

A crossover SAFT-VR equation of state for pure fluids: preliminary results for light hydrocarbons

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Abstract

SAFT is perhaps the most versatile, fundamentally, based engineering equation of state in use today. However, in common with all analytic equations of state, SAFT exhibits classical behavior in the critical region rather than the non-analytical, singular behavior seen in real fluids. Recently, so-called crossover equations of state have been developed which solve this shortcoming by incorporating the scaling laws valid asymptotically close to the critical point while reducing to the original classical equation of state far from the critical point. We have combined the SAFT-VR equation of state with an analytical crossover technique to obtain the SAFT-VRX equation of state. The SAFT-VRX approach combines the accurate low temperature behavior of SAFT-VR with a precise representation of the critical region. Preliminary results are presented for hydrocarbon systems which illustrate the accuracy of the SAFT-VRX approach over the entire fluid phase region.

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1. Introduction

The thermodynamics and phase behavior of fluid systems are central to chemical process and product design in the chemical and petrochemical industries, from standard separation techniques, through supercritical fluid extraction, to enhanced oil recovery. As the industrial need for accurate experimental data grows beyond the rate at which new experimental work is being carried out the importance of theoretical methods for interpreting and ultimately predicting experimental data increases.

Most engineering equations of state, such as the Peng and Robinson [1] or Redlich and Kwong [2] equations and their variants [3], which are based on van der Waals equation, with modifications being made to the treatment of the hard sphere repulsive term and/or (more commonly) the mean field attractive term can, with parameters fitted to experimental data, accurately reproduce the phase behavior of simple fluids and their mixtures. However, modeling more complex systems with these equations of state, such as polymers and associating systems (i.e., hydrogen-bonding fluids), usually involves introducing additional ad hoc parameters, since the

original equations of state have not been derived from a theoretical basis that accommodates the complexities of molecular shape and molecular association. Accounting for the latter has figured prominently in recent efforts to develop equations of state. For example, the perturbed hard chain theory (PHCT) [4,5], the associating perturbed anisotropic chain theory (APACT) [6], and their variants [3,7] have been widely used to correlate experimental data, but in common with the simpler cubic equations of state they appear to have limited predictive value far away from the systems and state conditions to which the model parameters were fitted [3–5,7].

Molecular-based equations of state, such as those derived from the SAFT approach [8,9], provide a framework in which the effects of molecular shape and interactions on the thermodynamic properties can be separated and quantified. In particular, the SAFT equation of state has the capability to accurately treat both simple spherical molecules and chain fluids. Furthermore, SAFT was developed from the thermodynamic perturbation theory of Wertheim which provides accurate expressions for the free energy contribution for associating chain fluids and so can also accurately describe associating systems. In its original formulation, SAFT was developed to model associating fluids as Lennard–Jones chains with short-range association sites. However, in recent

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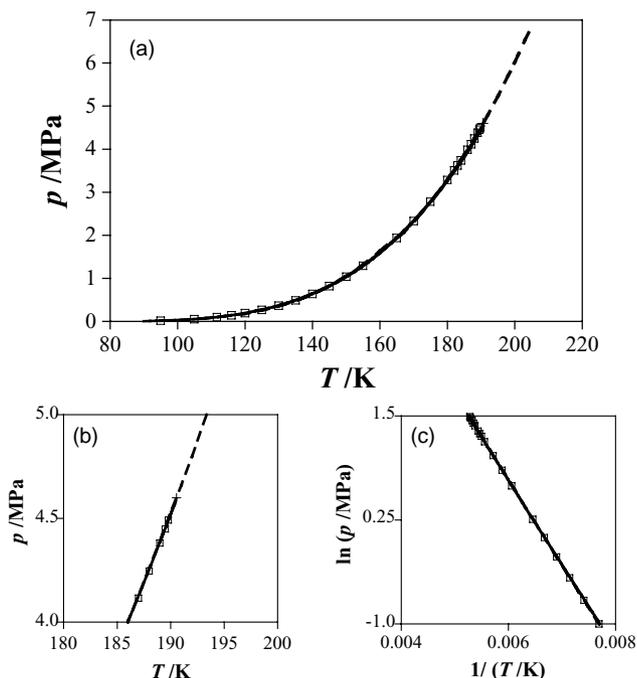


Fig. 1. Vapor pressure curve for methane (a), in the critical region (b) and as a Clausius–Clapeyron representation (c) from the SAFT-VRX (solid) and SAFT-VR (dashed) equations of state compared with experimental data [51] (symbols).

years, a number of modifications and extensions to the original expression have been presented which primarily differ in their treatment of the reference fluid [10,11]. In particular, SAFT has been extended to describe chain molecules formed from hard-core segments with attractive potentials of variable range (SAFT-VR) [12,13], typically a square well. SAFT-VR has been successfully used to describe the phase equilibria of a wide range of industrially important systems and provides significant improvement and predictive capability over the earlier formulations. For example, alkanes of low molecular weight through to simple polymers [14–17], and their binary mixtures [18–20], perfluoroalkanes [21], hydrogen fluoride [22], water [22,23], refrigerant systems [24], nitrogen [25], carbon dioxide [26], and electrolyte solutions [27,28], have all been modeled successfully using SAFT-VR.

While the SAFT-VR approach has been shown to be capable of predicting fluid phase equilibria in a wide variety of pure and mixed fluid systems, in common with essentially all empirical and theoretical equations of state, SAFT-VR exhibits classical behavior in the critical region rather than the non-analytical, singular behavior seen in real fluids [29]. This results in an over-prediction of the critical point, as illustrated by the dashed line in Fig. 1. However, in previous work, we have shown that when one is interested in the location of critical points and critical lines, it is possible to study the phase behavior of fluids and their mixtures in the critical region using the SAFT approach through re-scaling of the potential model parameters to the experimental crit-

ical temperature and pressure [14,16]. For example, using the pure-fluid re-scaled parameters and the cross-interaction parameters obtained from simple Lorentz–Berthelot combining rules, we were able to obtain excellent agreement between the predictions of the SAFT-VR equation of state and experimental data for the pure light *n*-alkanes and the critical lines of their binary mixtures without fitting to any binary mixture data [14]. However, the success of re-scaled parameters in describing mixture critical lines comes at the cost of significant deviations from experimental data at lower temperatures and pressures and for the coexisting densities. Thus, in common with all classical equations of state, a single set of parameters is unable to describe accurately both the near critical and subcritical regions. Hence, a better approach to describe the critical region with the SAFT-VR equation of state is needed.

An accurate thermodynamic description of the global phase diagram is possible through a so-called crossover equation of state which satisfies not only the asymptotic critical power laws, but also incorporates *crossover* to regular thermodynamic behavior far from the critical point. In earlier work, Kiselev and co-workers developed a crossover SAFT equation of state for non-associating [30–32] and associating fluids [33] based on the SAFT expressions of Huang and Radosz (SAFT-HR). The crossover SAFT-HR equation of state was applied to alkanes, and refrigerants and refrigerant mixtures and more recently to eight common pure supercritical fluids by Hu et al. [34]. The crossover formulation improved the theoretical description in the vicinity of the critical point, however in general deviations from experimental data were observed at lower temperatures. Hu et al. [35] have also proposed a crossover SAFT-BACK equation in which they have combined the empirical BACK equation of state with the association term due to Wertheim used in the SAFT approach. They found that for carbon dioxide (a non-associating fluid) the crossover formulation provided little improvement over the classical SAFT-BACK equation; however, for water (an associating fluid), significant improvement was achieved with the crossover equation. We note that while empirical equations of state can accurately correlate phase behavior for a pure fluid or for specific mixtures, little predictive value or molecular insight is derived from the parameters obtained. In work more closely related to the present paper, Jiang and Prausnitz have presented a crossover version of their molecular-based equation of state for non-associating chain fluids (EOSCF) [36,37]. However, they use the “globalized” renormalization-group (RG) procedure proposed by White and co-workers [38–42]. An advantage of the “globalized” RG [38–42] models is that they require only one additional parameter (beyond those of the classical EOS) as input. However, the resulting equation of state is not formulated in a closed mathematical form and so can only be solved numerically, requiring additional spline functions for the practical representation of the thermodynamic surface of real fluids.

In this work, we have combined the SAFT-VR equation of state with a crossover technique developed by Kiselev [43] to obtain the SAFT-VRX equation of state which incorporates the critical scaling laws valid asymptotically close to the critical point and reduces to the original classical equation of state far from the critical point. The remainder of the paper is organized as follows; in Sections 2 and 3, respectively, we give details of the SAFT-VRX approach and describe the molecular models used. Preliminary results for hydrocarbon systems will be presented in Section 4 and concluding remarks made in Section 5.

2. Theory

Following the seminal work of Wertheim [44–47], the SAFT free energy is written as the sum of four separate contributions:

$$\frac{A}{NkT} = \frac{A^{\text{ideal}}}{NkT} + \frac{A^{\text{mono.}}}{NkT} + \frac{A^{\text{chain}}}{NkT} + \frac{A^{\text{assoc.}}}{NkT} \quad (1)$$

where N is the number of molecules, k the Boltzmann's constant, and T the temperature. A^{ideal} is the ideal free energy, $A^{\text{mono.}}$ the contribution to the free energy due to the monomeric segments, A^{chain} the contribution due to the formation of a chain of m monomers, and $A^{\text{assoc.}}$ the contribution due to association. In the SAFT-VR approach the usual description of the monomer term by a hard-sphere fluid is replaced by a realistic potential of variable range, such as the square-well potential, which is used in this work. The dispersive interactions are treated via a second-order high-temperature perturbation expansion providing a more rigorous description of the thermodynamics than found in simpler versions of the SAFT approach, viz.

$$\frac{A^{\text{mono.}}}{NkT} = m \left(a^{\text{HS}} + \frac{a_1}{kT} + \frac{a_2}{(kT)^2} \right) \quad (2)$$

where m is the number of segments the model chain, a^{HS} the residual hard sphere free energy, a_1 the first perturbation term or mean attractive energy, and a_2 the second perturbation term. The contribution to the free energy due to chain formation is given by

$$\frac{A^{\text{chain}}}{NkT} = -(m-1) \ln y^{\text{SW}}(\sigma) \quad (3)$$

where $y^{\text{SW}}(\sigma)$ is the cavity distribution function of the reference square-well monomer fluid at contact. Finally, the free energy due to association is given by,

$$\frac{A^{\text{assoc.}}}{NkT} = \left[\sum_{a=1}^n \left(\ln X_a - \frac{X_a}{2} \right) + \frac{n}{2} \right] \quad (4)$$

where the sum is over all sites a on the model molecule and X_a is the fraction of molecules not bonded at site a . For full details of the SAFT-VR expressions the reader is directed to the original publication [12].

In order to derive the SAFT-VRX equation of state, we need to recast the classical expression for the Helmholtz free energy into dimensionless form,

$$\bar{A}(T, v) = \frac{A(T, v)}{NkT} = \Delta \bar{A}(\Delta T, \Delta v) - \Delta v \bar{P}_0(T) + \bar{A}_0^{\text{res}}(T) + \bar{A}^{\text{ideal}}(T) \quad (5)$$

where \bar{P}_0 is the dimensionless pressure, \bar{A}_0^{res} the residual Helmholtz free energy and \bar{A}^{ideal} the dimensionless temperature-dependent ideal gas term along the critical isochore, i.e., $v = v_{0,c}$. The critical part of the free energy, $\Delta \bar{A}$, is expressed as a function of the dimensionless deviations of the temperature from the classical critical temperature ($\Delta T = T/T_{0,c} - 1$) and molar volume from the classical molar volume $\Delta v = v/v_{0,c} - 1$.

$$\Delta \bar{A}(\Delta T, \Delta v) = \bar{A}^{\text{res}}(\Delta T, \Delta v) - \bar{A}_0^{\text{res}}(\Delta T) - \ln(\Delta v + 1) + \Delta v \bar{P}_0(\Delta T) \quad (6)$$

We then replace ΔT and Δv in the singular or critical term with renormalized values

$$\Delta T \rightarrow \bar{\tau} = \tau Y^{-\alpha/2\Delta_1} + (1 + \tau) \Delta \tau_c Y^{2(2-\alpha)/3\Delta_1} \quad (7)$$

$$\Delta v \rightarrow \Delta \bar{\eta} = \Delta \eta Y^{(\gamma-2\beta)/4\Delta_1} + (1 + \Delta \eta) \Delta v_c Y^{(2-\alpha)/2\Delta_1} \quad (8)$$

where Y is the crossover function, $\tau = T/T_c - 1$ the dimensionless deviation of the temperature from the real critical temperature T_c , $\Delta \eta = v/v_c - 1$ the dimensionless deviation of the molar volume from the real critical volume v_c and $\Delta \tau_c = T_c/T_{0,c} - 1$ and $\Delta v_c = v_c/v_{0,c} - 1$ the critical shifts. Hence, upon substitution, Eq. (6) becomes,

$$\bar{A}(T, v) = \Delta \bar{A}(\bar{\tau}, \Delta \bar{\eta}) - \Delta v \bar{P}_0(T) + \bar{A}_0^{\text{res}}(T) + \bar{A}^{\text{ideal}}(T) \quad (9)$$

The crossover function Y [48,49] asymptotically close to the critical point renormalizes ΔT and Δv in accordance with Eqs. (7) and (8), so giving the correct non-analytical asymptotic behavior of real fluids in the critical region. Far away from the critical point the crossover function $Y \rightarrow 1$, $\tau \rightarrow \Delta T$, and $\Delta \eta \rightarrow \Delta v$, and Eq. (5) is reduced to the classical Helmholtz free energy (1). Details of the crossover term can be found in the original papers [48,49], here we simply note that Y is a function of the Ginzburg number Gi , which characterizes the ratio of the intermolecular distance to the range of the potential. Now we have an expression for the free energy, which in the vicinity of the critical region incorporates scaling behavior with the correct critical exponents ($\gamma = 1.24$, $\beta = 0.325$, $\alpha = 0.112$, $\Delta_1 = 0.51$).

3. Molecular models

In this work, the molecules are described as chains of hard tangentially bonded spherical segments with the attractive

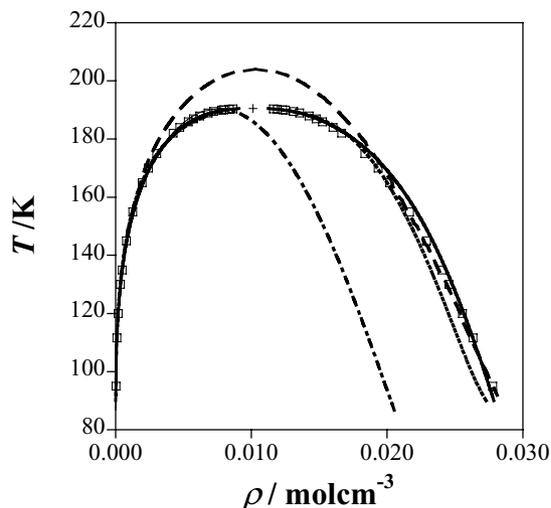


Fig. 2. Coexisting liquid and gas densities for methane from SAFT-VRX (solid line), SAFT-VR (dashed line), SAFT-VR with rescaled parameters (dashed-dotted line) and crossover SAFT-HR by Kiselev and Ely [50] (dotted line) compared with experimental data [51] (symbols).

interactions described by a square well potential of variable range;

$$u(r) = \begin{cases} +\infty, & \text{if } r < \sigma \\ -\varepsilon, & \text{if } \sigma \leq r < \lambda\sigma \\ 0, & \text{if } r > \lambda\sigma \end{cases} \quad (10)$$

In the description of non-associating molecules, which are considered in this preliminary work, three parameters (σ , ε and λ) are required to describe the strength of the molecular interactions and an additional parameter m is needed to determine the model chain length. In associating fluids two additional parameters are needed, however associating fluids are not considered in this preliminary study, but will be presented in a future publication. The inclusion of the crossover function into the SAFT-VR equation of state introduces three additional parameters: the Ginzburg number Gi , the rectilinear diameter amplitude d_1 , and an empirical coefficient v_1 related to the asymmetry of the vapor–liquid envelope [31,49]. Since the goal of this work is to evalu-

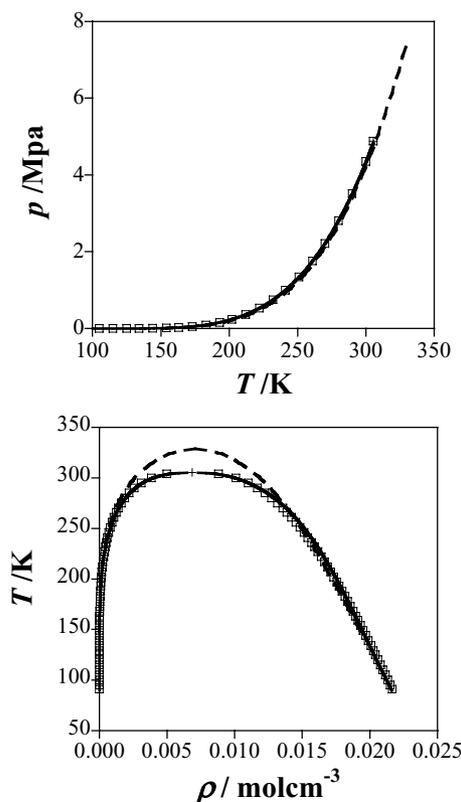


Fig. 3. Vapor pressure curve and coexisting liquid and gas densities for ethane from SAFT-VRX (solid line), SAFT-VR (dashed line) compared with experimental data [51] (symbols).

ate the ability of the SAFT-VRX equation to describe the thermodynamic properties of selected light hydrocarbons, all the parameters are determined by fitting to fluid property data, such as the vapor pressure curve, coexisting densities and PVT behavior. The parameters used in this work for the SAFT-VRX equation are presented in Table 1, along with those taken from earlier work for the SAFT-VR equation [12,16]. From the table we note that, for the alkanes beyond methane the potential model parameters (m , σ , ε and λ) increase fairly smoothly with molecular weight. The crossover parameters exhibit some scatter and it is difficult to determine from this limited study if a trend with molec-

Table 1

Summary of potential model parameters used to describe the hydrocarbons methane, ethane and hexane with the SAFT-VR and SAFT-VRX equations of state

SAFT	m	σ (Å)	ε/k (K ⁻¹)	λ	Gi	d_1	v_1
Methane							
VRX	1.00	4.126	166.9	1.409	0.302	0.380	7.47E-03
VR	1.00	3.670	168.8	1.444			
Ethane							
VRX	1.74	3.661	164.0	1.574	0.137	1.123	2.71E-03
VR	1.33	3.788	241.8	1.449			
<i>n</i> -Hexane							
VRX	3.55	3.987	170.4	1.664	0.187	0.510	4.34E-03
VR	2.67	3.920	250.4	1.552			

ular weight will develop. In comparison with the parameters from SAFT-VR, the number of segments representing a given alkane is larger for SAFT-VRX; however, the strength ($m\epsilon$) and range ($\lambda\sigma$) of the potential from both SAFT-VR and SAFT-VRX are approximately equal for each alkane. This provides encouraging evidence that we will be able to limit the reliance on experimental data when developing potential model parameters for the hydrocarbon homologous series, as was observed for SAFT-VR [16].

4. Results

In this work, we present preliminary results for methane, ethane, and hexane obtained from the SAFT-VRX approach. In Fig. 1a the SAFT-VRX prediction for the vapor pressure curve of methane is presented and compared with that from the original SAFT-VR approach and experimental data. From the figure we can see the over-prediction of the critical point with the SAFT-VR approach using the parameters of Table 1, compared to the excellent agreement obtained with the SAFT-VRX equation of state. With the SAFT-VRX equation we are able to achieve excellent agreement with experimental data both in the critical region (Fig. 1b) and at low temperatures and pressures, as seen in the Clausius–Clapyron representation of the vapor pressure curve (Fig. 1c). We also note that with the SAFT-VR de-

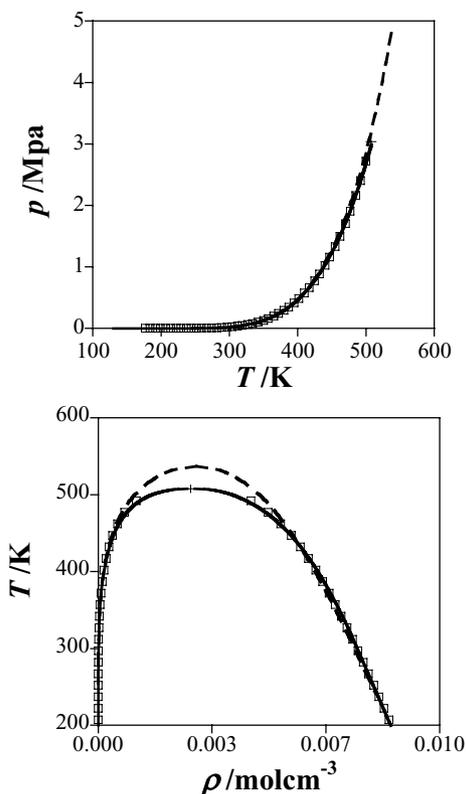


Fig. 4. Vapor pressure curve and coexisting liquid and gas densities for hexane from SAFT-VRX (solid line) and SAFT-VR (dashed line) compared with experimental data [51] (symbols).

scription, while we could improve on the prediction of the vapor pressure curve in the vicinity of the critical region if re-scaled parameters were used, this would be at the cost of the agreement with experimental data away from the critical region and for the coexisting densities. This is illustrated in Fig. 2 where we compare the SAFT-VRX description of the coexisting densities with that obtained from SAFT-VR with the optimized parameters given in Table 1 and re-scaled parameters [16]. In Fig. 2, we also compare with the crossover version of Huang and Radosz's SAFT (SAFT-HR) equation of state developed earlier by Kiselev and Ely [50]. From the figure we can see that while crossover SAFT-HR provides an excellent description of the critical region significant deviations are seen from experimental data at low temperatures compared to the SAFT-VRX approach. This is clearly a reflection of the more accurate classical equation of state being used in SAFT-VRX. Figs. 1 and 2 clearly demonstrate that with the SAFT-VRX approach we are able to accurately describe the phase behavior of methane over the entire fluid phase region. Similar excellent results were obtained for ethane and hexane (Figs. 3 and 4): For the saturated vapor pressure data in the temperature range $0.3T_c < T < T_c$ an average absolute deviation (AAD) of approximately 0.5–1% is achieved and for the saturated liquid densities

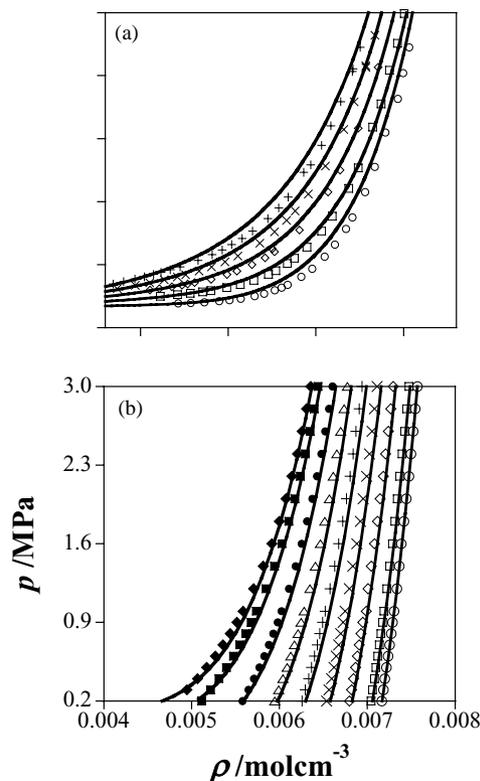


Fig. 5. $P\rho T$ behavior for hexane predicted from SAFT-VRX (solid line) compared with experimental data [52,53] (symbols). (a) Comparison in the supercritical region at (○) 523 K, (□) 548 K, (◇) 573 K, (×) 598 K and (+) 623 K; (b) comparison for the subcritical region (○) 343.15 K, (□) 353.15 K, (◇) 373.15 K, (×) 393.15 K and (+) 413.15 K, (△) 433.15 K, (●) 453.15 K, (◆) 483.15 K.

and vapor density an AAD of about 1 and 2–3% is obtained. Additionally for all substances, SAFT-VRX reproduces the PVT-data in the one phase region up to $T = 2T_c$ with an average absolute deviation (AAD) of approximately 2–3%. A representative comparison of the SAFT-VRX description compared to experimental data is given for hexane in Fig. 5.

5. Concluding remarks

We have presented preliminary results for the description of n -alkane phase behavior using the SAFT-VRX equation of state. Through the incorporation of a crossover function into the SAFT-VR equation, which exhibits classical behavior in the critical region rather than the non-analytical, singular behavior seen in real fluids we are able to provide an accurate description of the whole phase diagram using SAFT-VRX. The results presented here for selected n -alkanes are seen to be in excellent agreement with experimental data both near to and far from the critical region. We are currently optimizing the SAFT-VRX parameters for the n -alkane homologous series and developing simple relations for the SAFT-VRX parameters that will enable the estimation of parameters without fitting to experimental data and for molecules for which no experimental data is available. The molecular rather than empirical nature of the SAFT approach allows the development of such relations, which can then be used in a predictive sense, as was observed for SAFT-VR. The results presented here indicate that the SAFT-VRX parameters behave in a similar manner to those determined for SAFT-VR and so we anticipate the same predictive power will be realized, but with greater accuracy. The results of this more detailed study for the hydrocarbon homologous series, as well as associating fluids such as water and alcohols will be reported in a future publication.

List of symbols

a	Helmholtz free energy per segment
A	Helmholtz free energy per molecule
d_1	rectilinear diameter amplitude
G_i	Ginzburg number
k	Boltzmann constant
m	number of segments in model chain
n	total number of sites
N	number of molecules
p	pressure
T	temperature
u	square-well potential
v	molar volume
v_1	crossover parameter in Y
X_a	fraction of molecules not bonded at site a
y	cavity distribution function
Y	crossover function

Greek letters

α	universal critical exponent for specific heat
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β	universal critical exponent for the coexistence curve
ε	depth of square well potential
γ	universal critical exponent for susceptibility
$\Delta\eta$	order parameter
$\Delta\bar{\eta}$	renormalized order parameter
λ	width of square well potential
ρ	density
σ	hard core diameter
τ	reduced temperature difference
$\bar{\tau}$	renormalized temperature difference

Superscripts

cr	crossover
ideal	ideal-gas contribution
mono.	monomeric contribution
assoc.	association contribution
chain	chain contribution
res	residual

Subscripts

0	classical
c	critical
r	reduced

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