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Phase behavior of multi-component hydrocarbon systems in nano-pores using gauge-GCMC molecular simulation

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ABSTRACT

In recent years, the phase behavior of hydrocarbons in shale reservoirs has received significant attention. One of the main complexities in modeling the phase behavior in shale reservoirs is the confinement effect. Surface–fluid interactions in nanoscale shale pores can lead to a heterogeneous distribution of molecules and can significantly alter the phase behavior compared to that in bulk conditions. Molecular simulation has shown promising results in modeling phase behavior under confinement. In this study, we present a novel molecular simulation method for studying the confinement effect on the phase behavior of multicomponent systems. We validate our method by comparing the phase diagrams of pure and binary hydrocarbon systems with experimental data (where available) and the simulation results from other techniques. We also apply the proposed method in modeling the phase behavior of a ternary system (C_1/C_3C_5) under a 4 nm slit pore confinement. Our results show that critical density increases under confinement in binary and ternary systems, and the confinement effect produces in a significant shift in the composition of the critical point. Heavier components have a higher concentration in the adsorbed layers than that of lighter components, which results in significant phase density differences under confinement.

1. Introduction

Over the past few years, there has been a sharp increase in the production of tight oil and shale gas, which are projected to constitute the most significant energy supply for the U.S. in the coming decades. The U.S. oil and gas shale reserves are massive; however, achieving optimum production is a complex challenge. One of the complexities is the significant effect of porous media on the phase behavior of petroleum fluids in shale reservoirs. Shale matrices comprise micropores with diameters of less than 2 nm, mesopores with diameters between 2 and 50 nm, and macropores with diameters larger than 50 nm [1]. In such small pores, the pore surface molecules can significantly influence all the fluid molecules inside the pore space. This strong pore–fluid interaction and its competition with fluid–fluid interaction can lead to a heterogeneous distribution of fluid molecules in the pore space, which results in modified phase behavior [2,3].

Confined phase behavior has been experimentally studied in recent decades. Thommes and Findenegg tested the phase behavior of SF_6 in controlled pore glass (CPG) materials with mean pore diameters of 24 and 31 nm. They noted that the critical temperature of a pore fluid is lower than the bulk critical temperature, and the critical density of a pore fluid is shifted upward relative to bulk critical density [4]. Keizer, Michalski, and Findenegg studied the adsorption of SF_6 on CPG-10 in reduced temperatures, and found that there is a supercritical fluid at $T_r = 0.985$ inside a pore having a diameter of 7.7 nm [5]. Qiao, Bhatia, and Nicholson determined the adsorption isotherms of hexane on nanoporous MCM-41 silica for various pore diameters at several temperatures. Their results showed that the relative pressure of a phase transition increases with increasing temperature and pore size [6]. Luo, Lutkenhaus, and Nasrabadi presented experimental data on the nano-confinement effects on the bubble point of a binary mixture of octane and decane based on the differential scanning calorimetry method. The authors obtained a clear separation between the bubble points of bulk and confined fluids [7,8]. Recently, nano-channel chips have been used to study two–phase flow and phase behavior under confinement [9–12]. Although the best way to achieve confined phase behavior is experimentally, the data are still limited to a few types of fluids, pore materials, and ranges of

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temperature and pressure. For a better understanding of phase behavior under confinement, simulation allows for the study of complex fluid phase behavior in nanopores.

There are several methods for simulating fluid phase behavior in nanopores. An ideal adsorbed solution theory was proposed for calculating the adsorption equilibria of an ideal gas mixture [13], but the results may be not valid for non-ideal systems. Two other approaches – the Langmuir and Brunnauer–Emmet–Teller (BET) methods — have been applied widely to study the adsorption of mixtures under confinement [14–17]. An extended Langmuir model has also been applied to study multicomponent natural gas [14]. The Langmuir model is based on the assumption that adsorbed fluids act like ideal gases, and that there is only one layer of adsorbates near the solid surface without interaction between the adsorbed molecules. In domains far removed from the solid surface, the fluid assumes a bulk configuration. The BET model is an extension of the Langmuir method, which includes an infinite number of adsorbed layers near the solid surface without interaction between each layer. Use of the Langmuir and BET methods requires several parameters from experimental data, which limits the usage of both methods. Additional approximations are required for any extension of these methods. In addition, there may be interface related condensation and hysteresis under confinement, which cannot be simulated by these two methods [2].

In recent years, several theoretical studies have been carried out on confined fluid phase behavior, based on the equation of state (EOS). Capillary pressure is calculated using the Young–Laplace equation, and is included in the estimation of the liquid–vapor equilibrium [18–21]. But in shale reservoirs consisting of nanopores, a strong pore–fluid interaction, which is not included in the above procedure, has a significant influence on the fluid configuration and differs from the capillary effect [2]. Furthermore, hysteresis cannot be described from the capillary included EOS. Another method was also introduced for determining confined phase behavior, in which the critical properties of pure components are modified [21–24]. Based on the simulation results, the phase envelope is computed by including the shifted critical parameters. Since molecular simulation is only valid for specific models and force fields, these shifts could change in different situations.

Monte Carlo (MC) molecular simulations have been widely adopted to study fluid phase behavior under confinement [2,3,25]. These statistical thermodynamic approaches are based on the description of fluid–fluid and fluid–pore interactions, and are suitable for describing heterogeneous molecule distributions without additional assumptions. There are several MC simulation methods based on different ensembles [26,27], such as the Gibbs ensemble Monte Carlo (GEMC), the grand canonical Monte Carlo (GCMC), and the gauge-GEMC.

The GEMC was developed to simulate the phase equilibrium of pure substances and mixture systems in bulk situations. The volume shift move between two boxes makes the simulation straightforward, and provides accurate results when the temperature is below the critical temperature [28,29]. Although this technique has been applied in a number of tests under confinement [30,31], the volume shift move is computationally expensive because it includes pore molecules. Thus, the GEMC is not applied in this work.

The GCMC is a simulation method that uses just one system box with no volume shift move [32,33]. It can be used to generate the relationship between chemical potential and fluid density. This technique is quite suitable for simulating of simple systems under confinement, but many tests are required. The adsorption and desorption isotherms are calculated by gradually changing the chemical potential inputs, which are established after some trial-and-error testing. Typically, the GCMC is used only in pure substances and binary systems [34–40], since the total computation costs are prohibitive for simulating multicomponent systems. This method here is only included to provide comparison results for pure and binary systems. There are other simulation techniques such as grand canonical transition matrix Monte Carlo [41,42] that are not included in this work for the sake of brevity.

The gauge-GEMC is typically used to simulate pure substances in confined systems [43,44], and can also be applied in simulating multicomponent systems [45]. It provides the van der Waals relationship between the chemical potential and density, based on several tests. This method has a computation efficiency similar to the GCMC, and is easier to operate. It has been successfully applied in pure fluid simulations under confinement [43], but not in binary or multicomponent systems.

In this work, a modified version of the gauge-GEMC is presented and applied in the simulation of binary systems. To calculate the phase diagram for a multicomponent system under confinement, a new method is developed and named the gauge-GCMC, which combines the gauge-GEMC and GCMC methods, and it is applied in a ternary system in bulk and confinement conditions. Further details about these methods are included in the following sections.

The remainder of this article is organized as follows. First, we briefly present several MC methods (GCMC, gauge-GEMC, and gauge-GCMC). Next, simulation results are discussed with respect to the confinement effect on pure hydrocarbons and mixtures. Lastly, the main conclusions are summarized.

2. Methods

2.1. GCMC

A typical GCMC simulation, as described in Refs. [32,33], has been used in many studies [34–40]. This GCMC simulation, also called μVT simulation, establishs the box volume (V), temperature (T) and chemical potential for each component (μ_i) as constants (Fig. 1). During the MC simulation process, molecules are inserted into or deleted from the box by the configurational bias Monte Carlo method (CBMC) [46,47]. The initial configuration is important in the GCMC method. An adsorption isotherm is produced from an initial empty box, and a desorption isotherm is produced from an initial fully saturated box. The separation of these isotherms leads to hysteresis in MC molecular simulations [4,26,48].

The general simulation process in GCMC is described in the following example. To get the equilibrium state for the $C_1/C_3/nC_5$ system at temperature T_1, (μ_{C_1}, μ_{C_3}) are set as constant and a series of tests are conducted in a wide range of possible μ_{nC_5} with a large

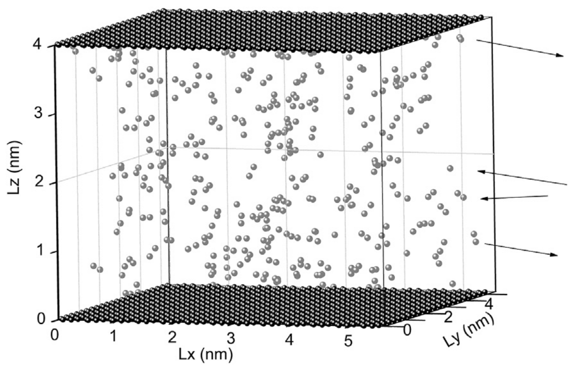

Fig. 1. Schematic of the GCMC method. Solid lines represent the box dimensions. Black and gray spheres are the molecules of the pore boundary and fluids, respectively. Arrows represent insertion/deletion MC move.