Thermodynamics phase changes of nanopore fluids

Akand W. Islam [a, *], Tad W. Patzek [b], Alexander Y. Sun [a]

[a] *Bureau of Economic Geology, University of Texas at Austin, Austin, TX, USA*
[b] *Earth Science and Engineering Division, King Abdullah University of Science & Technology, Thuwal, Saudi Arabia*

ABSTRACT

The van der Waals (vdW) equation (Eq.) is modified to describe thermodynamic of phase behavior of fluids confined in nanopore. Our aim is to compute pressures exerted by the fluid molecules and to investigate how they change due to pore proximity by assuming the pore wall is inert. No additional scaling of model parameters is imposed and original volume and energy parameters are used in the calculations. Our results clearly show the phase changes due to confinement. The critical shifts of temperatures and pressures are in good agreement compared to the laboratory data and molecular simulation. Peng-Robinson (PR) equation-of-state (EOS) has resulted in different effect than the vdW. This work delivers insights into the nature of fluid behavior in extremely low-permeability nanoporous media, especially in the tight shale reservoirs, below the critical temperatures.

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1. Introduction

The phase behavior of fluids confined in porous media is an important subject of many practical applications, such as separation processes, oil extraction, estimation of gas-in-place and reserves, heterogeneous catalysis, molecular transport, among others (Holt et al., 2006; Travalloni et al., 2010a; Didar and Akkutlu, 2013). The energy dissipated by the friction due to confinement induces liquid–gas phase transitions, chemical transformations, and also drastic changes of static and dynamic properties, such as shear stress, compressibility, coefficient of friction, and viscosity (Zarragoicoechea and Kuz, 2002). The dynamic and static property changes are different from bulk behavior even qualitatively (Singer and Pollock, 1992). The confinement effect becomes important as the dimensions of the pores shrink. Fluids confined within pores of nanometer are in between bulk matters and single atoms or molecules and, as a consequence, finite size and surface effects must be investigated (Singh et al., 2009). Any real system interfaces either with walls of a container, or with different phases of the substance under consideration. Fluids trapped in pore spaces with the dimensions of 5–10 molecules organize as layers, and within each layer lateral order exists. A particular structure exists across thin films and an oscillatory force decaying exponentially varies

between attraction and repulsion with a periodicity of the scale of molecular dimension (Zarragoicoechea and Kuz, 2002; McGuiggan and Israelachvili, 1990; Varnik et al., 2000). Pot et al. (1996) presented a lattice-gas cellular automata porous media model exhibiting vapor–liquid equilibrium of microscopic fluid on solid walls. Their study implicitly revealed a fluid in nanopore experiences tensorial effect. Thermodynamic model should describe this phenomenon. There are few laboratory experiments conducted to study the confinement at nanopore scale (Morishige et al., 1997; Morishige and Shikimi, 1998; Konno et al., 1985; Sakuth et al., 1998; Yun et al., 2004). Imaging tools although powerful are unable to provide us with an understanding of the underlying mechanisms of how fluids reside and flow in nanopores (Didar and Akkutlu, 2013). This shortcoming necessitates the employment of theoretical methods such as molecular simulation (Didar and Akkutlu, 2013; Singh et al., 2009; Coasne et al., 2009; Demontis et al., 2003; Dukovski et al., 2000; Giovambattista et al., 2009; Jiang and Sandler, 2006; Nicholson and Parsonage, 1982; Severson and Snurr, 2007; Diaz-Campos, 2010; Jiang et al., 2005; Jiang and Sandler, 2005; Binder et al., 2003) and density functional theories (Kotdawala et al., 2005; Travalloni et al., 2010b; Wu, 2006). However these tools are computationally expensive. Studying distributions of fluid mixtures in a large-scale heterogeneous porous matrix is not possible by using these schemes. Hence researchers (Zarragoicoechea and Kuz, 2002; Schoen and Diestler, 1998; Giaya and Thompson, 2002; Meyra et al., 2005; Derouane, 2007; Vakili-Nezhaad and Mansoori, 2006) have focused on developing

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Notations

A	pore cross sectional area [dm^2]	
a	vdW energy parameter [$Padm^6\ mol^{-2}$]	
b	vdW volume parameter [$dm^3\ mol^{-1}$]	
d_p	pore diameter [dm]	
F	Helmholtz free energy [$kg\ dm^2\ s^{-2}$]	
k	Boltzman constant	
L	length [dm]	
N	Avogadro number	
P	pressure [MPa]	
r_p	pore radius [dm]	
s	inter molecular distance [dm]	
R	universal gas constant [$dm^3\ MPa\ mol^{-1}\ K^{-1}$]	
T	temperature [K]	
v	specific volume [$dm^3\ mol^{-1}$]	
V	pore volume [dm^3]	

Greek symbol

σ	Lennard-Jones size parameter
ε	Lennard-Jones energy parameter

Subscripts

1,2	molecules id's
B	bulk
p	pore
red	reduced

Superscript

c	critical

Axes

x	axial direction
r	radial direction

analytical (semi empirical) EOS models. To study small systems one needs to modify the basic equations of the conventional (bulk) thermodynamics. The fundamental concept of phase equilibrium of nano systems was first introduced by Hill (2002) in early sixties. However there are still serious challenges in defining the environmental variables in nano systems, such as temperature and pressure. Parallel to thermodynamics of nano systems many attempts have been made by using the concept of non-extensive statistical mechanics and thermodynamics (Vakili-Nezhaad and Mansoori, 2006). Tsallis (1988, 1999) showed close relation between nanothermodynamics and non-extensive thermodynamics through the fundamental parameters (Vakili-Nezhaad and Mansoori, 2004). In this article we focus on an EOS to address the nano confinement effects (i.e., the pore size effect). The equation describes the fluid behavior from the bulk state to extreme confinement.

Extensions of the vdW EOS to confined fluids have been studied to predict the critical temperature change with pore size both qualitatively and quantitatively. Schoen and Diestler (1998) showed application of vdW to model fluids confined in slit pores based on perturbation theory. The capillary condensation and reduction in the critical temperature of the fluid due to confinement were predicted. The performance of the model near the critical point of bulk fluid was not satisfactorily. The assumption of a universal reference fluid could be the cause as observed by Travalloni et al. (2010b). Giaya and Thompson (2002) obtained good predictions of water adsorption on two different mesoporous formations. To study the phase behavior of confined fluids Zarragoicoechea and Kuz (2002) have improved the vdW considering the tensorial nature of pressure in nanopores. Their work was based on classical thermodynamics and aimed to understand fluids pressure tensor change due to pore size reduction. Therefore the pore-wall interaction was ignored. The capillary condensation measured was consistent with molecular simulation. However, the scaling relations are not good enough to show transition from a confined to bulk critical property. For instance, the critical temperature of bulk phase ($\sigma/r_p \rightarrow 10^{-5}$) CH_4 calculated is 113 K where the true value is 191 K. In a followed-up article (Zarragoicoechea and Kuz, 2004) they improved their model by regressing original energy and volume parameters of vdW. Here we show that even with no additional scaling of model parameters the vdW can be applied to confined fluids in nanopore. Our objective is to demonstrate the critical shifts both qualitatively and quantitatively. In addition,

comparison with another classical EOS, such as PR, is shown. A thorough literature survey (Didar and Akkutlu, 2013; Singh et al., 2009; Morishige et al., 1997; Morishige and Shikimi, 1998; Zarragoicoechea and Kuz, 2004; Vishnyakov et al., 2001; Ortiz et al., 2005; Jana et al., 2009; Devegowda et al., 2012) is performed to collect the critical shifts obtained from experiments and molecular simulation.

Other investigations on this subject include Vakili-Nezhaad and Mansoori (2006), who used the exact form of Zarragoicoechea and Kuz (2002) equation to interpret phase change or fragmentation. Derouane (2007) proposed a simple modification of the attractive part of vdW to apply for fluids in microporous solids far from saturation. Travalloni et al. (2010b) extended vdW to describe different types of adsorption isotherms. Later Travalloni et al. (2010a) presented critical behavior of pure confined fluids. The effects of pore size and intensity of the molecule—wall interaction were evaluated. However their new molecule—wall interaction term in the model equation is hypothetical and no suggestion is proposed for any particular pore wall structure.

2. Model

Here we show the model development. Pressure $\overrightarrow{P}$ is a diagonal tensor expressed as $\overrightarrow{P}(p_i, i = x, r)$. The pore model is shown in Fig. 1. The Helmholtz free energy of N particles interacting by a pair potential $U(s_{12})$ can be read as

$$F = f(T) - \frac{kTN^2}{2V^2} \iint \left(e^{-\frac{U(s_{12})}{kT}} - 1 \right) dV_1 dV_2. \tag{1}$$

Here $f(T)$ is the free energy of ideal gas. Because we are interested in measuring the pressure force exerted by the fluid molecules the pore wall is assumed to be non-wetting. For Lennard-Jones potential $U(s_{12})$ equals $4\varepsilon[(\sigma/s_{12})^{12} - (\sigma/s_{12})^6]$. By following the derivations shown by Zarragoicoechea and Kuz (2002) a form of F becomes
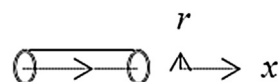

Fig. 1. Schematic diagram of pore model.