Molecular simulation of the pore size distribution effect on phase behavior of methane confined in nanopores

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A B S T R A C T

An understanding of the phase behavior of hydrocarbons is important in the petroleum reservoir simulation. However, fluid phase behavior in a shale reservoir is substantially different from conventional behavior. Since fluids are stored inside nanopores of shale rocks, there is a strong interaction between the pore boundary and fluid molecules. Due to this interaction, the fluid molecules are distributed heterogeneously inside the nanopores and the phase diagram is shifted under confinement. Advanced theoretical procedures such as molecular simulations are needed to properly model the heterogeneous molecular distribution inside the shale nanopores. Previous molecular simulation studies of nanoconfined hydrocarbon phase behavior have been limited to single pore size models. However, shale rocks usually have a wide pore size distribution (PSD) and single pore-size models are not accurate enough to represent a real shale system. In this work, to understand the PSD effect on the phase behavior, a recently proposed molecular simulation method, gauge-GCMC, is used to generate phase diagrams based on two types of cylindrical models (single pore and multiple pores, including one based on Eagle Ford shale rock). In single pore tests, the pore diameter is changed from 4 to 10 *nm*. Our results for multi-pore systems show that with an increasing pore size, the phase equilibrium properties approach the bulk values. Also, smaller pores cause a more significant shift in the phase diagram. Our results show that the small pores are filled before the large ones, which means that liquid will first be condensed in the small pores. In the Eagle Ford case, the pore model is designed by discretizing PSD data from experiments. The results show that it is possible to use a single pore model with a 10 *nm* diameter to represent the pore system of this shale sample.

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1. Introduction

Knowledge of hydrocarbon phase behavior is essential in reservoir simulation, well performance evaluation, and enhance oil recovery. Several equations of state (EOS) have been proposed in the past several decades to describe the fluid properties of conventional reservoirs. However, in a shale system, the fluid phase behavior differs significantly when compared with that of conventional reservoirs. Unlike conventional rocks, shale is composed of micropores (diameter less than 2 *nm*), mesopores (diameter between 2 and 50 *nm*), and macropores (diameter larger than 50 *nm*) [1]. Inside the micropores and mesopores, the pore surface has an important influence on the fluid molecules. It has been proposed that liquid and vapor phases can coexist within

nanopores with the same chemical potential [2]. Based on pore-fluid interactions, the fluid molecular distribution is heterogeneous and the phase equilibrium is achieved under confinement [3].

Shale consists of pores with different diameters, which is described using a pore size distribution (PSD) [4—8]. Many techniques have been used to determine this PSD, such as small-angle and ultra-small-angle neutron scattering (SANS and USANS) [4], low pressure adsorption isotherm [4,5,8], high pressure mercury intrusion [6—8], and nuclear magnetic resonance spectrum [7]. From these studies, the PSD of shale has been found to vary between regions and samples (Fig. 1). It should be noted that the fluids can stay in an equilibrium state inside these connected pores. Thus, the PSD effect needs to be considered in a phase behavior study.

To study the confined phase behavior, a direct method is measurement through experiments. The adsorption isotherm has been widely used in previous works to calculate the confined fluid

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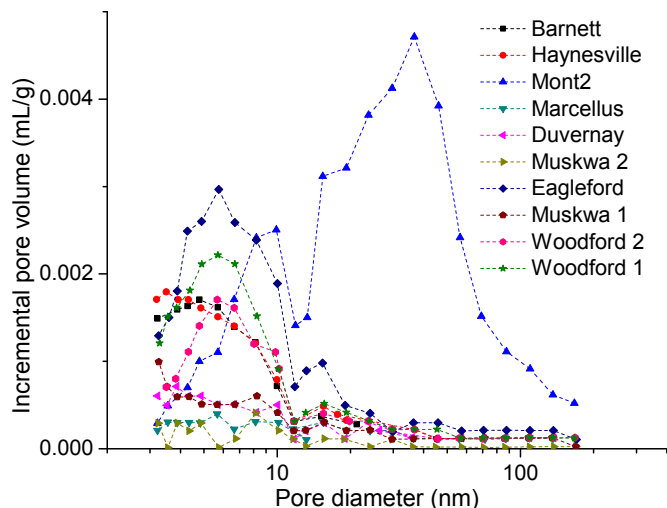 *E-mail address:* hadi.nasrabadi@tamu.edu (H. Nasrabadi).

Fig. 1. Incremental pore volume plot for shale samples from shale gas reservoirs in North America [4].

properties [9−12]. Several nanoporous materials (e.g., controlled pore glass, MCM-41 silica) are used to generate isothermal curves. From these experiments, the critical temperature of a confined fluid is reduced while the critical density is shifted upward when compared with bulk values. Luo, Lutkenhaus, and Nasrabadi [13−16] measured the bubble points of pure and binary fluids under confinement based on the differential scanning calorimetry method. They presented an obvious shift between the bubble points in bulk and confined conditions and observed the confinement-induced supercriticality. Another device, a nanochannel chip, has been adopted in case studies of fluid flow and phase equilibrium at atmospheric pressure under confinement [17−19]. Although experimentation is a direct way to capture the confinement effect, the data is restricted by the nanoporous material, pressure and temperature conditions, and fluid samples. Most experiments are conducted using pores with a single diameter and the PSD is barely used in the experiments.

Theoretical models have also been employed in the study of nanoconfined fluids. An ideal adsorbed solution theory was presented in the simulation of an ideal gas mixture [20]. Two adsorption models, the Langmuir and Brunnauer-Emmet-Teller (BET) models, have been used in studies of adsorption under confinement [21−24]. The Kelvin equation is generated to describe the pressure difference due to a curved liquid-vapor interface and is applied in studies of porous systems [25,26]. However, the hysteresis under confinement is not covered in these models [3,27].

Recently, several new applications of the EOS have been proposed in the study of confined phase behavior. Capillary pressure from the Young-Laplace equation is considered in the simulation of phase equilibrium based on the Peng-Robinson (PR) EOS [28−31]. However, the pore surface adsorption effect is not included in the assumptions, which limits the applicability of this method. In another approach, the confined critical parameters from previous molecular simulations are combined with traditional EOS applications [31−34]. This technique is restricted by those molecular simulation results. Travalloni et al. provided an extension of PR-EOS for a nanoporous system by introducing a pore size dependent term [35]. This EOS can be applied in confined phase behavior prediction when experimental data are available [15].

Monte Carlo (MC) molecular simulations have been used in confined phase behavior simulation for decades [27,36−39]. Based on the thermodynamic descriptions of interactions between

molecular particles, this method is capable of calculating the fluid properties in complex pore models. Simulations of hysteresis and the interface are also available using this statistical method. Several MC methods (GEMC [36,40,41], GCMC [42,43], gauge-GEMC [44−46], gauge-GCMC [3]) have been created for simulations in different ensembles [47,48]. Most studies have been performed using a single pore model.

In this paper, a MC molecular simulation method, gauge-GCMC from our previous work [3], is used to study the effect of PSD on the confined phase behavior of hydrocarbons. Molecular simulations are conducted for the phase diagrams of pure methane based on single pore models. Pore diameters range from 4 to 10 *nm*. Then, several multi-pore configurations are generated to test the PSD effect on the phase behavior, including an example based on Eagle Ford shale rock. The paper is finished with concluding remarks.

2. Method

2.1. Gauge-GCMC simulation

The gauge-GCMC method, modified from the gauge-GEMC method [44,46], is a technique for multicomponent system simulation under confinement [3]. Two boxes are involved in the simulation: one represents the fluid system and the other one is used as a gauge meter (Fig. 2). The volume of each box is fixed and several MC moves (insertion/deletion, translation and swap) are adopted during the simulation process. For a single-component fluid ($N = 1$), the method is equivalent to gauge-GEMC. For a system with N components, the input parameters are: temperature T, chemical potentials ($\mu_1, \mu_2, ..., \mu_{i-1}, \mu_{i+1}, ..., \mu_N$), and the total molecular number N_i of component i. The swap move helps the chemical potential of each component reach equilibrium between these two boxes. The insertion/deletion move keeps the chemical potentials ($\mu_1, \mu_2, ..., \mu_{i-1}, \mu_{i+1}, ..., \mu_N$) as the input parameters.

It takes 2 million MC steps for the pure methane to reach equilibrium in single pore cases and 4 million in multiple pore systems. For Eagle Ford model 5 million MC steps are required for equilibrium. After the equilibrium, additional 1−2 million MC steps are adopted to generate the average results. Since the capacity of the gauge meter is fixed, the property of a fluid system is gradually changed and the system can stay in any state. This method can generate the complete phase diagram (e.g., density vs. μ_i) in the form of a van der Waals loop, including unstable, meta-stable, and stable states [44]. Phase equilibrium points are computed following the thermodynamic integration of Maxwell equal area rule [49] (Fig. 3). The critical point is extrapolated from simulation results at lower temperatures based on the rectilinear diameter law [50] and the density scaling law [51]. The density mentioned above is the average density inside pore spaces. Since fluid molecules can still move inside pores under equilibrium, it is not recommended to pick a density change in some specific regions of the model.

2.2. Force field

The Lennard-Jones (LJ) 12−6 potential is used to calculate the non-bonded interaction energy U between molecular particles,

$$U(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \tag{1}$$

where r_{ij}, ε_{ij}, σ_{ij} are the separation distance, potential well depth, and finite distance where U is zero between particles i and j, respectively. The parameters (ε/k_B, σ) from the TraPPE force field [52] are (148 *K*, 0.373 *nm*) for CH4, and (30 *K*, 0.370 *nm*) for