



Capillary condensation and capillary pressure of methane in carbon nanopores: Molecular Dynamics simulations of nanoconfinement effects



Mohammad Sedghi*, Mohammad Piri

Department of Petroleum Engineering, University of Wyoming, 1000 E. University Avenue, Laramie, WY 82071, United States

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ABSTRACT

Two main groups of thought have emerged over the past decade to improve thermodynamic modeling of capillary condensation of nanoconfined fluids. One approach has been developed on the premise of using shifted critical parameters for the condensed phase to account for the wall-fluid interactions, while the other one considers a pressure difference across the interface between the condensed and the bulk phases. This pressure difference is the capillary pressure that exists across a curved meniscus formed in a capillary pore. For nanoconfinement, a modified Laplace equation has been utilized to calculate the capillary pressure to take into account the confinement effects that become more prominent as the pore size reduces. For small pores of a few nanometers in size, however, the impact of structural forces known as nanoconfinement effects, on the pressure of the confined phase becomes more significant. In this work, we studied the capillary pressure of methane at the capillary condensation point in graphite pores smaller than 7 nm, to verify whether the confined phase can experience a negative pressure at capillary condensation point and whether we can accurately predict this pressure from thermodynamic equations. For this purpose, we used Molecular Dynamics (MD) simulations to investigate the pressure of methane molecules confined in graphite pores of various sizes. Furthermore, normal and tangential pressures of methane in selected pore sizes were obtained during capillary condensation at constant pressure. Our results indicated that for small pores there is a critical size below which capillary condensation did not occur. For larger pores, on the other hand, capillary condensation could be identified with an abrupt drop in the pressure of the confined phase. The capillary pressure attained from the MD simulations were similar to the thermodynamic calculations provided the adsorbed phase was thick enough to screen out wall-fluid interactions.

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1. Introduction

Phase behavior of hydrocarbons in nanopores has attracted significant attention in recent years, largely due to the development of gas production from porous media with nanometer-sized pores in ultra-tight formations (e.g., shale and tight sandstones) [1–9]. Accurate assessment of hydrocarbon storage in and recovery from these reservoirs is of direct relevance to the thermodynamic phase prediction of nanoconfined fluids [5]. It is known that in nanopores, the effect of wall-fluid interactions on the phase behavior of confined fluids can be significant, causing a divergence from the phase behavior of the macroscopic bulk materials [9]. One particularly important example of this disparity is called capillary

condensation, a ubiquitous phenomenon occurring in both natural and synthetic nano-dimensional porous media. Capillary condensation describes condensation of the entrapped fluids at pressures below their bulk vapor saturation points [9–12].

The main challenge in modeling capillary condensation of nanoconfined fluids is to incorporate wall-fluid interactions, generally referred to as the confinement effect, into the equations of state. Two schools of thought have been developed to include the confinement effect in the phase equilibrium calculations. One approach, which has thus far been exclusive to the cubic equations of state, considers shifted critical parameters for the confined (condensed) phase [13–15]. In this approach, the same pressure can be used for both vapor and condensed phases. The second method, on the other hand, considers different pressures for the vapor (bulk) and condensed phases [6–8,16]. This pressure difference, called capillary pressure P_{cap} , is induced by highly curved

* Corresponding author.

E-mail address: msedghi@uwyo.edu (M. Sedghi).

menisci formed between the two phases. Implementation of this method in the PC-SAFT equation of state has shown promising results in modeling capillary condensation of associating and non-associating fluids in nanopores [6–8]. One of the main objectives of this work is to examine the validity of this technique, as outlined in the following paragraphs, for pore spaces of size < 7 nm.

For a cylindrical pore with a radius r_p , P_{cap} can be calculated by using the Laplace equation:

$$P_{cap} = P_{NW} - P_W = \frac{2\gamma}{r_p} \cos(\theta) \quad (1)$$

where γ is the surface tension and θ is the contact angle that the liquid-vapor interface creates with the pore wall and is measured through the condensed phase. Since the pore walls are completely covered by adsorbed layer(s) of the fluid, the contact angle can be reasonably considered zero at the condensation point [6]. W and NW subscripts denote wetting and non-wetting phases, respectively. It has been discussed that for the pores smaller than 45 nm, Eq. (1) becomes inaccurate based on two phenomena emerging in nanometer pores [6]: (1) strongly adsorbed fluid layers on the pore wall considerably reduce the effective size of the pore, and (2) curvature of the liquid surface leads to a reduction in the surface tension. Thus, a modified Laplace equation was introduced to account for these effects:

$$P_{cap} = \frac{2\gamma(r_p)}{r_p - t_p} \quad (2)$$

where t_p is the thickness of the adsorbed fluid and $\gamma(r_p)$ is the pore-size-dependent surface tension. It should be noted that at capillary condensation point inside slit pores (as considered in this study) the condensed phase forms a hemicylindrical surface. For this geometry, the principal radius normal to the walls is equal to the half of the pore width ($r_1 = \frac{d}{2}$), while the other radius parallel to the walls is infinite ($r_2 = \infty$). Thus, the curvature ($k = \frac{1}{r_1} + \frac{1}{r_2} = \frac{2}{r}$) of this surface is half of the curvature of a hemispherical surface formed in a cylindrical pore with radius of r_1 . Therefore, Eq. (2) can be applied to slit pores by removing coefficient 2 from the numerator.

To find the surface tension of the confined phase, Tan et al. [6,7] successfully used the well-known Parachor equation [17] to calculate the confined surface tension:

$$\gamma(T, r_p) = \left\{ \varphi \left(\rho^L(T, P^L) - \rho^V(T, P^V) \right) \right\}^4 \quad (3)$$

where φ is the parachor parameter that can be derived from the surface tension values of the bulk phase. In this equation, the surface tension is related to the difference between the density of the condensed phase (ρ^L) and that of the bulk vapor phase (ρ^V). One should note that calculating capillary pressure from Eqs. (2) and (3) requires an iterative method since the pressure of the condensed phase (P^L) is dependent upon the capillary pressure value as $P^L = P^v - P_{cap}$.

Other methods have also been proposed in the literature to estimate the surface tension of nanoconfined surfaces. A thermodynamic equation developed by Gibbs-Tolman-Koenig-Buff (GTKB) incorporates the Tolman length (δ) to relate the surface tension of a nanoscale surface (γ) to its macroscopic value (γ_∞). A simplified version of the GTKB can be derived by assuming $(\delta/r_p) \ll 1$ [18].

$$\gamma = \frac{\gamma_\infty}{1 + 2\delta/r_p} \quad (4)$$

However, the difficulty in calculating the Tolman length has hindered the application of this equation in the thermodynamic

models. Lu and Jiang derived a theoretical model that can calculate the surface tension of nano-sized droplets based on the readily attainable thermodynamic parameters of a given element [19].

$$\gamma = \gamma_\infty \left[1 - \frac{1}{4r_p/h - 1} \right] \exp \left[- \left(\frac{2S_b}{3R} \right) \frac{1}{4r_p/h - 1} \right] \quad (5)$$

where S_b is the entropy of vaporization, R is the ideal gas constant, and h is the effective molecular diameter. This model has been successfully applied to determine the surface tension of mercury droplets at various radii [20]. However, since in this work we are studying hemicylindrical surfaces, Lu-Jiang method cannot be used as it was developed for droplets with hemispherical surfaces.

Using the confined surface tension (Eq. (3)) in the modified Laplace equation (Eq. (2)), we can determine the pressure of the condensed phase. Subsequently, by integrating this capillary pressure into the phase equilibrium calculations, we can implicitly take into account the wall-fluid interactions. The underlying assumption in this method is that at capillary condensation, the pressure of the condensed phase is negative due to the large capillary pressure that exists across the interface between the confined and the bulk phase (Eq. (2)). However, before the condensation, the density of the confined phase is greater than that of the bulk phase (due to the tendency of gas molecules to strongly adsorb on the walls), therefore, the confined phase may have a slightly higher pressure than the bulk pressure. Immediately following the condensation, however, a curved interface will form between the confined and the bulk phases, across which the capillary pressure exists (Eq. (2)). Since the confined phase is the wetting phase, its pressure becomes less than the bulk pressure. Depending on the magnitude of the capillary pressure and the bulk pressure, the confined pressure could then become negative. To the best of our knowledge, this abrupt change of pressure during capillary condensation has not been studied in any modeling work. More importantly, the faithfulness of the modified Laplace equation and the thickness of the adsorbed phase has not been rigorously studied for extremely small pore sizes of less than 10 nm. For such small pore spaces, physical and chemical properties of the confined materials are impacted by the high pressures they may experience after condensation (due to nanoconfinement effects) [21,22]. In a recent study by Long et al. [23–25], Monte Carlo (MC) simulations were employed to investigate the pressure tensor components of confined argon in carbon nanoslits with various sizes between 0.7 and 2.8 nm. The simulations were run at the argon saturation point of 87 K and 1 bar so that the bulk phase would be liquid and no interface would exist between the confined and the bulk phases. Their simulation results demonstrated oscillation between positive and negative values in the normal pressure profile of the confined phase as the pore size varied. This oscillation was ascribed to the structural (solvent) forces described previously by Israelachvili [26]. These forces, as discussed further in Section 3, are originated from layered-structure formation of liquids entrapped in small nanoscale spaces. Similar oscillations were also observed in the normal pressure of argon, carbon tetrachloride, and water at or above their saturation points, confined in carbon nanopores of different geometries including cylindrical and spherical shapes [25]. Although the existence of the structural forces has been verified in both experimental and modeling studies, their impact on the phase behavior of confined materials has not been examined in the literature. Furthermore, it is not fully understood whether capillary pressure exists during capillary condensation of a confined phase under the influence of significant structural forces and if so whether the modified Laplace equation can be used to estimate its value.

In this study, using Molecular Dynamics (MD) simulations, we aimed to investigate validity of applying the modified Laplace equation to obtain the capillary pressure of methane in small carbon

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