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AN ENGINEERING EQUATION OF STATE: SQUARE-WELL STATISTICAL ASSOCIATING FLUID THEORY (SAFT)

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemical Engineering

by
Hertanto Adidharma
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To my parents,
Mariwati,
Widya,
and Lingga
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Notation

\(a\)  molar Helmholtz free energy

\(a_1, a_2\)  first and second perturbation terms of Helmholtz free energy, associated with the attractive energy \(u\)

\(A_V\)  Helmholtz energy per unit volume

\(\Delta A_V\)  critical part of the Helmholtz energy density

\(B\)  second virial coefficient

\(B_{\alpha\beta}\)  bond fraction of type \(\alpha\beta\)

\(c_i\)  variable defined in Equation (100)

\(c_v\)  molar isochoric heat capacity

\(c_p\)  molar isobaric heat capacity

\(C\)  a constant used in Equation (81)

\(C_k\)  scale factor defined in Equation (127)

\(d\)  temperature-dependent segment diameter

\(D\)  a function defined in Equation (118)

\(D_{ij}\)  universal constants used in Equation (23)

\(D_{mn}\)  universal constants used in \(a_t\)

\(e\)  a constant used in Equation (84)

\(f\)  proportionality function

\(f^{AB}\)  site-site Mayer \(f\)-function

\(g\)  radial distribution function

\(\bar{g}\)  modified radial distribution function defined in Equation (67)
$g_0$  radial distribution function calculated at zero density

$g_1$  first perturbation term of $g^{ren}$

$G$  shift crossover function defined in Equation (122)

$h$  molar enthalpy

$I$  integral defined in Equation (28)

$k$  Boltzmann constant

$K$  isothermal compressibility or a function defined in Equation (121)

$m$  number of segments per molecule

$N_{Av}$  Avogadro number

$P$  pressure

$r$  molecular distance

$R$  gas constant

$T$  temperature

$T^*$  dimensionless temperature

$S_k$  scale factor defined in Equation (126)

$u$  temperature-dependent well depth of the square-well potential

$\bar{u}$  adjustable crossover parameter, i.e. a coupling constant

$u^o$  temperature-independent well depth of the square-well potential

$u^*$  universal constant

$U$  a function defined in Equation (119)

$v$  molar volume

$v^{\infty}$  segment molar volume

$V$  volume
\( x \)  
reduced distance between two segments, \( r/\sigma \).

\( x_\alpha \)  
segment fraction

\( X \)  
mole fraction

\( \lambda' \)  
fraction of molecules that are not bonded at site A

\( Y \)  
crossover function

\( z_c \)  
coordination number

\( Z \)  
compressibility factor

**Greek**

\( \alpha \)  
universal critical exponent or a parameter used to calculate the renormalized potential

\( \beta \)  
\( 1/kT \)

\( \Delta_s \)  
universal correction-to-scaling exponent

\( \Delta^{AB} \)  
association strength

\( \varepsilon \)  
well depth of the site-site potential

\( \phi \)  
intermolecular potential

\( \phi_1 \)  
perturbation potential

\( \gamma \)  
universal critical exponent

\( \Gamma \)  
set of sites

\( \eta \)  
reduced density

\( \Theta \)  
renormalized potential

\( \kappa \)  
a measure of the distance from the critical point, defined in Equation (124) or SAFT parameter related to the volume available for bonding

\( \lambda \)  
reduced potential well range or adjustable crossover parameter
\( \Lambda \) adjustable crossover parameter, i.e. a dimensionless ultraviolet cutoff wave number of the long-range critical fluctuations

\( \mu \) background term

\( \nu \) universal constant

\( \theta \) angle between the vector connecting the centers of two molecules and the vector connecting the center of one molecule to an association site on that molecule

\( \rho \) molar density

\( \rho_n \) number density

\( \rho_s \) segment number density

\( \rho^* \) reduced number density

\( \sigma \) temperature-independent segment diameter

\( \tau \) a function defined in Equation (120)

\( \zeta \) reduced variable related to density

**Superscripts**

assoc association

disp dispersion

hs hard sphere

res constant-volume residual

res* constant-pressure residual

seg segment

sw square well

vap vaporization

\( \sim \) dimensionless
Subscripts

0 calculated at zero density
A, B association site
c observed critical point or cutoff value
c0 classical critical point
eff effective
i chain type or component
o per segment or based on the classical critical parameters
sh shift
t truncation-error correction
α, β segment type
x normalized properties
Abstract

Molecular thermodynamics is an engineering discipline rooted in molecular physics and physical chemistry and aimed at developing practical models that predict the properties of matter. The goal of this work is to develop a molecular thermodynamic model for predicting fluid densities, phase equilibria, and energy functions, such as enthalpy and heat capacity. Chemical engineers need these properties to develop and design new processes and materials, and to make these processes energy efficient and environmentally benign.

The approach is to hypothesize a mathematical approximation that captures interactions among real molecules on the basis of a molecular theory called the statistical associating fluid theory (SAFT). In this approximation, each molecule is composed of spherical segments that interact according to a square-well potential. These segments are allowed to form covalent or hydrogen bonds. A result of this approximation is an engineering equation of state referred to as SAFT1 that is found to be applicable to small and large molecules, associating and non-associating molecules, and to homopolymers and copolymers.

SAFT1 is tested on real-fluid properties, such as vapor pressure, vapor and liquid density, second virial coefficient, heat of vaporization, specific heat, and phase equilibria. For small n-alkanes, not only the vapor pressure and liquid density (that are correlated), but also the second virial coefficient, heat of vaporization, and heat capacity (that are predicted) are found to be accurate. For small alkanols-1, the vapor pressure and liquid density are also well correlated. The SAFT1 parameters for n-alkanes and
alkanols-1 are found to be well behaved and hence easy to estimate reliably for high-
molecular-weight molecules of corresponding homologs.

The SAFT1 equation of state developed in this work has already been applied by
others to calculate fluid-liquid and solid-fluid equilibria in solutions of \( n \)-alkanes and
polyolefins. More important, the knowledge and practical tools generated in this work
are applicable to developing new processes and materials that are less energy wasteful
and more environmentally benign.
Chapter 1
Introduction

Molecular thermodynamics is an engineering discipline rooted in molecular physics and physical chemistry and aimed at developing practical models that predict the properties of matter. Examples of such properties are densities, phase equilibria, chemical equilibria, and energy functions, such as enthalpy and heat capacity. Chemical engineers need these properties to develop and design new processes and materials, and to make these processes energy efficient and environmentally benign.

Chemical engineers cannot afford measuring, or having measured, all the needed properties in the laboratory, so they attempt to marry the available empirical knowledge with molecular theories. The fruit of this happy marriage has the form of practical computational tools that can be used to simulate the properties of matter at a great speed and with a minimum of cost. These powerful computational tools (perhaps we should call them toys), usually referred to as thermodynamic models or equations of state, are at the heart of all the modern process simulators.

The older thermodynamic models tend to be on the empirical side; they heavily rely on the experimental data, and hence they are not very predictive. The essence of progress is to make thermodynamic models less and less empirical, and hence more predictive, and to extend their applicability to more and more complex fluids and materials, such as associating and macromolecular fluids.
The most effective way to make thermodynamic models more predictive is to start with a realistic molecular theory, usually rooted in the statistical mechanics, and then to make the theory quantitative by fitting it carefully to accurate experimental data. Here are examples of theories that underpin modern engineering models: integral equation theory, renormalization group theory, lattice theory, and perturbation theory (Sandler, 1994). These molecular theories have been proven to have the capability to link the microscopic nature and behavior of molecules with the macroscopic properties of matter. Thus, the thermodynamic models emerging from these molecular theories are more predictive in accounting for complex-fluid behavior.

Most integral equations are based on the Ornstein-Zernike (OZ) relation, which needs a closure equation such as the Percus-Yevick, hypernetted chain, or mean spherical approximations. Typically, integral equations work best at low densities and high temperatures. The renormalization-group theory has been developed to deal with the effects of critical fluctuations. This theory is consistent with the universality of critical phenomena and the critical-region scaling laws; we are using this theory to develop crossover equations of state which incorporate the scaling laws asymptotically close to the critical point. The lattice theory of dense fluids is a common point of departure for developing activity-coefficient models in general and those for polymer solutions in particular (Danner and High, 1993).

In perturbation theory, the selected property (usually the Helmholtz free energy, configurational integral or partition function) of a system is expanded in Taylor series about the known property of a reference system. The accuracy of this model depends on the reference system chosen, and the number of terms included in the series; the closer
the reference system represents the real system and, in general, the more terms included in the series, the more accurate the model is.

Among the recent approaches to deriving thermodynamic models, the most popular is the so called SAFT (Statistical Associating Fluid Theory) approach which is rooted in perturbation theory. In the SAFT approach, the discrepancies between the predicted and experimental data are not due to the flaw of the statistical mechanics that underlies the models. These approximations are mathematical rather than physical. While not perfect, SAFT is a reliable theory for associating fluids as well as non-associating fluids. Another advantage of SAFT is that its approximations can be and have been tested against computer simulation data.

A preliminary SAFT model was proposed by Chapman et al. (Chapman et al., 1990) who applied the thermodynamic perturbation theory of the first order (TPT1) for associating fluids developed by Wertheim (Wertheim, 1984a; 1984b; 1986a; 1986b); Wertheim's work is the foundation of all SAFT developments. Huang and Radosz (Huang and Radosz, 1990; 1991) have developed an engineering version of the SAFT equation of state for pure components and mixtures. Much work has been done since then to refine SAFT approximations and to extend its applicability and accuracy.

For example, Banaszak et al. (Banaszak et al., 1993; Banaszak et al., 1994) improved the theory by incorporating explicitly the effect of chain connectivity. They allowed the reference fluids to be composed of attractive segments, e.g., they used square-well and Lennard-Jones fluids, rather than hard sphere segments, and they refer to these version of SAFT as SW-SAFT and LJ-SAFT, respectively. Their models agree well with the Monte Carlo data. Kraska and Gubbins (Kraska and Gubbins, 1996a;
independently developed another version of LJ-SAFT based on the work of Müller and Gubbins (Müller and Gubbins, 1995) in which they accounted for the long-range dipolar potential in addition to the Lennard-Jones repulsion-dispersion term.

Banaszak et al. (Banaszak et al., 1996) also extended the thermodynamic perturbation theory to heterobonded chains, such as heteronuclear and branched copolymers. Their model, referred to as Copolymer SAFT, explicitly accounts for the copolymer-solvent phase behavior. This model has been tested to calculate the cloud point pressure for binary solutions of ethylene-butene copolymers (EB) in propane and to calculate the Flory $\chi$ parameter for poly(ethylene-stat-butene) (PEB) blends.

Tavares et al. (Tavares et al., 1995) showed that TPT1 is equivalent to assuming that the free energy change on bond formation is proportional to the energy required to form a single dimer in a fluid of monomers; they refer to this perturbation theory as the monomer reference TPT1 (TPT1-M). They developed a dimer reference TPT1 (TPT1-D) that incorporates structural information on the square-well dimer fluid. They demonstrated that the inclusion of square-well dimer structural information in the TPT1-D model increases the accuracy of the predicted value for the compressibility factor of chain fluids in the broad range of density and temperature. Also Johnson (Johnson, 1996) applied TPT1-D for the Lennard-Jones dimer fluids.

Sear and Jackson (Sear and Jackson, 1994) implemented the Wertheim theory for ring formation in hard chain fluids. Ghonasgi et al. (Ghonasgi et al., 1994) and Ghonasgi and Chapman (Ghonasgi and Chapman, 1995), on the other hand, extended the Wertheim theory to systems that exhibit intramolecular association. By including the
intramolecular interaction, in addition to the intermolecular interaction, their extension also allows for the formation of ring-like chain molecules.

Gil-Villegas et al. (Gil-Villegas et al., 1997) have developed an equation of state for chain molecules of hard core segments with attractive potentials of variable range. Following the work of Chang and Sandler (Chang and Sandler, 1994) on the real function expression for the radial distribution function of hard sphere, Tavares et al. (Tavares et al., 1997) recently developed a completely analytic perturbation theory equation of state for freely jointed square-well chain fluid of variable well width.

Although many SAFT approximations have been proposed, such as those mentioned above, no new SAFT-based engineering equations of state have been proposed in which the ease of estimating parameters, the predictive power, and the accuracy are significantly improved. It is the goal of this work, therefore, to develop an enhanced engineering equation of state applicable over the whole density range to small and large molecules, associating and non-associating molecules, and to homopolymers and copolymers. The approach is to develop such an equation of state within the SAFT formalism using the square-well fluid as the reference fluid.

This dissertation is organized as a collection of stand-alone publishable chapters: In chapter 2, we characterize approaches to approximating the properties of the square-well fluid. In chapter 3, we present a prototype of an engineering equation of state for non-associating but heterosegmented fluids. In chapter 4, we document our effort to incorporate the critical fluctuations into SAFT equation of state. Finally, in chapter 5, we extend the applicability of the prototype presented in chapter 3 to associating fluids.
Chapter 2
A Study of Square-Well SAFT Approximations

2.1 Introduction

One of the approaches to developing equations of state for chain fluids is on the basis of Wertheim’s (Wertheim, 1984a; 1984b; 1986a; 1986b) thermodynamic perturbation theory of the first order (TPT1). A generic approach to implementing TPT1 to real fluids, referred to as the statistical associating fluid theory (SAFT), can be found in (Chapman et al., 1989).

The SAFT equations of state have the following terms: a segment term that accounts for the non-ideality of the reference fluid of non-bonded chain segments (monomers), a chain term that accounts for covalent bonding, and an association term that accounts for hydrogen bonding that leads to association. There may also be an optional term that accounts for polarity. The chain and association terms are estimated on the basis of the pair correlation function of the reference (non-bonded segment) fluid alone.

For example, Huang and Radosz (Huang and Radosz, 1990) developed a SAFT equation of state on the basis of an argon equation of state (the so-called BACK equation of state) for the segment term and a hard-sphere pair-correlation function for the chain

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1 Reprinted from Fluid Phase Equilibria, 161, Adidharma, H., Radosz, M., A study of square-well statistical associating fluid theory approximations, 1, Copyright 1999, with permission from Elsevier Science.
term. The Huang-Radosz version of SAFT has parameters that are well behaved and hence relatively easy to estimate for large molecules. Furthermore, this version has been extended to heterobonded chains by Banaszak et al. (Banaszak et al., 1996). That extension, referred to as copolymer SAFT, explicitly accounts for variable polyolefin microstructure due to the variability in comonomer incorporation.

The challenge is to make SAFT more predictive and to make the parameters even easier to estimate. Different approaches to improving SAFT fall into two categories: One approach utilizes the Lennard-Jones (LJ) fluid as the reference, as it is described, for example, by Banaszak et al. (Banaszak et al., 1994; Banaszak et al., 1995) and in the references therein. Another approach utilizes the square-well (SW) fluid as the reference, as it is described, for example, by Banaszak et al. (Banaszak et al., 1993) and in the references therein. In both approaches, we need two crucial expressions for the reference non-bonded fluid: an equation of state and a radial distribution function, both valid over the whole temperature, density, energy, and diameter ranges.

The focus of this work is on the SW-based SAFT. We build on theoretical concepts and data reported for SW fluids in (Barker and Henderson, 1972; Chang and Sandler, 1994; Tavares et al., 1995; Gil-Villegas et al., 1997).

The purpose of this work is to understand how different approaches to approximating the Helmholtz energy and the radial distribution function of the SW fluid affect the SAFT equations of state they underpin. Specifically, we look at the accuracy of correlating and predicting pure-alkane properties and mixed-alkane equilibria, and at the behavior of pure-component parameters. This is a narrow analysis, only from the SAFT
point of view, without an attempt to evaluate these approximations in general or to formulate a new equation of state.

2.2 Generic SAFT model

The generic SAFT model is based on Wertheim's TPT1. The constant volume residual Helmholtz energy per mole $a^{\text{res}}$, the residual Helmholtz energy for short, can be defined as

$$a^{\text{res}}(T,V,N) = a(T,V,N) - a^{\text{ideal}}(T,V,N)$$  \hspace{1cm} (1)

where $a(T,V,N)$ is the Helmholtz energy per mole of molecules of the real fluid and $a^{\text{ideal}}(T,V,N)$ is the Helmholtz energy per mole of the ideal gas at the same temperature and density. Dropping the (T,V,N) specification in our notation, the residual Helmholtz energy consists of three terms (Chapman et al., 1989):

$$a^{\text{res}} = a^{\text{seg}} + a^{\text{chain}} + a^{\text{assoc}}$$  \hspace{1cm} (2)

where $a^{\text{seg}}$ is the Helmholtz energy due to segment-segment within the reference system, $a^{\text{chain}}$ is the incremental Helmholtz energy due to chain formation, and $a^{\text{assoc}}$ is the incremental Helmholtz energy due to association, e.g., due to hydrogen bonding. The role of the unperturbed (reference) system can be assigned to any fluid having known Helmholtz energy and radial distribution function.

From Equation (2), the molar residual Helmholtz energy for non-associating alkane fluids studied in this work is given by

$$a^{\text{res}} = a^{\text{seg}} + a^{\text{chain}}$$  \hspace{1cm} (3)

The segment contribution can be expressed in term of the Helmholtz energy per segment, $a^{\text{seg}}_o$, that is
where $m$ is the number of segments per molecule. Tilde ($\sim$) used in this work means a dimensionless form of a variable. The chain contribution is related to the radial distribution function of the reference fluid at contact $g^\text{ref}(\sigma)$ as follows (Tavares et al., 1995)

$$\tilde{a}^{\text{chan}} = -(m-1)\left[ \ln g^\text{ref}(\sigma) - \ln g_0^\text{ref}(\sigma) \right]$$

where $g_0^\text{ref}(\sigma)$ is the radial distribution function of the reference monomer fluid at contact and at zero density.

2.3 Perturbation theory for SW fluid

The SW fluid has a steep repulsion at short distances and a short-ranged attraction at intermediate distances. Its potential model is characterized by three parameters, i.e. the hard-sphere diameter ($\sigma$), the well depth ($u$) and the reduced range of the potential well ($\lambda$), as shown in Figure 1.

Figure 1. The SW potential model
The potential energy for a pair of SW segments separated by a distance \( r \) is given by

\[
\phi(r) = \phi^\text{hs}(r, \sigma) - \phi_1(r, \lambda) \tag{6}
\]

where \( \phi^\text{hs} \) is the unperturbed potential, i.e. the hard-sphere potential, given by

\[
\phi^\text{hs}(r, \sigma) = \begin{cases} 
\infty & \text{if } r < \sigma \\
0 & \text{if } r > \sigma 
\end{cases} \tag{7}
\]

and \( \phi_1 \) is the perturbation given by

\[
\phi_1(r, \lambda) = \begin{cases} 
0 & r < \sigma \\
u & \sigma < r < \lambda \sigma \\
0 & r > \lambda \sigma 
\end{cases} \tag{8}
\]

The segment Helmholtz energy \( a_o^{\text{seg}} \) in Equation (4) and the radial distribution function in Equation (5) are estimated from the SW potential on the basis of perturbation theory for dense fluids developed by Barker and Henderson (McQuarrie, 1976). The segment term is then expressed as:

\[
\tilde{a}_o^{\text{sw}} = \tilde{a}_o^{\text{hs}} + \tilde{a}_o^{\text{disp}} \tag{9}
\]

where \( \tilde{a}_o^{\text{hs}} \) is the hard-sphere Helmholtz energy per segment, calculated from the Carnahan-Starling (CS) (Carnahan and Starling, 1969) equation, and \( \tilde{a}_o^{\text{disp}} \) is the dispersion term per segment given by (up to the second order):

\[
\tilde{a}_o^{\text{disp}} = \frac{1}{T^*} \tilde{a}_1 + \frac{1}{(T^*)^2} \tilde{a}_2 \tag{10}
\]

Here, \( T^* \) is the reduced temperature defined by \( kT/u \), \( k \) is the Boltzmann constant, \( T \) is the temperature, \( \tilde{a}_1 \) is the first perturbation term and \( \tilde{a}_2 \) is the second perturbation term.

For our purposes, it is convenient to rewrite Equation (10) as follows:
\[ \tilde{\alpha}_o^{disp} = \beta a_1 + \beta^2 a_2 \]  

where \( \beta \) is \( 1/kT \), \( a_1 \) and \( a_2 \) are the first two perturbation terms associated with the attractive energy \( u \), given by McQuarrie (McQuarrie, 1976):

\[ a_1 = u \tilde{a}_1 = -\frac{\rho_s}{2} \int \phi_1 g^{hs}(r)4\pi r^2 dr \]  

\[ a_2 = u^2 \tilde{a}_2 = -\frac{\rho_s}{4} \left( \phi_1 \right)^2 kT \frac{\partial (\rho_s g^{hs}(r))}{\partial P^{hs}} 4\pi r^2 dr \]  

Here, \( \rho \) is the number density, \( g^{hs}(r) \) is the hard-sphere radial distribution function at distance \( r \), and \( P^{hs} \) is the pressure of hard-sphere fluid. The first perturbation term \( a_1 \) corresponds to the average of the potential energy calculated with the hard-sphere structure. The second perturbation term \( a_2 \), so-called local-compressibility approximation, describes the fluctuation of the attractive energy. Equation (13) can be simplified further as

\[ a_2 = \frac{1}{2} u K^{hs} \rho_s \frac{\partial a_1}{\partial \rho_s} \]  

where \( K^{hs} \) is the hard-sphere isothermal compressibility defined as

\[ K^{hs} = kT \left( \frac{\partial \rho_s}{\partial P^{hs}} \right)_T \]  

The SW radial distribution function at contact, needed in Equation (5) is also calculated using the Barker-Henderson perturbation theory of the first order. A linear expansion of \( g(r) \) gives

\[ g^{sw}(\sigma) = g^{hs}(\sigma) + \beta u g_1(\sigma) \]  

and a logarithmic expansion of \( g(r) \) (Barker and Henderson, 1976) gives
where \( g^{hs}(\sigma) \) is the hard-sphere radial distribution function at contact, given by Carnahan-Starling (Reed and Gubbins, 1973), and \( g_1(\sigma) \) is the perturbation term given by (Henderson et al., 1976a)

\[
g_1(\sigma) = \frac{1}{4u} \frac{\partial \tilde{a}_1}{\partial \eta} + \lambda^3 g^{hs}(\lambda \sigma)
\]

or (Gil-Villegas et al., 1997)

\[
g_1(\sigma) = \frac{1}{4u} \left[ \frac{\partial \tilde{a}_1}{\partial \eta} - \frac{\lambda}{3\eta} \frac{\partial \tilde{a}_1}{\partial \lambda} \right]
\]

where \( \eta \) is the reduced density defined as

\[
\eta = \frac{\pi}{6} \sigma^3 \rho_s
\]

2.4 Approaches to estimating \( a_1, a_2 \) and \( g^{SW}(\sigma) \)

2.4.1 Empirical approach

For SW fluids, with \( \lambda = 1.5 \), Barker-Henderson (Barker and Henderson, 1972) correlated their MC data for \( a_1 \) and \( a_2 \) as follows:

\[
a_1 = uC_1 \left[ 1 - \exp \left( -\frac{\alpha_1 \rho^*}{\beta_1 - \rho^*} \right) - \frac{\alpha_1 \rho^*}{\beta_1} \right] + p_1 \rho^* + q_1(\rho^*)^2
\]

\[
a_2 = u^2C_2 \left[ 1 - \exp \left( -\frac{\alpha_2 \rho^*}{\beta_2 - \rho^*} \right) - \frac{\alpha_2 \rho^*}{\beta_2} \right] + p_2 \rho^* + q_2(\rho^*)^2
\]

where \( \rho^* \) is the reduced number density defined as \( \rho_s \sigma^3 \). The constants used in Equations (21) and (22) are listed in Table 1.
Chen and Kreglewski (Chen and Kreglewski, 1977) proposed an alternative equation for the dispersion term:

$$
\tilde{a}_o^{\text{disp}} = \sum_{i=1}^{4} \sum_{j=1}^{9} D_{ij} \left( \frac{u}{kT} \right)^i \left( \frac{\eta}{\tau} \right)^j
$$

(23)

where $\tau = 0.74048$ and $D_{ij}$'s are universal constants derived, for example, from fitting the argon data; such $D_{ij}$'s are used in the SAFT equation of state developed by Huang and Radosz (Huang and Radosz, 1990).

Table 1. The constants for $a_1$ and $a_2$ in Eqs. (21) and (22)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3.173136</td>
<td>-0.384466</td>
</tr>
<tr>
<td>$\alpha$</td>
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<td>9.75</td>
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<tr>
<td>$\beta$</td>
<td>$\sqrt{2}$</td>
<td>$\sqrt{2}$</td>
</tr>
<tr>
<td>p</td>
<td>-4.974192</td>
<td>-2.487096</td>
</tr>
<tr>
<td>q</td>
<td>5.134186</td>
<td>-0.047652</td>
</tr>
</tbody>
</table>

The radial distribution function of the reference at contact, $g^{\text{rw}}(\sigma)$, is obtained from Equations (16) and (18), where $g^{ht}(\lambda \sigma)$ is interpolated from fitting MC data (Banaszak et al., 1993),

$$
g^{ht}(1.5\sigma) = 1 + \gamma_1 \eta + \gamma_2 \eta^2 + \gamma_3 \eta^3 + \gamma_4 \eta^4
$$

(24)

where $\gamma_1$, $\gamma_2$, $\gamma_3$, and $\gamma_4$ are numerical coefficients listed in Table 2.

Table 2. The coefficients for $g^{ht}(1.5\sigma)$ in Eq. (24)

<table>
<thead>
<tr>
<th>$\gamma_i$</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>$\gamma_1$</td>
<td>0.653305</td>
</tr>
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<td>$\gamma_2$</td>
<td>-1.381460</td>
</tr>
<tr>
<td>$\gamma_3$</td>
<td>-7.558440</td>
</tr>
<tr>
<td>$\gamma_4$</td>
<td>8.401660</td>
</tr>
</tbody>
</table>
2.4.2 Analytical approach

Equation (12) can also be solved analytically; the result is dependent on the expression of the hard-sphere radial distribution function used. For example, Chang and Sandler (Chang and Sandler, 1994) proposed a real-function expression for \( g^h_r \) using the Percus-Yevick (PY) approximation. Their expression for the first shell, i.e. \( \sigma<r<2\sigma \), is as follows:

\[
g^h_r(x, \eta) = \frac{1}{x}[k_1 \exp\{A(x-1)\} + k_2 \exp\{B(x-1)\}\cos\{C(x-1)\} + k_3 \exp\{B(x-1)\}\sin\{C(x-1)\}]
\]

(25)

where the expressions of \( k_i \)'s, \( A, B \) and \( C \) are given in (Chang and Sandler, 1994) and \( x \) is the reduced distance between two segments, \( r/\sigma \). For \( 1<\lambda<2 \), Chang and Sandler (Chang and Sandler, 1994) solved Equations (12) and (14) to get:

\[
a_1 = -12u\eta I
\]

(26)

\[
a_2 = -6u^2 \eta \frac{(1-\eta)^4}{1 + 4\eta + 4\eta^2} \left[ I + \eta \frac{\partial I}{\partial \eta} \right]
\]

(27)

with

\[
I = \int g^h_r(x)x^2 \, dx = \sum_{n=1}^{3} k_n t_n
\]

(28)

where the expressions of \( t_n \)'s are given in (Chang and Sandler, 1994). In Equation (27), the PY approximation for the hard-sphere compressibility has been used.

Another approach to solving Equation (12) on the basis of a mean-value theorem has been proposed by Gil-Villegas et al. (Gil-Villegas et al., 1997); they solved the integral using the mean value of the hard-sphere radial distribution function, \( g^h_r(\xi) \).
Instead of using the mean value of distance $\xi$ in the hard-sphere radial distribution function directly, they used the contact value but evaluated at an effective reduced density $\eta_{\text{eff}}$. This way, the result is much simpler, even though a parameterization is still needed to make the equations tractable. Their final expression for $a_i$ is as follows:

$$a_i = -4\eta m(\lambda^2 - 1)g^{hs}(\sigma, \eta_{\text{eff}})$$  \hspace{1cm} (29)$$

where $\eta_{\text{eff}}$ is related to the real reduced density $\eta$ by a polynomial parameterization

$$\eta_{\text{eff}} = c_1\eta + c_2\eta^2 + c_3\eta^3$$  \hspace{1cm} (30)$$

and $c_1$, $c_2$ and $c_3$ are the polynomial coefficients. For $1.1 \leq \lambda \leq 1.8$, the coefficients have been obtained as functions of $\lambda$ using exact values of $a_i$ obtained by integrating Equation (12). Accurate values of $g^{hs}(r)$ calculated by solving the Ornstein-Zernike equation with Malijevsky and Labik formula have been used for this purpose.

The radial distribution function of the reference at contact, $g^{sw}(\sigma)$, is obtained from Equations (16) or (17) and (18) or (19).

### 2.5 Dimer SW reference

The Helmholtz energy contribution due to bond formation, $\tilde{\alpha}^{\text{chain}}$, given by Equation (5), is for a monomer reference TPT1. This contribution is equivalent to the change of the Helmholtz energy upon dimerization at constant temperature and monomer density (Tavares et al., 1995). Each bond in a chain is considered to be a dimer bond, and the interdependence of bonds is neglected.

This approach can be extended to a dimer reference TPT1 (TPT1-D) that incorporates the structural information on the SW-dimer fluid (Tavares et al., 1995). The chain formation is assumed to occur in two steps. The first step is the formation of
dimers from monomers, as in TPT1. The second step is the formation of chains from dimers; hence, dimers become the reference. The cumulative effect of bonding in the second step is estimated by multiplying the contribution due to forming one tetramer from dimers by the number of bonds required to form a chain of dimers.

The overall Helmholtz energy due to bond formation in TPT1-D, which supersedes Equation (5) in TPT1, is therefore calculated as follows

\[
\tilde{a}_{\text{chain}} = \frac{\mathcal{m}}{2} \left[ \ln g_{\text{sw-mono}}^{\text{mono}} (\sigma) - \ln g_{\text{sw-mono}}^{\text{mono}} (0) \right] \\
- \frac{m - 2}{2} \left[ \ln g_{\text{sw-dimer}} (\sigma) - \ln g_{\text{sw-dimer}}^{\text{mono}} (0) \right]
\]  

(31)

where \( g_{\text{sw-mono}} \) is the correlation function for SW monomers and \( g_{\text{sw-dimer}} \) is the site-site angle-averaged correlation function for SW dimer. The first term on the right side of Equation (31) is the energy contribution of the dimer bond formation (first step) and the second term on the right side of Equation (31) is the energy contribution of the chain formation (second step). Equation (31) can also be written as

\[
\tilde{a}_{\text{chain}} = -(m - 1) \left[ \ln g_{\text{sw-mono}}^{\text{mono}} (\sigma) - \ln g_{\text{sw-mono}}^{\text{mono}} (0) \right] \\
- \frac{m - 2}{2} \left[ \ln g_{\text{sw-corr}} (\sigma) - \ln g_{\text{sw-corr}}^{\text{mono}} (0) \right]
\]

(32)

where \( g_{\text{sw-corr}} \) is defined as

\[
g_{\text{sw-corr}} (\sigma) = \frac{g_{\text{sw-dimer}} (\sigma)}{g_{\text{sw-mono}} (\sigma)}
\]

(33)

Correlation for \( g_{\text{sw-corr}} \) has been developed (Tavares et al., 1995) using MC simulation data.
\[ g_{\text{nr-corr}}(\sigma) = \alpha_0(T^*) + \alpha_1(T^*) \rho^* + \alpha_2(T^*)(\rho^*)^2 + \alpha_3(T^*)(\rho^*)^3 \]
\[ + \alpha_4(T^*)(\rho^*)^4 \]  

\[ (34) \]

where \( \alpha_i \)'s are temperature-dependent parameters given in (Tavares et al., 1995).

### 2.6 Square-well SAFT models studied

We select six SW SAFT models for real fluids, numbered 1 through 6, by combining the different approaches discussed above. These models are defined in Table 3. For all models, as proposed in (Kreglewski and Wilhoit, 1974), we use a temperature-dependent potential-well depth \( u \) to account for the non-central forces:

\[ u = u^0 \left(1 + \frac{e}{kT}\right) \]  

\[ (35) \]

where \( u^0 \) is the temperature-independent potential-well depth and \( e/k \) is a constant (methane: \( e/k = 1 \), other \( n \)-alkanes: \( e/k = 10 \)). In all models, the radial distribution function is calculated using the linear expansion of \( g(r) \), Equation (16), and \( g_1(\sigma) \) is calculated using Equation (18) or (19). The expression of \( a_i \) used in Equation (18) or (19) is consistent with that in the dispersion term.

<table>
<thead>
<tr>
<th>Model</th>
<th>Dispersion term</th>
<th>Chain term</th>
<th>( g_m(\lambda \sigma) ) in Eq. (18)</th>
<th>( \lambda )</th>
<th>( m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Barker-Henderson's MC fit, Eqs. (21) and (22)</td>
<td>Monomer reference, Eq. (5)</td>
<td>Banaszak et al.'s MC fit, Eq. (24)</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>Argon fit, Eq. (23)</td>
<td>Monomer reference, Eq. (5)</td>
<td>Banaszak et al.'s MC fit, Eq. (24)</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>Analytic PY approximation, Eqs. (26) and (27)</td>
<td>Monomer reference, Eq. (5)</td>
<td>Banaszak et al.'s MC fit, Eq. (24)</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>(4)</td>
<td>Mean value theorem, Eqs. (29) and (14)</td>
<td>Monomer reference, Eq. (5)</td>
<td>Mean value theorem, see Eq. (19)</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td>Mean value theorem, Eqs. (29) and (14)</td>
<td>Monomer reference, Eq. (5)</td>
<td>Mean value theorem, see Eq. (19)</td>
<td>vary ( 1/(n_\sigma-1) )</td>
<td></td>
</tr>
<tr>
<td>(6)</td>
<td>Argon fit, Eq. (23)</td>
<td>Dimer reference, Eq. (32)</td>
<td>Banaszak et al.'s MC fit, Eq. (24)</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>
Model 1 is an empirical SW SAFT model. MC fit is used to calculate the dispersion term of the Helmholtz energy and $g^{hs}(\lambda \sigma)$. As in (Kreglewski, 1984), the segment diameter is temperature dependent, defined as

$$d = \int_0^\sigma [1 - \exp(-\beta \phi(r))] dr$$  \hspace{1cm} (36)

To integrate Equation (36), we apply the inverted SW model proposed by Kreglewski (Kreglewski, 1984) and obtain

$$d = \sigma \left[1 - 0.12 \exp \left(-\frac{3u^o}{kT}\right)\right]$$  \hspace{1cm} (37)

Thus, in this model, the reduced density $\eta$ and the reduced number density $\rho^*$ are defined in term of the effective segment diameter $d$, instead of $\sigma$.

Model 2 is also an empirical model. The dispersion term of the Helmholtz energy is the argon fit and the other equations are the same as that in model 1. This model is analogous to the Huang-Radosz version of SAFT (Huang and Radosz, 1990), except for $g^{hs}$.

Model 3 is a semi-analytical model that uses an analytical approach to calculate the dispersion term of the Helmholtz energy and an empirical approach to calculate $g^{hs}(\lambda \sigma)$. The reduced density $\eta$ and the reduced number density $\rho^*$ are defined in term of the effective segment diameter $d$.

Models 4 and 5 are analytical models based on the approach developed by Gil-Villegas et al. (Gil-Villegas et al., 1997). With the use of the mean value theorem and PY approximation for $K^{hs}$, the dispersion term of the Helmholtz energy and the radial distribution function are calculated analytically. As in their work, the segment diameter
is assumed to be independent of temperature, but the energy parameter is temperature
dependent according to Equation (35). Also, in model 4, we fix the value of \( \lambda (\lambda = 1.5) \),
whereas in model 5, we allow the value of \( \lambda \) to vary and use a simple correlation for \( m \) as
a function of molecular weight or number of carbon.

In model 6, which is empirical, we examine the effect of the inclusion of SW
dimer structural information in the chain term. Based on model 2, we replace Equation
(5) with the dimer reference chain term, Equation (32), and apply the MC fit, Equation
(34), to calculate \( g^{\text{sw-cor}}(\sigma) \).

2.7 Results and discussion

Before applying the models described above, we analyze the underlying
approximations, and illustrate their performance. Figure 2 illustrates behavior of the first
perturbation term \( \tilde{a}_1 \) as a function of reduced number density for models 1, 3, and 4 (or
5) calculated for \( \lambda = 1.5 \). It turns out that the curves calculated from the empirical and
analytical models nearly coincide.

Figure 3 illustrates the behavior of the second perturbation term \( \tilde{a}_2 \) for models 1,
3, and 4 (or 5) also calculated for \( \lambda = 1.5 \). We note that \( \tilde{a}_2 \) calculated from the local
compressibility approximation, in models 3 and 4, does not agree with the simulation
results. Besides the Barker-Henderson simulation result, which is model 1, we also show
the simulation result of Alder et al. (Alder et al., 1972).

Figure 4 illustrates the dispersion term per segment \( \tilde{a}_o^{\text{disp}} \) for models 1, 2, 3, and
4 (or 5) with \( \lambda = 1.5 \) and at \( T^* = 0.75 \). At this particular reduced temperature, models 1,
3, and 4 result in similar values of \( \tilde{a}_o^{\text{disp}} \), except in the high-density range. Although
Figure 2. The dimensionless first order perturbation term $\tilde{a}_1$ for $\lambda = 1.5$ as a function of reduced number density $\rho^*$ (dashed curve: model 1, dotted curve: model 3, solid curve: model 4 or 5).

$\tilde{a}_1$ of model 1 is very different from those of models 3 and 4, its contribution to $\tilde{a}_o^{\text{disp}}$ is not large. However, we may expect that the contribution of $\tilde{a}_2$ to the dispersion term will be larger at lower reduced temperatures. It is also interesting to note that the argon fit shown in Figure 4, which is model 2, has a much lower absolute value of the dispersion term than those of the other models.

Figure 5 illustrates the radial distribution function at contact for model 1 (or 2), 3, and 4 (or 5) at $\lambda = 1.5$, $T^* = 0.75$, and for hard-sphere fluid with CS approximation. The points are the MC simulation data (Henderson et al., 1976b). At this particular temperature, the radial distribution function calculated from all the models except CS are lower than those obtained from the MC simulation for $\rho^* < 0.8$. This figure also suggests

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Figure 3. The dimensionless second order perturbation term $\tilde{a}_2$ for $\lambda = 1.5$ as a function of reduced number density $\rho^*$ (dashed curve: model 1, dotted curve: model 3, solid curve: model 4 or 5). The dot-dashed curve is a smoothed curve of Alder's simulation results (Alder et al., 1972).

Figure 6 illustrates the chain contribution to the Helmholtz energy due to one bond formation, $\tilde{a}_{\text{bond}}$, for models 1 (or 2), 3, and 4 (or 5) with $\lambda = 1.5$ and at $T^* = 0.75$. We find that all these models imply similar estimates of $\tilde{a}_{\text{bond}}$.

Next, we fit all the models to experimental saturated-vapor pressure and saturated-liquid volume data for $n$-alkanes over the same temperature range as in reference (Huang and Radosz, 1990). In our optimization procedure, we give an equal weight to both properties. The results are presented in Table 4. The average values of...
Figure 4. The dispersion term per segment for $\lambda = 1.5$ at $T^* = 0.75$ as a function of reduced number density $\rho^*$ (dashed curve: model 1, dot-dashed curve: model 2, dotted curve: model 3, solid curve: model 4 or 5).

AAD (average absolute deviation) for the liquid volume and the vapor pressure are also shown in Table 4.

For all SW-SAFT models, the segment diameter $\sigma$ (or segment volume $v^\infty$) and the segment energy $u^\circ/k$ increase with increasing molecular weight, as shown in Figure 7 and 8. The segment volume is related to the segment diameter by the following equation:

$$v^\infty = \frac{\pi N_{AV}}{6\tau} \sigma^3 \quad (38)$$

where $N_{AV}$ is the Avogadro number.

Model 1 agrees with MC data (Banaszak et al., 1993), but it does not correlate the liquid volume well when it is applied to the real fluids, as shown in Table 4. As shown in Figures 7 and 8, model 1 also has large and variable values of the segment
Figure 5. Values of $g(\sigma)$ for hard-sphere fluid with CS (dot-dashed curve) approximation and for the SW fluid with $\lambda = 1.5$ at $T^* = 0.75$ (dashed curve: model 1 or 2, dotted curve: model 3, solid curve: model 4 or 5). The points are the MC data of Henderson et al. (Henderson et al., 1976b).

volume ($v^o$) and segment energy ($u^o/\k$) for long chains. This feature is undesirable for mixtures having large differences in molar mass (the difference in segment parameters becomes large). Figure 9 illustrates this problem for a mixture of ethane and $n$-decane (dashed curve represents model 1). The experimental data are taken from literature (Reamer and Sage, 1962).

Model 2 exhibits a better goodness of fit for the vapor pressure, as shown in Table 4. This is probably due to the fact that the universal constants of Equation (23) are obtained from data for a real substance, i.e. argon. Model 2 also gives lower values of the segment volume and energy for long chains, compared to model 1; the payoff (dotted curve) is shown in Figure 9. Let us note that model 2 is similar to the Huang-Radosz...
Figure 6. The chain contribution to the Helmholtz energy as a function of reduced number density $\rho^*$ (dashed curve: model 1 or 2, dotted curve: model 3, solid curve: model 4 or 5); $\lambda = 1.5$, $T^* = 0.75$.

SAFT equation of state (Huang and Radosz, 1990), except for the SW radial distribution function in the chain term, here used in place of the hard-sphere radial distribution function. Figures 10 and 11 show the effect of this difference; using the SW radial distribution function amounts to accounting for the attractive energy in determining the energy of bond formation. The examples in Figures 10 and 11 are for the coexisting vapor and liquid density of propane. Model 2 seems to improve slightly the representation of the vapor density, but there is little difference in the liquid density and critical region.

Model 3 does not fit the vapor pressure and liquid volume well, as shown in Table 4. It also has the same problem as model 1, i.e. it gives large values of the segment volume and energy for long chains. Recently, Tavares et al. (Tavares et al., 1997)
developed a completely analytic model. Their model, with temperature-independent parameters, is the same as model 3, except instead of applying the empirical Equation (24), they applied Equation (25) to calculate $g^{hs}(\lambda \sigma)$ and used a logarithmic expansion Equation (17) to calculate $g(r)$. Equation (17) gives the exact limit at zero density, $\exp(1/T*)$, whereas Equation (16) gives an approximate limit, $1+(1/T*)$. That model, with variable $\lambda$, was shown to fit the experimental vapor pressure and critical point data well. We instead fit it to experimental saturated-vapor pressure and saturated-liquid volume, and find that there is a problem with representing the saturated-liquid volume. This is probably due to the use of the PY approximation in calculating $g^{hs}(r)$ because the PY approximation does not give accurate values of the radial distribution function in the high-density range.
Table 4. The model parameters for $n$-alkanes

<table>
<thead>
<tr>
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<th>(2)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>$m$</td>
<td>$v^m$ (cc/mol)</td>
<td>$u^*/k$ (K)</td>
<td>AAD P/V (%)</td>
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<tr>
<td>Methane</td>
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<td>141.38</td>
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<td>Ethane</td>
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<td>239.71</td>
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<td>Propane</td>
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</tr>
</tbody>
</table>

Models 4 and 5 seem to give a good combination of the accuracy for the vapor pressure and liquid volume, as shown in Table 4, of the parameter behavior, as shown in Figures 7 and 8, and of the mixture phase behavior, as shown in Figure 9. These models are similar to the SAFT equation of state in representing the liquid density and critical region, as shown in Figures 11 and 12. In the pressure-density plane, as shown in Figure 11, the coexisting curve is better represented by SAFT. To characterize the performance at low densities, the estimated second virial coefficient is shown in Figure 13 for $n$-
Figure 8. The segment energy parameters for n-alkanes as a function of molecular weight.

octane; model 5 overestimates the second virial coefficient even at high temperatures.

The poor representation of the critical region and the second virial coefficient is probably due to the fact that the convergence of the Barker-Henderson perturbation theory is slow in the critical region and at low densities, and hence the first two perturbation terms alone may not be adequate.

Model 6 gives higher values of the segment parameters than those of model 2, as shown in Figures 7 and 8, which results in poor predictions for mixtures, as shown in Figure 9. Figure 13 shows a small improvement gained from the dimer reference for the second virial coefficient (dotted-dashed curve). One reaches the same conclusion if one includes the dimer structure information in the hard-chain term in the SAFT equation of state.
Figure 9. Vapor-liquid equilibria in ethane+n-decane at 378 K, experimental (Reamer and Sage, 1962) (points) and predicted (dashed curve: model 1, dotted curve: model 2, solid curve: model 5, dot-dashed curve: model 6).

Although the models considered here, except for model 2, represent almost the same Helmholtz energy, they significantly differ in representing real fluids. Models that result in high values of $\frac{u^0}{k}$ are less desirable because they cause lower values of $T^*$ ($=T/(u/k)$) and, hence, slower convergence of the perturbation series. This probably makes Equation (11) misrepresent the real systems. For example, a temperature of 303 K for n-octane corresponds to $T^*$ of 0.46 for model 1, 0.43 for model 3, 0.93 for model 4, and 1.42 for model 5; the lower the $T^*$, the slower the convergence. Also, a strong molecular weight dependence of $\frac{u^0}{k}$ and $\nu^\infty$ is undesirable because, as the mixture components differ more and more in the values of their parameters, the mixing rules become less and less reliable.
2.8 Conclusion

Six square-well SAFT models, fitted to the experimental saturated liquid volume and saturated vapor pressure for pure n-alkanes, are analyzed for predicting the coexisting densities, second virial coefficients, and binary phase equilibria. The models that result in low values of the segment energy and weak molecular weight dependence of the parameters are found to be more accurate for real fluids. For example, model 5 seems to provide a good basis for further development because it is based on an analytical approach, gives the lowest values of the segment energy and volume, and the smallest difference in the segment parameters between different molecules.
The inclusion of the dimer structure in the square-well chain term seems to produce no significant benefit for representing real substances. This is probably because the contribution of bond formation to the total Helmholtz energy is relatively small.

Figure 11. Coexisting vapor and liquid density for propane, experimental (Vargaftik, 1975) (points) and calculated (dashed curve: SAFT, dotted curve: model 2, dot-dashed curve: model 4, solid curve: model 5).
Figure 12. Coexisting vapor and liquid density for propane, experimental (Vargaftik, 1975) (points) and calculated (dashed curve: SAFT, dot-dashed curve: model 4, solid curve: model 5).

Figure 13. Second virial coefficient of n-octane, experimental (Dymond and Smith, 1980) (points) and predicted (dotted curve: model 2, solid curve: model 5, dotted-dashed curve: model 6).
Chapter 3

Prototype of an Engineering Equation of State for Heterosegmented Polymers

3.1 Introduction

In chemical and polymer technology, we need thermodynamic models that are more and more predictive, and less and less dependent on fitting to experimental data. The mathematical simplicity and the ease of coding, therefore, become relatively less important virtues, but the ease of estimating the parameters quickly and reliably becomes a very important virtue. One of the popular approaches to developing such thermodynamic models is rooted in perturbation theory, for example the statistical associating fluid theory (SAFT).

The SAFT equations of state have the following terms: a segment term that accounts for the non-ideality of the reference fluid of non-bonded chain segments (monomers), a chain term that accounts for covalent bonding, and an association term that accounts for hydrogen bonding that leads to association. There may also be an optional term that accounts for polarity. The main differences between different versions of SAFT stem from how the segment and chain terms are estimated.

For example, the original engineering version of SAFT was developed by Huang (Huang and Radosz, 1990; 1991) on the basis of an argon equation of state (the so-called

---

BACK equation of state) for the segment term and a hard-sphere pair-correlation function for the chain term. That version of SAFT has become popular because it is user friendly; its parameters are well behaved and hence relatively easy to estimate for new large molecules. Furthermore, SAFT has been extended to hetero-segmented chains by Banaszak (Banaszak et al., 1996). That extension, referred to as copolymer SAFT, explicitly accounts for variable polyolefin microstructure due to the variability in comonomer incorporation.

The challenge is to make SAFT even more predictive and to make the parameters even easier to estimate. We and others have used two approaches to improving SAFT for macromolecules. In both approaches, we need two crucial expressions for the reference non-bonded fluid: an equation of state and a radial-distribution function (rdf), both valid over the whole temperature, density, energy, and diameter ranges. One approach utilizes the Lennard-Jones (LJ) fluid as the reference, as it is described, for example, by Banaszak (Banaszak et al., 1994; Banaszak et al., 1995) and in the references therein. Examples of implementing a LJ-SAFT to alkanes are described in literature (Kraska and Gubbins, 1996a; 1996b; Chen et al., 1998). Another approach utilizes the square-well (SW) fluid as the reference, as it is described, for example, by Banaszak (Banaszak et al., 1993) and in the references therein. Our work builds on the SW-SAFT approach. A review and analysis of previous SW approximations within the SAFT framework, which has lead to this work, is presented in chapter 2.

The goal of this work is to develop a set of practical SW approximations with easy-to-estimate pure-component parameters, in the form of a prototype engineering equation of state that can be applied to hetero-segmented polymers. We define hetero-
segmented polymers as those composed of segments that may differ in volume or energy. For example, certain homopolymers, such as polyisobutylene and polybutene-1 can be considered heterosegmented if we assign different energy or volume or both to their segments, of the backbone type and of the branch type. We want to test such a prototype equation of state on pure normal alkanes, mixtures of alkanes, and polyolefin solutions, to find out if it is possible to predict mixture properties on the basis of pure component parameters alone. More work is needed for other systems.

3.2 Square-Well Potential Model

The square-well (sw) fluid has a steep repulsion at short distances and a short-ranged attraction at intermediate distances. The sw potential model is characterized by three parameters, i.e. the hard-core diameter ($\sigma$), the well depth ($u$) and the reduced range of the potential well ($\lambda$), as shown in Figure 1.

The potential energy for a pair of square-well segments separated by a distance $r$ can be represented by

$$\phi(r) = \phi^{hs}(r, \sigma) - \phi_1(r, \lambda)$$

(39)

where $\phi^{hs}$ is the unperturbed potential, i.e. the hard-sphere potential, given by

$$\phi^{hs}(r, \sigma) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases}$$

(40)

and $\phi_1$ is the perturbation given by

$$\phi_1(r, \lambda) = \begin{cases} 0 & r < \sigma \\ u & \sigma < r < \lambda \sigma \\ 0 & r > \lambda \sigma \end{cases}$$

(41)
3.3 SAFT1 Equation of State

We present the equation of state in a general form that is applicable to pure components and mixtures of homo-segmented and hetero-segmented molecules. For non-associating fluids, the dimensionless residual Helmholtz energy of chain molecules is given by

\[ \tilde{a}^{\text{res}} = \frac{a^{\text{res}}}{RT} = \tilde{a}^{\text{seg}} + \tilde{a}^{\text{chain}} \]

(42)

where \( \tilde{a}^{\text{seg}} \) is the segment term, which is the reference Helmholtz energy due to segment-segment interactions, and \( \tilde{a}^{\text{chain}} \) is the chain term, which is the perturbation Helmholtz energy due to chain formation. Tilde (~) used in this work means a dimensionless form of a variable.

The segment term can be expressed as

\[ \tilde{a}^{\text{seg}} = \left( \sum_i X_i m_i \right) \tilde{a}_o^{\text{seg}} \]

(43)

where \( m_i \) is the number of segments in chain \( i \) and \( X_i \) is the mole fraction of component (chain) \( i \) and \( \tilde{a}_o^{\text{seg}} \) is the Helmholtz energy per segment. For square-well segments, \( \tilde{a}_o^{\text{seg}} \) is approximated using the high-temperature expansion of the Barker-Henderson perturbation theory (Barker and Henderson, 1972; McQuarrie, 1976) as follows

\[ \tilde{a}_o^{\text{seg}} = \tilde{a}_o^{\text{hw}} = \tilde{a}_o^{\text{hw}} + \sum_{n=1}^\infty \frac{\tilde{a}_n}{(T^*)^n} \]

(44)

where \( \tilde{a}_o^{\text{hw}} \) is the hard-sphere free energy per segment, \( \tilde{a}_n \) is the n-th perturbation term, \( T^* \) is the dimensionless temperature \( kT/u \), \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. We can also rewrite Equation (44) as
\[ a^\alpha = \bar{a}_o^\alpha + \sum_{n=1}^{\infty} \beta^n a_n \]  

(45)

where \( \beta \) is \( 1/kT \) and therefore \( a_n = \bar{a}_n u^n \).

As in SAFT, the hard-sphere free energy is estimated from the Mansoori et al. equation (Mansoori et al., 1971):

\[
\bar{a}_o^{h2} = \frac{6}{\pi \rho N_A \sum_i X_i m_i} \left[ \frac{(\zeta_2)^3 + 3\zeta_1 \zeta_2 \zeta_3 - 3\zeta_1 \zeta_2 (\zeta_3)^2}{\zeta_3 (1 - \zeta_3)^2} \right] - \left( \zeta_0 - \frac{(\zeta_2)^3}{(\zeta_3)^2} \right) \ln(1 - \zeta_3) 
\]

(46)

where

\[
\zeta_k = \frac{\pi}{6} N_A \rho \sum_i X_i m_i \sum_\alpha x_\alpha (\sigma_\alpha)^k
\]

(47)

In Equation (47), \( N_A \) is the Avogadro number, \( \rho \) is the molar density, \( \sigma_\alpha \) is the diameter of segment \( \alpha \), and \( x_\alpha \) is the segment fraction defined as

\[
x_\alpha = \frac{\text{number of moles of segments } \alpha}{\text{total number of moles of all segments}}
\]

(48)

The first perturbation term in Equation (45) is summed over all segment-pair interactions,

\[
a_1 = \sum_\alpha \sum_\beta x_\alpha x_\beta a_{1,\alpha\beta}
\]

(49)

where \( \alpha \) and \( \beta \) are the segment types and \( a_{1,\alpha\beta} \) is the first-order binary term for \( \alpha-\beta \) segment interaction given by (Gil-Villegas et al., 1997)

\[
a_{1,\alpha\beta} = -4 \left( \frac{\pi}{6} \sigma_{\alpha\beta}^3 N_A \rho \sum_i X_i m_i \right) u_{\alpha\beta} (\lambda_{\alpha\beta}^3 - 1) \bar{a}_o^{h3} (\sigma_{\alpha\beta}, \zeta_{3,eff})
\]

(50)
where \( \sigma_{\alpha\beta} \) is the distance between centers of segment \( \alpha \) and \( \beta \) at contact, \( u_{\alpha\beta} \) is the well depth of the square-well potential for the \( \alpha-\beta \) interaction and \( \lambda_{\alpha\beta} \) is the reduced range of the potential well for the \( \alpha-\beta \) interaction. The Lorentz and Berthelot combining rules are used for \( \sigma_{\alpha\beta} \) and \( u_{\alpha\beta} \),

\[
\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_\alpha + \sigma_\beta) \tag{51}
\]

\[
u_{\alpha\beta} = (u_\alpha u_\beta)^{1/2} \tag{52}
\]

In Equation (52), the potential-well depth of segment \( \alpha \) is a function of temperature to account for the non-central forces (Kreglewski and Wilhoit, 1974):

\[
u_{\alpha} = u_\alpha^0 \left(1 + \frac{10}{T}\right) \tag{53}
\]

where \( u_\alpha^0 \) is the temperature independent potential-well depth of segment \( \alpha \).

A simple arithmetic-mean combining rule may be used for \( \lambda_{\alpha\beta} \), analogous to that for the segment diameters:

\[
\lambda_{\alpha\beta} = \frac{1}{2}(\lambda_\alpha + \lambda_\beta) \tag{54}
\]

Equation (50) has been obtained from the mean value theorem (Gil-Villegas et al., 1997). Instead of applying the mean value distance \( \xi \) in the hard-sphere radial distribution function directly, the contact value is used but evaluated at an effective reduced density. Thus, the pair radial distribution function for a mixture of hard spheres in Equation (50) is calculated using Carnahan-Starling’s equation (Reed and Gubbins, 1973), but evaluated at the effective reduced variable \( \zeta_{\text{eff}} \).
The effective reduced variable $\zeta_{3,\text{eff}}$ is approximated from (Gil-Villegas et al., 1997):

$$\zeta_{3,\text{eff}} = c_1 \zeta_3 + c_2 \zeta_3^2 + c_3 \zeta_3^3 \quad (56)$$

where coefficients $c_1$, $c_2$ and $c_3$ are functions of $\lambda_{\alpha\beta}$. For $1.1 \leq \lambda_{\alpha\beta} \leq 1.8$, the coefficients are as follows:

$$
\begin{pmatrix}
  c_1 \\
  c_2 \\
  c_3 \\
\end{pmatrix} =
\begin{pmatrix}
  2.25855 & -1.50349 & 0.249434 \\
  -0.669270 & 1.40049 & -0.827739 \\
  10.1576 & -15.0427 & 5.30827 \\
\end{pmatrix}
\begin{pmatrix}
  1 \\
  \lambda_{\alpha\beta} \\
  \lambda_{\alpha\beta}^2 \\
\end{pmatrix} \quad (57)
$$

These coefficients have been derived for pure fluid with exact values of $a_l$ obtained from integration using accurate values of $g^{kh}(r)$ calculated by solving Ornstein-Zernike equation with Malijevsky and Labik formula. Equation (56) and (57) are extensions for mixtures.

The effective reduced variable $\zeta_{2,\text{eff}}$ is calculated from

$$\zeta_{2,\text{eff}} = \frac{\zeta_2}{\zeta_3} \zeta_{3,\text{eff}} \quad (58)$$

The second perturbation term in Equation (45) has the same form as the first term:

$$a_2 = \sum_x \sum_{\beta} x_{\alpha} x_{\beta} a_{2,\alpha\beta} \quad (59)$$

where $a_{2,\alpha\beta}$ is related to $a_{1,\alpha\beta}$ (McQuarrie, 1976; Gil-Villegas et al., 1997), as follows:

$$a_{2,\alpha\beta} = \frac{1}{2} \mu_{\alpha\beta} K^{kh} \rho \frac{\partial a_{1,\alpha\beta}}{\partial \rho} \quad (60)$$
In Equation (60), $K^{hs}$ is the Percus-Yevick expression for the isothermal compressibility of hard-sphere fluid (Reed and Gubbins, 1973),

$$K^{hs} = \frac{\zeta_0 (1 - \zeta_3)^3}{\zeta_0 (1 - \zeta_3)^2 + 6\zeta_1 \zeta_2 (1 - \zeta_3) + 9 \zeta_2^3} \quad (61)$$

Equation (45) truncated after $a_2$ and used with Equations (49), (59) and (60) is found (Barker and Henderson, 1972) to be unreliable at high densities. Barker and Henderson (Barker and Henderson, 1972), therefore, propose an empirical equation for $a_2$ that is fitted to Monte Carlo data.

We find, however, that this empirical equation does not give good results for real substances (Adidharma and Radosz, 1999). One approach to improve it, for example, is to include three-body forces in the intermolecular potential where the three-body distribution function may be estimated from a superposition approximation. However, the superposition approximation is reasonable only if $a_2$ is small.

Another approach to improve Equation (45) truncated after $a_2$ is to add a truncation correction that accounts for higher order terms. The higher-order terms make little contribution to the Helmholtz energy at high densities because, at sufficiently high density, the hard cores prevent the occurrence of large local density fluctuations. For example, on the basis of molecular dynamics results at high density (Alder et al., 1972), all $a_n$ beyond the second term can be neglected. However, at lower densities, the convergence is slow, the magnitude of $a_1$ decreases and the impact of the higher-order terms increases (Hansen and McDonald, 1976). In the critical region, where large fluctuations due to clustering of particles occur, the convergence is slow and the first two $a_n$ terms alone are not adequate.
We therefore propose an empirical correction, reminiscent of the Alder model (Alder et al., 1972), that accounts for the truncation error of the second order perturbation theory as follows:

\[
\bar{a}_i = \sum_{m=1}^{4} \sum_{n=1}^{2} D_{mn} \left( \frac{u}{kT} \right)^m \left( \frac{u}{\tau} \right)^n
\]  

(62)

where \( D_{mn} \)'s are universal constants, \( \tau = \sqrt{2\pi/6} \), and \( u/kT \) is evaluated in the spirit of the van der Waals one-fluid theory (vdW-1),

\[
\frac{u}{kT} = \frac{\sum_{\alpha} \sum_{\beta} x_\alpha x_\beta \left[ \frac{u_{\alpha\beta}}{kT} \right] (v^{\infty})_{\alpha\beta}}{\sum_{\alpha} \sum_{\beta} x_\alpha x_\beta (v^{\infty})_{\alpha\beta}}
\]  

(63)

where \( (v^{\infty})_{\alpha\beta} = \left[ \frac{1}{2} \left( (v^{\infty}_\alpha)^{1/3} + (v^{\infty}_\beta)^{1/3} \right) \right]^3 \)  

(64)

The molar volume of segment \( \alpha \) is related to the segment diameter as follows:

\[
v^{\infty}_\alpha = \frac{\pi}{6\tau} \sigma_\alpha^3 N_{Av}
\]  

(65)

The chain contribution in Equation (42), summed over all components, is related to the radial distribution function of the reference (segment) fluid as follows:

\[
\bar{a}^{\text{chain}} = -\sum_i X_i (m_i - 1) \left[ \ln \bar{g}^{\infty}_i (\sigma_{\alpha\beta}) - \ln \bar{g}^{\infty}_0 (\sigma_{\alpha\beta}) \right]
\]  

(66)

where \( \bar{g}^{\infty}_i (\sigma_{\alpha\beta}) \) for chain \( i \) is defined as

\[
\ln \bar{g}^{\infty}_i (\sigma_{\alpha\beta}) \equiv \sum_{\beta \neq \alpha} B_{\alpha\beta,i} \ln g^{\infty}_{\alpha\beta} (\sigma_{\alpha\beta})
\]  

(67)

where the summation is over all the bonds in chain \( i \), \( B_{\alpha\beta,i} \) is the bond fraction of type \( \alpha\beta \) in chain \( i \) defined as
\[ B_{a\beta,i} = \frac{\text{the number of bonds of type } a\beta \text{ in chain } i}{\text{the total number of bonds in chain } i} \quad (68) \]

and \( g_{a\beta}^{\text{sw}}(\sigma_{a\beta}) \) is the pair radial distribution function for a mixture of square-well segments calculated at contact. In Equation (66), \( g_{a\beta}^{\text{sw}}(\sigma_{a\beta}) \) is \( g_{i}^{\text{sw}}(\sigma_{a\beta}) \) evaluated at zero density.

The pair radial distribution function for a mixture of square-well segments \( g_{a\beta}^{\text{sw}}(\sigma_{a\beta}) \) is determined using Barker-Henderson perturbation theory (Henderson and Barker, 1971) of the first order, as follows

\[ g_{a\beta}^{\text{sw}}(\sigma_{a\beta}) = g_{a\beta}^{\text{hs}}(\sigma_{a\beta}) + \beta u_{a\beta} g_{1a\beta}(\sigma_{a\beta}) \quad (69) \]

where \( g_{a\beta}^{\text{hs}}(\sigma_{a\beta}) \) is the pair radial distribution function for a mixture of hard spheres given by Carnahan-Starling's equation (Reed and Gubbins, 1973)

\[ g_{a\beta}^{\text{hs}}(\sigma_{a\beta}) = \frac{1}{1 - \zeta_{3}} + \frac{3\sigma_{a}\sigma_{\beta}}{\sigma_{a} + \sigma_{\beta}} \frac{\zeta_{2}}{1 - \zeta_{3}} + 2 \left( \frac{\sigma_{a}\sigma_{\beta}}{\sigma_{a} + \sigma_{\beta}} \right)^{2} \left( \frac{\zeta_{2}}{1 - \zeta_{3}} \right)^{2} \quad (70) \]

and \( g_{1a\beta}(\sigma_{a\beta}) \) is the perturbation term (Gil-Villegas et al., 1997),

\[ g_{1a\beta}(\sigma_{a\beta}) = \frac{1}{4u_{a\beta}} \left[ \frac{1}{\frac{\pi}{6} \sigma_{a\beta}^{3} N_{\text{av}} \sum_{i} X_{i} m_{i}} \frac{\partial \lambda_{a\beta}}{\partial \rho} \right. \]

\[ \left. - \frac{\lambda_{a\beta}}{3 \left( \frac{\pi}{6} \sigma_{a\beta}^{3} N_{\text{av}} \rho \sum_{i} X_{i} m_{i} \right)} \frac{\partial \lambda_{a\beta}}{\partial \lambda_{a\beta}} \right] \quad (71) \]
3.4 Application to pure normal alkanes

Equations (42) through (71), with \( X_i = 1 \) and \( x_a = 1 \), are applied to pure \( n \)-alkanes. These equations require three potential parameters, i.e. \( \sigma \) (or \( \nu^\infty \)), \( u^0 \) and \( \lambda \), and one size parameter \( m \). The parameter \( m \) means the number of effective tangent spheres in a chain. In real chainlike molecules, the segmental units overlap so that the bond lengths can be much less than the segment diameters. The parameter \( m \), therefore, can have values that are not necessarily integers. If \( b \) is defined as the ratio of the bond length to the segment diameter \( \sigma \), the following relation for \( m \) can be developed (see Figure 14):

\[
m = 1 + b(n - 1) \quad (72)
\]

where \( n \) is the number of overlapping segmental units. If \( b = \frac{1}{k} \), where \( k = 2, 3, 4, 5... \), the best value of \( k \) that leads to the smallest average absolute deviation (AAD) of the alkane vapor pressures and liquid volumes is found to be \( k = 3 \), which agrees with the value reported by Gil-Villegas et al. (Gil-Villegas et al., 1997).

![Figure 14. Overlapping segment units.](image)

An equivalent form of Equation (72) can be derived for \( m \) as a linear function of molecular weight:

\[
m = 0.023763 MW + 0.618823 \quad (73)
\]
Along with $v^\infty$, $u^0/k$ and $\lambda$, we obtain the universal constants ($D_{mn}$'s) in Equation (62) (truncation correction) by simultaneously fitting the second virial coefficient, saturated vapor pressure and saturated liquid volume of ethane; the results are shown in Table 5.

Using these ethane-derived $D_{mn}$'s, without further readjustment, we fit the saturated vapor pressures and saturated liquid densities of other $n$-alkanes to obtain $v^\infty$, $u^0/k$ and $\lambda$. The results are shown in Table 6; $v^\infty$ is in cm$^3$/mol and $u^0/k$ is in K. The experimental data and their temperature ranges are the same as in SAFT (Huang and Radosz, 1990). Table 6 suggests that $v^\infty$, $u^0/k$ and $\lambda$ approximately reach asymptotic values upon increasing the molecular weight, which is physically reasonable.

Table 5. The universal constants $D_{mn}$ in Equation (62)

| $D_{11}$ | 0.2933 |
| $D_{21}$ | 2.8222 |
| $D_{31}$ | -8.9554 |
| $D_{32}$ | 3.4764 |
| $D_{12}$ | 0.9358 |
| $D_{22}$ | 6.8199 |

Table 6. The SAFT1 parameters for $n$-alkanes

<table>
<thead>
<tr>
<th>$n$-alkane</th>
<th>$m$</th>
<th>$v^\infty$</th>
<th>$u^0/k$</th>
<th>$\lambda$</th>
<th>AAD P (%)</th>
<th>AAD V (%)</th>
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<tbody>
<tr>
<td>methane</td>
<td>1</td>
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<td>0.80</td>
<td>1.2</td>
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<td>193.223</td>
<td>1.6914</td>
<td>0.95</td>
<td>0.87</td>
</tr>
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<td>n-butane</td>
<td>2</td>
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<td>210.600</td>
<td>1.6797</td>
<td>1.8</td>
<td>1.1</td>
</tr>
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<td>0.58</td>
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<td>1.5</td>
<td>0.62</td>
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<td>231.353</td>
<td>1.6793</td>
<td>1.3</td>
<td>0.68</td>
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<td>n-octane</td>
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<td>1.6758</td>
<td>0.97</td>
<td>0.42</td>
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<td>1.6798</td>
<td>0.57</td>
<td>0.43</td>
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<td>1.6703</td>
<td>0.50</td>
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<td>1.6</td>
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<td>1.6646</td>
<td>1.8</td>
<td>0.06</td>
</tr>
</tbody>
</table>
We plot the parameters against the molecular weight as shown in Figure 15. The parameters are well behaved, and can be represented by the following equations:

\[ m v^\infty = 0.59911 MW + 4.64026 \]  \hspace{1cm} (74)

\[ \frac{m u^o}{k} = 6.70234 MW + 19.67793 \]  \hspace{1cm} (75)

\[ m\lambda = 0.039308 MW + 1.104297 \]  \hspace{1cm} (76)

\( m v^\infty \) in Equation (74) is the volume occupied by a mole of molecules in a close-packed arrangement. Equations (74)-(76) provide a basis for estimating \( u^o/k \) and \( \lambda \) for \( n \)-alkanes if there are no experimental data available. The fact that linear functions fit the data well makes it possible to extrapolate to higher molecular weights.

Figure 15. SAFT1 parameters for \( n \)-alkanes as functions of molecular weight.
In Figure 16 and 17, the AAD for the saturated liquid volume and saturated vapor pressure are plotted against the carbon number. A substantial improvement in fitting the saturated liquid is likely attributable to a better representation of the attractive forces in SAFT1; SAFT does not account for the effect of attractive forces on the chain formation.

Figure 16. Percent average absolute deviation (AAD) of the calculated values from the experimental values for the molar liquid volume of n-alkanes, in the state of saturation.

The parameters reported in Table 6 are used without further readjustment to predict other properties. For example, Figure 18 and 19 illustrate the prediction of the second virial coefficient. This is a good test in the low-density limit, where the convergence of Equation (45) is slow. Figure 18 shows the importance of including the truncation correction for n-butane using SW-SAFT (without the correction) (Adidharma and Radosz, ) and SAFT1 (with the correction), with all the other elements of our
approach being the same. We find that, without the truncation correction, SW-SAFT systematically overpredicts the second virial coefficient at all temperatures. Figure 19, on the other hand, presents a comparison with SAFT. While not perfect, especially at low temperatures, SAFT1 is more accurate in estimating the second virial coefficient.

In another example, the coexisting vapor and liquid densities for propane are plotted as T-p and P-p diagrams in Figure 20 and 21. This is a further illustration of how significant the truncation correction can be, away and near the critical region.

Further examples compare SAFT1 to SAFT in reproducing the coexisting vapor and liquid density for propane and n-octane in a T-p diagram in Figure 22, and the saturated vapor pressure in Figure 23. Figure 24 illustrates similar comparisons for the Sanchez-Lacombe and Peng-Robinson equation of state.
SAFT1 is also used to predict the thermal properties, such as the heat of vaporization and the heat capacity. Figure 25 shows an example for the heat of vaporization of ethane and n-octane at the boiling point. The prediction agrees well with the experimental data, except near the critical point because no crossover correction is included in this example. A good representation of the heat of vaporization is not surprising because SAFT1 well represents the vapor pressure.

Figures 26 and 27 are examples of the estimated heat capacity for liquid n-octane and ethane. In Figure 26, the heat capacity of liquid n-octane is predicted in the state of saturation. The examples for the other equations are only to illustrate the extent of possible error; these equations of state were not intended, but are used, for thermal properties. In Figure 27, the heat capacity of ethane is predicted near and above its critical point.
Figure 19. Second virial coefficients of n-alkanes, C_1 to C_4, experimental (Dymond and Smith, 1980) (points) and predicted (curves).

Figure 20. Effect of adding the truncation-error correction on the coexisting vapor and liquid density of propane (T-\rho diagram), experimental (Vargaftik, 1975) (points) and calculated (curves).
Figure 21. Effect of adding the truncation-error correction on the coexisting vapor and liquid density of propane (P-$\rho$ diagram), experimental (Vargaftik, 1975) (points) and calculated (curves).

Figure 22. Coexisting vapor and liquid density for propane and $n$-octane, experimental (Vargaftik, 1975) (points) and calculated (curves).
Figure 23. Saturated vapor pressure for propane and n-octane, experimental (Vargaftik, 1975) (points) and calculated (curves).

Figure 24. Coexisting vapor and liquid density for n-octane, experimental (Vargaftik, 1975) (points) and calculated (curves).
Figure 25. Heat of vaporization of ethane and n-octane at the boiling point, experimental (Vargaftik, 1975) (points) and predicted (curves).

Figure 26. Heat capacity for liquid n-octane, experimental (points (Vargaftik, 1975) and dashed lines (Stull et al., 1969)) and predicted (solid curves).
3.5 Application to mixtures

We apply SAFT1 to predict the phase equilibria in mixtures without using any adjustable binary parameters: such a parameter is introduced in Equation (52), but it is arbitrarily set equal to zero in this work. Our focus is not on the quality of fit, but on what can be predicted without fitting.

Figure 28 illustrates the prediction of equilibrium phase compositions for an asymmetric mixture of small molecules, such as ethane+n-decane. The result suggests that both SAFT and SAFT1 can reasonably represent the experimental data. In this case, and in other figures, SAFT is also used with the binary interaction parameter set equal to zero. As reported by Pan (Pan and Radosz, 1998), however, a small but constant value of $k_{ij} = 0.03$ will make SAFT nearly as accurate as SAFT1 for such systems.
Figure 28. Vapor-liquid equilibria in ethane+n-decane system at 378 K, experimental (Reamer and Sage, 1962) (points) and predicted (curves).

Figure 29 is an example of predicted cloud points for a homo-segmented polymer solution, such as propane+polyethylene. The experimental data are taken from literature (Ehrlich and Kurpen, 1963). The SAFT1 parameters for the polymer are estimated from Equations (73) through (76). This example is used to probe the sensitivity of the cloud-point predictions to small changes in parameter $\lambda$ ($\lambda$ for the polymer estimated from Equation (76) is 1.654). These results suggest that the predicted phase equilibria sensitively depend on $\lambda$. Hence, the Equation (76) or the mixing rule for $\lambda$ may need further refinements.

Figure 30 is an example of cloud-point pressures for a hetero-segmented polymer solution, such as propane+poly(ethylene-co-hexene-1) (Chan and Radosz, 1998).
Poly(ethylene-co-hexene-1) is a random copolymer with butyl branches attached to a polyethylene backbone. The size parameter $m$ is calculated from Equation (73) and the other parameters are estimated as follows. We model the polymer as a macromolecule consisting of two types of segments, i.e. the backbone type and the branch type, which have different SAFT1 parameters ($v^\infty$, $u^\infty/k$ and $\lambda$); see Figure 31. For the backbone-type segments, the parameters are estimated from Equation (74) through (76); they are practically constant at this molecular weight. Since each side branch contains 4 carbons, the branch-type segments are assumed to have the same SAFT1 parameters as $n$-butane. We use the same method for the copolymer SAFT (Banaszak et al., 1996) prediction. The results in Figure 30 suggest that SAFT1 can quantitatively predict the cloud point.
curve; copolymer SAFT can be used to estimate such data with a non-zero binary parameter (Pan and Radosz, 1998).

Figure 30. Cloud point pressure of EH+propane system at 453 K as a function of polymer composition, experimental (Chan and Radosz, 1998) (points) and predicted (curves).

Figure 31. Segment model for poly(ethylene-co-hexene-1).
Figure 32 shows a similar example for two propane+poly(ethylene-butene-1) solutions (Chen et al., 1995). This example is calculated using the same approach as that in Figure 30, except the branch-segment parameters are taken to be the same as those for ethane.

The preliminary examples used in this work are to demonstrate that it is possible to predict the alkane-mixture properties on the basis of pure-component parameters alone. Much more work is needed to demonstrate that this approach can be more general.

3.6 Conclusion

The square-well-fluid thermodynamics and liquid structure derived from Barker Henderson’s perturbation theory, including a truncation correction, are used within a SAFT framework to develop a prototype of an engineering equation of state for alkane
chains. The truncation correction is found to improve the representation of pure-component properties in the low-density range, high-density range and critical region. The critical region representation is further improved using a crossover correction.

For small \textit{n}-alkanes, not only the vapor pressure and liquid density (that are correlated), but also the second virial coefficient, heat of vaporization, and heat capacity (that are predicted) are found to be more accurate. Their parameters are found to be well behaved, and hence easy to estimate reliably for high-molecular-weight alkanes and polyolefins. For mixtures of small and large, homo- and hetero-segmented, molecules, the phase equilibria are found to be reasonably predicted.
Chapter 4
Crossover SAFT Equation of State

4.1 Introduction

Many molecular-thermodynamic based equations of state have been developed in the past few years to accurately represent the thermodynamic properties of fluids and fluid phase equilibria both in the sub- and supercritical regions. However, all of them, including equations of state developed in the SAFT framework, fail to represent correctly the critical region. In particular, they predict coexistence curves and pressure-density isotherms that are insufficiently flat in the critical region.

In the classical theory (mean field theory), each molecule is subject to the effect of all other molecules while fluctuations are neglected. It is this assumption that makes the classical equations of state misrepresent the critical region. In the critical region, long-range density fluctuations exist well beyond the extent of the range of molecular potentials. This long-range fluctuations cause singular behavior of thermodynamic properties and affect these properties in a substantial range of temperatures and densities around the critical point (Sengers, 1994).

According to the classical mean-field concept of critical phenomena, asymptotically close to the critical point, any classical equation of state can be expanded in a Taylor series in density and temperature (van Pelt and Sengers, 1995); the expansion is referred to as the Landau expansion. Although this Landau expansion yields the functional form of the power laws close to the critical point, it does not reproduce the
correct critical exponents. For example, the asymptotic temperature dependence of the coexistence density from this expansion is parabolic, i.e. the critical exponent is 0.5, while the non-classical critical exponent for this property is 0.326.

Renormalization-group theory has been developed to deal with the effects of critical fluctuations and the so-called Wegner expansion has been obtained (Ley-Koo and Green, 1981). This non-classical expansion gives the correct exponents of the power laws. The so-called crossover procedure can be applied to modify the Landau expansion of the classical equation of state, in such a way that close to the critical point it will reproduce the Wegner expansion.

In this work, we apply this crossover procedure to SAFT equation of state (Huang and Radosz, 1990), so that the equation of state will reproduce the correct physical behavior of properties in the asymptotic critical region. The theoretical approach we implement here has been originally developed by Sengers (Chen et al., 1990) and has been modified and applied to some simple empirical equations of state such as van der Waals (Wyczalkowska et al., April 1998) and Carnahan-Starling-DeSantis (van Pelt et al., 1994; Edison, 1998), but it has not been implemented to theoretical-based equations of state.

4.2 SAFT equation of state and its parameters

The SAFT equation of state is defined in terms of the residual Helmholtz energy per mole, $a^{\text{res}}$. For non-associating molecules, the molar residual Helmholtz energy consists of two terms (Huang and Radosz, 1990):

$$\frac{a^{\text{res}}}{RT} = \tilde{a}^{\text{res}} = \tilde{a}^{\text{seg}} + \tilde{a}^{\text{chain}} \quad (77)$$
where $\tilde{\alpha}\text{seg}$ is the Helmholtz energy due to segment-segment interactions, and is considered to be the reference term; $\tilde{\alpha}\text{chain}$ is the incremental Helmholtz energy due to chain formation. Tilde (~) in this work means a dimensionless form of a variable.

The segment contribution is given by

$$\tilde{\alpha}\text{seg} = m(\tilde{\alpha}_o^{hs} + \tilde{\alpha}_o^{disp})$$

(78)

where $m$ is the number of segments per molecule, the first parameter of the SAFT equation of state, and $\tilde{\alpha}_o^{hs}$ is the Helmholtz energy of hard-sphere fluids per segment given by Carnahan-Starling (Carnahan and Starling, 1969):

$$\tilde{\alpha}_o^{hs} = \left[\frac{4\eta - 3\eta^2}{(1 - \eta)^2}\right]$$

(79)

In Equation (79), $\eta$ is the reduced density (segment packing fraction or volume fraction of segment) defined as

$$\eta = \frac{\pi N_{Av}}{6} \rho m d^3$$

(80)

Here, $N_{Av}$ is the Avogadro number, $\rho$ is the molar density and $d$ is the effective diameter of the hard spherical segment (the temperature-dependent segment diameter). Using the inverted square-well potential, Chen and Kreglewski (Chen and Kreglewski, 1977) expressed $d$ as

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

(81)

where $\sigma$ is the center-to-center distance between two segments, at which the pair potential of the real fluid is zero (the temperature-independent segment diameter), $k$ is the Boltzmann constant ($1.381 \times 10^{-23}$ J/K), $C = 0.12$ for all fluids except those strongly
associated, and \( u^0/k \) is the temperature-independent well depth of the square-well potential, the second SAFT parameter. The temperature-independent segment diameter, \( \sigma \), provides basis for the third SAFT parameter, which is the temperature-independent segment molar volume in a closed-packed arrangement defined per mole of segments:

\[
v^{\infty} = \frac{\pi N_A \sigma^3}{6}
\]

where \( \tau = \sqrt{2\pi}/6 \).

The dispersion part in Equation (78), \( \tilde{a}_o^{\text{disp}} \), is given by (Chen and Kreglewski, 1977):

\[
\tilde{a}_o^{\text{disp}} = \sum_i \sum_j D_{ij} \left[ \frac{u}{kT} \right]^i \left[ \frac{\eta}{\tau} \right]^j
\]

where \( D_{ij} \)'s are universal constants and \( u \) is the temperature-dependent well depth defined as

\[
u = u^0 \left[ 1 + \frac{e}{kT} \right]
\]

Here, \( e/k \) is a constant that is related to Pitzer’s acentric factor and the critical temperature, but since the energy parameter is for segments rather than for molecules, \( e/k = 10 \) for SAFT molecules (Huang and Radosz, 1990).

The chain contribution, \( \tilde{a}_\text{chain} \) in Equation (77), is related to the radial distribution function of the hard-sphere fluid at contact, \( g^{hs}(d) \), as follows:

\[
\tilde{a}_\text{chain} = -(m-1) \ln g^{hs}(d)
\]

where

\[
g^{hs}(d) = \frac{1 - \frac{1}{2 \eta}}{(1-\eta)^3}
\]
4.3 The classical Helmholtz energy density

4.3.1 The SAFT parameters are closely related to the classical critical parameters

We find that the parameter \( v^\infty \) controls only the classical critical molar volume (or critical density), while the parameter \( u^o/k \) controls only the classical critical temperature. Let us relate the SAFT parameters to the classical critical parameters by solving the criticality conditions

\[
\left( \frac{\partial P}{\partial \rho} \right)_T = \left( \frac{\partial^2 P}{\partial \rho^2} \right)_T = 0
\]

where \( P \) is the pressure, \( \rho \) is the molar density and \( T \) is the temperature.

We use this approach to build correlations for \( v^\infty \) and \( u^o/k \). In general, for a pure substance, the classical critical molar volume changes linearly with \( v^\infty \), and the classical critical temperature changes linearly with \( u^o/k \). For example, we can develop general expressions for \( n \)-alkanes that relate the SAFT parameters \( v^\infty \) and \( u^o/k \) to the classical critical points as follows:

\[
v^\infty = f_v(m)v_{co}
\]

\[
u^o/k = f_T^o(m)T_{co}
\]

where \( v_{co} \) is the classical critical molar volume, \( T_{co} \) is the classical critical temperature, \( f_v(m) \) and \( f_T^o(m) \) are the proportionality functions fitted to the calculated data, as shown in Figures 33 and 34,

\[
f_v(m) = 0.00836 + 0.12526e^{\frac{m-1}{0.5225}} + 0.09177e^{\frac{m-1}{2.56707}}
\]

\[
f_T^o(m) = 0.26993 + 0.376976e^{\frac{m-1}{0.54850}} + 0.34323e^{\frac{m-1}{3.37972}}
\]
4.3.2 Reduced form of SAFT

In the crossover procedure, one needs to represent the equation of state in terms of the dimensionless variables reduced with the classical critical parameters $\rho_{co}$, $T_{co}$ and $P_{co}$. Therefore, we define

\[ \Delta \tilde{\rho}_o = \frac{\rho - \rho_{co}}{\rho_{co}} \]  
\[ \Delta \tilde{T}_o = \frac{T - T_{co}}{T} \]  
\[ \tilde{P} = \frac{P}{P_{co}} \frac{T_{co}}{T} \]  
\[ \tilde{A}_v = \frac{A}{V} \frac{T_{co}}{T} \frac{1}{P_{co}} \]  

[Figure 33. Proportionality function for $\nu^\infty$ of $n$-alkanes.]

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Figure 34. Proportionality function for $u^o/k$ of $n$-alkanes.

We also define reduced SAFT parameters

\[
\tilde{\nu}^\infty = \frac{\nu^\infty}{\nu_{co}} = f_\nu(m)
\]

(96)

\[
\tilde{u}^o = \frac{u^o}{kT_{co}} = f_T^o(m)
\]

(97)

In terms of these reduced variables and reduced parameters, the Helmholtz energy density of SAFT, i.e. the Helmholtz energy per unit volume, can be written as:

\[
\tilde{\Lambda}_v(\Delta \rho_o, \Delta T_o) = \frac{(\Delta \rho_o + 1)}{Z_{co}} \left[ m \left\{ \frac{4c_1 (\Delta \rho_o + 1) - 3c_1^2 (\Delta \rho_o + 1)^2}{(1-c_1(\Delta \rho_o + 1))^2} \right\} 
+ m \sum_i \sum_j D_y(i) \left( \frac{c_1 (\Delta \rho_o + 1)}{\tau} \right)^j \right]
\]

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-(m-1)\ln\left\{\frac{2-c_1(\Delta \tilde{\rho}_o+1)}{2(1-c_1(\Delta \tilde{\rho}_o+1))^3}\right\} + \ln(\Delta \tilde{\rho}_o+1) \quad (98)

where
\[ Z_{co} = \frac{P_{co} v_{co}}{RT} \quad (99) \]
\[ c_1 = mn \tilde{v}_oo \left[1 - C \exp(3 \tilde{\nu}_o (\Delta \tilde{T}_o - 1))\right] \quad (100) \]
\[ \tilde{\nu} = f_T(m) \left[1 - \frac{\tilde{\nu}}{k} \Delta \tilde{T}_o \right] (1 - \Delta \tilde{T}_o) \quad (101) \]
\[ \frac{\tilde{e}}{k} = \frac{e}{kT_{co}} - \frac{f_T^o(m)}{f_T(m)} \quad (102) \]

In Equations (101) and (102), \( f_T(m) \) is a proportionality function that relates \( u/k \) calculated at the classical critical temperature to the classical critical temperature

\[ \left( \frac{u}{k} \right)_{T=T_{co}} = f_T(m)T_{co} \quad (103) \]

and is also fitted to the calculated data, as shown in Figure 35,

\[ f_T(m) = 0.27191 + 0.374516e^{-0.60\tilde{\nu}} + 0.34887e^{-0.33\tilde{\nu}} \quad (104) \]

The reduced SAFT equation for pressure is given by:

\[ P(\Delta \tilde{\rho}_o, \Delta \tilde{T}_o) = \frac{(\Delta \tilde{\rho}_o+1)}{Z_{co}} \left[ m \left\{ \frac{4c_1(\Delta \tilde{\rho}_o+1) - 2c_1^2(\Delta \tilde{\rho}_o+1)^2}{(1-c_1(\Delta \tilde{\rho}_o+1))^3} \right\} \right. 
\[ + m \sum \sum_j jD_j(\tilde{\nu})^j \left( \frac{c_1(\Delta \tilde{\rho}_o+1)}{\tau} \right)^j 
\[ - (m-1) \left\{ \frac{5c_1(\Delta \tilde{\rho}_o+1) - 2c_1^2(\Delta \tilde{\rho}_o+1)^2}{(1-c_1(\Delta \tilde{\rho}_o+1))(2-c_1(\Delta \tilde{\rho}_o+1))} \right\} + 1 \right] \quad (105) \]
4.3.3 The expression for the critical part of the Helmholtz energy density

Asymptotically close to the critical point, SAFT Helmholtz energy density, i.e. Equation (98), can be expanded in a Taylor series in density and temperature. After collecting terms, the Helmholtz energy density can be rewritten as the summation of three terms

$$
\tilde{A}_v(\Delta \tilde{\rho}, \Delta \tilde{T}) = \tilde{A}_{v0}(\Delta \tilde{T}) + \Delta \tilde{\rho} \tilde{\mu}_0(\Delta \tilde{T}) + \Delta \tilde{A}_v(\Delta \tilde{\rho}, \Delta \tilde{T})
$$

(106)

The first two terms on the right side of Equation (106), i.e. the terms that are zeroth and first order in $\Delta \tilde{\rho}$, are referred to as the background terms and given by the following expressions:
The third term, that represents the remaining higher order terms, is the critical part of the Helmholtz energy density,

\[
\tilde{A}_{\nu}(\Delta \tilde{T}_o) = \frac{1}{Z_{co}} \left[ m \left\{ \frac{4c_1 - 3c_1^2}{(1-c_1)^2} \right\} + m \sum_i \sum_j D_y(u) \left( \frac{c_1}{\tau} \right)^j \right] \\
- (m - 1) \ln \left[ \frac{2 - c_1}{2(1-c_1)^3} \right] 
\]

(107)

\[
\tilde{\mu}_0(\Delta \tilde{T}_o) = \tilde{A}_{\nu}(\Delta \tilde{T}_o) + \tilde{P}(\Delta \tilde{\rho}_o = 0, \Delta \tilde{T}_o) 
\]

(108)

It is this term that plays a role in the critical behavior of fluids.

4.4 The renormalized Helmholtz energy density

The extended crossover procedure is used to renormalize the critical part of the Helmholtz energy density. A detailed and comprehensive description on this procedure is given in the literature (Edison, 1998).
A renormalized SAFT Helmholtz energy density, \( \tilde{A}_{V,x} \), which incorporates the
effects of the critical fluctuations, can be obtained by applying the following
transformation:

\[
\tilde{A}_{V,x} = \tilde{A}_{V,0}(\Delta \tilde{T}_o) + \Delta \tilde{\rho}_o \tilde{\mu}_0(\Delta \tilde{T}_o) + \Delta \tilde{A}_{V,x}
\]  

(110)

with

\[
\Delta \tilde{A}_{V,x} = \Delta \tilde{A}_v \left( \Delta \tilde{\rho}_v = \Delta \tilde{\rho}_x, \Delta \tilde{T}_v = \Delta \tilde{T}_x \right) - \frac{1}{2} S_\xi \Delta \tilde{T}^2 K
\]

(111)

where

\[
\Delta \tilde{\rho}_x = \Delta \tilde{\rho} D^2 U^4 - (1 + \Delta \tilde{\rho}) \Delta \tilde{\rho}_{sh} G U^{-2}
\]

(112)

\[
\Delta \tilde{T}_x = \Delta \tilde{T} \tau U^{-2} + (1 - \Delta \tilde{T}) \Delta \tilde{T}_{sh} G U^{-2}
\]

(113)

\[
\Delta \tilde{\rho}_{sh} = \frac{\rho_{co} - \rho_c}{\rho_{co}}
\]

(114)

\[
\Delta \tilde{T}_{sh} = \frac{T_{co} - T_{co}}{T_c}
\]

(115)

\[
\Delta \tilde{\rho} = \frac{\rho - \rho_c}{\rho_c}
\]

(116)

\[
\Delta \tilde{T} = \frac{T - T_c}{T}
\]

(117)

The functions \( D, U, \tau, K \) and \( G \) used in this transformation are defined in terms of a
crossover function \( Y \) as follows:

\[
D = Y^{\Delta s}
\]

(118)

\[
U = Y^{\Delta s}
\]

(119)

\[
\tau = Y^{\Delta s}
\]

(120)
\[
K = \frac{\nu}{\alpha u \Lambda} \left[ Y^{-\Delta_1} - 1 \right] 
\]

\[
G = \left[ \frac{\lambda}{1 - (1 - \lambda)Y} \right]^{2\nu} Y^{\Delta_2} 
\]

where \( \alpha, \gamma, \nu, \) and \( \Delta_1 \) are the universal critical exponents (see Table 7), and \( \lambda, \bar{u} \) and \( \Lambda \) are the crossover parameters that need to be determined from experimental data. The shift crossover function \( G \) governs how the critical parameters of the model change from the classical critical parameters to the observed (real) critical parameters (van Pelt et al., 1994).

The crossover function \( Y \) is determined from

\[
l - (l - \bar{u})Y = \bar{u} \left[ 1 + \left( \frac{\Lambda}{\kappa} \right)^2 \right]^{\frac{1}{2}} Y^{\Delta_1} 
\]

where

\[
\kappa^2 = C_k Y^{2\Delta_1} \kappa_o^2(\Delta \tilde{\rho}_x, \Delta \tilde{T}_x) 
\]

\[
\kappa_o^2(\Delta \tilde{\rho}_o, \Delta \tilde{T}_o) = \frac{\partial^2 \Delta \tilde{A}_y(\Delta \tilde{\rho}_o, \Delta \tilde{T}_o)}{\partial \Delta \tilde{\rho}_o^2} 
\]

The variable \( \kappa^2 \) is a measure of the distance from the observed critical point. From Equation (123), it follows that \( Y \to 1 \) as \( \kappa^2 \to \infty \) and the classical expression is recovered.

The scale factors \( S_k \) and \( C_k \) that appear in Equations (111) and (124) are calculated from

\[
S_k = \left( \frac{\mu^* \bar{u} \Lambda}{\tilde{A}_{40}} \right) \tilde{A}_{21}^2 
\]
where \( u^* \) is a universal constant (see Table 7), and \( \tilde{A}_{21} \) and \( \tilde{A}_{40} \) are calculated from SAFT:

\[
\tilde{A}_{21} = \left( \frac{\partial^3 \tilde{A}}{\partial \rho_o^2 \partial T_o} \right)_{\Delta \rho_o=0, \Delta T_o=0} = 8.9914
\]

\[
\tilde{A}_{40} = \left( \frac{\partial^4 \tilde{A}}{\partial \rho_o^4} \right)_{\Delta \rho_o=0} = 8.0646
\]

We will refer to the model described in this section as crossover SAFT.

4.5 Coexisting curves and vapor pressure of propane

Using parameters and constants listed in Table 7, we fit the experimental saturated liquid volume and vapor pressure of propane to obtain the adjustable crossover parameters, i.e. \( \lambda, \bar{u}, \) and \( \Lambda. \)

Figure 36 illustrates the coexisting curves (T-\( \rho \) diagram) calculated using SAFT and crossover-SAFT. We notice that the critical region is well represented by crossover-SAFT. However, the liquid density representation becomes slightly worse. Using the same set of crossover parameters, but without the density shift, i.e. by setting \( \Delta \bar{\rho}_{sh} = 0 \) in Equation \((112)\), improves the representation of the liquid density. The result is shown with the solid curve in Figure 36.

Next, by trial and error, we find another set of crossover parameters without the density shift that best represent T-\( \rho \), P-\( \rho \) and P-T diagrams. These parameters are used to calculate examples shown in Figures 37, 38 and 39.
Table 7. Non-adjustable parameters and constants in the Crossover SAFT equation of state for propane

<table>
<thead>
<tr>
<th>Universal critical exponents</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu = 0.63$ \hspace{1cm} $\gamma = 1.24$ \hspace{1cm} $\Delta_\alpha = 0.51$ \hspace{1cm} $\alpha = 2 - 3\nu$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Observed critical parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c = 369.8$ K \hspace{1cm} $P_c = 42.48$ bar \hspace{1cm} $\rho_c = 5.000 \times 10^{-3}$ mol/cc</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Classical critical parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{co} = 388.05$ K \hspace{1cm} $P_{co} = 52.29$ bar \hspace{1cm} $\rho_{co} = 4.545 \times 10^{-3}$ mol/cc</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Universal constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$u^* = 0.472$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SAFT parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m = 2.696$ \hspace{1cm} $v^\infty = 13.457$ \hspace{1cm} $u^*/k = 193.03$</td>
</tr>
</tbody>
</table>

While not perfect, the crossover SAFT improves the critical region representation. Also, as we notice from Figure 37, 38 and 39, the crossover SAFT does not deteriorate the performance of the classical SAFT in the range far away from the critical region.

However, we find that this procedure behaves incorrectly in the supercritical region very close to the critical point; note the behavior of the isotherms in Figure 40. We suspect that the temperature shift, i.e. Equation (113), may not be implemented correctly; the renormalization changes the sign of temperature distance from positive to
negative before reaching the critical point. We will address this problem in our future work.

Another challenge we should resolve in our future work is how to keep the number of parameters low. There is a total of nine parameters in this crossover SAFT, three classical SAFT parameters, i.e. $m$, $v^\infty$ and $u^0/k$, three crossover parameters, i.e. $\lambda$, $\bar{u}$ and $\Lambda$, and three critical parameters, i.e. $T_c$, $P_c$ and $\rho_c$. One possibility is to develop correlations between the classical critical parameters and the real critical parameters. Another possibility is to develop simple correlations of the crossover parameters, e.g. as functions of molecular weight.
Figure 37. Calculated coexisting vapor and liquid density (T-\(\rho\) diagram) for propane using SAFT and Crossover SAFT (without density shift and using the best set of crossover parameters), experimental (Vargaftik, 1975) (points) and calculated (curves).

4.6 Conclusion

The crossover procedure, with and without the density shift, is applied to incorporate the effect of the critical fluctuations into the SAFT equation of state. We find that the procedure without the density shift seems to be more suitable for SAFT. Much work needs to be done to correct the temperature shift and develop correlations for the parameters.
Figure 38. Calculated coexisting vapor and liquid density (P-\(\rho\) diagram) for propane using SAFT and Crossover SAFT (without density shift and using the best set of crossover parameters), experimental (Vargaftik, 1975) (points) and calculated (curves).
Figure 39. Calculated vapor pressure for propane using SAFT and Crossover SAFT (without density shift and using the best set of crossover parameters), experimental (Vargaftik, 1975) (points) and calculated (curves).

Figure 40. Isotherms of propane in the supercritical region very close to the critical point.
Chapter 5
SAFT1 for Associating Fluids: Pure Alkanols

5.1 Introduction

In order to predict the physical properties and phase behavior of self- and cross-associating fluids, such as \( n \)-alkanols, one needs thermodynamic models that account for specific interactions that lead to molecular association. One approach to developing such models is on the basis of perturbation theory, such as Statistical Associating Fluid Theory (SAFT).

An early engineering version of SAFT (Huang and Radosz, 1990), which treats molecules as chains of hard-sphere repulsive segments with dispersion interactions, has been applied to many real associating fluids. There are other versions of SAFT that have also been applied to associating fluids. For example, SAFT-HS, which treats molecules as chains of repulsive hard-sphere segments with van der Waals interactions, has been applied to model hydrogen fluoride, water, and alkanols (Galindo et al., 1997; Garcia-Lisbona et al., 1998). SAFT-LJ, which treats molecules as chains of Lennard-Jones segments, has been applied to model alkanols and water (Kraska and Gubbins, 1996a; Blas and Vega, 1998).

On the other hand, SAFT1 (Adidharma and Radosz, 1998), which treats molecules as chains of square-well segments, similar to SAFT-VR (Gil-Villegas et al., 1997), has been found to be attractive for macromolecular systems, but it has not been extended to model associating fluids yet. It is, therefore, the purpose of this work to
extend SAFT1 to associating fluids and test it on pure alkanols. This is a preliminary step toward extending SAFT1 to associating polymers, which is our long-range goal.

5.2 Potential model

The general form of the total potential of the associating fluids consists of a core potential and association site potentials:

$$\phi(12) = \phi_{\text{core}}(r) + \sum_{A \in \Gamma} \sum_{B \in \Gamma} \phi_{AB}(r_{AB})$$

in which \((12)\) designates the distance and orientation coordinates between molecules 1 and 2, \(r\) is the center-to-center distance between cores (segments), and \(r_{AB}\) is the center-to-center distance between association site \(A\) and \(B\). The summation in Eq. (128) is carried out over the set of association sites denoted by \(\Gamma\).

To use Eq. (128), potential models for the core and association sites must be postulated. For the core, we postulate a SW potential as in SAFT1 for non-associating fluids (Adidharma and Radosz, 1998). For the association sites, we neglect long-range interactions, e.g. electrostatic interaction, and assume their potential to be of a simple SW type too, as proposed by Jackson et al. (Jackson et al., 1988).

Various kinds of geometry of the site potential have been used in the previous studies of Wertheim's theory (Jackson et al., 1988; Chapman, 1990; Walsh and Gubbins, 1993), but we only apply one kind of geometry that is mathematically simple, as shown in Figure 41 (Jackson et al., 1988). Therefore, our SAFT1 associating molecules consist of SW cores with off-center SW association sites. In this model, bonding between two sites occurs only if the molecules are close enough to bond (within a certain cutoff radius...
and if the molecules are in the correct orientations (within the constraints $|\theta_1| \leq \theta_c$ and $|\pi - \theta_2| \leq \theta_c$). Thus, the SW site-site interaction is given by

$$\phi_{AB}(r) = \begin{cases} 
-\varepsilon_{AB} & r \leq r_c \text{ and } |\theta_1| \leq \theta_c \text{ and } |\pi - \theta_2| \leq \theta_c \\
0 & r > r_c \text{ and } |\theta_1| > \theta_c \text{ and } |\pi - \theta_2| > \theta_c 
\end{cases} \quad (129)$$

where $\varepsilon_{AB}$ is the well depth of the site-site potential.

![Figure 41. Schematic representation of the associating sites.](image)

5.3 SAFT1 equation of state

For associating fluids, the dimensionless residual Helmholtz energy of chain molecules is given by

$$\tilde{a}^{\text{res}} = \frac{a^{\text{res}}}{RT} = \tilde{a}^{\text{seg}} + \tilde{a}^{\text{chain}} + \tilde{a}^{\text{assoc}} \quad (130)$$

where $\tilde{a}^{\text{seg}}$ is the segment term, which is the reference Helmholtz energy due to segment-segment interactions, $\tilde{a}^{\text{chain}}$ is the chain term, which is the perturbation Helmholtz energy due to chain formation, and $\tilde{a}^{\text{assoc}}$ is the association term, which is the Helmholtz energy change due to association. Tilde ($\tilde{\cdot}$) used in this work means a dimensionless form of a variable.

The segment term (Adidharma and Radosz, 1998), derived on the basis of the Barker-Henderson perturbation theory, is given by
where $m$ is the number of segments in a chain, $\tilde{a}_o^{hs}$ is the hard-sphere Helmholtz energy per segment, $\beta$ is $1/kT$, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $a_1$ is the first perturbation term, $a_2$ is the second perturbation term, and $\tilde{a}'$ is the empirical correction to account for the truncation error of the second-order perturbation theory.

The chain term is given by

$$\tilde{a}_{\text{chain}} = -(m-1)\left[ln g^{sw}(\sigma) - ln g_0^{sw}(\sigma)\right]$$

where $g^{sw}(\sigma)$ is the pair radial distribution function of square-well segments calculated at contact and $g_0^{sw}(\sigma)$ is $g^{sw}(\sigma)$ evaluated at zero density.

The association term, derived on the basis of Wertheim's thermodynamic perturbation theory, is given by

$$\tilde{a}_{\text{assoc}} = \sum_{\text{sites}} \left[\ln X^A - \frac{X^A}{2}\right] + \frac{n(I)}{2}$$

where $n(I)$ is the number of attraction sites on the molecule and $X^A$ is the fraction of molecules that are not bonded at site A. The expression for $X^A$ is also obtained from Wertheim's theory:

$$X^A = \frac{1}{I + \sum_{\text{sites}} n(I) X^B \Delta^{AB}}$$

where $n(I)$ is the number density and $\Delta^{AB}$ is the association strength given by

$$\Delta^{AB} = 4\pi \int_{\sigma}^r g^{\text{ref}}(r) f^{AB}(r)\,r^2 dr$$
In Eq. (135), \( \sigma \) is the core diameter, \( g^{ref}(r) \) is the pair distribution function of the reference fluid, which is a SW fluid in this work, so \( g^{ref}(r) = g^{sw}(r) \), and \( \left<f^{AB}(IJ)\right>_{\alpha_1,\alpha_2} \) is the angle average of the site-site Mayer \( f \)-function over orientations of molecules 1 and 2.

To solve Eq. (135), we need the pair distribution function of SW fluid, \( g^{sw}(r) \), which can only be approximated. We apply two approximations. Firstly, we replace the pair distribution function of the SW chain fluid by the pair distribution function of SW segments, evaluated at the same temperature and segment density. Secondly, we apply the exponential approximation of Andersen and Chandler (Andersen and Chandler, 1972), which is derived from the optimized cluster expansions, to obtain the pair distribution function of SW segments:

\[
g^{sw}(r) \approx g^{hs}(r) e^{\beta \vartheta} \tag{136}
\]

where \( g^{hs}(r) \) is the pair distribution function of hard-sphere segments and \( \vartheta \) is the renormalized potential, which can be represented by

\[
\vartheta = \alpha(\rho) u \tag{137}
\]

In Eq. (137), \( \alpha(\rho) \) is a parameter that accounts for the effect of density on fluid structure and \( u \) is the well depth of the SW potential. Using the local composition model, Vimalchand et al. (Vimalchand et al., 1992) showed that by assuming \( \alpha = 0.5 \), the properties of the SW fluids were well predicted and in good agreement with molecular dynamics data of Alder (Alder et al., 1972). However, with this constant \( \alpha \), Eq. (136) clearly does not give the correct low-density limit.
In another study, Lee and Chao (Lee and Chao, 1987) carried out Monte Carlo simulations to obtain the coordination number of SW fluids ranging from dilute gas to dense liquid. They fitted the data to a new model, which reduces to

\[
Z_c = \frac{4}{3} \pi (\lambda^3 - 1)(1 + 0.57 \rho^* \rho^* e^{\beta_a(\rho) u}}{1 + \rho^* (e^{\beta_a(\rho) u} - 1)}
\]  \hspace{1cm} (138)

for pure component. In Eq. (138), \( \lambda \) is the reduced range of the potential well, \( \rho^* \) is the reduced density given by

\[
\rho^* = \rho \sigma^3
\]  \hspace{1cm} (139)

and \( \alpha(\rho) \) is given by

\[
\alpha(\rho) = 1 + 0.1044 \rho^* - 2.8469 (\rho^*)^2 + 2.3785 (\rho^*)^3
\]  \hspace{1cm} (140)

This new model of the coordination number can also be derived using the local composition model if Eqs. (136), (137) and (140) are used to represent the SW pair distribution function and if the density-related parameter \( \zeta \) (Vimalchand et al., 1992) is assumed to be \( \rho^* \). Note that Eq. (140) makes Eq. (136) satisfy the low-density limit.

Using Eqs. (136), (137) and (140) to represent the SW pair distribution function, one can reduce Eq. (135) to

\[
\Delta^{AB} = 4\pi e^{\beta_a(\rho) u} \int_0^{r_c} g^{ha}(r) (f^{AB}(lz))_{a_1 a_2} r^2 dr
\]  \hspace{1cm} (141)

For simple geometry depicted in Figure 41, the angle average of the site-site Mayer \( f \)-function is independent of \( r \) (Jackson et al., 1988), so we can integrate Eq. (141) analytically. In order to avoid unnecessary mathematical complexity, following Jackson (Jackson et al., 1988), we make further approximation:
\[ r^2 g^{kz}(r) \approx \sigma^2 g^{kz}(\sigma) \]  
\[ (142) \]

to obtain

\[ \Delta^{AB} = F^{AB} e^{\beta a(\rho)_{m}^{kz}(\sigma)} \left( \sigma^3 \kappa^{AB} \right) \]  
\[ (143) \]

where \( F^{AB} \) is given by

\[ F^{AB} = e^{\left( \frac{\epsilon^{AB}}{kT} \right)} - 1 \]  
\[ (144) \]

and \( \sigma^3 \kappa^{AB} \) is a measure of the volume available for bonding.

5.4 How to approximate association sites for alkanols

To obtain specific expressions for \( \tilde{a}^{assoc} \) and \( \chi^A \), one has to hypothesize the number of association sites and make simplifying approximations for the association strength of site-site interactions. Figure 42 shows two examples of bonding models for alkanols (Huang and Radosz, 1990), which are used in this work: a less rigorous model (2B) and a more rigorous model (3B).

![Figure 42. Types of bonding in alkanols.](image)
In model 2B, the 1-alkanol is modelled as an associating chain molecule with two association sites, i.e. off-center SW association sites, which represent the terminal hydroxyl group. Both sites represent the lone pairs of electrons of oxygen. In model 3B, on the other hand, three association sites are assigned, two of which represent the lone pairs of electrons of oxygen and one represents the hydrogen.

These examples are chosen so that there are only two additional parameters needed in the association term.

5.5 Results and Discussion

The SAFT1 equation of state for alkanols has a total of 6 parameters that need to be estimated, i.e. \( m, v^\infty, u^\circ/k, \lambda, \varepsilon, \) and \( \kappa; \) the last two parameters are specifically from the association term. We initially fit these parameters to experimental saturated-vapor pressure and saturated-liquid volume data for several alkanols using the bonding models of type 2B and 3B; the results are shown in Table 8.

Table 8. Parameters for several alkanols as a result of six-parameter fitting

<table>
<thead>
<tr>
<th>Type 2B</th>
<th>( m )</th>
<th>( v^\infty ) (cm(^3)/mol)</th>
<th>( u^\circ/k ) (K)</th>
<th>( \lambda )</th>
<th>( \varepsilon/k ) (K)</th>
<th>( \kappa )</th>
<th>AAD P/V (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>1.319</td>
<td>19.954</td>
<td>387.875</td>
<td>1.5141</td>
<td>2544.13</td>
<td>0.002451</td>
<td>0.73/0.55</td>
</tr>
<tr>
<td>propanol-1</td>
<td>1.652</td>
<td>21.560</td>
<td>308.154</td>
<td>1.5991</td>
<td>2554.97</td>
<td>0.005155</td>
<td>0.39/0.25</td>
</tr>
<tr>
<td>butanol-1</td>
<td>1.986</td>
<td>22.000</td>
<td>277.654</td>
<td>1.6484</td>
<td>2658.09</td>
<td>0.005439</td>
<td>0.40/1.3</td>
</tr>
<tr>
<td>pentanol-1</td>
<td>2.319</td>
<td>22.147</td>
<td>294.975</td>
<td>1.6319</td>
<td>2582.62</td>
<td>0.004345</td>
<td>0.21/1.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type 3B</th>
<th>( m )</th>
<th>( v^\infty ) (cm(^3)/mol)</th>
<th>( u^\circ/k ) (K)</th>
<th>( \lambda )</th>
<th>( \varepsilon/k ) (K)</th>
<th>( \kappa )</th>
<th>AAD P/V (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>1.409</td>
<td>18.919</td>
<td>378.381</td>
<td>1.5124</td>
<td>2148.58</td>
<td>0.002850</td>
<td>0.73/0.49</td>
</tr>
<tr>
<td>propanol-1</td>
<td>1.742</td>
<td>20.608</td>
<td>312.148</td>
<td>1.5864</td>
<td>2190.61</td>
<td>0.004479</td>
<td>0.52/0.28</td>
</tr>
<tr>
<td>butanol-1</td>
<td>2.076</td>
<td>21.210</td>
<td>278.442</td>
<td>1.6347</td>
<td>2281.85</td>
<td>0.005586</td>
<td>0.68/1.3</td>
</tr>
<tr>
<td>pentanol-1</td>
<td>2.409</td>
<td>21.200</td>
<td>292.600</td>
<td>1.6298</td>
<td>2254.32</td>
<td>0.003845</td>
<td>0.63/2.4</td>
</tr>
</tbody>
</table>

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The data presented in Table 8 suggest that applying model 3B does not necessarily improve the goodness of fit. This more rigorous model is probably more realistic if the association strength between A and B is not assumed zero, but this would introduce additional parameters, which we do not want. Hence, we proceed to use SAFT1 with model 2B only.

The parameters shown in Table 8 have physically realistic values but result in no clear correlations. Hence, in an effort to reduce the number of parameters to be fitted, we set the segment volume \( v^{\infty} \) equal to 22 cm\(^3\)/mol and refit the other parameters to experimental saturated-vapor pressure and saturated-liquid volume data for propanol-1 and butanol-1. Then, on the basis of \( m \) for propanol-1 and butanol-1 only, we develop an empirical expression for \( m \):

\[
m = (2.61638 \times 10^{-2})MW + (4.76587 \times 10^{-2})
\]

(145)

To develop correlations for parameters, we do not consider methanol and ethanol because their long-range electrostatic interactions are expected to be of greater relative importance (Kraska and Gubbins, 1996a); a model that neglects these long-range interactions is likely to result in parameters for these alkanols that do not follow the parameter trends for the other alkanols.

Next, using \( v^{\infty} = 22 \) cm\(^3\)/mol and Eq. (145), we refit the experimental saturated-vapor pressure and saturated-liquid volume data again for other alkanols to obtain the other parameters; the results are shown in Table 9. The experimental data and their temperature ranges are the same as in SAFT (Huang and Radosz, 1990).

Figures 43 and 44 illustrate the goodness of fit, in terms of the average absolute deviation (AAD) of the saturated-liquid volumes and vapor pressures plotted against the
carbon number. Comparing the SAFT1 and SAFT results shown in Figure 43, we observe a substantial improvement in fitting the saturated liquid volume that is likely attributable to a better representation of the liquid structure in SAFT1; in SAFT, the liquid is assumed to have the hard-sphere liquid structure. Except for n-decanol, where SAFT1 is much more accurate, as it is shown in Figure 44, both models result in similar goodness of fit for the saturated vapor pressure.

Table 9. SAFT1 parameters for 1-alkanols

<table>
<thead>
<tr>
<th>SAFT1</th>
<th>m</th>
<th>$V^\infty$ (cm$^3$/mol)</th>
<th>$u^0/k$ (K)</th>
<th>$\lambda$</th>
<th>$\delta/k$ (K)</th>
<th>$\kappa$</th>
<th>AAD P/V (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>0.986</td>
<td>17.956</td>
<td>247.367</td>
<td>1.5535</td>
<td>2765.64</td>
<td>0.028831</td>
<td>0.83/0.33</td>
</tr>
<tr>
<td>ethanol</td>
<td>1.319</td>
<td>19.954</td>
<td>387.875</td>
<td>1.5141</td>
<td>2544.13</td>
<td>0.002451</td>
<td>0.73/0.55</td>
</tr>
<tr>
<td>propanol-1</td>
<td>1.620</td>
<td>22.000</td>
<td>307.979</td>
<td>1.5998</td>
<td>2581.25</td>
<td>0.005153</td>
<td>0.33/0.27</td>
</tr>
<tr>
<td>butanol-1</td>
<td>1.987</td>
<td>22.000</td>
<td>277.388</td>
<td>1.6485</td>
<td>2660.03</td>
<td>0.005416</td>
<td>0.30/1.3</td>
</tr>
<tr>
<td>pentanol-1</td>
<td>2.354</td>
<td>22.000</td>
<td>261.405</td>
<td>1.6779</td>
<td>2694.50</td>
<td>0.005647</td>
<td>0.48/1.6</td>
</tr>
<tr>
<td>hexanol-1</td>
<td>2.721</td>
<td>22.000</td>
<td>254.698</td>
<td>1.6910</td>
<td>2662.50</td>
<td>0.006300</td>
<td>0.88/2.2</td>
</tr>
<tr>
<td>heptanol-1</td>
<td>3.088</td>
<td>22.000</td>
<td>250.397</td>
<td>1.6985</td>
<td>2679.03</td>
<td>0.006406</td>
<td>0.87/4.6</td>
</tr>
<tr>
<td>octanol-1</td>
<td>3.455</td>
<td>22.000</td>
<td>248.305</td>
<td>1.7035</td>
<td>2665.00</td>
<td>0.006209</td>
<td>0.75/4.6</td>
</tr>
<tr>
<td>decanol-1</td>
<td>4.189</td>
<td>22.000</td>
<td>245.334</td>
<td>1.7065</td>
<td>2694.95</td>
<td>0.006492</td>
<td>0.92/4.8</td>
</tr>
</tbody>
</table>

Figures 45 and 46 provide further comparisons of SAFT1 to SAFT in reproducing the coexisting vapor and liquid densities in T-p and P-p diagrams for propanol-1 and hexanol-1; while not perfect, SAFT1 improves the representation of the coexisting liquid density. Figure 47 compares the corresponding saturated vapor pressure; both SAFT and SAFT1 can correlate the experimental data equally well.

The SAFT1 parameters from Table 9 are plotted against the molecular weight in Figure 48. These parameters are found to be well behaved so that they can be
extrapolated to higher alkanols. The following equations are developed for higher alkanols:

\[
m^\frac{\mu^o}{k} = 5.98096 \text{MW} + 80.03215 \quad (146)
\]

\[
m \lambda = 0.04635 \text{MW} - 0.15792 \quad (147)
\]

\[
m^\frac{c}{k} = 71.54733 \text{MW} - 50.4074 \quad (148)
\]

\[
m \kappa = (1.97875 \times 10^{-4}) \text{MW} - 0.0042 \quad (149)
\]

Figure 43. Percent average absolute deviation (AAD) of the calculated values from the experimental values for the molar liquid volume of 1-alkanols, in the state of saturation.

Thus, for high-molecular-weight molecules, such as polymers, all parameters except \( m \) can have practically constant values. Therefore, Eqs. (146)-(149) represent a very
simple empirical method for estimating SAFT1 parameters for hydroxy polymers. These equations, however, are not accurate for and should not be applied to small alkanols. We will test them on polymers in future work.

![Graph showing percent average absolute deviation (AAD) of calculated values from experimental values for vapor pressure of 1-alkanols, in the state of saturation.](image)

Figure 44. Percent average absolute deviation (AAD) of the calculated values from the experimental values for the vapor pressure of 1-alkanols, in the state of saturation.

### 5.6 Conclusion

The SAFT1 equation of state is extended using Wertheim’s theory to model associating fluids and tested on pure alkanols. For small 1-alkanols, the SAFT1 more accurately correlates the vapor pressure and liquid density. Their parameters are found to be well behaved and hence easy to estimate reliably for high-molecular-weight 1-alkanols.
Figure 45. Coexisting vapor and liquid density for propanol-1 and hexanol-1 (T-p diagram), experimental (points) and calculated (curves).

Figure 46. Coexisting vapor and liquid density for propanol-1 and hexanol-1 (P-p diagram), experimental (points) and calculated (curves).
Figure 47. Saturated vapor pressure for propanol-1 and hexanol-1, experimental (points) and calculated (curves).

Figure 48. SAFT1 parameters for 1-alkanols as functions of molecular weight.
Chapter 6
Conclusions

The square-well fluid thermodynamics and liquid structure are used within a SAFT framework to develop a prototype of an engineering equation of state. Each molecule is considered to be composed of spherical segments that interact according to a square-well (SW) potential. These segments are allowed to form covalent or hydrogen-type bonds. As a result of this SW SAFT approximation, an engineering model referred to as SAFT1 has been developed in this work. SAFT1 is found to be applicable to small and large molecules, associating and non-associating molecules, and to homopolymers and copolymers.

SAFT1 is tested on real-fluid properties, such as vapor pressure, vapor and liquid density, second virial coefficient, heat of vaporization, specific heat, phase equilibrium. For small n-alkanes, not only the vapor pressure and liquid density (that are correlated), but also the second virial coefficient, heat of vaporization, and heat capacity (that are predicted) are found to be accurate. For small alkanols-1, the vapor pressure and liquid density are also well correlated.

The SAFT1 parameters for n-alkanes and alkanols-1 are found to be well behaved and hence easy to estimate reliably for high-molecular-weight molecules of corresponding homologs. For example, these parameters reach asymptotic values upon increasing the molecular weight, except for the chain length m.
To improve the SAFT representation of the coexisting curves in the critical region, a crossover procedure is used to incorporate the effect of the critical fluctuations. This procedure is found to improve the representation of the coexisting curves in the region close to the critical point.

In this pursuit of a reliable thermodynamic model, the molecular theories confirm their usefulness in estimating the behavior of real molecules. It is demonstrated that the molecular structure could be the only information needed to predict and understand the behavior of the macromolecular systems, such as polyolefins.

At the same time, this work also identifies opportunities for improvement. For example, a group-contribution approach may be an attractive route for estimating model parameters for small and large molecules because the model parameters are well-behaved. Another example of a possible improvement is to explore the Lennard-Jones fluid; the current hurdle is the lack of reliable models for the LJ structure.
References


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Tavares, F. W.; Chang, J.; Sandler, S. I. A completely analytic equation of state for the square-well chain fluid of variable well width. *Fluid Phase Equilib.*, 1997, 140, 129.


Appendix A
Expressions of Thermodynamic Properties

SAFT1 is defined in terms of the residual Helmholtz energy. This section provides other functions needed to calculate the thermodynamic properties.

Compressibility Factor

\[ Z = 1 + \rho \left( \frac{\partial \bar{a}_{\text{res}}}{\partial \rho} \right)_{T,X} \]  \hspace{1cm} (A.1)

Second Virial Coefficient

\[ B = \lim_{\rho \to 0} \left( \frac{\partial \bar{a}_{\text{res}}}{\partial \rho} \right)_{T,X} \]  \hspace{1cm} (A.2)

Heat of Vaporization

\[ \frac{h_{\text{res}}(V,T,n)}{RT} = \frac{h_{\text{res}}^\diamond(P,T,n)}{RT} = \tilde{h}_{\text{res}} = -T \left( \frac{\partial \bar{a}_{\text{res}}}{\partial T} \right)_{p,X} + Z - 1 \]  \hspace{1cm} (A.3)

\[ \Delta h_{\text{vap}} = (\tilde{h}_{\text{res},\text{vapor}} - \tilde{h}_{\text{res},\text{liquid}})RT \]  \hspace{1cm} (A.4)

Heat Capacity

\[ \frac{c_v^{\text{res}}}{R} = \bar{c}_v^{\text{res}} = -T \left[ 2 \left( \frac{\partial \bar{a}_{\text{res}}}{\partial T} \right)_{p,X} + T \left( \frac{\partial^2 \bar{a}_{\text{res}}}{\partial T^2} \right)_{p,X} \right] \]  \hspace{1cm} (A.5)

\[ \frac{c_p^{\text{res}}}{R} = \bar{c}_p^{\text{res}} = \bar{c}_v^{\text{res}} - 1 + \frac{T}{R \rho^2} \left( \frac{\partial P}{\partial T} \right)_{p,X} \left( \frac{\partial P}{\partial \rho} \right)_{T,X}^{-1} \]  \hspace{1cm} (A.6)

\[ \left( \frac{\partial P}{\partial T} \right)_{p,X} = \frac{P}{T} + \rho^2 RT \left[ \frac{\partial}{\partial T} \left( \frac{\partial \bar{a}_{\text{res}}}{\partial \rho} \right)_{T,X} \right]_{p,X} \]  \hspace{1cm} (A.7)

\[ \left( \frac{\partial P}{\partial \rho} \right)_{T,X} = RT \left[ 1 + 2 \rho \left( \frac{\partial \bar{a}_{\text{res}}}{\partial \rho} \right)_{T,X} + \rho^2 \left( \frac{\partial^2 \bar{a}_{\text{res}}}{\partial \rho^2} \right)_{T,X} \right] \]  \hspace{1cm} (A.8)
Appendix B

Expression of Pressure for Crossover SAFT

This section describes how we calculate the pressure from the crossover SAFT equation of state.

\[ P = \rho RT \left[ 1 + \rho \left( \frac{\partial \tilde{a}^{\text{res}}}{\partial \rho} \right)_T \right] \]  \hspace{1cm} (B.1)

where \( \tilde{a}^{\text{res}} = \frac{P_{co}}{RT_{co}} \tilde{A}_V x - \ln \frac{\rho}{\rho_{co}} \) \hspace{1cm} (B.2)

\[ \left( \frac{\partial \tilde{a}^{\text{res}}}{\partial \rho} \right)_T = \frac{P_{co}}{RT_{co}} \left[ -\frac{1}{\rho^2} \tilde{A}_V x + \frac{1}{\rho} \left\{ \frac{1}{\rho_{co}} \tilde{\mu}_o + \frac{1}{\rho_c} \left( \frac{\partial \tilde{A}_V x}{\partial \tilde{\rho}} \right)_{\Delta \tilde{r}} \right\} \right] - \frac{1}{\rho} \] \hspace{1cm} (B.3)

\[ \left( \frac{\partial \Delta \tilde{A}_V x}{\partial \Delta \tilde{\rho}} \right)_{\Delta \tilde{r}} = \left( \frac{\partial \Delta \tilde{A}_V}{\partial \Delta \tilde{\rho}_x} \right)_{\Delta \tilde{r}} \left( \frac{\partial \Delta \tilde{\rho}_x}{\partial \Delta \rho} \right)_{\Delta \tilde{r}} + \left( \frac{\partial \Delta \tilde{A}_V}{\partial \Delta \tilde{r}_x} \right)_{\Delta \tilde{r}} \left( \frac{\partial \Delta \tilde{r}_x}{\partial \Delta \rho} \right)_{\Delta \tilde{r}} \] \hspace{1cm} (B.4)
Appendix C

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Appendix D

Publications and Presentations

Publications


8. Adidharma, H.; Radosz, M. Crossover SAFT. Drafted but incomplete.

Presentations


7. Adidharma, H.; Radosz, M. SAFT and SAFT1 Modeling of Polymer Solutions in Sub- and Supercritical Fluids. Submitted for The Fifth International Symposium on Supercritical Fluids, ISSF 2000, Atlanta, Georgia, April 8-12, 2000.

Vita

On April 25, 1963, Hertanto Adidharma was born as the second child of Tan Boen Hwa and Poo Lee Djoe in Mojokerto, Indonesia. He grew up there and attended Taruna Nusa Harapan Elementary School. His high school education was completed in 1982 from Santa Maria High School in Malang, Indonesia, from which he graduated with honors.

He studied chemical engineering at the Institute of Technology 10 Nopember, Surabaya, Indonesia, and graduated with a bachelor of science degree with honors in 1987.

He worked at Sungei Pinang Palm Oil Company and Surya Kertas Pulp and Paper Industry before joining the University of Surabaya in 1989. One year after joining the university, he married Mariwati who gave him two adorable daughters, Widya and Lingga.

In 1995, he continued the study of chemical engineering at Louisiana State University, Baton Rouge, by entering the Graduate School. He was permitted to pursue the doctorate under the direction of Professor Maciej Radosz in the area of thermodynamics; the degree of Doctor of Philosophy will be awarded on December 17, 1999.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Hertanto Adidharma

Major Field: Chemical Engineering

Title of Dissertation: An Engineering Equation of State: Square-Well Statistical Associating Fluid Theory (SAFT)

EXAMINING COMMITTEE:

Martin Hirs, 
David W., 
Frank R. 

Date of Examination: October 5, 1999