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On the linear approximation of mixture internal energies of departure

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Professor Rafiq Gani, Editor
Computers & Chemical Engineering Journal

10/21/2015

Dear Professor Gani:

Please consider the revised article entitled " On the Linear Approximation of Mixture Internal Energies of Departure" by R.B. Kelly and A. Lucia for publication as a Short Note in Computers and Chemical Engineering.

Sincerely,

Angelo Lucia

Detailed Response to Reviews

In the revision, we have addressed all reviewer comments regarding the use of Monte Carlo simulation section 2.4 and the sensitivity of the mixture energy parameter to uncertainty in the internal energy of departure in section 4 - both of which are additions to the original manuscript. More specifically we have

- 1) Added a flowchart description of the Monte Carlo simulation methods used in our work in section 2.3.
- 2) Validated the use of Monte Carlo simulation by comparisons with simulations of other workers in the field and experimental data in Section 2.4 of the revised manuscript.
- 3) Added an analysis of the sensitivity of the mixture energy parameter and mixture molar volume to uncertainty in internal energies of departure and provided two illustrations in Figures 2 and 3.

Highlights

- Linear mixing rule for mixture internal energies of departure validated
- Comparisons are made to direct Monte Carlo simulation in the NPT ensemble
- Gas-oil, oil-oil and oil-water mixtures are considered
- Sensitivity analysis of a_M and V_M to uncertainty in U_M^D presented

On the Linear Approximation of Mixture Internal Energies of Departure

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Abstract

Direct Monte Carlo simulation of internal energies of departure for binary mixtures of geological interest are gathered and compared to those calculated using a linear mixing rule. Simulation results for gas-oil, oil-oil, and oil-water mixtures show that the linear mixing rule used in the Gibbs-Helmholtz Constrained (GHC) equation of state framework gives accurate approximations of binary mixture internal energies of departure. A flowchart for computing internal energies of departure using Monte Carlo simulation is included along with a sensitivity analysis for the GHC mixture energy parameter with respect to uncertainty in internal energies of departure.

Keywords: internal energy of departure; direct Monte Carlo simulation; linear mixing rule; geological binary mixtures; equations of state

1. Introduction

The Gibbs-Helmholtz Constrained (GHC) equation of state (EOS) is a multi-scale adaptation of the Soave form (Soave 1972) of the Redlich-Kwong EOS (Redlich and Kwong 1949),

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad (1)$$

where the energy parameter, a , given by

$$a(T, P) = \left[\frac{0.42748R^2T_c}{P_c} + \frac{bU^D}{T_c \ln 2} + \frac{2bR \ln T_c}{\ln 2} \right] T - \frac{bU^D}{\ln 2} - \left[\frac{2bR}{\ln 2} \right] T \ln T \quad (2)$$

is derived analytically by constraining $a(T, P)$ to satisfy the Gibbs-Helmholtz equation

$$\left(\frac{\partial \ln \phi}{\partial T} \right)_P = - \frac{H^D}{RT^2} \quad (3)$$

The resulting expression for the energy parameter shown in Eq. 2 is an explicit function of temperature and has implicit dependence on temperature and pressure through the functionality of the internal energy of departure, U^D . The dependence of the energy parameter on U^D – which can be computed for pure components and mixtures via molecular simulation – makes the GHC equation a multi-scale EOS.

For mixtures, single fluid theory is applied to the EOS so that Kay's rules

$$M_{cM} = \sum_{i=1}^C x_i M_{ci} \quad (4)$$

are used for estimating mixture critical properties (M is any critical property) and linear mixing rules

$$b_M = \sum_{i=1}^C x_i b_i \quad (5)$$

$$U_M^D = \sum_{i=1}^C x_i U_i^D \quad (6)$$

are used for the mixture molecular co-volume, b_M , and mixture internal energy of departure, U_M^D , respectively. These quantities are needed in the expression for the mixture energy parameter, which is given by

$$a_M(T, P, x) = \left[\frac{0.42748R^2 T_{cM}}{P_{cM}} + \frac{b_M U_M^D}{T_{cM} \ln 2} + \frac{2b_M R \ln T_{cM}}{\ln 2} \right] T - \frac{b_M U_M^D}{\ln 2} - \left[\frac{2b_M R}{\ln 2} \right] T \ln T \quad (7)$$

Furthermore, the GHC equation, originally proposed by Lucia (2010), is thermodynamically consistent (Lucia and Henley 2013) and has been used successfully to predict density and phase equilibrium of geological systems such as carbon dioxide-aqueous electrolytes mixtures (Lucia et al., 2012), hexagonal ice and structure I hydrates (Henley et al., 2014), and salt precipitation in systems with multiple salts (Lucia et al., 2015).

The objective of this note is to present numerical evidence that shows that the linear mixing for U_M^D is valid for gas-oil, oil-oil, and oil-water mixtures. Accordingly, the sections of this short note are organized as follows. Section 2 provides molecular simulation details, describes the computational procedure used to determine binary mixture U_M^D , and validates the use of Monte Carlo simulation. Section 3 compares results for U_M^D from direct Monte Carlo simulation with those using the linear mixing rule. Section 4 gives a sensitivity analysis of the GHC mixture energy parameter with respect to uncertainty in U_M^D and provides two numerical illustrations. Finally, closing remarks are given in Section 5.

2. Computational Procedure for the Internal Energy of Departure

This section presents many of the details of the Monte Carlo simulations in this work.

2.1 Internal Energy of Departure

The internal energy of departure is defined as

$$U^D(T, P) = U(T, P) - U^{ig}(T) \quad (8)$$

where the superscript *ig* denotes ideal gas.

2.2 Simulation and Force Field Details

MCCCS Towhee version 7.1.0 (Martin 2013) was used for all Monte Carlo simulations.

TraPPE-UA (Martin and Siepmann 1998; 1999) and TraPPE-EH (Potoff and Siepmann 2001) force field models were used for oil-oil and gas-oil mixtures using the parameters provided in Towhee. The TIP4P-Ew force field (Horn et al. 2004) was used for water and standard Lorentz-Berthelot mixing and combining rules were used for all mixtures.

2.3 Molecular Simulation Procedure

A flowchart for computing $\langle U_i^D \rangle$ and $\langle U_M^D \rangle$ is given in Figure 1.

Figure 1: Flowchart for Computing Internal Energies of Departure

For all ensembles, 40,000 - 100,000 equilibration and production cycles were used. The number of molecules was $N = 32 - 128$ for pure components (see Table 3) and $N = 100$ for mixtures. Mixture internal energies of departure were calculated for various compositions using the largest pure component radial cutoff distance(s). In the canonical (NVT) ensemble, reference state U_i^D for each pure component account for intra-molecular interactions (i.e. electrostatic, torsion, etc.) and were computed by placing a single molecule in a box with radial cutoff distance(s) large enough to capture all intra-molecular effects. Ensemble averages, $\langle U_i^D \rangle$ and $\langle U_M^D \rangle$, were calculated by set averaging.

2.4 Are Monte Carlo Simulation Results Accurate?

Comparisons of calculated properties with experimental data are generally used to validate the accuracy of Monte Carlo simulation results. For example, Table 4 in Martin and Siepmann (1998) shows a comparison of experimental saturated liquid densities at standard conditions with those computed using the TraPPE force field for n-pentane, n-octane, and n-dodecane. Average root mean square errors reported in that table are quite small (i.e., $\sim 10^{-3}$). Table 1 shows that the Monte Carlo simulation densities in this work match both those from Martin and Siepmann (1998) and experimental data quite well.

Horn et al. (Table V, p. 9672, 2004) have validated the TIP4P-Ew model with experimental data for liquid water for a wide range of conditions and have calculated average densities and heats of vaporization, which show very good agreement with experimental data. In addition, they report average U^D values for water over a range of temperatures, which allows direct comparison with results in this work. Specifically, Table 2 shows that the

TIP4P-Ew simulation results for $\langle U^D \rangle$ of water used in this work closely matches those reported in Horn et al., where slight differences can be attributed to the statistical nature of Monte Carlo simulation and ensemble size.

In our opinion, these comparisons demonstrate that the Monte Carlo simulation results in this study represent accurate values of internal energies of departure.

3. Main Computational Results and Discussion

Table 3 lists pure component data used in this study while Tables 4-6 show comparisons of $\langle U_M^D \rangle$ from direct Monte Carlo simulation of mixtures with those for the linear mixing rule for n-octane-methane, 5-butylnonane-carbon dioxide, and n-heptane-n-dodecane. The numbers to the immediate right of $\langle U_M^D \rangle$ shown in parentheses correspond to standard deviations. The average absolute deviations (AAD) % errors for the linear mixing rule were 0.80, 1.75, and 0.73% respectively.

Table 7 lists values of $\langle U_M^D \rangle$ calculated from direct Monte Carlo simulation and the linear mixing rule for various compositions of n-hexane-water at 290 K and 150 bar. This mixture exhibits a rather large region of immiscibility (i.e., overall compositions ranging from 4.21×10^{-10} to 99.996 mol% hexane). Moreover, while the error is much larger in the region of immiscibility, this is unimportant in practice because the error in the linear mixing rule is small for dilute solutions of n-hexane and water, especially those far from the plait point. For example, Table 7 shows that for a mixture of 99 mol% n-hexane and 1 mol% water at 290 K and 150 bar, the linear mixing rule gives a value of $U_M^D = -281959 \text{ cm}^3\text{bar/mol}$, which is an error of 1.99%. A small error is also observed for the water-rich composition of 99 mol% water-1 mol% n-hexane.

4. Sensitivity Analysis

Figure 7 in Lucia et al. (p. 85, 2012) shows that U^D has a small impact on the molar volume, V_M , of liquid water. In this section, a more detailed study of the sensitivity of a_M and V_M with respect to U_M^D is presented. From Eq. 7, it is easily seen that the change in a_M with respect to changes in U_M^D is given by

$$\left(\frac{\partial a_M}{\partial U_M^D}\right) = \left[\frac{T}{T_{cM}} - 1\right] \left(\frac{b_M}{\ln 2}\right) \quad (9)$$

and the local change in a_M with respect to changes (or uncertainty) in U_M^D is given by

$$\Delta a_M = \left[\frac{T}{T_{cM}} - 1\right] \left(\frac{b_M}{\ln 2}\right) \Delta U_M^D = \left[\frac{T}{T_{cM}} - 1\right] \left(\frac{b_M}{\ln 2}\right) \sum_{i=1}^C x_i \Delta U_i^D \quad (10)$$

where Δ denotes perturbation. Figure 2 gives plots showing relative changes in a_M for $\Delta U_i^D = 0.05 U_i^D$, $i = 1, 2$ as a function of composition for two mixtures studied in Section 3.

Note that the relative sensitivity of a_M to 5% change in U_M^D is $< 4\%$ everywhere and for methane-octane it is zero at $x_{CH_4} \approx 0.7$. This is because a_M is independent of U_M^D at the point where T_{cM} from Kay's rule is equal to the specified temperature $T = 300 \text{ K}$.

Figure 2: Sensitivity of a_M to 5% Change in U_M^D

Figure 3 shows the corresponding relative sensitivity of molar volume, where molar volumes were computed by the GHC EOS using the pure component data shown in Table 8.

Figure 3: Sensitivity of V_M to 5% Change in U_M^D

Note that the relative sensitivity of V_M to changes in U_M^D is less than 1.5% over the entire composition range.

5. Conclusions

Direct Monte Carlo simulation was used to compare binary mixture internal energies of departure to those computed using the linear mixing proposed by Lucia et al. (2012).

AAD% errors clearly show that the linear mixing rule provides very good approximations of U_M^D for gas-oil, oil-oil, and oil-water mixtures and validates the use of the linear mixing rule in the GHC EOS framework. Finally, a sensitivity analysis for the mixture energy parameter as a function of U_M^D was conducted. Results show that uncertainty in U_M^D (from the linear mixing rule) has a small impact on a_M and fluid molar volume.

Table 1: Comparison of Monte Carlo Simulation Densities

Species	ρ (g/mL)*	ρ (g/mL)**	ρ^{exp} (g/mL)*
n-octane	0.705	0.704	0.7025
n-dodecane	0.754	0.756	0.7487

* taken from Table 4 in Martin & Siepmann (1998)

** this work

Table 2: Comparison of U^D for Water Using the TIP4P-Ew Force Field

T (K)	U^D (kcal/mol)*	U^D (kcal/mol)**	% Difference
298	-5687.4	-5697.2	0.17
310.5	-5596.8	-5603.3	0.12
323	-5496.6	-5510.9	0.26
335.5	-5401.2	-5418.4	0.32
348	-5311.0	-5326.0	0.28
360.5	-5219.3	-5236.1	0.32
373	-5128.2	-5146.6	0.36
400	-4939.7	-4953.4	0.27

* taken from Table V in Horn et al. (2004)

** this work; N = 32, P = 1 bar

Table 3: Force Field, N, T, P, Ensemble Average, and Reference Internal Energy

Species	Force Field	N	T (K)	P (bar)	$\langle U_i^D(T, P) \rangle$	$\langle U_i^o(T, V) \rangle$
Methane	TraPPE-UA	64	300	200	-23652 (173)	--
Octane	TraPPE-UA	64	300	200	-192344 (221)	177400 (483)
Carbon Dioxide	TraPPE-EH	128	273.15	100	-112930 (671)	--
5-Butylnonane	TraPPE-UA	64	273.15	100	-350234 (2416)	240875 (568)
Water	TIP4P-Ew	128	290	150	-470000 (299)	--
Hexane	TraPPE-UA	32	290	150	-170109 (640)	109950 (58)
Heptane	TraPPE-UA	32	350	300	-132594 (436)	171700 (163)
Dodecane	TraPPE-UA	32	350	300	-159070 (1521)	359150 (640)

* All energies are in units of $\text{cm}^3\text{bar/mol}$.

Table 4: Comparison for Octane-Methane*

x_{octane}	x_{methane}	$U_M^D(T, P)$	$\sum_{i=1}^C x_i U_i^D(T, P)$	% Error
0.80	0.20	-297270	-300525	1.10
0.50	0.50	-195125	-196698	0.81
0.30	0.70	-126840	-127480	0.50
AAD				0.80

* N = 100, T = 300 K, P = 200 bar. All energy units are in cm³bar/mol.

Table 5: Comparison for 5-Butylnonane-Carbon Dioxide*

$x_{\text{5-butylnonane}}$	$x_{\text{carbon dioxide}}$	$U_M^D(T, P)$	$\sum_{i=1}^C x_i U_i^D(T, P)$	% Error
0.80	0.20	-491200	-495473	0.87
0.50	0.50	-343638	-352020	2.44
0.20	0.80	-204600	-208566	1.94
AAD				1.75

* N = 100, T = 273.15 K, P = 100 bar. All energy units are in cm³bar/mol.

Table 6: Comparison for Heptane-Dodecane*

x_{heptane}	x_{dodecane}	$U_M^D(T, P)$	$\sum_{i=1}^C x_i U_i^D(T, P)$	% Error
0.75	0.25	-353588	-357775	1.18
0.50	0.50	-408900	-411257	0.58
0.25	0.75	-462688	-464739	0.44
AAD				0.73

* N = 100, T = 350 K, P = 300 bar. All energy units are in cm³bar/mol.

Table 7: Comparison for Hexane-Water*

x_{water}	x_{hexane}	Single Phase Stability	$U_M^D(T, P)$	$\sum_{i=1}^C x_i U_i^D(T, P)$	% Error
0.99	0.01	Unstable	-467050	-468101	0.23
0.75	0.25	Unstable	-386463	-422515	9.33
0.50	0.50	Unstable	-338725	-375030	10.72
0.25	0.75	Unstable	-301038	-327545	8.81
0.01	0.99	Unstable	-276451	-281959	1.99
AAD					6.21

* N = 100, T = 290 K, P = 150 bar. All energy units are in cm³bar/mol.

Table 8: Pure Component Fluid Properties

Species	T_c (K)	P_c (bar)	b (cm ³ /mol)
Methane	190.58	45.92	29.614
Octane	568.83	24.86	143.145
Water	647.37	221.20	16.363
Hexane	507.60	30.20	110.309

<i>Nomenclature</i>	
a, a_M	pure component liquid energy parameter, liquid mixture energy parameter
b, b_i, b_M	molecular co-volume, ith component molecular co-volume, mixture molecular co-volume
C	number of components
H^D	enthalpy of departure
N	number of molecules
P, P_c, P_{cM}	pressure, critical pressure, mixture critical pressure
R	gas constant
T, T_c, T_{cM}	absolute temperature, critical temperature, mixture critical temperature
U_i^D, U_i^o	i th component internal energy of departure, reference state internal energy
V_M	mixture molar volume
x, x_i	mole fraction, ith component mole fraction
<i>Greek Symbols</i>	
φ	fugacity coefficient
ρ	mass density

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