

Perspective

Fluid phase behavior of tight and shale reservoirs: Monte Carlo simulations

Wenzhen Chu, Kaiqiang Zhang^{✉*}

Institute of Energy, Peking University, Beijing 100871, P. R. China

Keywords:

Monte Carlo simulation
tight and shale reservoirs
nanopores
phase behavior
confinement effect

Cited as:

Chu, W., Zhang, K. Fluid phase behavior of tight and shale reservoirs: Monte Carlo simulations. *Advances in Geo-Energy Research*, 2023, 7(2): 132-135.
<https://doi.org/10.46690/ager.2023.02.06>

Abstract:

Tight and shale reservoirs are forming important components of the global hydrocarbon landscape, which impede the free thermal movement of fluid molecules, with numerous nanoscale pores. The confined hydrocarbons in the nanopores cannot be industrially produced from conventional exploration and development methods, with deviated fluid phase behavior under nano-confinement effects. Most commonly important fluid phase behavior in nanopores has been simulated and compared with the bulk cases previously, including phase coexistence, critical properties, and density distribution of confined fluids. This paper focuses on the deviated fluid phase behavior under nano-confinement effects by Monte Carlo modeling. The Monte Carlo simulation is still limited to modeling the macroscopic pore-related behavior like capillarity and complex fluid and solid materials. Moreover, the Monte Carlo simulation is usually scale-restricted and the pore-size range where the nano-confinement effect fails to work needs to be quantitatively determined. Overall, for the tight and shale fluid phase behavior, a functional Monte Carlo model, coupled with the long-range correction and configuration bias techniques, is suggested to include both the multi-component fluids and skeleton.

1. Introduction

Owing to the continuous depletion of conventional petroleum resources, tight and shale reservoirs have become increasingly important in the world energy landscape in the last decade. Locked in abundant nanoscale pores, shale and tight fluids in porous media can hardly be explored from conventional extraction methods. As phase behavior is a fundamental property in the progress of hydrocarbon production, understanding the deviated fluid phase behavior in nanopores is crucial for the tight and shale fluid recovery. The current laboratory technologies are limited for fluid phase behavior in nanopores, which cannot model the actual subsurface reservoir in an efficient and economical manner.

Combining theoretical methods with computational techniques, molecular simulation has provided new avenues for nano-fluid modeling, which includes molecular dynamics simulation, Monte Carlo (MC) simulation, density functional theory, lattice Boltzmann method, etc. Among these methods, the molecular dynamics and MC simulations are the most used

in simulating nano-fluids. The molecular dynamics simulation uses the variation of motion trajectories with time to yield kinetic properties, which is dependent on initial conditions and constrained by energy conservation due to the nanosecond time step (Liu and Zhang, 2019). Instead, the MC simulation uses probability walks to generate microstates, which is capable to handle conformational changes more effectively when dealing with nonphysical motions (Leach, 2001) and meanwhile, converge more quickly when facing simple molecular systems. Given the strong functions of the MC simulation, this paper presented a perspective on the MC simulation of calculating phase behavior under nano-confinement and discussed the gaps that need to be solved in future research.

2. Nano-confined phase behavior

The reduced pore dimension results in the restricted free thermal motion of fluid molecules and the enhanced interplay of fluid-wall and fluid-fluid forces (Devegowda et al., 2012). The fluid phase behavior at the nanoscale is very different

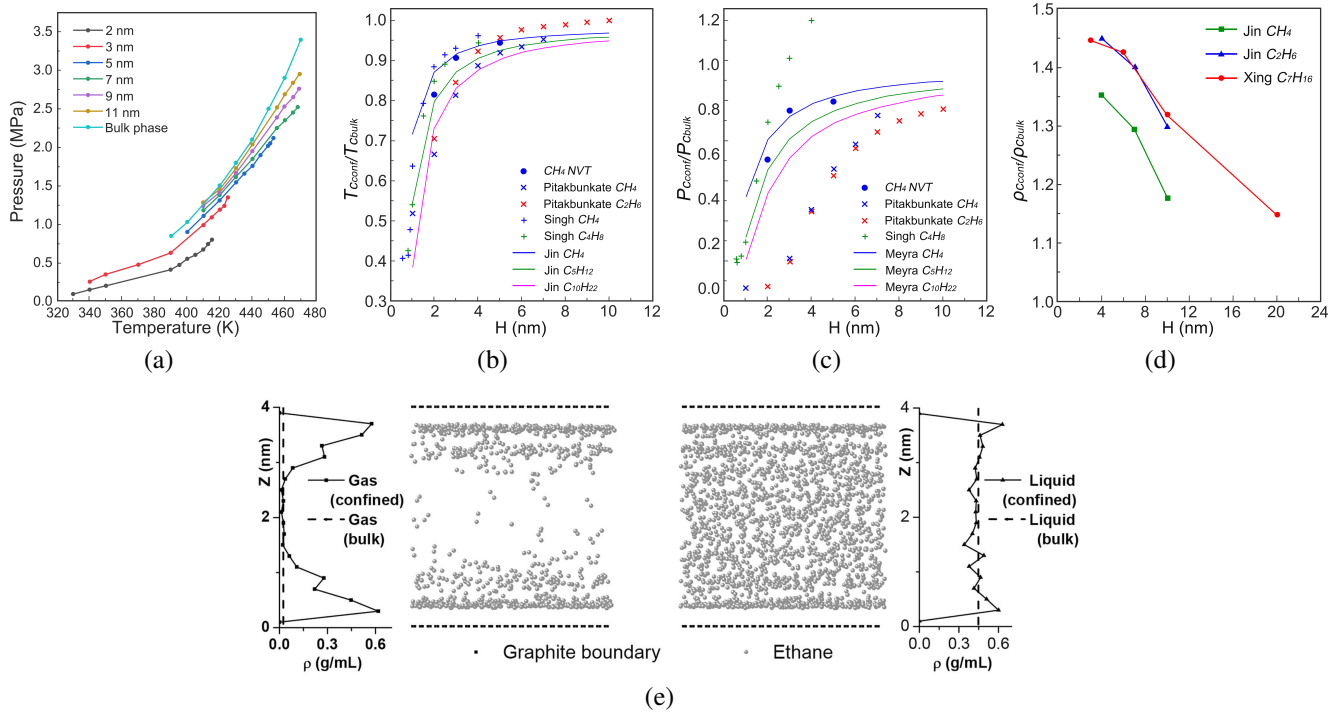


Fig. 1. (a) *n*-pentane phase diagram in 5 nm silica slit (Yu et al., 2022); comparison of critical (b) temperature, (c) pressure (Sobecki et al., 2019) and (d) density (Jin and Nasrabadi, 2016; Xing et al., 2021) versus pore length evolution with literature; (e) two phase snapshots of ethane at 250 K in 4 nm slit pore model (Jin and Nasrabadi, 2016).

from that at the macroscale. The phase coexistence, critical parameters, and density heterogeneity in nanopores have been studied by the MC simulation, as shown in Fig. 1.

2.1 Phase coexistence properties

Singh et al. (2009) investigated the phase coexistence properties of *n*-alkanes in the slit range of 0.5 to 1.5 nm. They calculated the deviation of the saturation pressure in nanopores from that of the bulk phase, which gradually disappeared as the temperature approached the critical temperature. Comparing in multidimensional pores, they found that the deviation was positive and negative for 40 and 8 Å pores, respectively. In the simulation by Pitakbunkate et al. (2016), the phase diagram of the methane-ethane mixtures shrunk in nanopores, and the bubble point pressure increased slightly below 200 K while the dew point pressure became higher. Sobecki et al. (2019) analyzed the phase coexistence properties of the confined mixtures, which also showed that the dew point pressure increased and the bubble point pressure decreased under confinement. Xing et al. (2021) proposed that the confinement affected the equilibrium phase composition. As the simulated size increased from 3 to 20 nm, the dew point pressure of the CO_2/C_7 system performed a downward concave pattern and the bubble point pressure monotonically increased. At 20 nm, the bubble point line agreed with that in the bulk phase, while the dew point line did not. Accordingly, they supposed that the pore size-induced nano-effect cannot be accurately determined from the bubble or dew point pressure. Using grand canonical Monte Carlo (GCMC) simulation, Yu et al. (2022) obtained

the deviated phase diagram of the confined *n*-pentane and the deviation was gradually diminished as the pore size increased from 2 to 11 nm.

2.2 Critical parameters

Table 1 summarized the confined critical parameters compared to the bulk phase by the MC simulation. Singh et al. (2009) studied the variation of critical parameters of pure hydrocarbons in nano-slits. As the system approached the two-dimensional regime, the critical temperature and pressure decreased to constant values, while the critical density increased. The critical parameters of nano-confined methane (Didar and Akkutlu, 2013), ethane, methane-ethane mixtures (Pitakbunkate et al. 2016), and methane-ethane-pentane mixtures (Jin and Nasrabadi, 2016) were simulated, which came to the similar conclusions. The variation of the critical temperature and pressure under confinement was also verified by Sobecki et al. (2019). Xing et al. (2021) established the relationship between the pore size and the shift from critical temperature to the bulk value, which followed a power function coupled with the coefficient. Moreover, the shift of C_7 was wider than CO_2 for stronger interaction between alkanes and organic pores. The minimum miscible temperature and pressure of the binary system were lower in nanopores, which contributes to higher oil recovery by CO_2 injection. Yu et al. (2022) found that the critical temperature of confined *n*-pentane can be treated with the bulk one at the pore size beyond 10 nm, so was the critical pressure at the pore size larger than 30 nm.

Table 1. Monte Carlo simulations for the confined critical parameters compared to the bulk.

Reference	Fluid system	Pore	Critical radius (nm)	Temperature	Pressure	Density
Jiang et al. (2004)	C ₂ , C ₃ , nC ₄	Graphite cylinder	3.074	<	-	>
Mota and Esteves (2007)	C ₃	Graphite slit	2-4	<	-	>
Singh et al. (2009)	C ₁ -C ₈	Graphite/mica slit	0.5-1.5	<	<	>
Didar and Akkutlu (2013)	C ₁ , C ₁ /C ₂ , C ₁ /C ₃	Graphite slit	3	<	<	-
Pitakbunkate et al. (2016)	C ₁ , C ₂ , C ₁ /C ₂	Graphite slit	1-10	<	<	>
Jin and Nasrabadi (2016)	C ₁ , C ₂ , C ₁ /C ₂ , C ₁ /C ₃ /C ₅	Graphite slit	4-10	<	-	>
Jin et al. (2017)	C ₁	Graphite cylinder	4-10	<	-	>
Pathak et al. (2017)	C ₁₀ , C ₁ /C ₁₀	Graphite slit	3.5	<	<	<
Lowry and Piri (2018)	C ₂	FCC carbon Disordered carbon Amorphous silica	3-6	<	-	>
Sobecki et al. (2019)	C ₁ , C ₂ , nC ₅ , nC ₁₀ , C ₁ /C ₂ , C ₂ /nC ₁₀	Graphite slit	2-7	<	<	-
Xing et al. (2021)	CO ₂ , C ₇ , CO ₂ /C ₇	Graphite slit	3-20	<	<	>
Yu et al. (2022)	C ₅	SiO ₂ slit	2-11	<	<	-

2.3 Adsorption layers and density distribution

Peterson and Gubbins (1987) plotted the adsorption isotherms and density profiles of Lennard-Jones fluids in cylindrical pores, which indicated the fluid density near the pore wall was higher than that in the center. Mota and Esteves (2007) proposed that the number of the adsorption layers reduced as the pore size decreases. They distinguished the adsorption layer number and profile morphology of the vapor and liquid states. Didar and Akkutlu (2013) found that the heavier fractions of the fluid system tended to form layers along the walls. Pitakbunkate et al. (2016) fixed the overall fraction of the methane-ethane system and found that the heavier components were enriched under confinement. Accordingly, they supposed that during the production of the nano hydrocarbons, the heavier hydrocarbons began to release after the lighter ones almost drained out. Jin and Nasrabadi (2016) found that the fluid density in the pore center was closer to the bulk one, and multiple adsorption layers existed near the pore walls with higher concentrations of heavy hydrocarbons in the layers. Xing et al. (2021) proposed that the absorption led to a higher equilibrium vapor phase density while the capillary coalescence led to a lower liquid phase density. Since the van der Waals force is the main factor affecting the nano-fluid phase state, Yu et al. (2022) quantitatively characterized the relationship between the van der Waals force and the pore size. The van der Waals force, which arose as the temperature decreased and pressure increased, fluctuated at 1.4 MPa and 450 K, where the vapor-liquid phase transition performed. The larger the absolute force value, the more adsorptions of *n*-pentane and easier conversions from the vapor to liquid phase occurred.

In addition, the effect of the pore material properties on

the phase behavior of the confined fluid has been studied. Singh et al. (2009) studied the phase transition of pure hydrocarbons in nano-slits with graphite and mica surfaces. They also simulated a square-well fluid to perform the phase transition in flat pores (Singh et al., 2010) and cylindrical pores (Singh and Singh, 2011). Jin et al. (2017) investigated the impact of pore size distribution on fluid confinement effects using the gauge-GCMC simulation. However, they considered the porous media only as parallel pores of different sizes, which didn't reflect the pore correlation. Lowry and Piri (2018) used the GCMC to simulate the confined ethane in three different pore structures (FCC carbon, disordered carbon, and amorphous silica pores), which showed the disorder and surface chemistry of the pore material influenced the critical point.

3. Summary

The MC simulation has been proven to be effective for the nano-confined fluid phase behavior and applicable for the tight and shale hydrocarbon reservoirs. However, the MC simulation needs further modifications in terms of the following shortcomings. First, the MC simulation is inapplicable for the pore-related properties, like capillary pressure and wettability, and the dynamic properties, such as viscosity and boundary slip. As another major limit of the MC simulation, most studies relevant to the nano reservoirs focused on simple-molecule fluids, while the tight and shale hydrocarbon is composed of complex saturated, aromatic, and non-hydrocarbons, as well as impurities like water and inorganic gas. Furthermore, the skeleton material affects the phase properties of the confined fluids. Most previous studies simply used graphene to substitute kerogen as the pore material, while the tight and shale

formations are complex with multiple components, consisting of both organic and inorganic minerals to be considered, such as quartz, feldspar, calcite, and clay (Feng et al., 2020). Beyond the complex material composition, nanopores range from several to 100 nm, but the confined behavior of nano-fluids by the MC simulation has been mainly restricted to the scale below 20 nm. Within nanoscales, the MC simulation can handle conformational changes effectively, but once the spatial scale rises, it can hardly guarantee data validity. Therefore, how to improve the scale of molecular simulations is to be solved. Moreover, the size range where the nano-effect fails to work needs to be quantitatively determined.

Here are several suggestions to improve the MC simulation for fluid phase behavior in nanopores. First, the long-range correction is believed to handle the density heterogeneity caused by pore dimension reduction. Second, the configurational bias technique is found to be effective in dealing with complex MC simulation systems. Furthermore, to investigate the effect of matrix properties on the fluid phase behavior deviation, the skeletal model is suggested to be coupled with the material, surface chemistry, shape, and mutual connectivity of the pores. Overall, for the phase behavior of tight and shale fluids, a systematic, mature, and highly reductive molecular model is suggested, including both the multi-component fluids and the skeleton model.

Acknowledgements

The authors want to acknowledge the research funding from the China National Petroleum Corporation-Peking University Strategic Cooperation Project of Fundamental Research, and Peking University-Ordos Carbon Neutrality Joint Laboratory.

Conflict of interest

The authors declare no competing interest.

Open Access This article is distributed under the terms and conditions of the Creative Commons Attribution (CC BY-NC-ND) license, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

References

- Devegowda, D., Sapmanee, K., Civan, F., et al. Phase behavior of gas condensates in shales due to pore proximity effects: Implications for transport reserves and well productivity. Paper SPE 160099 Presented at SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA, 8-10 October, 2012.
- Didar, B. R., Akkutlu, I. Y. Pore-size dependence of fluid phase behavior and properties in organic-rich shale reservoirs. Paper SPE 164099 Presented at SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, USA, 8-10 April, 2013.
- Feng, Q., Xu, S., Xing, X. et al. Advances and challenges in shale oil development: A critical review. *Advances in Geo-Energy Research*, 2020, 4(4): 406-418.
- Jiang, J., Sandler, S. I., Smit, B. Capillary phase transitions of *n*-alkanes in a carbon nanotube. *Nano Letters*, 2004, 4(2): 241-244.
- Jin, B., Bi, R., Nasrabadi, H. Molecular simulation of the pore size distribution effect on phase behavior of methane confined in nanopores. *Fluid Phase Equilibria*, 2017, 452: 94-102.
- Jin, B., Nasrabadi, H. Phase behavior of multi-component hydrocarbon systems in nano-pores using gauge-GCMC molecular simulation. *Fluid Phase Equilibria*, 2016, 425: 324-334.
- Leach, A. R. *Molecular Modelling: Principles and Applications*. London, UK, Pearson, 2001.
- Liu, X., Zhang, D. A review of phase behavior simulation of hydrocarbons in confined space: Implications for shale oil and shale gas. *Journal of Natural Gas Science and Engineering*, 2019, 68: 102901.
- Lowry, E., Piri, M. Effects of chemical and physical heterogeneity on confined phase behavior in nanopores. *Microporous and Mesoporous Materials*, 2018, 263: 53-61.
- Mota, J. P. B., Esteves, I. A. A. C. Simplified gauge-cell method and its application to the study of capillary phase transition of propane in carbon nanotubes. *Adsorption*, 2007, 13: 21-32.
- Pathak, M., Cho, H., Deo, M. Experimental and molecular modeling study of bubble points of hydrocarbon mixtures in nanoporous media. *Energy & Fuels*, 2017, 31(4): 3427-3435.
- Peterson, B. K., Gubbins, K. E. Phase transitions in a cylindrical pore. *Molecular Physics*, 1987, 62(1): 215-226.
- Pitakbunkate, T., Balbuena, P. B., Moridis, G. J., et al. Effect of confinement on pressure/volume/temperature properties of hydrocarbons in shale reservoirs. *SPE Journal*, 2016, 21(2): 621-634.
- Singh, S. K., Singh, J. K. Effect of pore morphology on vapor-liquid phase transition and crossover behavior of critical properties from 3D to 2D. *Fluid Phase Equilibria*, 2011, 300(1-2): 182-187.
- Singh, S. K., Sinha, A., Deo, G. et al. Vapor-liquid phase coexistence, critical properties, and surface tension of confined alkanes. *The Journal of Physical Chemistry C*, 2009, 113(17): 7170-7180.
- Singh, S. K., Saha, A. K., Singh, J. K. Molecular simulation study of vapor-liquid critical properties of a simple fluid in attractive slit pores: Crossover from 3D to 2D. *Journal of Physical Chemistry B*, 2010, 114(12): 4283-4292.
- Sobecki, N., Wang, S., Ding, D. et al. Tight oil and shale gas PVT modelling for flow simulation with matrix-fracture interaction. Paper SPE 193867 Presented at SPE Reservoir Simulation Conference, Galveston, Texas, USA, 10-11 April, 2019.
- Xing, X., Feng, Q., Zhang, W. et al. Vapor-liquid equilibrium and criticality of CO₂ and *n*-heptane in shale organic pores by the Monte Carlo simulation. *Fuel*, 2021, 299: 120909.
- Yu, C., Zhao, J., Wang, Z. et al. Vapor-liquid phase equilibrium of *n*-pentane in quartz nanopores by grand canonical Monte Carlo calculation. *Journal of Molecular Liquids*, 2022, 365: 120075.