

The thermodynamics of heteronuclear molecules formed from bonded square-well (BSW) segments using the SAFT-VR approach

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We broaden the scope of the statistical associating fluid theory for potentials of variable attractive range (SAFT-VR) to treat heteronuclear chain molecules formed from bonded square-well (BSW) segments. The ideas of the bonded hard sphere (BHS) treatment for distributed-site models composed of hard-sphere segments are applied to square-well sites with the SAFT-VR approach. The results of isothermal–isobaric Monte Carlo simulations are reported for heteronuclear square-well diatomics with different sets of energy and range parameters. The SAFT-VR approach provides an excellent description of the equation of state of the diatomic systems for a wide range of densities. The goal of the work is to provide a rigorous treatment of distributed-site models of fluids, and to establish a framework for a group contribution approach with SAFT-VR.

1. Introduction

The statistical associating fluid theory (SAFT) [1, 2] was developed in the late 1980s to model associating Lennard-Jones chains [1, 2], based on the thermodynamic perturbation theory of Wertheim [3–8] for associating systems. The SAFT approach has since been used to examine the phase behaviour of a wide range of pure components and their mixtures (e.g. [9, 10]) and is now widely accepted as one of the most powerful predictive tools for the study of fluid phase equilibria. Since the introduction of SAFT there have been many variations on the original approach, the simplest of which describes chains of hard-sphere (HS) segments with attractive interactions described at the mean-field level of van der Waals (which we refer to as SAFT-HS [11, 12]). The SAFT-HS equation of state has been successfully used to study the phase behaviour and critical lines of systems in which at least one of the components is strongly associated, such as alkanes + water [13], refrigerants + hydrogen fluoride [14] and water + alkylpolyoxyethylenes [15, 16]. In these cases the hydrogen bonding is dominant, and the weak dispersive attraction can be described by a background mean-field interaction. The SAFT-HS treatment is not as adequate for systems where the dispersive interactions are domi-

nant such as the alkanes [17, 18]. The SAFT-HS equation of state was also applied to the treatment of heteronuclear molecules using the bonded hard sphere (BHS) approach proposed by Archer and Jackson [19]. Initially only heteronuclear diatomic molecules were examined and the theoretical predictions compared with isothermal–isobaric Monte Carlo simulation results. Amos and Jackson [20] later extended the BHS expressions to treat heteronuclear triatomic molecules and provided the basis for the generalization of the theory to arbitrary polyatomic molecules [21, 22]. Preliminary comparisons with experimental data were made using the BHS model for the *n*-alkanes [23].

Extensions of the SAFT expressions to obtain a more precise description of the thermodynamics of real systems and to describe higher-order terms are numerous (see [24] for an overview). In particular, Blas and Vega [25] have proposed a version of SAFT for homo- and heteronuclear chains based on an extension of Wertheim's theory for Lennard-Jones fluids due to Johnson *et al.* [26]. Heteronuclear Lennard-Jones diatomics were studied and good agreement was achieved with Monte Carlo simulation data. In a recent extension of SAFT, chain molecules formed from hard-core monomers with attractive potentials of variable range (VR) [24, 27] were examined. This allows the treatment of non-conformal systems and provided a more accurate

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description of the thermodynamics due to dispersion forces compared with the mean-field treatment used in SAFT-HS. Furthermore, the equation of state is more compact than the Lennard-Jones versions while achieving the same degree of accuracy [24]. The SAFT-VR approach has been successfully used in the description of the fluid phase behaviour of a wide range of industrially important systems, e.g. alkanes, perfluoroalkanes and their mixtures [17, 18, 24, 28], hydrogen fluoride + water [29], refrigerant systems [30], hydrogen chloride + *n*-alkanes [31], and reacting systems such as formaldehyde + water [32]. In this earlier work the molecules are described by a united atom model where each segment represents a group of atoms; the tangentially bonded segments are of equal diameters σ with the attractive interactions described by a potential of variable range. The adequacy of the SAFT-VR approach in describing the phase equilibria of chain molecules formed from tangent square-well [24], Lennard-Jones [33], and Yukawa [34] segments is already firmly established. We should however note that the united atom model is too crude to reproduce some of the finer details of the properties of real chain molecules; for example, with the *n*-alkane homologous series one cannot describe the anomalously low critical pressure of methane [23]. An atomistic or distributed-site model where the molecule is represented by a number of linked spherical sites which usually coincide with the individual atoms forming the molecule, provides a more explicit description of chain molecules such as the *n*-alkanes.

The application of the SAFT-VR equation of state to describe heteronuclear molecules is a natural step towards more accurate models for the treatment of real substances. For example, a study of heteronuclear models allows us to model molecules formed from groups of different sizes, such as the perfluoroalkyl-alkanes (or semi-fluorinated *n*-alkanes) which are an important class of amphiphile formed by bonding together a hydrocarbon and a fluorocarbon chain. In this work we present the SAFT-VR expressions which allow the description of such heteronuclear models. In particular we examine models composed of bonded square-well segments which we have called the bonded square-well (BSW) model. The theoretical predictions for heteronuclear diatomics are studied and compared with exact results from isothermal-isobaric Monte Carlo simulations as an initial test of the SAFT-VR approach for the BSW model.

2. Models and theory

We consider heteronuclear molecules formed from *n* tangentially bonded square-well (BSW) segments. The segment-segment square-well interaction is given by

$$u_{ij}(r) = \begin{cases} +\infty, & \text{if } r < \sigma_{ij}, \\ -\varepsilon_{ij}, & \text{if } \sigma_{ij}r \leq r < \lambda_{ij}\sigma_{ij}, \\ 0, & \text{if } r \geq \lambda_{ij}\sigma_{ij}, \end{cases} \quad (1)$$

where r is the distance between the two spheres, σ_{ij} is the diameter of the interaction, and λ_{ij} the range and ε_{ij} the depth of the square-well potential. We should note that although we consider SAFT-VR for the square-well potential in this work, the Sutherland, Lennard-Jones or Yukawa potentials can be treated within the same theory [24]. In contrast to the original SAFT approach, where homonuclear molecules with segments of equal diameter are tangentially bonded together to form a linear chain, heteronuclear molecules can be formed from spherical segments of different sizes. Examples of BSW models are found in figure 1: a heteronuclear chain molecule formed from two tangentially bonded chains with spherical segments of different diameter (figure 1(a)) could describe amphiphilic molecules such as the perfluoroalkylalkanes and even block copolymers.

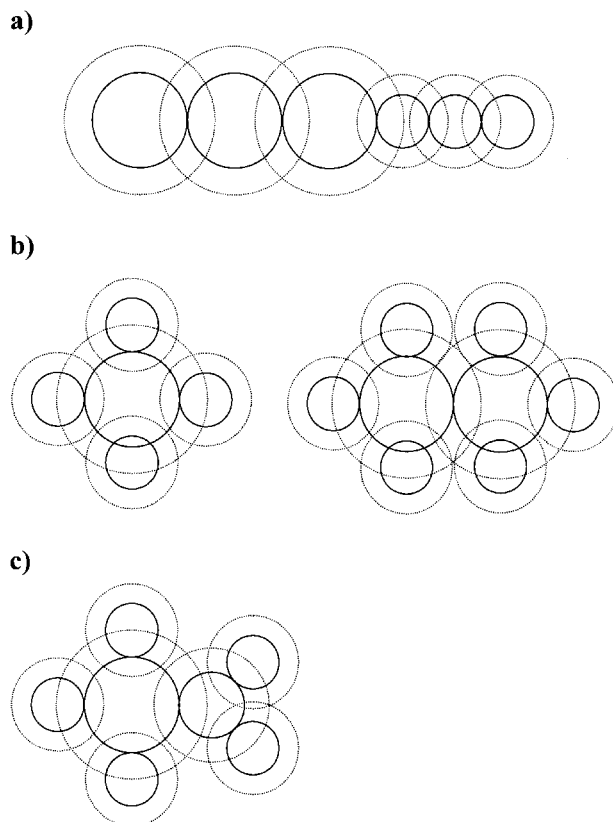


Figure 1. The BSW model of heteronuclear molecules: (a) linear heteronuclear chain molecules formed from tangentially bonded square-well segments; (b) alkane-like molecules formed from smaller square-well segments bonded to a larger central segment; (c) a general polyatomic molecule.

Table 1. Potential parameters for the three heteronuclear dimer systems studied. σ_{ij} is the hard-core diameter, λ_{ij} the range of the square-well interaction, and ε_{ij} the attractive square-well energy of segment i .

System	I	II	III
σ_{22}/σ_{11}	0.5	0.5	0.5
$\varepsilon_{22}/\varepsilon_{11}$	1.0	1.0	0.5
λ_{11}	1.5	1.5	1.5
λ_{22}	1.5	1.25	1.25

The heteronuclear diatomic molecules studied in this work are formed from tangentially bonded square-well segments with diameters σ_{11} and σ_{22} , where $\sigma_{22} = \sigma_{11}/2$ in all cases: in system I both segment 1 and 2 have equal well depths and potential ranges; in system II the depth of the potential well for the two segments remains identical, although the range of interaction now differs; and in system III the segments have different depths and ranges of the attractive potential (see table 1 for details). Note that the unlike size and energy parameters have been determined using the Lorentz–Berthelot combining rules [35],

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \quad (2)$$

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}, \quad (3)$$

and the unlike range parameter is obtained from the arithmetic mean,

$$\lambda_{ij} = (\lambda_{ii}\sigma_{ii} + \lambda_{jj}\sigma_{jj})/(\sigma_{ii} + \sigma_{jj}). \quad (4)$$

The generalization of the SAFT-VR equation of state to treat heteronuclear molecules is a straight forward procedure. We present the SAFT-VR expressions for the treatment of polyatomic heteronuclear molecules followed by the specific equations for a heteronuclear diatomic composed of two segments of diameter σ_{11} and σ_{22} . Within the SAFT formalism the Helmholtz free energy A can be written in terms of the various contributions as

$$\frac{A}{NkT} = \frac{A^{\text{IDEAL}}}{NkT} + \frac{A^{\text{MONO}}}{NkT} + \frac{A^{\text{BOND}}}{NkT}, \quad (5)$$

where N is the total number of molecules, A^{IDEAL} is the ideal free energy, A^{MONO} is the residual free energy due to the monomer segments, and A^{BOND} the contribution due to bond formation. The chain term as presented in the original SAFT-VR equation of state is the specific case for homonuclear chains. Note we have not included the association term characteristic of the SAFT approach as the systems studied in this work are non-associating.

The ideal contribution to the free energy is given by [36]

$$\frac{A^{\text{IDEAL}}}{NkT} = \ln \rho \Lambda^3 - 1, \quad (6)$$

where $\rho = N/V$ is the number density of the fluid, Λ is the thermal de Broglie wavelength (strictly the ideal term should also contain the inertial contributions, but these do not affect the phase equilibria of the system), and V is the volume of the system.

We express the monomer Helmholtz free energy as a sum over all segments i ,

$$\begin{aligned} \frac{A^{\text{MONO}}}{NkT} &= \sum_{i=1}^n \frac{A^M}{N_s kT} \\ &= 2a^M, \end{aligned} \quad (7)$$

where N_s is the total number of spherical segments and $a^M = A^M/N_s kT$ the excess Helmholtz free energy *per* segment. This is expressed as a high-temperature expansion about a hard-sphere reference system using the perturbation theory of Barker and co-workers [37] for mixtures,

$$a^M = a^{\text{HS}} + \beta a_1 + \beta^2 a_2, \quad (8)$$

where $\beta = 1/kT$, a^{HS} is the free energy of the reference hard sphere term and a_1 and a_2 are the first two perturbative terms. Note that although we are considering a pure heteronuclear fluid the terms in equation (8) correspond to a mixture of segments of different sizes; for example, a heteronuclear diatomic molecule is treated as an equimolar binary mixture. The expression of Boublík [38] and Mansoori *et al.* [39] for a multicomponent mixture of hard spheres is used for the reference hard-sphere term,

$$\begin{aligned} a^{\text{HS}} &= \frac{6}{\pi\rho_s} \left[\left(\frac{\zeta_3^3}{\zeta_3} - \zeta_0 \right) \ln(1 - \zeta_3) \right. \\ &\quad \left. + \frac{3\zeta_1\zeta_2}{(1 - \zeta_3)} + \frac{\zeta_3^3}{\zeta_3(1 - \zeta_3)^2} \right], \end{aligned} \quad (9)$$

where ρ_s is the total number density of spherical segments and ζ_i are the reduced densities defined by

$$\begin{aligned} \zeta_i &= \frac{\pi\rho_s}{6} \left[\sum_{i=1}^m x_{s,i} \sigma_{ii}^3 \right] \\ &= \frac{\pi\rho_s}{6} \left[\frac{1}{2}\sigma_{11}^3 + \frac{1}{2}\sigma_{22}^3 \right]. \end{aligned} \quad (10)$$

Here, σ_{ii} is the diameter and $x_{s,i}$ is the mole fraction of spherical segments of type i . The mean-attractive energy represented by the a_1 term is obtained from the sum of

the partial terms corresponding to each type of pair interaction [24, 27],

$$\begin{aligned} a_1 &= \sum_{i=1}^n \sum_{j=1}^n x_{s,i} x_{s,j} a_1^{ij} \\ &= \frac{1}{4} a_1^{11} + \frac{1}{2} a_1^{12} + \frac{1}{4} a_1^{22}, \end{aligned} \quad (11)$$

where

$$a_1^{ij} = -2\pi\rho_s \varepsilon_{ij} \int_{\sigma_{ij}}^{\infty} r_{ij}^2 g_{ij}^{\text{HS}}[r_{ij}; \zeta_3] dr_{ij}. \quad (12)$$

Using the mean-value theorem [24, 27] we obtain an expression for a_1 in terms of the contact value of the radial distribution function for a mixture of hard-spheres g_{ij}^{HS} :

$$a_1 = -\rho_s \sum_i \sum_j x_{s,i} x_{s,j} \alpha_{ij}^{\text{VDW}} g_{ij}^{\text{HS}}[\sigma_{ij}; \zeta_3^{\text{eff}}], \quad (13)$$

where

$$\alpha_{ij}^{\text{VDW}} = 2\pi\varepsilon_{ij}\sigma_{ij}^3(\lambda_{ij}^3 - 1)/3 \quad (14)$$

is the van der Waals attractive constant for the i - j interaction and ζ_3^{eff} is an effective packing fraction. The parametrization obtained in the original SAFT-VR paper [24] for a pure fluid is used to determine the dependence on the actual packing fraction of the system ζ_3 ;

$$\zeta_3^{\text{eff}}(\zeta_3, \lambda_{ij}) = c_1(\lambda_{ij})\zeta_3 + c_2(\lambda_{ij})\zeta_3^2 + c_3(\lambda_{ij})\zeta_3^3, \quad (15)$$

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 2.25855 & -1.50349 & 0.249434 \\ -0.669270 & 1.40049 & -0.827739 \\ 10.1576 & -15.0427 & 5.30827 \end{pmatrix} \begin{pmatrix} 1 \\ \lambda_{ij} \\ \lambda_{ij}^2 \end{pmatrix}. \quad (16)$$

The contact value of the radial pair distribution function for a mixture of hard spheres $g_{ij}^{\text{HS}}[\sigma_{ij}; \zeta_3^{\text{eff}}]$ is obtained from the expression of Boublík [38],

$$g_{ij}^{\text{HS}}[\sigma_{ij}; \zeta_3^{\text{eff}}] = \frac{1}{1 - \zeta_3^{\text{eff}}} + 3 \frac{D_{ij} \zeta_3^{\text{eff}}}{(1 - \zeta_3^{\text{eff}})^2} + 2 \frac{(D_{ij} \zeta_3^{\text{eff}})^2}{(1 - \zeta_3^{\text{eff}})^3}, \quad (17)$$

where for convenience the equation is written in terms of the parameter D_{ij} ,

$$D_{ij} = \frac{\sigma_{ii}\sigma_{jj} \sum_{i=1}^n x_{s,i} \sigma_{ii}^2}{\sigma_{ii} + \sigma_{jj} \sum_{i=1}^n x_{s,i} \sigma_{ii}^3}. \quad (18)$$

The first fluctuation term a_2 is given by the local compressibility approximation [24, 27] as applied to mixtures [40, 41],

$$\begin{aligned} a_2 &= \sum_{i=1}^n \sum_{j=1}^n x_{s,i} x_{s,j} a_2^{ij} \\ &= \frac{1}{4} a_2^{11} + \frac{1}{2} a_2^{12} + \frac{1}{4} a_2^{22}, \end{aligned} \quad (19)$$

where the terms a_2^{ij} are obtained from the expressions for a_1^{ij} ,

$$a_2^{ij} = \frac{1}{2} K^{\text{HS}} \varepsilon_{ij} \rho_s \frac{\partial a_1^{ij}}{\partial \rho_s}, \quad (20)$$

and K^{HS} is the hard-sphere isothermal compressibility of Percus–Yevick [42],

$$K^{\text{HS}} = \frac{\zeta_0(1 - \zeta_3)^4}{\zeta_0(1 - \zeta_3)^2 + 6\zeta_1\zeta_2(1 - \zeta_3) + 9\zeta_2^3}. \quad (21)$$

Finally, the contribution to the free energy due to bond formation between two segments is expressed in terms of the contact value of the segment–segment background correlation function [24, 27],

$$\begin{aligned} \frac{A^{\text{BOND}}}{NkT} &= - \sum_{ij \text{ bonds}} \ln y_{ij}^{\text{SW}}(\sigma_{ij}) \\ &= - \ln y_{12}^{\text{SW}}(\sigma_{12}), \end{aligned} \quad (22)$$

where

$$y_{ij}^{\text{SW}}(\sigma_{ij}) = g_{ij}^{\text{SW}}(\sigma_{ij}) \exp(-\beta\varepsilon_{ij}), \quad (23)$$

and is determined from the high-temperature expansion of $g_{ij}^{\text{SW}}(\sigma_{ij})$ to first order,

$$g_{ij}^{\text{SW}}(\sigma_{ij}) = g_{ij}^{\text{HS}}(\sigma_{ij}) + \beta\varepsilon_{ij} g_{ij}^{\text{SW}}(\sigma_{ij}). \quad (24)$$

The radial distribution function $g_{ij}^{\text{SW}}(\sigma_{ij})$ is obtained from a self-consistent method for the pressure p from the Clausius theorem and from the density derivative of the Helmholtz free energy [24, 27],

$$\begin{aligned} g_{ij}^{\text{SW}}[\sigma_{ij}; \zeta_3] &= g_{ij}^{\text{HS}}[\sigma_{ij}; \zeta_3] + \beta\varepsilon_{ij} \left[g_{ij}^{\text{HS}}[\sigma_{ij}; \zeta_3^{\text{eff}}] \right. \\ &\quad \left. + (\lambda_{ij}^2 - 1) \frac{\partial g_{ij}^{\text{HS}}[\sigma_{ij}; \zeta_3^{\text{eff}}]}{\partial \zeta_3^{\text{eff}}} \right. \\ &\quad \left. \times \left(\frac{\lambda_{ij}}{3} \frac{\partial \zeta_3^{\text{eff}}}{\partial \lambda_{ij}} - \zeta_3 \frac{\partial \zeta_3^{\text{eff}}}{\partial \zeta_3} \right) \right]. \end{aligned} \quad (25)$$

It is clear that the chain contribution for homonuclear molecules of m segments is a special case in which all $(m-1)$ i - j bonds are equivalent. Hence,

$$\frac{A^{\text{BOND}}}{NkT} = -(m-1) \ln y^{\text{SW}}(\sigma), \quad (26)$$

which is analogous to the chain contribution for a pure fluid (equation (106) of [24]).

3. NpT Monte Carlo simulations

Simulations were carried out in the isothermal-isobaric (NpT) ensemble using the Monte Carlo method of Wood [43]. Although similar studies on homo- and heteronuclear square-well diatomics have been carried out by Lisal and Nezbeda [44] using Monte Carlo simulations in the canonical and Gibbs ensembles, we do not make direct comparisons with their results as the majority of the molecules examined are fused diatomics.

At the start of the simulations 250 heteronuclear diatomics are placed at random orientations on the sites of a face centred cubic lattice with the usual periodic boundary conditions (PBC) and minimum image convention (MIC). A cycle in the simulation consists of N trial re-orientations and displacements of the molecules and one volume change (see [19] for details). The extent of the particle displacements and reorientations is adjusted so that the separate acceptance probabilities are almost equal and the overall acceptance probability is about 40%. The random changes in volume are achieved by varying the hard-core diameters with

Table 2. Isothermal-isobaric Monte Carlo simulation results for system I with parameters: $\sigma_{22} = 0.5\sigma_{11}$; $\varepsilon_{22} = \varepsilon_{11}$; $\lambda_{11} = \lambda_{12} = \lambda_{22} = 1.5$. The fixed variables during the simulation are the number of particles $N = 250$, the reduced pressure $p^* = p\pi\sigma_{11}^3/(6kT)$, and the reduced temperature $T^* = kT/\varepsilon_{11}$. The packing fraction is given by ζ_3 and the reduced energy per molecule $E^* = E/\varepsilon_{11}N$; the uncertainties correspond to one standard deviation.

T^*	p^*	ζ_3	E^*
1.0	0.1698	0.418 ± 0.005	-10.47 ± 0.13
1.0	0.3739	0.424 ± 0.005	-10.60 ± 0.12
1.0	0.7553	0.438 ± 0.004	-10.92 ± 0.11
1.0	1.2408	0.453 ± 0.004	-11.25 ± 0.10
1.5	0.0849	0.316 ± 0.008	-7.54 ± 0.21
1.5	0.3929	0.363 ± 0.006	-8.67 ± 0.17
1.5	1.6116	0.408 ± 0.004	-9.77 ± 0.12
2.0	0.0657	0.104 ± 0.007	-2.62 ± 0.20
2.0	0.0908	0.148 ± 0.001	-3.59 ± 0.09
2.0	0.1259	0.211 ± 0.009	-4.84 ± 0.24
2.0	0.2016	0.255 ± 0.008	-5.78 ± 0.20
2.0	0.3854	0.309 ± 0.004	-7.01 ± 0.14
2.0	0.8055	0.360 ± 0.007	-8.31 ± 0.21
2.0	1.6777	0.407 ± 0.005	-9.52 ± 0.15
3.0	0.0904	0.100 ± 0.005	-2.04 ± 0.14
3.0	0.1584	0.155 ± 0.007	-3.09 ± 0.18
3.0	0.2516	0.204 ± 0.007	-4.18 ± 0.18
3.0	0.4085	0.252 ± 0.007	-5.29 ± 0.18
3.0	0.6955	0.301 ± 0.007	-6.49 ± 0.20
3.0	1.2306	0.354 ± 0.006	-7.86 ± 0.17
3.0	2.2083	0.403 ± 0.004	-9.17 ± 0.12

respect to the box length to again give an acceptance of about 40%. The packing fraction $\zeta_3 = \pi N(\sigma_{11}^3 + \sigma_{22}^3)/(6V)$ and the energy $E^* = E/\varepsilon_{11}N$ of the system corresponding to a given reduced pressure $p^* = p\pi\sigma_{11}^3/(6kT)$ are obtained as ensemble averages and the errors estimated by determining the standard deviation. Initially the system is equilibrated for 10000 cycles and a further 10000 to 20000 cycles are performed to accumulate the averages.

4. Results

The isothermal-isobaric Monte Carlo data for the three heteronuclear diatomic systems are compared with the theoretical predictions from the SAFT-VR approach. The simulation data for system I in which the heteronuclear diatomic segments interact through potentials of identical range and well depth ($\varepsilon = \varepsilon_{11} = \varepsilon_{12} = \varepsilon_{22}$; $\lambda_{11} = \lambda_{12} = \lambda_{22} = 1.5$) are presented in table 2. The isotherms studied are shown in figure 2 where we compare the results of the SAFT-VR equation of state with the simulation data. Good agreement between the theoretical predictions and simulation data over the entire fluid range is achieved, although

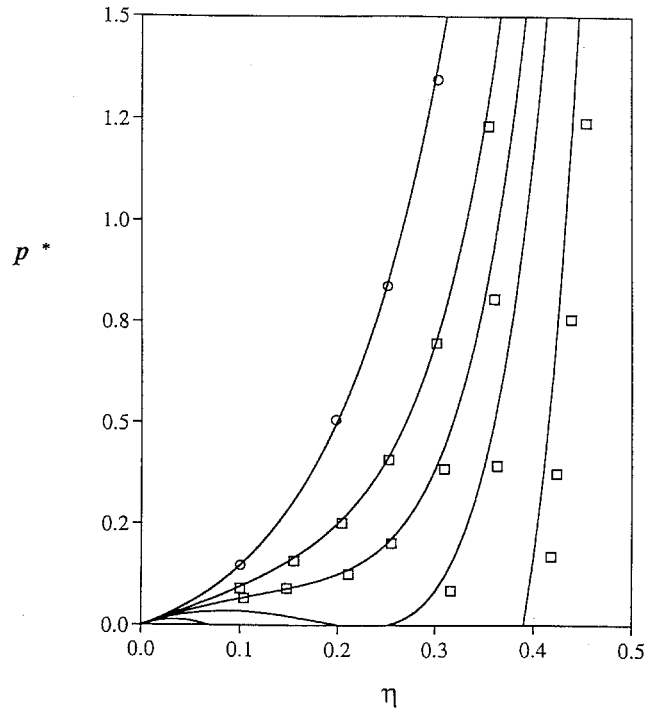


Figure 2. Isotherms for the square-well heteronuclear diatomic with diameter ratio $\sigma_{22} = 0.5\sigma_{11}$, well depth $\varepsilon_{22} = \varepsilon_{11}$, and range $\lambda_{11} = \lambda_{12} = \lambda_{22} = 1.5$. The squares represent the results of isothermal-isobaric Monte Carlo simulations and the circles those of Archer and Jackson [19] for the hard system (infinite temperature). The continuous curves correspond to theoretical predictions using the SAFT-VR equation of state.

Table 3. Isothermal-isobaric Monte Carlo simulation results for system II with parameters: $\sigma_{22} = 0.5\sigma_{11}$; $\varepsilon_{22} = \varepsilon_{11}$; $\lambda_{11} = 1.5$, $\lambda_{12} = 1.42$, and $\lambda_{22} = 1.25$. See table 2 for details.

T^*	p^*	ζ_3	E^*
1.0	0.3576	0.420 ± 0.004	-9.64 ± 0.12
1.0	0.5484	0.425 ± 0.006	-9.76 ± 0.15
1.0	1.0438	0.443 ± 0.004	-10.12 ± 0.11
1.0	1.7221	0.459 ± 0.004	-10.46 ± 0.10
1.5	0.0501	0.171 ± 0.007	-4.21 ± 0.21
1.5	0.0542	0.216 ± 0.018	-4.95 ± 0.34
1.5	0.0863	0.280 ± 0.013	-6.07 ± 0.25
1.5	0.2064	0.323 ± 0.009	-6.95 ± 0.20
1.5	0.5351	0.363 ± 0.007	-7.86 ± 0.18
1.5	1.2890	0.409 ± 0.005	-8.96 ± 0.14
2.0	0.0749	0.105 ± 0.007	-2.23 ± 0.17
2.0	0.1124	0.160 ± 0.012	-3.27 ± 0.24
2.0	0.1668	0.209 ± 0.015	-4.20 ± 0.31
2.0	0.2681	0.265 ± 0.009	-5.33 ± 0.21
2.0	0.4781	0.311 ± 0.008	-6.35 ± 0.19
2.0	0.9131	0.357 ± 0.006	-7.46 ± 0.16
2.0	1.7746	0.409 ± 0.005	-8.71 ± 0.14
2.5	0.0439	0.051 ± 0.003	-0.97 ± 0.10
2.5	0.0908	0.101 ± 0.006	-1.90 ± 0.14
2.5	0.1491	0.155 ± 0.008	-2.90 ± 0.18
2.5	0.2345	0.206 ± 0.010	-3.89 ± 0.22
2.5	0.3792	0.259 ± 0.009	-4.99 ± 0.21
2.5	0.6453	0.308 ± 0.006	-6.12 ± 0.17
2.5	1.1456	0.354 ± 0.006	-7.23 ± 0.16
2.5	2.0724	0.404 ± 0.004	-8.44 ± 0.13
3.0	0.0464	0.051 ± 0.003	-0.89 ± 0.09
3.0	0.1011	0.102 ± 0.005	-1.79 ± 0.13
3.0	0.1731	0.153 ± 0.007	-2.71 ± 0.15
3.0	0.2798	0.204 ± 0.007	-3.69 ± 0.16
3.0	0.4541	0.251 ± 0.008	-4.69 ± 0.20
3.0	0.7585	0.305 ± 0.001	-5.92 ± 0.17
3.0	1.3031	0.353 ± 0.006	-7.08 ± 0.17
3.0	2.2736	0.402 ± 0.004	-8.28 ± 0.13

slightly larger deviations are seen at higher densities. We have included the simulation results of [19] for the hard sphere system with $\sigma_{22} = \sigma_{11}/2$ for comparison with the SAFT-VR theory at an infinite temperature; as expected we see excellent agreement between the theoretical predictions of SAFT-VR and the exact simulation results for the HS system.

In table 3 we present the NpT -MC simulation results for system II, where the heteronuclear diatomic segments now interact through potentials of differing range but equal well depths ($\varepsilon = \varepsilon_{11} = \varepsilon_{12} = \varepsilon_{22}$; $\lambda_{11} = 1.5$, $\lambda_{12} = 1.42$, and $\lambda_{22} = 1.25$). The isotherms for system II, shown in figure 3, have a steeper pressure-density dependence when compared with those of

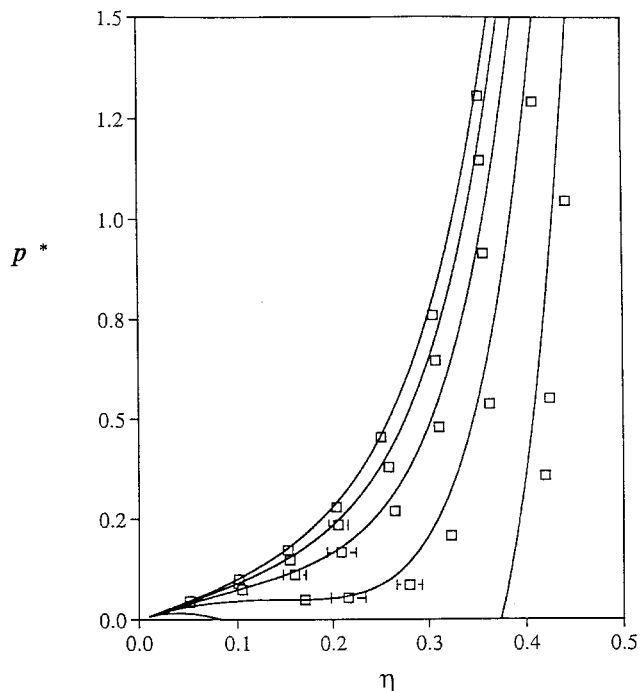


Figure 3. Isotherms for the square-well heteronuclear diatomic with diameter ratio $\sigma_{22} = 0.5\sigma_{11}$, well depth $\varepsilon_{22} = \varepsilon_{11}$, and range $\lambda_{11} = 1.5$, $\lambda_{12} = 1.42$, and $\lambda_{22} = 1.25$. The squares represent the results of isothermal-isobaric Monte Carlo simulations and the continuous curves correspond to theoretical predictions using the SAFT-VR equation of state.

the previous system. Good agreement between the exact simulation results and the SAFT-VR approach is found.

Finally the results of the NpT -MC simulations for system III where the segments have different depths and ranges of the attractive potential ($\varepsilon_{22} = 0.5\varepsilon_{11}$ and $\varepsilon_{12} = 0.7\varepsilon_{11}$; $\lambda_{11} = 1.5$, $\lambda_{12} = 1.42$, and $\lambda_{22} = 1.25$) are presented in table 4 and the corresponding isotherms in figure 4. From a comparison of figures 3 and 4 it is apparent that reducing the depth of the potential well of the smaller sphere has little noticeable effect on the thermodynamics of the system. Again the theory provides a good description of the simulation data over the entire fluid range.

5. Conclusions

We have generalized the SAFT-VR equation of state to heteronuclear chain molecules. Isotherms for three heteronuclear diatomic models are compared with isothermal-isobaric Monte Carlo simulation results and good agreement is found. This encouraging preliminary study sets the basis for the future examination of more complex heteronuclear models. For example a natural extension of our previous work on n -alkane + perfluoro- n -alkane mixtures [17, 18, 28] will be to examine the

Table 4. Isothermal-isobaric Monte Carlo simulation results for system II with parameters: $\sigma_{22} = 0.5\sigma_{11}$; $\varepsilon_{22} = 0.5\varepsilon_{11}$; $\lambda_{11} = 1.5$, and $\lambda_{12} = 1.42$, $\lambda_{22} = 1.25$. See table 2 for details.

T^*	p^*	ζ_3	E
1.0	0.105	0.378 ± 0.006	-7.41 ± 0.13
1.0	0.770	0.413 ± 0.005	-8.09 ± 0.12
1.5	0.058	0.105 ± 0.010	-2.17 ± 0.21
1.5	0.076	0.151 ± 0.010	-2.96 ± 0.19
1.5	0.102	0.203 ± 0.010	-3.78 ± 0.20
1.5	0.168	0.259 ± 0.010	-4.70 ± 0.20
1.5	0.340	0.314 ± 0.007	-5.73 ± 0.17
1.5	0.739	0.362 ± 0.005	-6.71 ± 0.13
1.5	1.575	0.406 ± 0.004	-7.62 ± 0.10
2.0	0.083	0.101 ± 0.006	-1.75 ± 0.12
2.0	0.131	1.153 ± 0.009	-2.59 ± 0.17
2.0	0.202	0.200 ± 0.008	-3.38 ± 0.17
2.0	0.331	0.254 ± 0.007	-4.34 ± 0.16
2.0	0.581	0.309 ± 0.007	-5.43 ± 0.15
2.0	1.070	0.355 ± 0.006	-6.39 ± 0.14
2.0	1.993	0.404 ± 0.004	-7.40 ± 0.10
2.5	0.097	0.101 ± 0.005	-1.60 ± 0.11
2.5	0.163	0.150 ± 0.007	-2.39 ± 0.13
2.5	0.263	0.202 ± 0.006	-3.26 ± 0.13
2.5	0.430	0.251 ± 0.006	-4.14 ± 0.14
2.5	0.729	0.305 ± 0.006	-5.22 ± 0.15
2.5	1.273	0.353 ± 0.006	-6.23 ± 0.14
2.5	2.249	0.403 ± 0.004	-7.27 ± 0.11
3.0	0.106	0.099 ± 0.005	-1.48 ± 0.11
3.0	0.185	0.152 ± 0.006	-2.32 ± 0.12
3.0	0.303	0.200 ± 0.006	-3.14 ± 0.14
3.0	0.497	0.253 ± 0.007	-4.12 ± 0.15
3.0	0.829	0.301 ± 0.005	-5.07 ± 0.13
3.0	1.410	0.352 ± 0.005	-6.14 ± 0.13
3.0	2.422	0.402 ± 0.005	-7.19 ± 0.12

phase behaviour of perfluoroalkylalkanes. The application of the united atom mode to tangentially bonded heteronuclear chains would also allow the treatment of copolymers such as those examined by Gulati *et al.* [45] with the generalized Flory equation of state. Furthermore, the BSW model allows a more atomistic approach to the modelling of molecules, which would enable a group contribution like treatment of real molecules, where the various atoms and functional groups are treated independently and are therefore transferable. It is also straightforward to extend the approach to treat associating models, as in the original SAFT-VR approach, and to mixtures of BSW models (cf. [21]).

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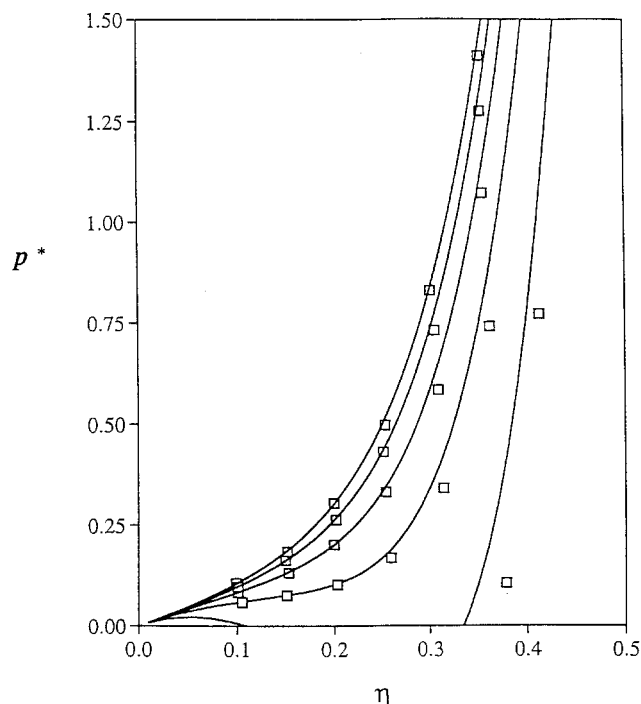


Figure 4. Isotherms for the square-well heteronuclear diatomic with diameter ratio $\sigma_{22} = 0.5\sigma_{11}$, well depth $\varepsilon_{22} = 0.5\varepsilon_{11}$, and range $\lambda_{11} = 1.5$, $\lambda_{12} = 1.42$, and $\lambda_{22} = 1.25$. The squares represent the results of isothermal-isobaric Monte Carlo simulations and the continuous curves correspond to theoretical predictions using the SAFT-VR equation of state.

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