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Cubic equations of state extended to confined fluids: New mixing rules and extension to spherical pores

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HIGHLIGHTS

- A Peng-Robinson-based model of confined fluid mixtures was modified.
- More explicit and consistent mixing rules were adopted.
- An improved performance in mixture adsorption predictions was obtained.
- The adopted pore geometry can affect significantly the model performance.

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ABSTRACT

The thermodynamic behavior of fluids confined in nanopores is highly influenced by the interaction between fluid molecules and pore walls. The most accurate approaches for modeling confined fluids are too computationally demanding for practical engineering requirements, such as process simulation. Thus, several efforts have been made to develop analytical equations of state suitable for confined fluids. The scope of this work consists of a modification to our previous modeling of fluid confinement in cylindrical pores based on cubic equations of state. By using new, more explicit mixing rules, a more consistent description of confined mixtures is obtained. Additionally, this modeling approach is extended to spherical pores. The proposed models displayed good predictive performance for the adsorption of binary and ternary mixtures, based on pure fluid adsorption data only, with an improvement relative to the previous modeling. It is shown that the adopted pore geometry can significantly affect the model performance.

1. Introduction

The thermodynamic properties of fluids confined in nanometric porous media can differ significantly from those of the bulk fluids, due to the inhomogeneity imposed by the geometric constraint and the interaction between fluid molecules and pore walls (molecule-wall interaction). The modeling of such properties is of practical importance to several applications, including gas and oil recovery from shale reservoirs. Thus, much work has been dedicated to studying the behavior of confined fluids (Peng and Yu, 2008; Vanzo et al., 2015; Tan and Piri, 2017). For instance, regarding the phase behavior, theoretical studies (Truskett et al., 2001; Zeng et al., 2010) and molecular simulations (Alvarez et al., 1999; De Grandis et al., 2007; Singh and Singh, 2011) indicate that a pure confined fluid may have a second critical point, related to a liquid-liquid transition. Regarding the adsorption phenomenon, Balbuena and Gubbins (1994) used density functional theory (DFT) to model a Lennard-Jones fluid and evaluate the effects of the interaction potential parameters and of the pore geometry (slit-like or cylindrical) on the adsorption amount and isosteric heat. These authors reported that the adopted confinement geometry plays an important role, especially for small pores, in which the fluid approaches a one-dimensional structure for cylindrical pores, or a two-dimensional structure for slit pores.

In an attempt to avoid computationally cumbersome modeling approaches, such as molecular simulations and DFT, several efforts have been made to develop analytical equations of state for confined fluids, which would be more suitable for process simulation.

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List of symbols

a	energy parameter of the equation of state for bulk fluids
a_p	energy parameter modified by confinement
b	volume parameter of the equation of state for bulk fluids
b_p	volume parameter modified by confinement
E_{conf}	configurational energy
F_p	fraction of fluid molecules interacting with the pore walls
F_{pr}	value of F_p for random distribution of the fluid molecules
h	function of confinement in the expression of E_{conf}
k	Boltzmann constant
N	number of fluid molecules
N_{av}	Avogadro number
N_c	coordination number in a bulk fluid
NC	number of fluid components
P	pressure
q	internal partition function
Q	canonical partition function
R	ideal gas constant
r_p	pore radius
T	temperature
v	molar volume
V	total volume
V_f	free volume
V_p	pore volume
x	mole fraction

Greek letters

δ_p	molecule-wall interaction range
ε	intermolecular interaction energy
ε_p	molecule-wall interaction energy
θ	function of confinement in the expression of F_p
λ	de Broglie wavelength
μ	chemical potential
ρ	molecular density
σ	molecular diameter
ψ	attractive term of the equation of state for confined fluids

Subscripts

i, j	fluid component
max	maximum value (for molecular packing)

Superscripts

c	cylindrical confinement
PR	model based on the Peng-Robinson equation of state
s	spherical confinement
vdW	model based on the van der Waals equation of state

Many of the models proposed in the literature were obtained as extensions of usual models, such as the van der Waals equation of state (Schoen and Diestler, 1998; Zhu et al., 1999; Truskett et al., 2001; Giaya and Thompson, 2002; Zarragoicoechea and Kuz, 2002; Holovko and Dong, 2009; Travalloni et al., 2010; Kim et al., 2011; Dong et al., 2016), the Peng-Robinson equation of state (Travalloni et al., 2014; Barbosa et al., 2016), and SAFT (statistical associating fluid theory) equations of state (Martínez et al., 2007, 2017; Tan and Piri, 2015; Franco et al., 2017). In these publications, the confining pores are generally assumed to be slit-like or cylindrical. The different modeling approaches include the interfacial theory (Zhu et al., 1999), perturbation theory (Schoen and Diestler, 1998; Truskett et al., 2001; Giaya and Thompson, 2002; Martínez et al., 2007, 2017; Franco et al., 2017), scaled particle theory (Holovko and Dong, 2009), generalized van der Waals theory (Travalloni et al., 2010, 2014; Barbosa et al., 2016), and hybrid approaches (Tan and Piri, 2015; Dong et al., 2016), combining a bulk equation of state with the Young-Laplace equation. However, there is still room to further modeling efforts, with the aim of attaining an equation of state able to describe the complex behavior of confined fluids accurately.

In previous work (Travalloni et al., 2010), the van der Waals equation of state was extended to fluids confined in cylindrical pores, based on the generalized van der Waals theory and empirical expressions for some structural properties of the fluid. The obtained model relates the PVT variables with the pore radius and two additional parameters for each fluid, which are related to the molecule-wall interaction. The pure fluid model was successfully applied to the correlation of adsorption data. In addition, the extension of this model to fluid mixtures revealed its potential to predict the adsorption behavior of binary and ternary mixtures. The same methodology was used to extend the Peng-Robinson equation of state to confined fluids (Travalloni et al., 2014). However, the models proposed for confined mixtures in these publications were straightforward extensions of the models developed for pure fluids. In this way, despite the good performance when predicting mixture adsorption, the confined mixture modeling proved to be inconsistent with the ideal solution limit, as discussed in the next section. Nonetheless, our modeling of pure confined fluids (Travalloni et al., 2010, 2014) has no such drawback.

In this work, we start from our models for pure fluids confined in cylindrical pores, based on cubic equations of state (Travalloni et al., 2010, 2014), and propose a consistent way to extend them to confined mixtures, with more explicit mixing rules. We follow a similar approach for model development, using the empirical formulation of the confined fluid structural properties. Additionally, we extend this modeling to confinement in spherical pores, which are characteristic of certain materials, such as X- and Y-type zeolites (Auerbach et al., 2003). The predictive performance of the new models is evaluated against experimental mixture adsorption data, revisiting some of the adsorption systems considered in previous work in order to assess the effect of the new mixing rules. Also, the effect of the adopted pore geometry is evaluated and confined fluid models based on different equations of state for bulk fluids (van der Waals or Peng-Robinson) are compared.

2. Inconsistency in previous modeling of confined mixtures

In our previous work (Travalloni et al., 2010, 2014), conventional cubic equations of state were extended to fluids confined in cylindrical pores. First, models were developed for pure fluids. For example, the extension of the van der Waals equation to pure confined fluids was:

$$P = \frac{RT}{v - b_{pi}} - \frac{a_{pi}}{v^2} - \theta_i \frac{b_{pi}}{v^2}\left(1 - \frac{b_{pi}}{v}\right)^{\theta_i - 1} \times (1 - F_{pr,i})\left(RT\left(1 - \exp\left(-\frac{N_{av}\varepsilon_{pi}}{RT}\right)\right) - N_{av}\varepsilon_{pi}\right) \quad (1)$$

where P is the pressure, R is the ideal gas constant, T is the absolute temperature, v is the molar volume of the fluid, N_{av} is the Avogadro number, and the other variables (a_{pi}, b_{pi}, ε_{pi}, θ_i, and $F_{pr,i}$) depend on