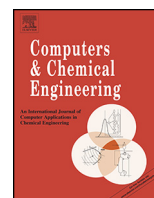




Contents lists available at ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

Multi-scale equation of state computations for confined fluids

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ARTICLE INFO

Article history:

Received 23 September 2016
Received in revised form 25 May 2017
Accepted 31 May 2017
Available online xxx

Keywords:

Confined fluids
Monte Carlo simulation
GHC equation of state
Sensitivity analysis
Bubble point pressure

ABSTRACT

Fluid properties of five binary mixtures relevant to shale gas and light tight oil in confined nano-channels are studied. Canonical (NVT) Monte Carlo simulations are used to determine internal energies of departure of pure fluids using the RASPA software system (Dubbeldam et al., 2015). The linear mixing rule proposed by Lucia et al. (2012) is used to determine internal energies of departure for mixtures, U_M^D , in confined spaces and compared to U_M^D from direct NVT Monte Carlo simulation. The sensitivity of the mixture energy parameter, a_M , for the Gibbs–Helmholtz constrained (GHC) equation, confined fluid molar volume, V_M , and bubble point pressure are studied as a function of uncertainty in U_M^D . Results show that the sensitivity of confined fluid molar volume to 5% uncertainty in U_M^D is less than 1% and that the GHC equation predicts physically meaningful reductions in bubble point pressure for light tight oils.

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1. Introduction

Shale gases and light tight oils (LTO) are important unconventional resources with enormous potential as clean and abundant energy sources. Shales are ‘tight’ porous media with pore radii < 50 nanometer and permeability < 0.1 millidarcies. Recent improvements in shale gas and LTO economics are the result of hydraulic fracturing (‘fracking’) and horizontal well completion; thus shale gas and LTO production is, and will remain, an important part of the US energy portfolio for years to come (for projections to the year 2040; see p. 20, DOE/EIA, 2015).

One of the many open challenges in developing consistent models that couple fluid phase behavior in tight porous media (i.e., confined spaces) with models for multi-phase flow and transport is the accurate description of rigorous phase behavior in tight porous media. The Gibbs–Helmholtz Constrained (GHC) equation is a predictive, multi-scale equation of state (EOS) that up-scales molecular information in the form of internal energies of departure, U_M^D , which is solely determined from Monte Carlo simulations, to the bulk length scale to build estimates a_M of the well known cubic equation energy parameter.

The energy parameter is then used to determine molar volume and, in turn, pressure. Details of the derivation of the GHC equation

can be found in Lucia et al. (2012). In a recent paper, Kelly and Lucia (2016) have validated the linear mixing rule

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

for mixture internal energies of departure, U_M^D , in unconfined spaces in the NPT ensemble. In Eq. (1) x_i denotes the mole fraction of the i^{th} component, U_i^D is the pure component internal energy of departure for component i , C is the number of components in the mixture, and the superscript D denotes departure. The fact that Eq. (1) is valid for mixtures is important because only pure component internal energies, U_i^D , as functions of temperature, T , and pressure, p , are needed to model mixtures. The internal energy of departure, $U^D = U - U^{\text{ig}}$, is negative of the residual internal energy (e.g., see p.128 in Walas, 1985).

This paper focuses on the computation and accuracy of using Eq. (1) to model mixture internal energies of departure in confined spaces and the resulting sensitivity of the energy parameter, molar density, and bubble point pressure to uncertainty in U_M^D .

The open literature is surveyed in Section 2. Section 3 describes the methodology used to compute internal energies of departure in confined spaces. Section 4 presents the main computation results, which compare U_M^D in confined spaces computed using the linear mixing rule to those from direct Monte Carlo simulation. Sensitivity analyses for the energy parameter, molar volume and bubble point pressure to uncertainty (or changes) in U_M^D are presented in Section 5 and conclusions are drawn in Section 6. Appendices A–E contain details for the computational results in Sections 4 and 5.

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Nomenclature

a, a_M	Pure component liquid energy parameter, mixture liquid energy parameter
b, b_M	Pure component molecular co-volume, mixture molecular co-volume
C	Component
E	Total energy in system
L	Liquid
N	Number of molecules
P	Pressure
R, r	Gas constant, radius
T, T_M, T_{cM}	Absolute temperature, critical temperature, mixture critical temperature
U_i^D, U_M^D	Pure component internal energy of departure, mixture internal energy of departure
V, V_i, V_M	Volume, pure component molar volume, mixture molar volume
x	Mole fraction
<i>Greek symbols</i>	
σ	Interfacial tension
<i>Subscripts/superscripts</i>	
D	Departure function
M	Mixture

2. Literature survey

Interest in physical properties and phase behavior of shale gas and LTO is relatively recent and the open literature on the subject is somewhat sparse. Early studies in reservoir and petroleum engineering from the 1940's to 2000 (Wang et al., 2013) suggested that capillary effects on phase behavior were negligible. However, all recent studies, which are largely numerical in nature, include interfacial tension between immiscible phases as part of the model. See Du and Chu (2012), Nojabaei et al. (2012), Honarpour et al. (2012), and Pang et al. (2012).

The current approach to modeling fluid properties and phase equilibrium in tight pores in reservoir simulation consists of

- 1) An equation of state [e.g., Peng and Robinson (1976), extended Peng-Robinson (Travalloni et al., 2014), Perturbed Chain (PC)–SAFT (Tan and Piri, 2015)].
- 2) A correlation [e.g., the parachor equation or MacLeod-Sugden correlation (Sugden, 1924)] to calculate interfacial tension, σ .
- 3) An estimate of capillary pressure, $p^{cap} = \frac{2\sigma}{r}$ (e.g., using the Young-Laplace equation or Leverett J functions) [see Xiong et al., 2012].
- 4) A difference in phase pressures for each immiscible phase given by $p^{cap} = p^V - p^L$.

Table 1
Comparison of Unconfined NPT U_i^D Using MCCCSTowhee and RASPA.

Species	Force field	N	T (K)	P (bar)	U_i^D ($cm^3 bar/mol$)		% difference
					Kelly and Lucia (2016)*	This work**	
methane	TraPPE-UA	64	300	200	-2.365×10^4 (1.73×10^2)	-2.300×10^4 (7.2×10^1)	2.79
CO ₂	TraPPE	128	273.15	100	-1.1293×10^5 (6.71×10^2)	-1.1563×10^5 (3.26×10^2)	2.36
hexane	TraPPE-UA	32	290	150	-2.8005×10^5 (6.98×10^2)	-2.8103×10^5 (5.13×10^2)	0.35
octane	TraPPE-UA	64	300	200	-3.697×10^5 (7.04×10^2)	-3.695×10^5 (5.85×10^3)	0.054
Water	TIP4P-Ew	128	290	150	-4.7000×10^5 (2.99×10^2)	-4.7103×10^5 (7.61×10^2)	0.22

*MCCCSTowhee version 7.10 (Martin, 2013).

**RASPA version 2.0 (Dubbeldam et al., 2015).

Table 2
Comparison of Methane/Octane NPT U_M^D Using MCCCSTowhee and RASPA^a.

x_{CH_4}	$U_M^D(T, P)$		% difference
	Kelly and Lucia (2016) ^b	This work ^c	
0.20	-2.9727×10^5	-3.1063×10^5 (3.8×10^3)	4.40
0.50	-1.9512×10^5	-1.9879×10^5 (2.30×10^2)	1.86
0.70	-1.2468×10^5	-1.2433×10^5 (8.90×10^2)	2.81
		ADD	2.18

^a N = 100, T = 300 K, p = 200 bar.

^b MCCCSTowhee version 7.10 (Martin, 2013).

^c RASPA version 2.0 (Dubbeldam et al., 2015).

For example, Tan and Piri (2015) use the PC-SAFT and Young-Laplace equations and a surface tension correlation to model light gas/oil phase behavior in nanopores. However, all current methods for fluid properties and phase behavior in confined spaces (1) rely heavily on empirical relationships such as correlations for interfacial phenomena (or capillary pressure) that require accurate phase densities and/or regression to experimental data, (2) are correlative, not predictive, and (3) can be inaccurate (i.e., give poor estimates of phase properties and equilibrium in pores).

3. Computational procedure for internal energies of departure

The material in this section describes the Monte Carlo simulation methodologies used to model physical properties of unconfined and confined fluids.

3.1. The unconfined NPT ensemble

Kelly and Lucia (2016) have clearly demonstrated that the linear mixing rule given by Eq. (1) can be used to estimate internal energies of departure of mixtures in the unconfined NPT ensemble and that uncertainties in any pure component U_i^D introduce very little error in the resulting computation of fluid density. See Kelly and Lucia (2016) for the details used in computing internal energies of departure in the NPT ensemble using the MCCCSTowhee software system, version 7.10 (Martin, 2013).

In this work, the more recent RASPA software (Dubbeldam et al., 2015) was used for all Monte Carlo simulations. Therefore, the first issue to be resolved is to show that the same statistical results for unconfined NPT Monte Carlo simulations can be obtained for mixtures studied by Kelly and Lucia (2016) using RASPA. Table 1 shows a comparison of NPT Monte Carlo simulation using MCCCSTowhee and RASPA for pure components while Tables 2 and 3 compare results for mixtures. The numbers in parentheses in Tables 1–3 represent standard deviations.

For these unconfined NPT simulations, volume, translation, and rotation move frequencies were set to 2.48%, 48.78%, and 48.78% respectively while radial cutoff distances were adjusted to include all interactions in the system. For electrostatic forces, Coulomb

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