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# Bubble/dew point and hysteresis of hydrocarbons in nanopores from molecular perspective

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ABSTRACT

The effect of nano-confinement on the thermodynamic behavior and saturation properties of petroleum fluids in nanoporous media are important parameters for shale gas/oil production. Confined petroleum fluids can have hysteresis and bubble/dew point behaviors can be very different depending on the thermodynamic route. In this work, we use grand canonical Monte Carlo (GCMC) simulations and engineering density functional theory (DFT) to study the effect of pressure, temperature, and nanopore sizes on the bubble/dew point and hysteresis of hydrocarbons in nanopores. By comparing to GCMC simulations, engineering DFT reliably predicts the vapor-liquid equilibrium of confined hydrocarbon fluids. We also find that dew point of pure confined fluids approaches bulk saturation point as pore size increases, but bubble point can be very different from bulk even for very large pores. As a result, the hysteresis between bubble and dew points increases with pore size. For single-component, the hysteresis decreases as pressure approaches critical pressure. For binary mixtures, the dependence of hysteresis on temperature is dependent on the pore sizes. The cricondentherm point of confined mixtures is shifted toward higher temperatures comparing to the bulk.

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## 1. Introduction

Shale gas and tight oil have become important energy resources in the past few years [1]. Shale reservoirs are very different from the conventional reservoirs due to widely distributed nanopores, ranging from a few nanometers to micrometers [2]. Phase behaviors of nano-confined petroleum fluids are very different from the bulk [3], which play a critical role in predicting the well productivity. Therefore, the effect of nano-confinement on the thermodynamic behaviors and saturation properties of petroleum fluids in nanoporous media is an important parameter for shale gas/oil production [4]. It has been shown that in nanopores, the bubble point of petroleum fluids is shifted [5–9]. The bubble point represents the liquid to vapor transition at which the first bubble forms. On the other hand, the dew point represents the vapor to liquid transition at which the first droplet forms.

Kelvin equation has been widely used to predict the vapor pressure of fluid forming liquid droplet in a capillary considering the surface tension and interface curvature. It predicts that the vapor pressure decreases with increasing interface curvature [10]. However, the Kelvin equation does not consider the inhomogeneity of density distributions under nano-confinement [11] and assumes that interfacial tension is the same as bulk. In nanoscale, the interfacial tension can be very different from bulk [12,13]. Kelvin equation also ignores the fluid-surface interactions and surface adsorptions which play an important role in phase behaviors of nano-confined fluids [1,3].

There have been a number of experimental works on the liquid-vapor equilibrium of confined fluids at isothermal conditions [14–17]. In the hexane adsorption on MCM-41 silica, Qiao found that the condensation phase transition pressure shifted to the higher relative pressure [18]. Recently, Nasrabadi and his coworkers have used differential scanning calorimetry approach to measure the bubble point temperature of confined pure hydrocarbons and their mixtures in controlled pore glasses [4,7,19]. They found that the bubble point of confined petroleum fluids is 20 K higher than the bulk saturation point. Recently, Alfi *et al.* [9] found that there is a shift of bubble point temperature from bulk saturation point even for pore diameter of 100 nm. Computer simulations and theoretical calculations have also been used to study the liquid-vapor equilibrium. Using GCMC simulations, Walton and Quirke [20] reported that the condensation pressure is less than the bulk saturation pressure, shifting to lower values with decreasing pore size.

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Wongkoblap found that the hysteresis loop area of argon in cylindrical carbon nanopores increase with the pore size [11]. By using engineering DFT, Li *et al.* found that for binary mixtures of $C_1$-$C_3$, the critical temperature of confined fluids, which is the highest temperature when capillary condensation/evaporation can appear, can be higher than the bulk cricondentherm temperature [1]. Later, Jin and Firoozabadi used engineering DFT and GCMC simulations to show that both critical pressure and temperature of pure hydrocarbons in carbon nanopores are reduced [3]. Although these studies provide important insights into the understanding of phase behavior of nano-confined fluids, the complete view of the effect of pressure, temperature, and pore sizes on the bubble/dew point and the hysteresis of hydrocarbon fluids in nanopores is still lacking.

In this work, we use GCMC simulations and engineering DFT to study the nano-confinement effect on the phase behavior of pure hydrocarbons and their mixtures. GCMC simulations can explicitly consider the intermolecular interactions and molecular configurations. Singh *et al.* used GCMC simulation to reproduce the experimental data on the liquid-vapor phase equilibrium and interfacial tensions of bulk hydrocarbon fluids [21]. Despite of great success of GCMC simulations on phase behavior of confined fluids, sometimes it comes with expensive computational cost, especially for heavier hydrocarbons. In previous works [1,3], we used an engineering DFT with Peng Robinson (PR)-EOS to study the hydrocarbon adsorption/desorption isotherms as well as gas sorption in shale media and showed good agreement with experimental data. Engineering DFT extends the PR-EOS to inhomogeneous conditions by using weighted density approximations (WDA) [22], treating the fluid molecules as a structureless sphere. Without confinement, engineering DFT with PR-EOS reduces to PR-EOS [1]. Engineering DFT can significantly reduce the calculation time, but might lose information on the intermolecular interactions and molecular configurations. In our previous work [3], we compared the dew points of confined pure $nC_4$ from engineering DFT and GCMC simulations, which have shown excellent agreement. However, we did not compare the average densities of confined fluids from these two different approaches. In addition, the comparison on the properties of confined hydrocarbon mixtures has not been reported yet. In this work, we will first calibrate our engineering DFT by comparing to GCMC simulations on the phase behavior and average densities of pure $nC_8$ and $C_1$-$nC_6$ mixtures in nanopores. Then, we will use engineering DFT to study the bubble/dew point and the hysteresis of nano-confined hydrocarbons. Similar to our pervious works [1,3], for simplicity, we use a structureless carbon slit-pore model to describe the nanopores.

## 2. Molecular model, theory, and simulation

Phase behavior and bubble/dew points of hydrocarbons confined in nanopores are studied in open system settings. In an open system, a system with a constant volume is in equilibrium with an infinite fictitious bulk reservoir of particles imposing chemical potentials and temperature. The outside bulk reservoir has the composition, temperature and pressure fixed and these properties do not change with the conditions in nanopores. In this work, GCMC simulations and engineering DFT are suited for open system study.

### 2.1. Grand canonical Monte Carlo simulation

In grand canonical ensemble, the chemical potentials $\mu$ of fluids, system volume $V$ and temperature $T$ are fixed. The chemical potentials describe the properties of fictitious bulk reservoirs. Because the number of molecules within the volume fluctuates throughout the simulation, the ensemble averaged number of molecules is fully determined by the chemical potentials.

We use the united atom model [23] to simulate different hydrocarbon molecules. Non-bonded site-site interactions between groups on different molecules and groups belonging to the same molecule separated by more than three bonds are described by the modified Buckingham exponential-6 intermolecular potential [24], for which the pairwise additive interaction potential $U(r)$ is presented as

$$U(r) = \left\{ \frac{\varepsilon}{1-\frac{6}{\alpha}} \left[ \frac{6}{\alpha} \exp\left( \alpha \left[ 1 - \frac{r}{r_m} \right] \right) - \left( \frac{r_m}{r} \right)^6 \right] \right\}, \quad r > r_{\max} \\ = \infty, r < r_{\max} \tag{1}$$

in which $\varepsilon$, $r_m$, and $\alpha$ are exponential-6 parameters. The variable $r_m$ is the radial distance at which $U(r)$ reaches a minimum, and the cutoff distance $r_{\max}$ represents the smallest radial distance for which $dU(r)/dr = 0$ [21]. The reason a cutoff distance is required is that at very short distances, the original Buckingham exponential-6 potential becomes negative [24]. The parameters $\varepsilon$, $\sigma$ and $\alpha$ are 129.63 K, 0.3679 nm, and 16, respectively, for the methyl group (-$CH_3$), 73.5 K, 0.4 nm, and 22, respectively, for the methylene group (-$CH_2$-), and 160.3 K, 0.373 nm, 15, respectively, for $CH_4$. The following combining rules are used to determine the cross parameters [21]:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \tag{2}$$

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}, \tag{3}$$

$$\alpha_{ij} = (\alpha_i \alpha_j)^{1/2}. \tag{4}$$

The bond lengths $CH_3$-$CH_2$ and $CH_2$-$CH_2$ are 0.1687 nm and 0.1535 nm, respectively. The bond bending potential is given as [25].

$$U_{bend}(\theta) = \frac{K_\theta}{2}(\theta - \theta_{eq})^2, \tag{5}$$

where $K_\theta = 62500$ K/rad$^2$ and $\theta_{eq} = 114^\circ$. Torsion energy is given as [26].

$$U_{tor}(\varphi) = V_0 + \frac{V_1}{2}(1 + \cos\varphi) + \frac{V_2}{2}(1 - \cos 2\varphi) + \frac{V_3}{2}(1 + \cos 3\varphi), \tag{6}$$

where $V_0 = 0$, $V_1 = 355.03$ K, $V_2 = -68.19$ K, and $V_3 = 791.32$ K.

In this work, pores are of slit geometry with smooth and structureless carbon surfaces. We use 10-4-3 Steele potentials to describe the fluid-wall interaction $\varphi_{wf}$ [27],

$$\varphi_{wf}(z) = 2\pi\rho_w\varepsilon_{wf}\sigma_{wf}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{wf}}{z}\right)^{10} - \left(\frac{\sigma_{wf}}{z}\right)^4 - \frac{\sigma_{wf}^4}{3\Delta(0.61\Delta + z)^3}\right], \tag{7}$$

where $\rho_w = 114$ nm$^{-3}$, $\varepsilon_w = 28$ K, $\sigma_w = 0.3345$ nm, and $\Delta = 0.335$ nm, respectively. The external potential $\Psi$ in a slit pore is expressed as

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