



Note

On the linear approximation of mixture internal energies of departure



Robert B. Kelly, Angelo Lucia*

Department of Chemical Engineering, University of Rhode Island, Kingston, RI 02881, United States

ARTICLE INFO

Article history:

Received 8 October 2015

Received in revised form 21 October 2015

Accepted 22 October 2015

Available online 30 October 2015

Keywords:

Internal energy of departure

Direct Monte Carlo simulation

Linear mixing rule

Geological binary mixtures

GHC equation of state

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.

© 2015 Elsevier Ltd. All rights reserved.

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

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

Furthermore, the GHC equation, originally proposed by Lucia (2010), is thermodynamically consistent (Lucia and Henley, 2013)

* Corresponding author. Tel.: +1 401 874 2814.
E-mail address: alucia@uri.edu (A. Lucia).

Nomenclature

a, a_M	pure component liquid energy parameter, liquid mixture energy parameter
b, b_i, b_M	molecular co-volume, i th 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^0	i th component internal energy of departure, i th component reference state internal energy
V_M	mixture molar volume
x, x_i	mole fraction, i th component mole fraction

Greek symbols

φ	fugacity coefficient
ρ	mass density

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.

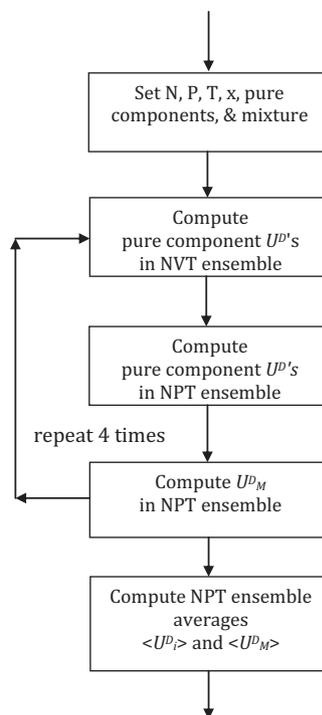


Fig. 1. Flowchart for computing internal energies of departure.

2.3. Molecular simulation procedure

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

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

Table 1
Comparison of Monte Carlo simulation densities.

Species	ρ (g/mL) ^a	ρ (g/mL) ^b	ρ^{exp} (g/mL) ^a
n -Octane	0.705	0.704	0.7025
n -Dodecane	0.754	0.756	0.7487

^a Taken from Table 4 in Martin and Siepmann (1998).

^b This work.

Download English Version:

<https://daneshyari.com/en/article/172138>

Download Persian Version:

<https://daneshyari.com/article/172138>

[Daneshyari.com](https://daneshyari.com)