



Equation-of-state modeling of confined-fluid phase equilibria in nanopores



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ABSTRACT

Perturbed-chain statistical associating fluid theory (PC-SAFT) is coupled with Young–Laplace equation to investigate and represent fluid-phase equilibria in nanosize pores. The calculated pure-substance properties at capillary condensation (critical temperature, critical pore radius, surface tension, condensed-phase equilibrium pressure, and saturated densities) are found to be consistent with experimental data, theoretical models, and molecular simulation. The information obtained for pure substances can then be applied to predict the phase equilibria of fluid mixtures in porous mediums. The promising results presented in this work establish a strong platform for further development of an effective model toward engineering applications in real settings of confined fluids such as chemical systems encountered in unconventional reservoirs (e.g., shale oil and shale gas).

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1. Introduction

It has been known for a long time that the confinement in porous mediums introduces significant effects to many physical properties of fluids entrapped inside the pores including the phase equilibria [1,2]. Due to the strong interaction between the solid wall of the pores and the fluid molecules in the confined space, phase transitions such as capillary condensation occur at temperatures and pressures different from those outside the pores. For example, the vapor pressure of a pure chemical species generally decreases in the confining pores, which means, at a fixed temperature the vapor phase of the fluid condenses at a lower pressure than it does in the bulk phase outside the porous medium.

This kind of phenomena is well known and many models have been proposed to give the correct representation, ranging from the very simple form of the Kelvin equation [3–6] to those based on the sophisticated density functional theory (DFT) [7–11]. While the former has been applied for practical applications in a very wide range of disciplines, the latter is, due to its intensive mathematical and computational framework, generally intended for theoretical and simulation studies on the confined fluids. However, the DFT has contributed numerous plausible

descriptions on the underlying mechanisms that, at least for now, are inaccessible to experimental measurements, including its use as a reliable way to estimate pore radii [12].

Regardless of being simple or sophisticated, the existing models are shadowed with a common drawback, that is, the exact nature of the interaction between the solid walls and the fluid molecules is unknown in the first place. There are many factors that come into play, which make it difficult, or even impossible, for analytical approaches to mimic the factual interaction. In many cases, this kind of interaction may be approximated and derived from experimental observations, which in turn advantages simpler approaches for practical applications.

This is the very reason why simple approaches such as Kelvin's equation and its variants have survived until today in their applications. However, the simplicity does not give much information on the underlying physics. Moreover, the phase equilibrium in Kelvin's equation is assumed to occur between an ideal gas and an incompressible liquid phase. This assumption is not valid for fluids in confined space, in particular if the pore size is in the order of few diameters of the fluid molecules.

Some authors have attempted to use simple molecular theories and empirical approaches to account for the interaction between the pore walls and the fluid, but still without considerable applications in real systems. An example is the model proposed by Travalloni et al. [13], which is able to describe the adsorption isotherms of some real fluids and their mixtures in various porous mediums. It applies the van der Waals equation of state (EOS) [13,14], later also the Peng–Robinson (PR) cubic EOS [15], and a simplified wall–fluid interaction model that is represented by two

Abbreviations: EOS, equation of state; PC-SAFT, perturbed-chain statistical associating fluid theory; VLE, vapor–liquid equilibria.

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Nomenclature

\tilde{A}	Dimensionless Helmholtz energy
b_{ij}	Coefficients in Eq. (18) for λ parameter
c_{ij}	Binary parameter for the surface tension
f_i	Fugacity of component i in phase- π mixture (MPa)
k_B	Boltzmann constant ($\text{J K}^{-1} \text{mol}^{-1}$)
k_{ij}	Binary interaction parameter
ℓ	Liquid mole fraction
m	Segment number parameter
N	Number of components
P	Pressure (bar = 10^{-1} MPa)
φ	Parachor ($\text{dn}^{1/4} \text{cm}^{11/4} \text{mol}^{-1}$)
R	Gas constant ($\text{J K}^{-1} \text{mol}^{-1}$)
r_p	Pore radius (nm)
T	Temperature (K)
t_p	Adsorbed fluid layer thickness (nm)
$\mathbf{x} = \{x_i\}$	Mole fractions in adsorbed phases
$\mathbf{y} = \{y_i\}$	Mole fractions in the bulk vapor phase
$\mathbf{z} = \{z_i\}$	Overall mole fractions
Z	Compressibility factor

Greek letters

α	Measured amount of adsorbed fluid (mol/g-adsorbent)
β	Volumetric saturation
μ_i	Chemical potential of component i
ε_i	LJ energy depth; segment energy parameter of component i ($k_B K$)
λ	Parameter
γ	Surface tension (mN/m)
δ	Tolman's length (nm)
σ_i	Segment diameter parameter of component i (\AA)
ρ	Molar density (mol/cm^3), (mol/L), (g/cm^3)
θ	Contact angle
$\hat{\phi}_i^\pi$	Fugacity coefficient of component i in phase- π mixture
ϕ	Total volume of the pores ($\text{cm}^3/\text{g-adsorbent}$)
ξ	Reciprocal of fluid–fluid interaction decay distance

Subscripts/superscripts

π	Phases (A: adsorbed light phase; V: vapor phase; L: liquid or condensed phase)
C	Critical
res	Residual
hs	Hard sphere
chain	Chain
disp	Dispersion
sat	Saturated
p	Pore
cap	Capillary
∞	Flat surface
i, j	Of component i, j
ij	Between component i and j

additional EOS parameters. Though this model can theoretically calculate the capillary condensation, it has not been verified to represent the condensation of real systems in confined space. Nevertheless, this approach is applied to describe the phase behavior in organic shale nanopores [16], which shows an urgent need for such a tool. Another model, which is based on Kelvin's equation with an additional temperature-dependent parameter, was proposed to describe the adsorption isotherms and the capillary condensation, but the comparison between the model and experiments is only for pure argon [17].

In this paper, we use a robust thermodynamic EOS, i.e., the perturbed-chain statistical associating fluid theory (PC-SAFT) [18], which is a reliable EOS widely used in petrochemical industries [19], coupled with the Young–Laplace equation (Laplace equation for short) [1], to describe the confined fluid phase equilibrium in nanosize pores. PC-SAFT can deal with non-ideality of fluids very well, thus removes the assumption that is imposed in Kelvin's equation. Laplace equation, on the other hand, is a successful model to represent the effects of surface curvature of fluid on the pressure difference across the surface, which is the boundary of the equilibrium phases. It applies macroscopic property of the fluid, i.e., the surface tension, as well as the geometry of the confined space (size and shape), while the interaction between the fluid and the pore wall is usually accounted for by the so-called contact angle of the surface to the wall. A further discussion on the equation, including its extension to nanoscale applications will be given later in the paper.

The PC-SAFT/Laplace is used here to deal with the capillary condensation, i.e., the phase transition that occurs in confined space, but not the adsorption that occurs prior to condensation. We are only interested in the phase equilibrium as it applies to shale oil and gas that have been condensed in the shale for a very long time. Crude oil and gas condensate are recovered from shales that often have pores of nanometer size. The information on the phase transitions in the shales is crucial in such applications, where the miscibility of the injected gas and the trapped oil is necessary to achieve high recovery. The number of existing phases is also required to appropriately represent the multiphase flow in the recovery processes. Furthermore, accurate prediction of the fluid properties will reduce the uncertainty in fluid-in-place estimates, which is an important issue in reservoir modeling.

In shale-oil applications, simple molecular-based and empirical models are often used to simulate the multicomponent systems [20] without prior systematic studies. In fact, prior to such applications, systematic studies must be performed first with pure chemical species, then binary mixtures, and eventually with multicomponent systems, to build a robust model that can provide reliable predictions. Such an approach has been well established for fluid phases in the bulk. The study with pure-component systems is expected to provide us with information of the confined-phase behavior as a result of interaction between the pore walls and the fluid molecules, while the study with binary mixtures will provide the information on how to represent the molecular interaction of the fluids under the influence of the confinement of porous mediums. Finally, the study with multicomponent systems will apply the results from the preceding studies in a more realistic setting of applications.

This paper introduces an effective and practical EOS that can handle conditions in confined spaces for challenging applications such as in the recovery from shale oil and gas reservoirs. To the best of our knowledge, it is the first time for an EOS-based modeling of confined-fluid phase equilibrium to be systematically developed from the case of pure substances to that of mixtures supported by experimental data. The advantage of this EOS is that it applies the widely used algorithm of flash calculations with only minor modifications due to the confined space so that it is readily implemented in both applications and model simulations. Furthermore, the good accuracy of PC-SAFT makes it possible for this work to get new insights on the confined-fluid phase equilibria that can be contributed to the long-standing studies using other techniques such as molecular simulations [21–26].

In the next section, the description of all equations needed to deal with confined-fluid phase equilibrium is given, followed by the description of capillary condensation data that are used in deriving the extra parameter due to the confined space. In Section 3, the modeling results for pure substance and binary mixtures are presented. Properties of pure fluids in porous

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