

A Computationally Efficient Approach to Applying the SAFT Equation for CO₂ + H₂O Phase Equilibrium Calculations

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Received: 4 July 2013 / Accepted: 25 September 2013 / Published online: 4 December 2013
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Abstract The statistical associating fluid theory equation of state (EoS) is employed in a time efficient way for the correlation and prediction of vapor–liquid equilibrium of the CO₂ + H₂O binary system for the temperature (10–100 °C) and pressure (1–600 bar) ranges suitable for simulation of CO₂ geologic sequestration. The effective number of segments and energy parameter are correlated with the reduced temperature. Simple mixing rules are applied to obtain binary interaction parameters. Assigning a fixed H₂O composition in the mixing rule makes the phase equilibrium calculations relatively fast compared to other EoS's. The results obtained by the model used were found to be in satisfactory agreement with the literature data.

Keywords SAFT · CO₂ + H₂O · Phase equilibrium · Geologic sequestration · Efficient computation

Abbreviations

<i>A</i>	Helmholtz energy (J)
<i>d</i>	Hard-sphere diameter (10 ⁻¹⁰ m)
<i>g</i>	Radius distribution function
<i>k</i>	Boltzman-constant (J·K ⁻¹)
<i>M</i>	Number of associated sites
<i>N</i>	Number of molecules
<i>N_{AV}</i>	Avogadro's number (6.02217 × 10 ²³ mol ⁻¹)
<i>p</i>	Pressure (bar)
<i>P_c</i>	Critical pressure (for CO ₂ 73.83 bar, for H ₂ O 220.55 bar)
<i>T_c</i>	Critical temperature (for CO ₂ 304.2 K, for H ₂ O 647.1 K)
<i>T</i>	Absolute temperature (K)
<i>t</i>	Celsius temperature (°C) (<i>T</i> /K) –273.15
<i>R</i>	Gas constant (J·K ⁻¹ ·mol ⁻¹)

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x	Mole fraction in liquid phase
X_i^A	Mole fraction of molecule i not bonded at site A
y	Mole fraction in vapor phase
Z	Compressibility factor
β	$1/KT$
$\frac{\epsilon}{k}$	Energy parameter of dispersion (K)
$\frac{\epsilon^{AB}}{k}$	Energy parameter of association between sites A and B
κ^{AB}	Bonding volume
Δ^{AB}	Association strength between sites A and B
μ	Chemical potential
ρ	Molar density ($\text{mol}\cdot\text{m}^{-3}$)
ρ_n	Number density (m^{-3})
A, B, C, D, E, F	Constants
abs	Absolute
assoc	Association interaction
chain	Hard-sphere chain
disp	Dispersion interaction
hs	Hard sphere
obj	Objective function
lit	Literature value
cal	Calculated value

1 Introduction

For reducing the amount of CO_2 emitted to the atmosphere the underground sequestration of CO_2 is considered to be a useful method [1–3]. Injecting CO_2 into oil (hydrocarbon) reservoirs is a recognized technology for enhancing oil production and CO_2 injection into depleted oil and/or natural gas reservoirs is already underway to reduce CO_2 emission to the atmosphere [4]. Predicting the sequestration potential and long term behavior of man-made geologic reservoirs requires calculating $\text{CO}_2 + \text{H}_2\text{O}$ phase equilibrium at depths where the temperature remains below $100\text{ }^\circ\text{C}$ and pressures may reach up to several hundred bars. At temperatures below $100\text{ }^\circ\text{C}$, the amount of H_2O in the CO_2 rich phase is very small, such that CO_2 properties can be assumed fairly well by those of pure CO_2 [5, 6].

A number of models are available to calculate phase equilibrium between CO_2 and H_2O for a wide temperature and pressure range [6–20]. In addition to these models, SAFT is a molecular based theory which is designed to account for effects of molecular association (i.e., H-bonding, charge transfer, etc.), chain flexibility, and more usual effects due to repulsive and dispersion effects. This is a very successful approach to predict the phase behavior [21–26]. This approach, based on Wertheim's first order perturbation theory [27–29], has been used to determine the phase behavior of several pure components and mixtures in a broad range of thermodynamic conditions and is becoming a standard equation for engineering purposes. There are some investigations [23, 30–38] where $\text{CO}_2 + \text{H}_2\text{O}$ phase equilibrium calculations were carried out using the statistical associating fluid theory (SAFT) equation. Sun and Dubessy [39] presented a nice review in this regard. The objective of this paper is to show the usability of the SAFT equation for the

range of temperature 10–100 °C at pressures up to 600 bar in a time efficient manner, so that this approach can be used in numerical simulations of CO₂ flows in geologic reservoir.

2 Equation of State (EoS)

Here carbon dioxide is considered as a homonuclear chainlike molecule. This is an approximation because the actual molecules are heteronuclear. Therefore, a molecule of the polar fluid is assumed to be composed of m hard-spherical segments of diameter σ tangentially bonded together to form chains. The equation of state is written in terms of the Helmholtz energy for a binary mixture of associating chain molecules. It can be expressed as the sum of hard-sphere repulsion, hard-chain formation, dispersion, and association terms. Mathematically:

$$A^{\text{res}} = A^{\text{hs}} + A^{\text{chain}} + A^{\text{disp}} + A^{\text{assoc}}, \tag{1}$$

where A^{hs} is the free energy of hard-sphere fluid; A^{chain} is the free energy associated with the formation of chains from hard spheres; A^{disp} and A^{assoc} are the contributions to the free energy of dispersion and association interactions, respectively. Based upon Eq. 1, detailed descriptions of the equations involved in the computation process are discussed in the following subsections.

2.1 Hard-Sphere Repulsion Term

Following the Boublik–Mansoori–Carnahan–Starling–Leland [40, 41] equation, the hard sphere term A^{hs} is expressed as:

$$\frac{A^{\text{hs}}}{RT} = \frac{\sum_{i=1}^N x_i m_i}{\pi \rho_s} \left[\frac{3\zeta_1 \zeta_2 - \zeta_2^3 / \zeta_3^2}{1 - \zeta_3} + \frac{\zeta_2^3 / \zeta_3^2}{(1 - \zeta_3)^2} + \frac{\zeta_2^3}{\zeta_3^2} \ln(1 - \zeta_3) \right] - \sum_{i=1}^N x_i m_i \ln(1 - \zeta_3) \tag{2}$$

where

$$\zeta_j = \frac{\pi}{6} \rho_n \sum_{i=1}^N x_i m_i d_i^j \quad (j=0, 1, 2, 3) \tag{3}$$

and

$$\rho_s = \rho_n \sum_{i=1}^N x_i m_i \tag{4}$$

To make Eq. 2 applicable for the temperature and pressure ranges, the effective number of segments, m_i , is correlated with reduced temperature (T_r) in a very simple way:

$$m_i = A_i + B_i T_r. \tag{5}$$

Here d_i is the hard sphere diameter of segment i which relates with the soft-sphere diameter, σ_i , based on Barker–Henderson perturbation theory and is expressed as [42]:

$$\frac{d_i}{\sigma_i} = \frac{1 + 0.2977kT/\varepsilon_i}{1 + 0.33163kT/\varepsilon_i + 0.001047(kT/\varepsilon_i)^2} \quad (6)$$

where ε_i is the energy parameter of the L–J (Lennard–Jones) potential. Like Eq. 5, this is also expressed as:

$$\varepsilon_i/k = D_i + E_i T_R. \quad (7)$$

2.2 Hard-Chain Formation Term

A^{chain} is presented as [21]:

$$\frac{A^{\text{chain}}}{RT} = \sum_{i=1}^N x_i (1 - m_i) \ln[g_i^{\text{hs}}(d_i)], \quad (8)$$

where

$$g_i^{\text{hs}}(d_i) = \frac{1}{1 - \zeta_3} + \frac{3d_i \zeta_2}{2(1 - \zeta)^2} + \frac{d_i^2}{2(1 - \zeta_3)^3}, \quad (9)$$

and for binary mixtures:

$$g_{ij}^{\text{seg}}(d_{ij}) = g_{ij}^{\text{hs}}(d_{ij}) = \frac{1}{1 - \zeta_3} + \frac{3d_i d_j}{d_i + d_j} \frac{\zeta_2}{(1 - \zeta_3)^2} + 2 \left(\frac{d_i d_j}{d_i + d_j} \right)^2 \frac{\zeta_2^2}{(1 - \zeta_3)^3}. \quad (10)$$

2.3 Dispersion Term

A^{disp} is computed from the expression of Ref. [42] based on the L–J potential. This reads:

$$\frac{A^{\text{disp}}}{RT} = \sum_{i=1}^N x_i m_i \frac{1}{T_R} (A_1^{\text{disp}} + A_2^{\text{disp}}/T_R), \quad (11)$$

where

$$A_1^{\text{disp}} = \rho_R (-8.5959 - 4.5424\rho_R - 2.1268\rho_R^2 + 10.285\rho_R^3), \quad (12)$$

$$A_2^{\text{disp}} = \rho_R (-1.9075 + 9.9724\rho_R - 22.216\rho_R^2 + 15.904\rho_R^3), \quad (13)$$

$$T_R = kT/\varepsilon_x, \quad (14)$$

$$\rho_R = \frac{6}{\sqrt{2\pi}} \zeta_3, \quad (15)$$

$$\varepsilon_x \sigma_x^3 = \sum_{i=1}^N \sum_{j=1}^N y_i y_j \varepsilon_{ij} \sigma_{ij}^3, \quad (16)$$

$$y_i = \frac{x_i m_i}{\sum_{j=1}^N x_j m_j}. \quad (17)$$

The cross parameters between segments, ε_{ij} and σ_{ij} , are calculated from following combining rules:

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2, \tag{18}$$

$$\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_i\varepsilon_j}. \tag{19}$$

k_{ij} is the binary interaction parameter. To make the calculation fast we have fixed $y_{\text{H}_2\text{O}} = 0.0001$. This helps avoid extra iterations in the mixing rule. This assumption is legitimate because the amount of H_2O in the CO_2 -rich phase is quite small, and this phase can fairly be approximated as pure CO_2 as mentioned in the Introduction.

2.4 Association Term

The Helmholtz energy due to association is calculated using following expression [22]:

$$\frac{A^{\text{assoc}}}{RT} = \sum_i x_i \left[\sum_{A_i} (\ln X^{A_i} - X^{A_i}/2) + .5M_i \right]. \tag{20}$$

Here m_i is the number of associating sites on molecule i . X^{A_i} is the mole fraction of molecules i , in mixtures with other components, not bonded at site A and is given by:

$$\Delta^{A_i B_j} = d_{ij}^3 g_{ij}(d_{ij})^{\text{seg}} \kappa^{A_i B_j} [\exp(\varepsilon^{A_i B_j}/kT) - 1]. \tag{21}$$

κ^{AB} is the bonding volume, and ε^{AB}/k is the associating energy. For mixtures, the following combining rules are applied:

$$\kappa^{A_i B_j} = \kappa^{A_j B_i} = (\kappa^{A_i B_i} + \kappa^{A_j B_j})/2, \tag{22}$$

$$\varepsilon^{A_i B_j} = \varepsilon^{A_j B_i} = (1 - k_{ij}^{AB})\sqrt{\varepsilon^{A_i B_i} \varepsilon^{A_j B_j}}, \tag{23}$$

where k_{ij}^{AB} is the binary associating interaction parameter. Calculations of chemical potentials, compressibility factor, and other properties of the components are shown in the Appendix.

3 Parameter Estimation

Three pure component parameters for the nonassociating fluid CO_2 and five parameters for the associating fluid H_2O are L–J potential well depth (ε/k), the soft-sphere diameter of the segments (σ), the number of the segments in the molecule (m), the bonding volume (κ^{AB}), and the associating energy between sites A and B (ε^{AB}) are estimated from regression of density [43, 44] and $\text{CO}_2 + \text{H}_2\text{O}$ phase equilibrium data [5, 45–60] simultaneously. A summary of the experimental phase equilibrium data used in the data reduction process is shown in Table 1. Van der Waals one fluid mixing rules with the binary interaction parameter k_{ij} for the dispersion interactions and the parameter k_{ij}^{AB} for the associating interactions are applied. k_{ij} is estimated to be 0.585. Since CO_2 is a non-associating fluid, k_{ij}^{AB} is set to zero. Four-site model [61, 62] is used for the water molecule. The regressed segment parameters are shown in Table 2.

To keep numerical values of m and ε/k positive, absolute values are used during the regression process. In all cases the objective function was set as:

Table 1 Experimental data used for the parameterization

Ref	<i>p</i> range (bar)	<i>t</i> range (°C)
[5]	51.7–243.2	12–40
[60]	50.7–557.3	25– 5
[59]	50.7–506.6	12–40
[58]	25.3–608	50–100
[47]	22.7–51.5	25–100
[57]	200–500	50–100
[51]	344.8	50–75
[53]	100–600	21
[56]	64.4–294.9	15–20
[52]	9.2–23	100
[50]	50.7–202.7	15.6–93.3
[46]	68.2–176.8	50
[49]	101.3– 52	50–75
[54]	103.4–209.4	75
[48]	101–301	50
[55]	34.5–73.9	12–31.06
[45]	40.5–141.1	50–80
[66]	48	100
[65]	50–202	100

Table 2 Segment parameters for pure fluids

	CO ₂	H ₂ O
<i>p</i> (bar)	10–600	10–600
<i>t</i> (°C)	0–100	0–100
<i>m</i> [Eq. 5]		
<i>A</i>	1,014.96007	–43.6716186
<i>B</i>	–58.5377031	–2.28211080
σ (10 ^{–10} m)	0.218976799	34.7032841
ε/k (<i>k</i>) [Eq. 7]		
<i>D</i>	0.721973786	–4.85199626
<i>E</i>	0.633929370	10.3010420
ε^{AB}/k (K)		1195.00
κ		0.04

$$F_i(\text{obj}) = \sum_k^{N_k} \sum_i^{N_i} \frac{1}{N} \frac{\text{abs}[F_{i,k}(\text{lit}) - F_{i,k}(\text{cal})]}{F_{i,k}(\text{lit})} \quad (24)$$

where $N = N_k \times N_i$, N_i number of data points and N_k total number of properties [such as $k = 1$ (density), and $k = 2$ (phase equilibrium)].

4 Results and Discussion

To check the reliability of the estimated parameters, density data for pure CO₂ and H₂O were generated at different temperatures and pressures. These are shown in Fig. 1 where

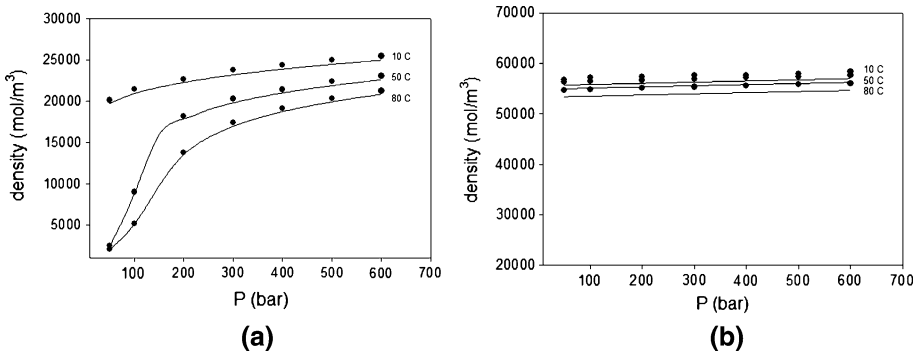


Fig. 1 Reproducibility of pure component density data for **a** CO₂ and **b** H₂O. Lines represent this study and symbols are from computed literature values [16, 63]

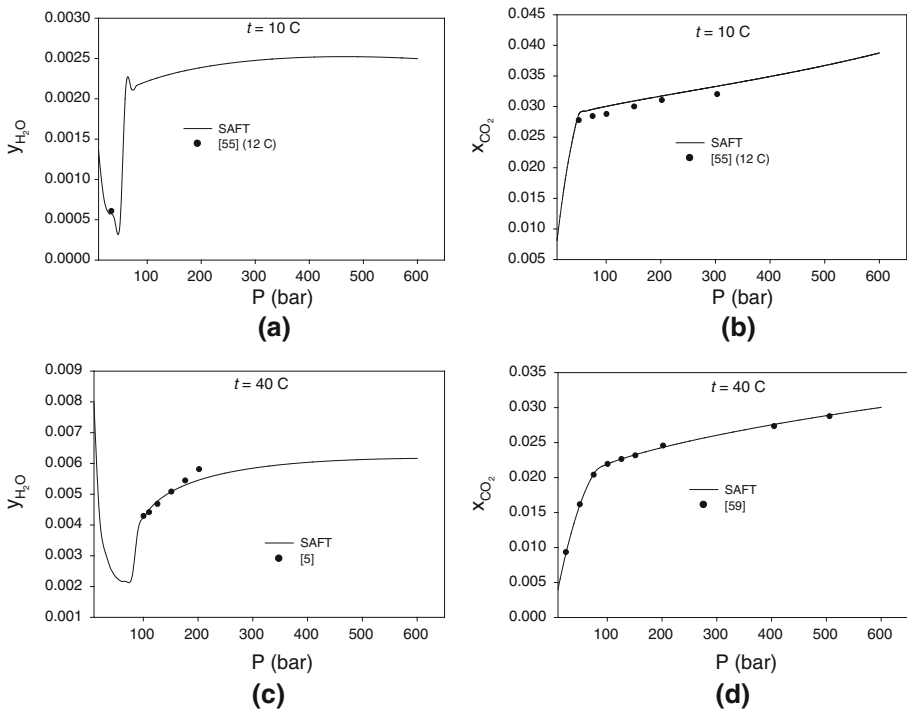


Fig. 2 Comparisons between calculated and experimental mutual solubilities of CO₂ and H₂O

the reproducibility observed is within 2.5 % of the calculated literature values from Span and Wagner [16] and Wagner et al. [63], respectively. Calculated mutual solubilities through the discussed SAFT model are shown in Fig. 2 along with literature data for comparison. Isotherm results are shown at the temperatures 10, 40, 80, and 100 °C. For cases where we did not have data at the exact temperature (i.e., 10 °C), comparison is shown with available data at the nearest temperature. As seen in the figures, the overall agreement between the calculated and experimental solubilities is quite good and generally

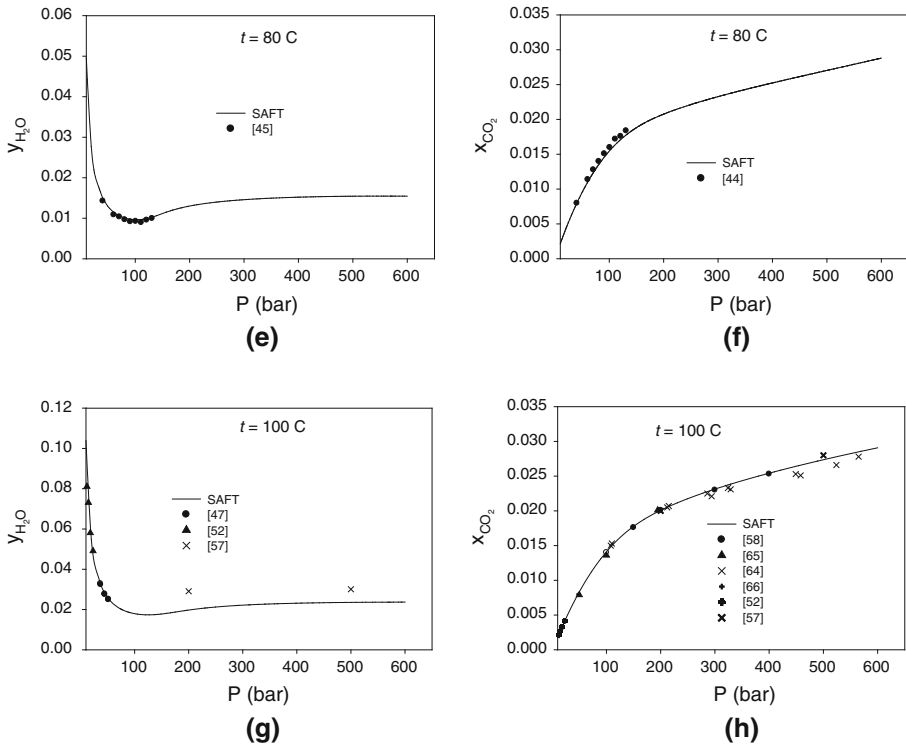


Fig. 2 continued

within a few percent up to pressures 600 bar. The calculated results tend to follow any of the trends established by cases where the experimental data differ significantly among the references. The results do so within 2 % deviation. Each data source has its own share of assumptions and potential problems, which cause differences. At 100 °C and pressures above 50 bar the accuracy of the model for estimating H_2O solubility is difficult to evaluate since only one data source [57] was found. The CO_2 solubility data are reproduced within less than 1 % of those reported by [52, 57, 58, 64–66].

Now we show how the calculation process using the SAFT model presented can save computational costs (cost per CPU time or memory) with respect to other EoS (Span and Wagner (S–W) [16], Duan et al. (D et al.) [67], and Redlich–Kwong [68] (R–K) modified by Spycher and Pruess [6]). These models are chosen because they are used very frequently in numerical simulations of geologic sequestration of CO_2 . Table 3 shows the comparisons of execution times. The SAFT model performs 1.93 to 3.68 times faster phase equilibrium calculation on a notebook of average configuration (for example, 3 GB RAM, Dual-core CPU T4500 @ 2.3 GHz). In a fairly high configuration workstation (for example, 11.57 GB RAM and i7-920 @ 2.67 GHz processor), this calculation is 2.0–3.4 times faster than the others. Here the absolute savings are on the order of fractions of seconds; however, we have already shown in our study [69] that this small difference can make the execution time variations from a couple of hours up to days after integrating with a numerical simulator for an increased number of time steps.

Table 3 Comparisons of execution times

Computation time (CPU time in s)							
Notebook ^a				Lab workstation ^b			
SAFT	S–W	D et al.	R–K	SAFT	S–W	D et al.	R–K
0.016	0.059	0.047	0.031	0.010	0.034	0.024	0.02

^a 3 GB RAM, Dual-core CPU T4500 @ 2.3 GHz

^b 11.57 GB, i7-920 CPU @ 2.67 GHz

5 Conclusions

The SAFT EoS is employed to compute the phase equilibria for CO₂ + H₂O binary system over a temperature range of 10–100 °C and pressures of up to 600 bar. We have used this equation in such a way that it performed 2 to 4 times faster computations than other EoS’s. Pure component and binary interaction parameters applying simple mixing rules estimated from the density and vapor–liquid equilibrium data were implemented. A satisfactory agreement between predicted values and experimental data was found.

Acknowledgments The work was conducted with the support of the Reservoir Simulation Joint Industry Project, a consortium of operating and service companies for Petroleum and Geosystems Engineering at The University of Texas at Austin.

Appendix

This section provides necessary functions to calculate chemical potential μ_i , compressibility factor Z , and fugacity coefficient ϕ_i . First, μ_i , which is a derivative of A^{res} with respect to the mole number of component i at constant T , volume V , and non- i components, is shown.

Expression for Chemical Potential

We discuss μ_i in the order used to present the corresponding Helmholtz energy terms, i.e., hard-sphere, chain, dispersion, and association terms. The expression is:

$$\mu_i^{\text{res}} = \mu_i^{\text{hs}} + \mu_i^{\text{chain}} + \mu_i^{\text{disp}} + \mu_i^{\text{assoc}}. \tag{25}$$

The hard-sphere contribution to the chemical potential, μ_i^{hs} , can be expressed as:

$$\begin{aligned} \frac{\mu_i^{\text{hs}}}{RT} = & \frac{m_i d_i^3 \zeta_0 + 3m_i d_i^2 \zeta_1 + 3m_i d_i \zeta_2 - 3m_i d_i^2 \zeta_2^2 / \zeta_3^2 + 2m_i d_i^3 \zeta_2^3 / \zeta_3^3 - m_i d_i^3 \zeta_2^3 / \zeta_3^2}{1 - \zeta_3} \\ & + \frac{3m_i d_i^3 \zeta_1 \zeta_2 + 3m_i d_i^2 \zeta_2^2 / \zeta_3^2 - m_i d_i^3 \zeta_2^3 / \zeta_3^2 - 2m_i d_i^3 \zeta_2^3 / \zeta_3^3}{(1 - \zeta)^2} + \frac{2m_i d_i^3 \zeta_2^3 / \zeta_3^2}{(1 - \zeta_3)^3} \\ & + \frac{(3m_i d_i^2 \zeta_2^2 \zeta_3 - 2m_i d_i^3 \zeta_2^3) \ln(1 - \zeta_3)}{\zeta_3^3} - m_i \ln(1 - \zeta_3). \end{aligned} \tag{26}$$

μ_i^{chain} , the chain contribution to the chemical potential, is expressed as:

$$\frac{\mu_i^{\text{chain}}}{RT} = (1 - m_i) \ln[g_i^{\text{hs}}(d_i)] + \rho \sum_{i=1}^N \frac{x_i(1 - m_i)}{g_i^{\text{hs}}(d_i)} \left[\frac{\partial g_i^{\text{hs}}}{\partial \rho_i} \right]_{T,V,\rho_{j \neq i}}, \quad (27)$$

where

$$\left[\frac{\partial g_i^{\text{hs}}(d_i)}{\partial \rho_i} \right]_{T,V,\rho_{j \neq i}} = \frac{\pi}{6} m_i d_i^2 N_{\text{AV}} \left[\frac{d_i}{(1 - \zeta_3)^2} + \frac{3d_i(1 - \zeta_3 + 2d_i\zeta_2)}{2(1 - \zeta)^3} + \frac{d_i^2(2\zeta_2 - 2\zeta_2\zeta_3 + 3d_i\zeta_2^2)}{2(1 - \zeta_3)^4} \right]. \quad (28)$$

The dispersion contribution to the chemical potential, μ_i^{disp} is expressed as:

$$\frac{\mu_i^{\text{disp}}}{RT} = \frac{m_i A_1^{\text{disp}}}{T_R} + \frac{m_i A_2^{\text{disp}}}{T_R^2} + \frac{\rho_s}{T_R} \left[\frac{\partial A_1^{\text{disp}}}{\partial \rho_i} \right]_{T,V,\rho_{j \neq i}} - \left(\frac{\rho_s A_1^{\text{disp}}}{T_R^2} + 2 \frac{\rho_s A_2^{\text{disp}}}{T_R^3} \right) \left[\frac{\partial T_R}{\partial \rho_i} \right]_{T,V,\rho_{j \neq i}}, \quad (29)$$

where

$$\left[\frac{\partial A_1^{\text{disp}}}{\partial \rho_i} \right]_{T,V,\rho_{j \neq i}} = \frac{m_i d_i^3}{\sqrt{2}} (-8.5959 - 9.0848\rho_R - 6.3807\rho_R^2 + 41.141\rho_R^3), \quad (30)$$

$$\left[\frac{\partial A_2^{\text{disp}}}{\partial \rho_i} \right]_{T,V,\rho_{j \neq i}} = \frac{m_i d_i^3}{\sqrt{2}} (-1.9075 + 19.9449\rho_R - 66.648\rho_R^2 + 63.616\rho_R^3), \quad (31)$$

$$\left[\frac{\partial T_R}{\partial \rho_i} \right]_{T,V,\rho_{j \neq i}} = \frac{2m_i \rho \left(\varepsilon_x \sum_{l=1}^N x_l m_l \rho_{il}^3 - \sum_{l=1}^N x_l m_l \rho_{il}^3 \varepsilon_{il} \right)}{\beta \varepsilon_x^2 \sigma_x^3 \rho_s^2}. \quad (32)$$

μ_i^{assoc} , the association contribution to the chemical potential can be expressed as:

$$\frac{\mu_i^{\text{assoc}}}{RT} = \left\{ \sum_{A_i} (\ln X^{A_i} - .5X^{A_i}) + .5M_i + \sum_j x_j \rho \sum_{A_j} \left[\left(\frac{\partial X^{A_j}}{\partial \rho_i} \right)_{T,\rho_{j \neq i}} \left(\frac{1}{X^{A_j}} - .5 \right) \right] \right\}, \quad (33)$$

where

$$\left(\frac{\partial X^{A_j}}{\partial \rho_j} \right)_{T,\rho_{j \neq i}} = -(X^{A_j})^2 N_{\text{AV}} \left\{ \sum_{B_i} X^{B_i} \Delta^{A_j B_i} + \rho \sum_k \sum_{B_k} X_k \left[\Delta^{A_j B_k} \left(\frac{\partial X^{B_k}}{\partial \rho_i} \right)_{T,\rho_{l \neq i}} + X^{B_k} \left(\frac{\partial \Delta^{A_j B_k}}{\partial \rho_i} \right)_{T,\rho_{l \neq i}} \right] \right\}. \quad (34)$$

$\left(\frac{\partial X^{B_k}}{\partial \rho_i} \right)_{T,\rho_{l \neq i}}$ and so forth can be found similarly following Eq. 34. Now the expression for $\left(\frac{\partial \Delta^{A_j B_k}}{\partial \rho_i} \right)_{T,\rho_{l \neq i}}$ is given by:

$$\left(\frac{\partial \Delta^{A_j B_k}}{\partial \rho_i} \right)_{T,\rho_{l \neq i}} = d_{jk}^3 \left[\frac{\partial g_{jk}(d_{jk})^{\text{hs}}}{\partial \rho_i} \right]_{T,\rho_{l \neq i}} [\exp(\varepsilon^{A_j B_k}/kT) - 1] \kappa^{A_j B_k}, \quad (35)$$

where

$$\left[\frac{\partial g_{jk}(d_{jk})^{\text{hs}}}{\partial \rho_i} \right]_{T, \rho_{i \neq i}} = \frac{\pi N_{\text{AV}}}{6} m_i \left\{ \frac{d_i^3}{(1 - \zeta_3)^2} + 3 \frac{d_j d_k}{d_j + d_k} \left[\frac{d_i^2}{(1 - \zeta_3)^2} + \frac{2d_i^3 \zeta_2}{(1 - \zeta_3)^3} \right] + 2 \left(\frac{d_j d_k}{d_j + d_k} \right)^2 \left[\frac{2d_i^2 \zeta_2}{(1 - \zeta_3)^3} + \frac{3d_i^3 \zeta_2^2}{(1 - \zeta_3)^4} \right] \right\}. \tag{36}$$

Expression for Compressibility Factor Z

The compressibility factor is calculated from the Helmholtz energy, *A*, through:

$$Z = \rho \left[\frac{\partial(A/RT)}{\partial \rho} \right]_{T,N} = 1 + Z^{\text{hs}} + Z^{\text{disp}} + Z^{\text{chain}} + Z^{\text{assoc}}, \tag{37}$$

where:

$$Z^{\text{hs}} = \frac{\sum_{i=1}^N x_i m_i}{\zeta_0} \left[\frac{6\zeta_1 \zeta_2 - \zeta_2^2/\zeta_3 - \zeta_2^3/\zeta_3 + \zeta_0 \zeta_3}{1 - \zeta_3} + \frac{6\zeta_1 \zeta_2 \zeta_3 - 3\zeta_1 \zeta_2 - 2\zeta_2^3/\zeta_3 + 2\zeta_2^3/\zeta_3^2}{(1 - \zeta_3)^2} + \frac{3\zeta_2^3/\zeta_3 - \zeta_2^3/\zeta_3^2}{(1 - \zeta_3)^3} \right], \tag{38}$$

$$Z^{\text{disp}} = \sum_{i=1}^N x_i m_i \left(Z_1^{\text{disp}}/T_R + Z_2^{\text{disp}}/T_R^2 \right), \tag{39}$$

and

$$Z_1^{\text{disp}} = \rho_R (-8.5959 - 9.0848 \rho_R - 6.3807 \rho_R^2 + 41.1416 \rho_R^3), \tag{40}$$

$$Z_2^{\text{disp}} = \rho_R (-1.9075 + 19.9449 \rho_R - 66.648 \rho_R^2 + 63.616 \rho_R^3), \tag{41}$$

$$Z^{\text{chain}} = \sum_{i=1}^N \frac{x_i (1 - m_i)}{g_i^{\text{hs}}(d_i)} \left[\frac{\zeta_3 + 1.5 d_i \zeta_2}{(1 - \zeta_3)^2} + \frac{3 d_i \zeta_2 \zeta_3 + d_i^2 \zeta_2^2}{(1 - \zeta_3)^3} + \frac{1.5 d_i^2 \zeta_2^2 \zeta_3}{(1 - \zeta_3)^4} \right], \tag{42}$$

$$Z^{\text{assoc}} = \frac{1}{RT} \left[\sum_i x_i \mu_i^{\text{assoc}} - A^{\text{assoc}} \right]. \tag{43}$$

Here μ_i^{assoc} and A^{assoc} are presented by Eqs. 33 and 20, respectively.

Expression for Fugacity Coefficient

The relation between ϕ_i (fugacity coefficient) and the residual chemical potential of component *i* is as follows:

$$\ln \varphi_i = \frac{\mu_i^{\text{res}}}{RT} - \ln Z. \quad (44)$$

μ_i^{res} and Z can be obtained from Eqs. 25 and 37, respectively.

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