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Extension of an Improved One-Fluid Conformal Solution Theory to Real Fluid Mixtures with Large Size Differences[1]

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Conformal solution theories have been shown to be inadequate as the size ratio of the molecules in a mixture increases. We present an improved van der Waals-1 fluid conformal solution theory which incorporates a correction term developed using statistical mechanical perturbation theory. The correction addresses the effect of different size molecules on the Helmholtz free energy of the mixture. Results of the new model are compared with other conformal solution theories for model Lennard–Jones systems. We also show how to extend the model to perform computations on real fluid mixtures. Results for selected hydrocarbon mixtures are given.

KEY WORDS: conformal solution theory; corresponding states; Lennard–Jones mixtures.

1. INTRODUCTION

The most successful predictive models for the calculation of the equilibrium thermodynamic properties of mixtures are those based upon a corresponding states or conformal solution principle. When the mixture contains molecules which do not differ much in size, the van der Waals one-fluid (VDW-1) approximation developed by Leland and co-workers [1] has been shown to perform well [2–4]. When the molecules in the mixture do have large size differences, studies have shown that these types of models tend to fail [5, 6]. Several approaches have been used to improve conformal solution models, such as the use of theoretically derived mixing rules

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[7], and the use of a correction factor to the mean density approximation (MDA) of Mansoori and Leland [8], developed using statistical mechanical perturbation theory [9]. In this work we present a new conformal solution theory which incorporates the VDW-1 concept and statistical mechanical perturbation theory.

A conformal solution is one in which all the molecules obey the same reduced intermolecular potential function, which may be written as the product of an energy parameter and a universal function F. A simple example, which is used in this work, is the Lennard-Jones 12-6 potential

$$u_{ij}(r) = 4\varepsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^{6}] = \varepsilon_{ij}F(r/\sigma_{ij}) \tag{1}$$

where ε_{ij} and σ_{ij} are the energy and distance parameters for the potential, and F is a universal function for all species. Given this type of potential, simple scaling arguments applied to the canonical ensemble partition function enable us to express the properties of fluid i in terms of some known reference fluid properties [10];

$$A_i^{\mathrm{r}}(T, V) = f_{ii}A_0^{\mathrm{r}}(T/f_{ii}, V/h_{ii}) \tag{2}$$

and

$$Z_i^{\mathrm{r}}(T, V) = Z_0^{\mathrm{r}}(T/f_{ii}, V/h_{ii}) \tag{3}$$

where A^{r} and Z^{r} denote the residual Helmholtz energy and compressibility factor, the subscript 0 refers to the reference fluid, and the factors f_{ii} and h_{ii} are called equivalent substance reducing ratios, defined as $h_{ii} = (\sigma_{ii}/\sigma_{00})^3$ and $f_{ii} = (\varepsilon_{ii}/\varepsilon_{00})$. Equations (2) and (3) are an expression of the law of corresponding states. Since all points on the PVT surface of any conformal substance may be represented by scaling the PVT surface of the reference substance, we may express the equivalent substance reducing ratios in terms of the critical volumes and critical temperatures, $h_{ii} = (V_i^{\mathrm{cr}}/V_0^{\mathrm{cr}})$ and $f_{ii} = (T_i^{\mathrm{cr}}/T_0^{\mathrm{cr}})$. If the fluids are not conformal, we can use the concept of extended corresponding states, developed by Leland and co-workers [11–13], which introduces the use of shape factors Φ_{ii} and Θ_{ii}. These are density- and temperature-dependent factors which force conformality by modifying the equivalent substance reducing ratios,

$$h_{ii} = (V_i^{\mathrm{cr}}/V_0^{\mathrm{cr}})\,\Phi_{ii} \tag{4}$$

$$f_{ii} = (T_i^{\mathrm{cr}}/T_0^{\mathrm{cr}})\,\Theta_{ii} \tag{5}$$

Extension of these scaling arguments to mixtures is not successful since the potential energy depends on the assignment of the positions of the molecules in each configuration. It is therefore necessary to adopt empirical combining and mixing rules, such as the Lorentz–Berthelot combining rules,

$$f_{ij} = (f_{ii} f_{jj})^{1/2} (1 - k_{ij}) \tag{6}$$

$$h_{ij} = 0.125 (h_{ii}^{1/3} + h_{jj}^{1/3})^3 (1 - l_{ij}) \tag{7}$$

where k_{ij} and l_{ij} are binary interaction parameters. For mixing rules, the van der Waals mixing rules,

$$h_x = \sum_i \sum_j x_i x_j h_{ij} \tag{8}$$

and

$$f_x h_x = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \tag{9}$$

are often used. Corresponding states may then be applied to the mixture using

$$A_x^{\mathrm{r}}(T, V) = f_x A_0^{\mathrm{r}}(T/f_x, V/h_x) \tag{10}$$

and

$$Z_x^{\mathrm{r}}(T, V) = Z_0^{\mathrm{r}}(T/f_x, V/h_x) \tag{11}$$

This is known as the van der Waals one-fluid model.

2. IMPROVED VDW-1 THEORY

The approach to improving the VDW-1 fluid theory is similar to the method used to develop an improved n-fluid theory in Ref. 9. The essential idea is to use perturbation theory to correct conformal solution theory, rather than to express thermodynamic properties solely in terms of perturbations about hard spheres.

The perturbation theory expansion of a mixture's Helmholtz free energy to order $1/T$ is [14]

$$\frac{A_{\mathrm{mix}}^{\mathrm{r}}}{RT} = \frac{A_{\mathrm{mix}}^{\mathrm{HS,r}}}{RT} + \frac{2\pi\rho}{kT} \left[\sum_i \sum_j x_i x_j \int_{d_{ij}}^{\infty} u_{ij}(r)\, g_{ij}^{\mathrm{HS}}(r, \rho, \{d_{ml}\})\, r^2\, dr \right] \tag{12}$$

where R is the gas constant, k is the Boltzmann constant, g is the radial distribution function, d denotes an effective hard sphere diameter, and the superscript HS refers to a hard sphere property. A similar expansion for a hypothetical pure fluid yields

$$\frac{A_x^{\mathrm{r}}}{RT}=\frac{A_x^{\mathrm{HS,r}}}{RT}+\frac{2\pi\rho}{kT}\left[\int_{d_x}^{\infty} u_x(r)\; g_x^{\mathrm{HS}}(r,\rho,d_x)\, r^2\, dr\right] \tag{13}$$

where the subscript x denotes the hypothetical pure fluid. Subtracting Eq. (13) from Eq. (12) gives

$$\frac{A_{\mathrm{mix}}^{\mathrm{r}}}{RT}=\frac{A_x^{\mathrm{r}}}{RT}+\left[\frac{A_{\mathrm{mix}}^{\mathrm{HS,r}}}{RT}-\frac{A_x^{\mathrm{HS,r}}}{RT}\right]+\frac{2\pi\rho}{kT}\left[I_{\mathrm{mix}}-I_x\right] \tag{14}$$

with

$$I_{\mathrm{mix}}=\left[\sum_i\sum_j x_i x_j \int_{d_{ij}}^{\infty} u_{ij}(r)\; g_{ij}^{\mathrm{HS}}(r,\rho,\{d_{ml}\})\, r^2\, dr\right]$$

and

$$I_x=\left[\int_{d_x}^{\infty} u_x(r)\; g_x^{\mathrm{HS}}(r,\rho,d_x)\, r^2\, dr\right]$$

If the hypothetical pure fluid is chosen according to the VDW-1 fluid model, Eqs. (6)–(11), then Eq. (14) represents a mixture model which gives a correction term for the effect of size on the VDW-1 fluid model.

In order to apply this model, the effective hard sphere diameters for the components, d_{ij}, and the equivalent hard sphere diameter of the pure fluid, d_x, must be specified. Possible choices include the Barker–Henderson diameter [15], the temperature-dependent part of the Chandler–Weeks–Andersen diameter [16], and the empirical correlation of Elliot and Daubert [17]. In this work, the calculations were insensitive to the choice of d_{ij}, and thus we chose simply to set d_{ij} equal to the Lennard–Jones σ_{ij}. A mixing rule to determine d_x can be found by setting $A_{\mathrm{mix}}^{\mathrm{HS}}=A_x^{\mathrm{HS}}$. An alternative mixing rule for the determination of d_x can be found by forcing $Z_{\mathrm{mix}}^{\mathrm{HS}}=Z_x^{\mathrm{HS}}$, resulting in

$$\sum_i\sum_j x_i x_j d_{ij}^3\, g_{ij}^{\mathrm{HS}}(d_{ij})=d_x^3\, g_x^{\mathrm{HS}}(d_x) \tag{15}$$

which permits us to solve for d_x in terms of the d_{ij}, the mole fractions x_i, and the hard sphere contact values of the radial distribution functions. For the hard sphere contact values we used the Percus–Yevick virial values [18, 19]. In our Lennard–Jones studies, we found the mixing rule Eq. (15) generally superior to the mixing rule obtained by setting $A_{\mathrm{mix}}^{\mathrm{HS}}=A_x^{\mathrm{HS}}$, and we therefore report results using only Eq. (15).

The integral terms, I_{mix} and I_x, are found using the Lennard–Jones potential function. This requires evaluation of the hard sphere radial distribution functions for both pure fluids and mixtures, not just at contact, but as a function of *r*. This may be done numerically using the algorithm of Perram [20] to generate the hard sphere distribution functions and numerically evaluating the integrals. The calculational time, however, may be significantly reduced by expressing the integrals in terms of Laplace transforms, as shown in Refs. 21 and 22. The advantage of this formulation is that the Laplace transforms of the hard sphere radial distribution functions have been found analytically for the Percus–Yevick approximation [23] and may be computed rapidly.

3. COMPARISONS WITH LENNARD–JONES SIMULATION DATA

The hard sphere corrected van der Waals model (VDW-HSC), as given by Eqs. (12)–(15), was tested by comparing with computer simulation data for binary Lennard–Jones 6-12 mixtures. The equation of state of Nicolas et al. [24] for Lennard–Jones fluids was used in the conformal solution calculations. Table I shows comparisons of predicted pressures with the simulation data of Ely and Huber [25], for a size ratio (σ_{22}/σ_{11}) of two and a range of compositions and energy ratios. Table I also includes the predictions obtained from the uncorrected VDW-1 model and the perturbation theory of Lee and Levesque [26]. The VDW-HSC is generally superior to VDW-1 for these mixtures, especially in the mid-composition ranges. The improvement in pressure prediction over VDW-1 is very good for the 0.25, 0.50, and 0.75 mole fractions, especially at the largest energy ratio. At these compositions, the perturbation theory gives the best predictions. The VDW-HSC does, however, seem to represent the composition extremes better than the perturbation theory, except at the lowest energy ratio.

Table II gives comparisons for density prediction using the simulation data of Shukla and Haile [27] for equimolar mixtures with equal energies, at several size ratios. The VDW-HSC is superior to VDW-1, especially when the size ratio is large, although the perturbation theory is slightly better. In Table II the version of perturbation theory is that given by Shukla and Haile [27, 28], which combines elements of the Lee–Levesque and Grundke–Henderson [29] perturbation theories, along with an improved method of finding the hard sphere diameter.

4. REAL FLUID MIXTURE RESULTS

In order to extend the conformal solution calculations with the VDW-HSC model to real fluids, the pure fluids must first be made conformal. This is done using the extended corresponding states formalism described in Section 1. Propane was chosen as the reference fluid, and its properties were calculated with a 32-term BWR equation of state [30]. Binary interaction parameters were set to zero.

In addition, the correction terms to the VDW-1 conformal solution model, which involve integrals of the potential functions [see Eq. (14)],

Table I. Equation of State Comparisons for Lennard-Jones Mixtures with $\sigma_{22}/\sigma_{11} = 2$, $T^* = 2$; Percentage Deviations of Pressure for Simulation Data of Ely and Huber [25]

x_1	$\varepsilon_{22}/\varepsilon_{11}$	ρ^*	p^*	VDW	VDW-HSC	PT[a]
0.05	0.5	0.0910	0.5073	−2.67	−2.18	−0.54
0.10	0.5	0.0945	0.5072	−3.47	−2.56	−0.67
0.25	0.5	0.1070	0.5090	−5.70	−4.00	−1.53
0.50	0.5	0.1371	0.5093	−7.10	−5.84	−2.89
0.75	0.5	0.1901	0.5005	−4.13	−5.38	−3.77
0.90	0.5	0.2470	0.4941	−0.77	−2.92	−3.67
0.95	0.5	0.2742	0.4956	−0.36	−1.91	−3.45
0.05	1.0	0.0979	0.5100	−3.93	−2.15	−2.87
0.10	1.0	0.1019	0.5093	−6.22	−2.86	−2.96
0.25	1.0	0.1170	0.5212	−12.12	−5.21	−3.45
0.50	1.0	0.1530	0.5252	−17.25	−9.10	−5.00
0.75	1.0	0.2180	0.5197	−12.07	−8.75	−5.74
0.90	1.0	0.2800	0.5122	−3.86	−4.52	−5.79
0.95	1.0	0.2981	0.5050	−1.70	−2.57	−4.95
0.05	1.5	0.1050	0.5052	−5.78	−1.55	−2.90
0.10	1.5	0.1095	0.5060	−10.19	−2.16	−2.87
0.25	1.5	0.1260	0.5183	−21.72	−4.97	−3.48
0.50	1.5	0.1650	0.4968	−31.33	−9.54	−4.40
0.75	1.5	0.2435	0.5440	−24.22	−10.49	−5.12
0.90	1.5	0.3058	0.5077	−7.13	−4.76	−6.48
0.95	1.5	0.3215	0.5161	−3.11	−2.88	−6.15
0.05	2.0	0.1113	0.5107	−9.69	−1.78	−2.65
0.10	2.0	0.1162	0.5146	−16.82	−1.73	−2.80
0.25	2.0	0.1338	0.5207	−35.49	−3.70	−3.36
0.50	2.0	0.1772	0.5042	−51.10	−7.09	−4.19
0.75	2.0	0.2571	0.4799	−38.40	−8.08	−5.77
0.90	2.0	0.3315	0.5112	−12.44	−4.87	−9.04
0.95	2.0	0.3387	0.5123	−4.28	−2.62	−7.86
Overall avg. absolute Percentage deviation				12.61	4.51	4.08

$\rho^* = \rho\sigma_{11}^3$, $p^* = p\sigma_{11}^3/\varepsilon_{11}$, $T^* = kT/\varepsilon_{11}$

[a] Perturbation theory of Lee and Levesque [26].

Table II. Comparison of Density Prediction for Equimolar Lennard-Jones Mixtures with Equal Energy Ratios; Percentage Deviations of Density from Simulation Data of Shukla and Haile [27]

T^*	P^*	ρ^*	σ_{22}/σ_{11}	VDW	VDW-HSC	PT[a]
1.0	0.5	0.5319	1.25	1.07	0.06	0.62
1.0	0.5	0.3762	1.50	3.00	0.07	0.16
1.0	0.5	0.2400	1.85	6.38	0.70	−0.25
1.0	0.5	0.2008	2.00	7.87	1.15	−0.35
2.0	1.2	0.4091	1.25	2.08	1.53	1.86
2.0	1.2	0.3142	1.50	2.90	1.47	1.02
2.0	1.2	0.2418	1.75	4.14	1.58	0.25
2.0	1.2	0.1875	2.00	5.87	2.11	−0.11
3.0	2.5	0.4133	1.25	1.31	1.14	0.53
3.0	2.5	0.3232	1.50	2.38	1.57	0.37
3.0	2.5	0.2527	1.75	3.68	1.92	−0.04
3.0	2.5	0.1992	2.00	5.07	2.20	−0.55
Overall avg. absolute Percentage deviation				3.81	1.29	0.51

$\rho^* = \rho\sigma_{11}^3$, $p^* = p\sigma_{11}^3/\varepsilon_{11}$, $T^* = kT/\varepsilon_{11}$

[a] Perturbation theory of Shukla and Haile [27, 28].

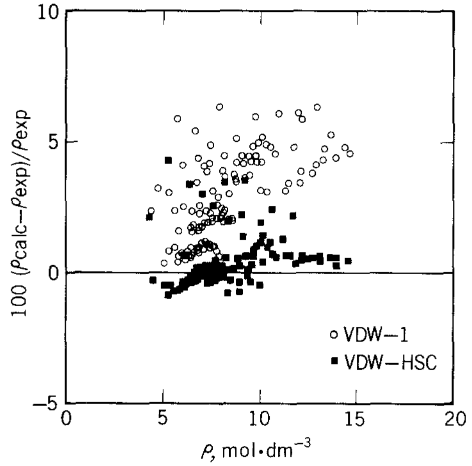

Fig. 1. Density prediction of VDW-1 model (circles) and VDW-HSC (squares) for methane–heptane data of Ref. 31.

must be computed. Thus, effective Lennard–Jones potential parameters for propane, which in principle are functions of temperature, density and composition, must be found. In this work, an average value for the potential parameters was found by optimizing *PVT* or phase equilibrium results over a range of temperatures, compositions, and densities. The results were sensitive to the values of the propane Lennard–Jones parameters, and we also found that the optimum value of ε_0/k and σ_0 for *PVT* calculations differed from that for phase equilibria, suggesting that our method of using an average ε_0/k and σ_0 is too crude. The results do, however, provide an idea of the type of improvement in predictive capability possible with this approach.

Figure 1 shows the percentage error in density prediction for the VDW-1 method (circles) and VDW-HSC (squares), for a methane–heptane system [31]. This system has a size ratio σ_{22}/σ_{11} of 1.64 and an energy ratio $\varepsilon_{22}/\varepsilon_{11}$ of 2.83. Figure 2 shows the results for the percent error in density prediction for a methane–decane system [32], which has size ratio 1.83 and energy ratio 3.24. For methane, exact shape factors were found by pointwise mapping onto the reference fluid, while a generalized method was used for the heptane and decane shape factors [33]. The calculations were made using effective average potential parameters of $\sigma_0 = 0.4848$ nm and $\varepsilon_0/k = 179.52$ K. The improvement with VDW-HSC is quite good for both the methane–heptane and the methane–decane systems.

Table III compares the Henry's constant of methane in decane for the VDW-1 and VDW-HSC models with the experimental data of Beaudoin

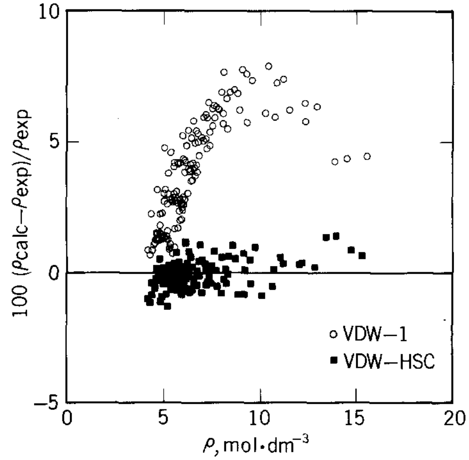

Fig. 2. Density prediction of VDW-1 model (circles) and VDW-HSC (squares) for methane–decane data of Ref. 32.

Table III. Henry's Law Constant for Methane in Decane; Experimental Data from Ref.34

T (K)	ρ (mol · dm^{-3})	Henry's constant (bar)	% error	
			VDW-1	VDW-HSC
248.15	5.374	138	−66	−14
273.15	5.239	168	−55	−8.3
298.15	5.104	193	−46	−2.1
323.15	4.971	215	−36	2.8
348.15	4.835	239	−29	3.8
373.15	4.696	260	−23	3.5
423.15	4.400	283	−14	3.5

and Kohn [34]. For the VDW-HSC, $\sigma_0 = 0.4570$ nm, $\varepsilon_0/k = 145$ K. Table III shows that the VDW-HSC model gives much better predictions than the VDW-1.

5. CONCLUSIONS

A modified van der Waals 1-fluid theory has been developed which uses a hard sphere correction term that accounts for size differences in mixtures. The model has been tested on model Lennard–Jones binary mixtures and found to be superior to VDW-1 theory, although not quite as good as perturbation theory. The model has been extended to perform calculations on real fluid mixtures using extended corresponding-states theory. Sample *PVT* calculations on methane–decane and methane–heptane and Henry's constant calculations for methane–decane show the model to be a significant improvement over VDW-1 fluid theory.

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