

Article

Phase Behavior and Critical Properties of Hydrocarbons in Shale Illite Nanopores

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Abstract

Clay minerals are significant constituents of shale reservoirs, yet the confinement-induced phase behavior of hydrocarbons within clay nanopores has received comparatively less attention than in carbonaceous materials. In this study, Grand Canonical Monte Carlo (GCMC) simulations were performed to investigate the confinement-induced shifts in the critical properties of hydrocarbons within illite slit pores ranging from 2 to 20 nm. The simulation results indicate apparent reductions in both critical temperature (T_c) and critical pressure (P_c) under confined conditions. The relative shift in critical properties is more pronounced for n-pentane than for methane, which is attributed to the larger molecular size and complex chain-like structure of n-pentane compared to methane. The simulation results also show that the extent of these shifts varies among different pore geometries and materials due to the differences in fluid–solid interactions and specific surface areas. Illite exerts a weaker confinement effect than graphite, while cylindrical pores intensify the shift compared to slit pores. As the pore size increases from 2 to 20 nm, the nanoconfinement-induced shifts in the critical properties of alkanes in illite slit pores progressively diminish, and the critical properties approach their corresponding bulk values at a pore size of 20 nm. Finally, new correlations are proposed to quantify the critical property shifts in illite slit nanopores. Overall, this study provides a quantitative characterization of confinement-induced critical-property shifts for the investigated hydrocarbons in illite slit nanopores.

Keywords: shale; hydrocarbons; critical properties; illite nanopores; molecular simulation; confinement effect



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1. Introduction

Shale reservoirs contain abundant nanopores, which are mainly hosted in organic matter and clay minerals and serve as important storage sites for hydrocarbons [1–5]. When hydrocarbons are confined within nanopores, their physicochemical properties change, resulting in phase behavior that differs from bulk behavior [6–10]. Understanding these confinement-induced changes is essential for accurately modeling hydrocarbon storage and transport in shale nanopores. Compared with organic nanopores, clay nanopores have received relatively limited attention with respect to confinement-induced shifts in critical

properties. Illite is often the predominant component of the clay fraction in shale formations [11–13]. Therefore, illite was selected as a representative clay mineral to investigate the confined phase behavior of hydrocarbons. Understanding these phenomena is vital to the accurate modeling of hydrocarbon storage and transport in shale nanopores.

Currently, studies on the phase equilibrium of confined hydrocarbons are generally divided into two approaches: experimental and molecular simulation. Experimental techniques include gas physisorption, differential scanning calorimetry (DSC), lab-on-a-chip platforms, etc. Qiao et al. [14], Nguyen et al. [15], and Al-Garadi et al. [16] measured hydrocarbon adsorption and desorption isotherms in the ordered mesoporous material MCM-41 at various temperatures to investigate confined vapor–liquid phase equilibrium. Their findings indicate that as the pore size increase, the capillary condensation pressures increase. Luo et al. [17], Pathak et al. [18], and Qiu et al. [19] employed DSC to study the phase equilibrium of hydrocarbons in synthetic porous materials, such as MCM-41, SBA-15, and CPG-35. Their findings reveal that the bubble points of confined hydrocarbons differ from those in bulk conditions. Lab-on-a-chip platforms enable direct observation of vapor–liquid phase equilibrium at the nanoscale [20]. Parsa et al. [21] found that the critical pressure of propane dropped markedly in nanochannels compared to that in bulk conditions. Zhong et al. [22] utilized a nanofluidic device to study the bubble point of a methane/propane mixture and found that its bubble point is suppressed compared with that in bulk conditions. Wang et al. [23] used a chip containing multi-scale nanopores to investigate the phase behavior of condensate gas and found that condensate gas in small-scale pores condenses first.

The experimental studies mentioned above are confined to silicon-based materials. However, shale porous media is far more complex than silicon-based materials. Moreover, laboratory tests are often costly and time consuming, whereas molecular simulation offers a more convenient approach and provides a powerful computational complement to experimental methods. In particular, Monte Carlo (MC) methods are widely used to investigate the phase equilibrium of confined hydrocarbons, including Grand Canonical Monte Carlo (GCMC) and Gibbs Ensemble Monte Carlo (GEMC) methods, along with their gauge cell extensions (gauge-GCMC and gauge-GEMC). By employing GCMC simulations, Pitakbunkate et al. [24] examined the phase equilibrium of methane, ethane, and their binary mixtures within graphite slit pores. They found that as nanopore size decreases, both the critical parameters (T_c and P_c) of methane and ethane are suppressed relative to their bulk counterparts. Lowry and Piri [25] employed GCMC simulations to examine the influence of porous materials on the critical properties of ethane, revealing that its critical point is significantly modulated by pore wall–fluid interactions. Pathak et al. [26] investigated the critical properties of pure decane and a methane-decane mixture in 3.5 nm graphite slit pores by GEMC simulations. The simulation results indicate that the confinement effect leads to a decrease in both critical temperature and bubble point pressure relative to bulk conditions. Zhou et al. [27] used gauge-GEMC simulations to study the effect of pore geometry on the phase behavior of confined hydrocarbons. Xing et al. [28] also employed gauge-GEMC simulations to investigate the phase behavior of a binary CO_2/nC_7 system within graphite slit pores. The simulation shows that the binary system exhibits a decrease in bubble point pressure and an increase in dew point pressure under confinement.

Currently, molecular simulation studies focus on carbon-based materials, such as graphite and carbon nanotubes. Some researchers [8,24,29–31] have developed critical property shift equations based on molecular simulations of graphite slit pores and carbon nanotubes. Furthermore, these carbon-based structures are often employed as simplified models to represent organic pores in shale. Consequently, these critical property shift equations have been incorporated into reservoir simulations to study the influence of con-

finement on shale oil and gas production. Clay minerals are significant constituents of shale, yet molecular simulation research regarding phase behavior within clay nanopores remains limited, leading to a lack of critical property shift correlations tailored to hydrocarbons confined in clay nanopores. Carbonaceous materials and clay minerals generate distinct fluid-wall potential fields, which can lead to material-dependent shifts in critical properties. Therefore, correlations developed for carbonaceous materials may not be directly applicable to clay nanopores, motivating the development of clay-specific correlations in this study.

This study aims to elucidate the confinement-induced shifts in the critical properties of hydrocarbons within illite nanopores using GCMC simulations. Finally, the critical point is identified via density-pressure isotherms [32], enabling a quantitative assessment of the confinement-induced shifts in critical temperature and pressure relative to their bulk values, as illustrated in Figure 1.

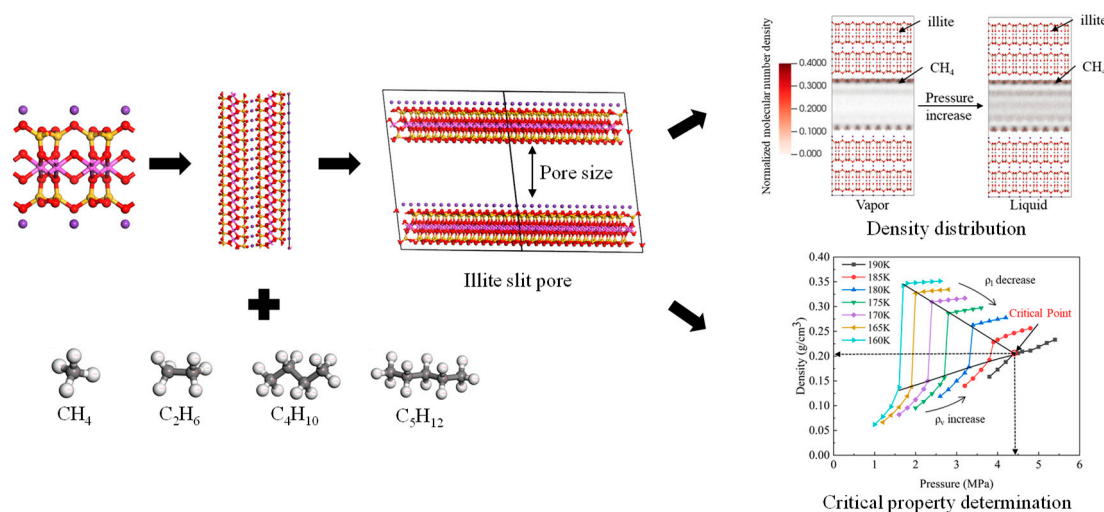


Figure 1. Schematic of the molecular simulation workflow for determining critical properties of hydrocarbons within illite nanopores.

2. Methodology

2.1. Molecular Models for Clay Nanopores and Hydrocarbons

Clay minerals typically constitute a significant fraction of shale, ranging from approximately 10% to 80%, and commonly include kaolinite, smectite, illite, and chlorite [33]. Among these, illite often represents the predominant component [11–13]. Therefore, illite is selected as the representative clay mineral of shale in this study. Illite nanopores are simplified as slit-shaped pores because illite is a layered phyllosilicate mineral, and the interlayer spaces between mineral sheets can be reasonably represented by parallel-wall slit geometries in molecular simulations. Such slit-pore models have been widely adopted to investigate fluid phase behavior, transport, and adsorption in nanopores [34,35]. However, natural illite structures are more complex than the idealized models and may exhibit lattice defects, heterogeneous distributions of isomorphic substitutions, and distinct basal and edge surface configurations. Moreover, clay nanopores generally exhibit geometries more complex than ideal slit-pore models. These structural and geometric factors may alter fluid–solid interactions and molecular organization within nanopores, thereby affecting the magnitude of confinement-induced shifts in critical properties. Therefore, further studies incorporating more realistic mineral structures and pore geometries are needed.

The slit-pore model was constructed using an illite unit cell sourced from the Crystallography Open Database (COD) [36]. The unit cell was first orthogonalized and subsequently expanded into an $8 \times 4 \times 2$ supercell ($41.58 \text{ \AA} \times 36.51 \text{ \AA} \times 20.26 \text{ \AA}$) to construct the mineral walls. The interlayer charge originates from the isomorphic substitution of

Si by Al in the tetrahedral sheets, with the constraint that no two adjacent Al tetrahedra occur simultaneously. This yields a layer charge of approximately -0.65 e per unit cell, corresponding to a basal surface charge density of -1.40 e/nm². Charge neutrality is satisfied by 0.65 K⁺ per unit cell, which in the final $8 \times 4 \times 2$ supercell amounts to approximately 42 K⁺ ions. The K⁺ ions reside in the interlayer region, preferentially above the tetrahedral substitution sites, forming inner-sphere complexes with the basal oxygen atoms. To ensure sufficient potential energy summation and avoid boundary effects, the wall thickness along the z-direction was designed to surpass the cutoff radius of 17.5 Å. Two such walls were superimposed to create slit nanopores with sizes in the range of 2–20 nm. The simulation utilized periodic boundary conditions in the *x* and *y* planes to represent an infinite pore surface. Four representative hydrocarbons (CH₄, C₂H₆, n-C₄H₁₀, and n-C₅H₁₂) were studied as model fluids to quantify their confined phase behavior in illite nanopores.

2.2. Simulation Details

Although GCMC, gauge-GEMC and gauge-GCMC methods are based on different statistical ensembles, previous studies have demonstrated that they yield consistent phase behavior results under equivalent thermodynamic conditions [37]. We used the GCMC method in this study, and all GCMC simulations were performed using the RASPA software (v2.0.41) [38], a specialized tool for simulating adsorption and diffusion of molecules in nanoporous materials.

The intermolecular interactions for illite were described by the ClayFF force field [39], while the hydrocarbons were modeled using the TraPPE-UA force field [40]. The corresponding force field parameters are summarized in Table 1. GCMC simulations were performed across a range of different temperatures, pressures, and pore sizes to obtain the density-pressure isotherms. At each temperature, only adsorption sweeps were conducted by progressively increasing pressure. Desorption sweeps were not performed in this study. Possible adsorption–desorption hysteresis and metastable behavior near the critical region were not evaluated and will be examined in future work. Moreover, the pressure was converted to fugacity using the Peng–Robinson equation of state. For each state point, the simulation consisted of 1×10^6 equilibration cycles followed by 1×10^6 production cycles.

Table 1. Force field parameters for the ClayFF (illite) and TraPPE-UA (hydrocarbon) models.

Atom Type	ϵ/k_b (K)	σ' (Å)
CH ₄	148	3.73
CH ₃	98	3.75
CH ₂	46	3.95
Al	6.69×10^{-4}	4.27
Si	9.26×10^{-4}	3.3020
O in bridging oxygen	78.26	3.1655
O in octahedral substitution	78.26	3.1655
O in O–H	78.26	3.1655
H in O–H	-	-
K	50.32	3.3350

Note: ϵ is the depth of the potential well (J), k_b is the Boltzmann constant (1.381×10^{-23} J/K), σ' is the collision diameter (Å). All structural oxygen atoms share identical Lennard–Jones parameters per the ClayFF convention [39].

2.3. Determination and Verification of Critical Properties

GCMC simulations were used to determine the number of hydrocarbon molecules within a slit pore at given conditions. Subsequently, the density of the confined hydrocarbons was derived based on these results

$$\rho = \frac{n \times M}{N_A \times V} \quad (1)$$

where n is the number of hydrocarbon molecules, M is the molar mass of hydrocarbon (g/mol), N_A is the Avogadro constant (6.022×10^{23} /mol), and V is the pore volume (cm^3). The pore volume V was calculated as $V = L_x L_y L$, where $L_x = 41.58 \text{ \AA}$ and $L_y = 36.51 \text{ \AA}$ are the lateral dimensions of the illite supercell, and L is the slit-pore size.

Below the critical temperature, increasing pressure induces a first-order gas–liquid transition, leading to an abrupt jump in hydrocarbon density [41]. Above the critical temperature, the fluid density increases continuously without a phase boundary. By computing fluid density over a range of temperatures and pressures, one can construct a phase envelope that encloses the two-phase (vapor–liquid) region. The apex of this envelope corresponds to the critical point, where vapor–liquid coexistence ends. This approach is commonly referred to as the phase envelope method [32].

3. Results and Discussion

3.1. Effect of Pore Size on Phase Behavior of Hydrocarbons

In this study, GCMC simulations were conducted for four representative hydrocarbons, including methane, ethane, n-butane, and n-pentane. Figure 2a shows the calculated methane density over a range of temperatures and pressures at a pore size of 20 nm. By employing the phase-envelope method, the critical point of methane was determined to be $T_c = 190 \text{ K}$ and $P_c = 4.4 \text{ MPa}$. The corresponding results for other hydrocarbons are summarized in Figure 2.

Table 2 compares the critical properties of the investigated hydrocarbons under bulk conditions with those obtained in a 20 nm illite slit pore. Only small deviations are observed between the two sets of values, indicating that the critical properties in the 20 nm pore are close to their corresponding bulk values.

Table 2. Comparison of hydrocarbon critical properties under bulk conditions and in a 20 nm illite slit pore.

Hydrocarbons	Bulk Conditions		20 nm	
	$T_c \text{ (K)}$	$P_c \text{ (MPa)}$	$T_c \text{ (K)}$	$P_c \text{ (MPa)}$
CH ₄	190.60	4.64	190.00	4.40
C ₂ H ₆	305.3	4.87	305.00	4.90
n-C ₄ H ₁₀	425.10	3.80	425.00	3.70
n-C ₅ H ₁₂	469.70	3.39	470.00	3.30

The following discussion focuses on the simulation results for methane and n-pentane as representative cases. The density isotherms for the other hydrocarbons are documented in Figures S1 and S2 within the Supporting Information. Figures 3 and 4 present the density–pressure isotherms for methane and n-pentane confined within illite nanopores of varying pore sizes (2–20 nm), respectively. At subcritical temperatures, all isotherms exhibit a distinct discontinuity in density, signifying a first-order phase transition wherein the gas phase condenses into a liquid state. The region enclosed by the saturation branches defines the vapor–liquid coexistence envelope. To provide microscopic insights into the observed phase transitions, representative simulation snapshots are presented in Figures 5 and 6. Figure 5 shows that at 1.5 MPa, methane molecules preferentially accumulate near the illite surfaces, forming adsorption layers due to the strong surface potential, while the pore center remains in a gas state. Compared to methane, n-pentane displays more pronounced structural layering and increased adsorption layer thickness, as

shown in Figure 6, which can be attributed to its stronger fluid-wall interactions. Figure 5 shows that upon an incremental increase in pressure (from 1.5 to 1.6 MPa), a dramatic transition to the liquid state occurs. This visual evidence corresponds to the sharp density jump observed in the density-pressure isotherms. Figure 5 also shows that an increase in pressure from 1.6 to 1.7 MPa results in a continuous density rise rather than a discrete phase transition. The snapshot demonstrates that above the critical point, increased pressure leads to a progressive accumulation of methane molecules within the nanopore, representing a continuous transition toward a dense fluid phase. Figure 6 shows that n-pentane exhibits a similar transition.

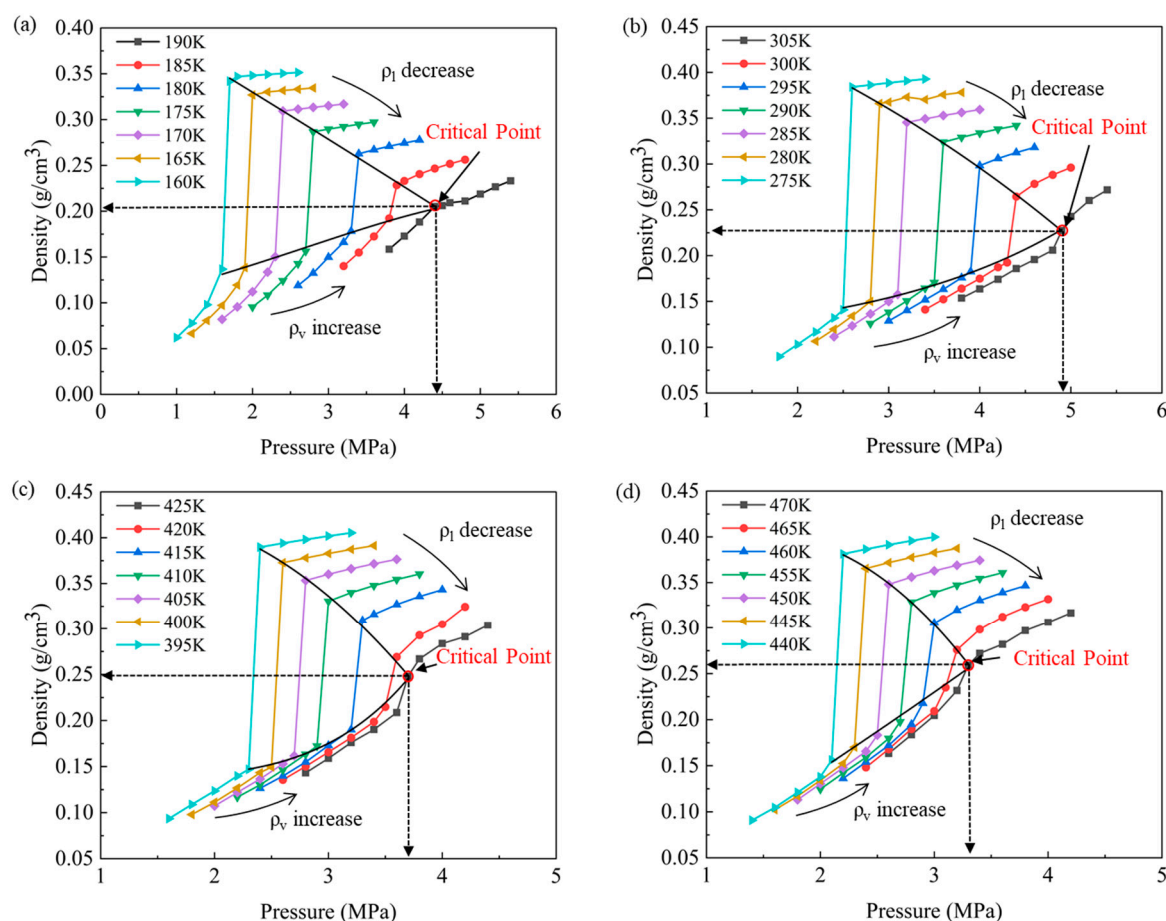


Figure 2. Calculated fluid densities as a function of pressure for different hydrocarbons at a pore size of 20 nm: (a) CH_4 ; (b) C_2H_6 ; (c) $\text{n-C}_4\text{H}_{10}$; (d) $\text{n-C}_5\text{H}_{12}$.

Figures 3 and 4 also show that as the pore size decreases, a confinement-induced suppression of the critical parameters is observed. Specifically, the critical pressure of methane drops from 4.4 MPa in a 20 nm pore to 0.73 MPa at 2 nm, representing a significant reduction of 83.41%. The relative shift in critical properties is slightly greater for n-pentane than for methane under identical pore sizes. This discrepancy is linked to the larger molecular size and the complex chain-like structure of n-pentane. Unlike the simple spherical methane molecule, the multi-segment nature of n-pentane leads to a slightly greater reduction in critical properties within the 2–20 nm illite slit pores [26]. The critical property shifts in different hydrocarbons in 2–20 nm illite nanopores are illustrated in Figures 7 and 8. With the pore size reaching 20 nm, the critical property shifts gradually diminish, and the critical properties of these hydrocarbons converge toward their bulk values. This trend arises because, in larger pores, the overlap of wall-potential fields weakens, thereby reducing the confinement effect and its associated impact on critical

properties. Conversely, smaller pores enhance this overlap, intensifying the confinement effect and producing more pronounced shifts in critical properties. This diminishing confinement effect in a 20 nm pore is consistent with previous studies on hydrocarbons in nanoporous media [8,42].

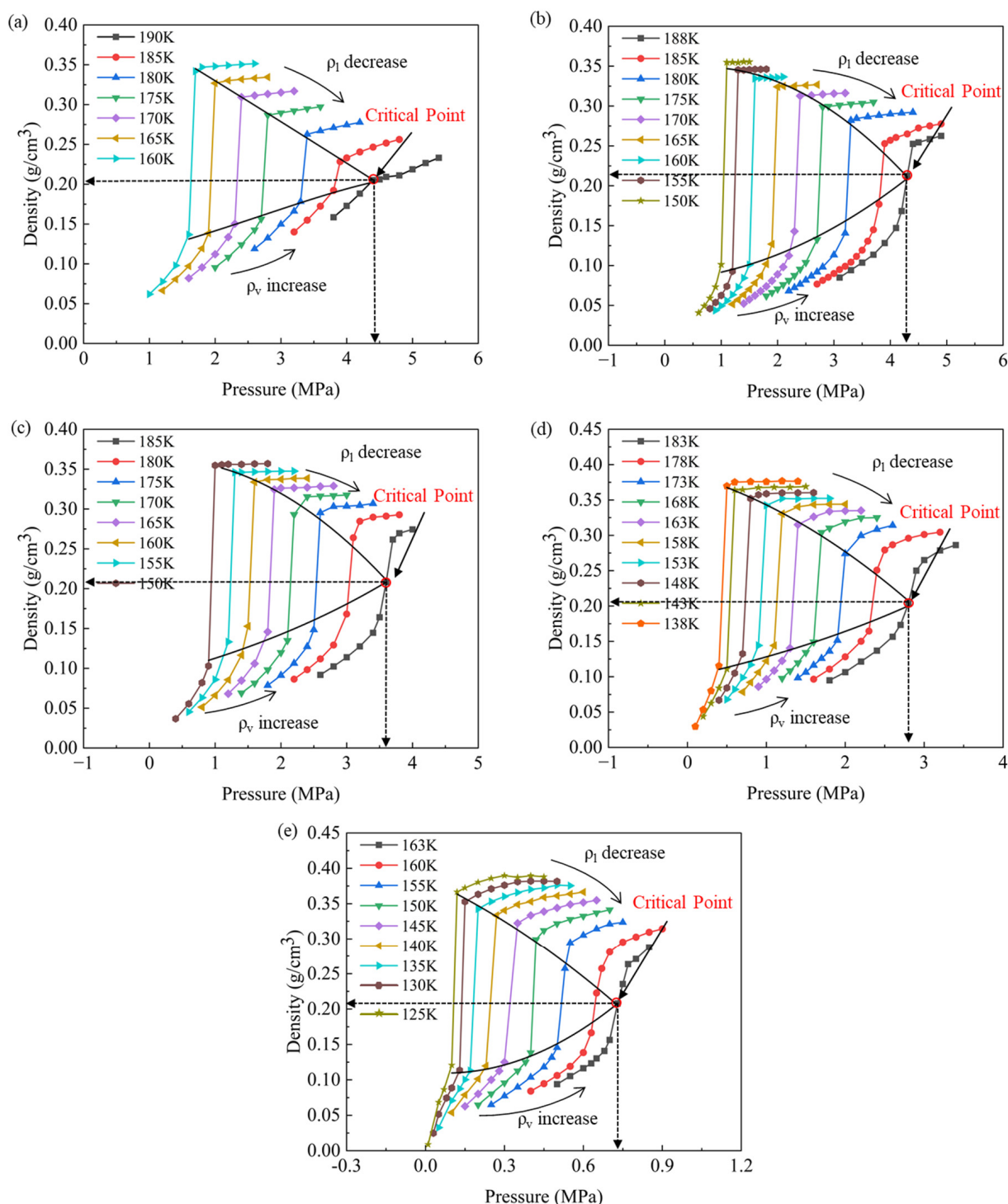


Figure 3. Density-pressure isotherms of methane in illite nanopore: (a) 20 nm; (b) 10 nm; (c) 7 nm; (d) 4 nm; (e) 2 nm. The red circles denote the estimated critical points, while the solid black curves represent the vapor–liquid coexistence envelopes.

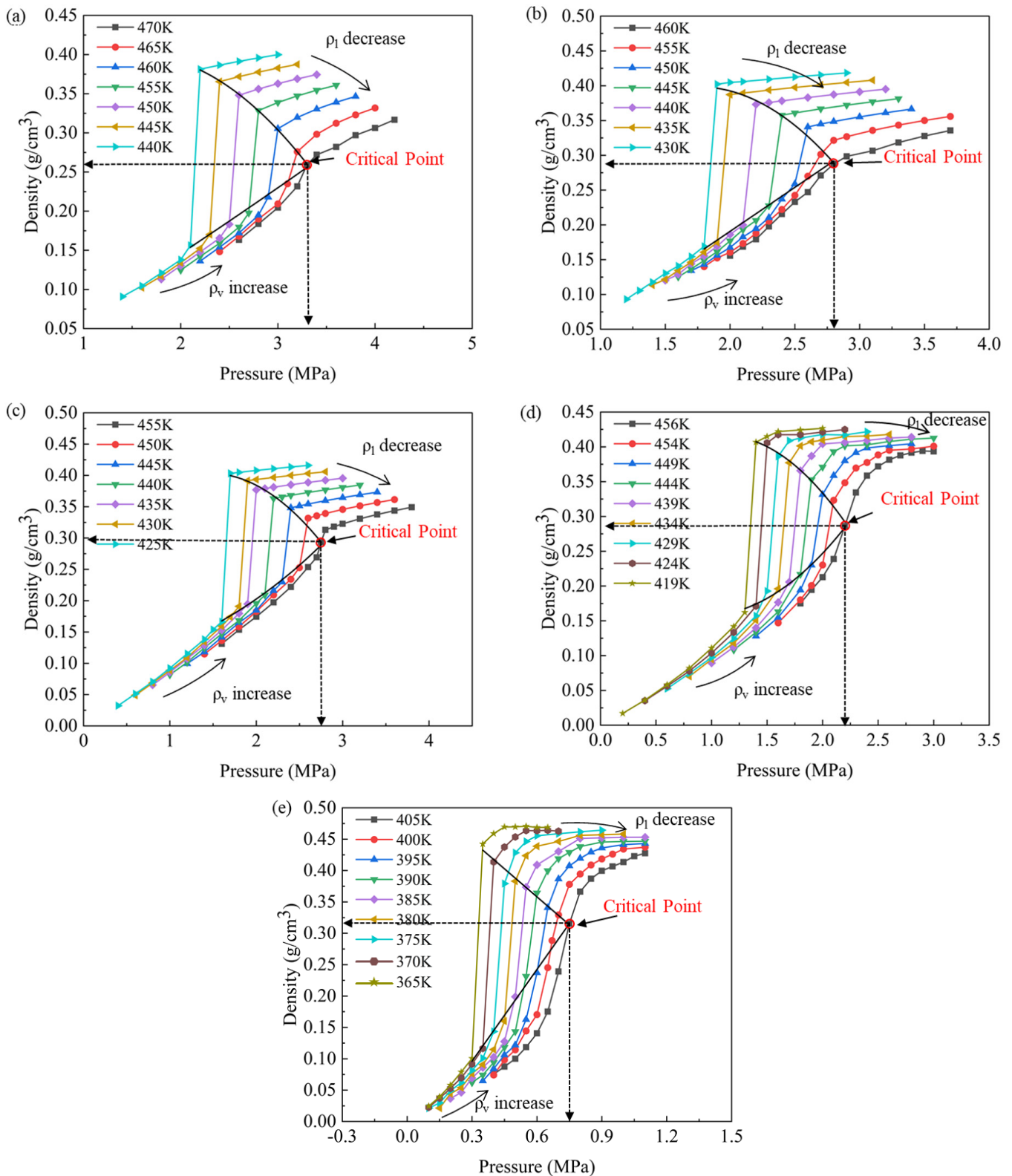


Figure 4. Density-pressure isotherms of n-pentane in illite nanopore: (a) 20 nm; (b) 10 nm; (c) 7 nm; (d) 4 nm; (e) 2 nm. The red circles denote the estimated critical points, while the solid black curves represent the vapor–liquid coexistence envelopes.

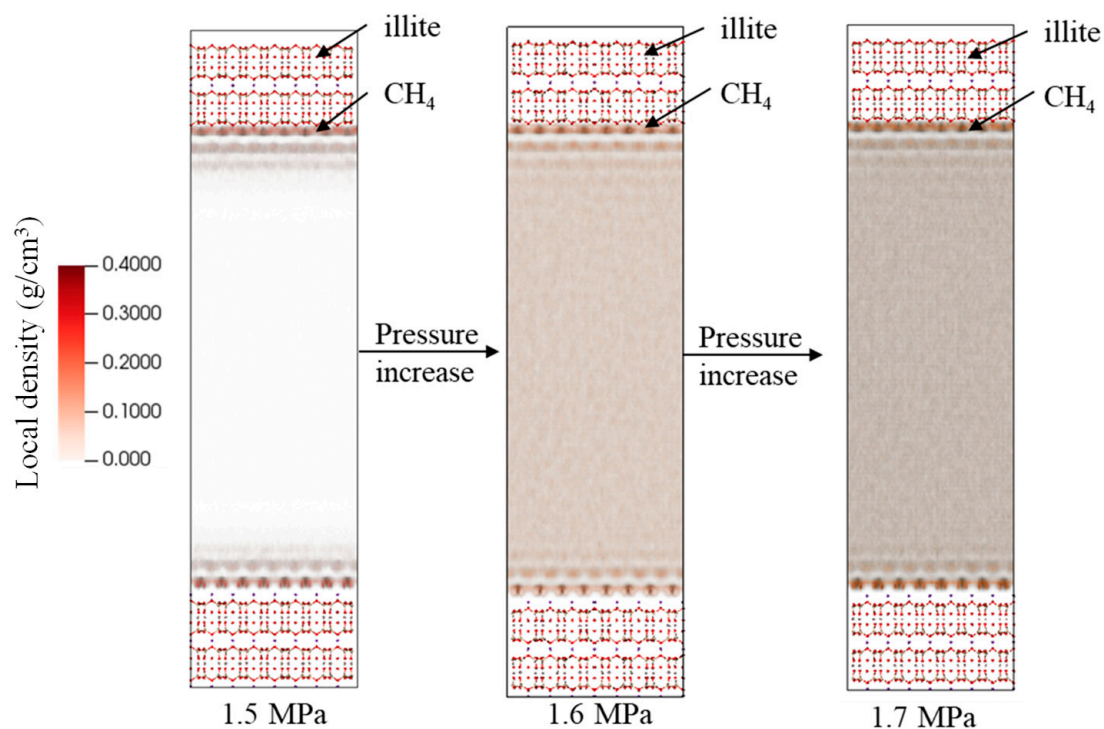


Figure 5. Representative simulation snapshots and corresponding local density of methane confined in a 10 nm illite nanopore at $T = 160$ K.

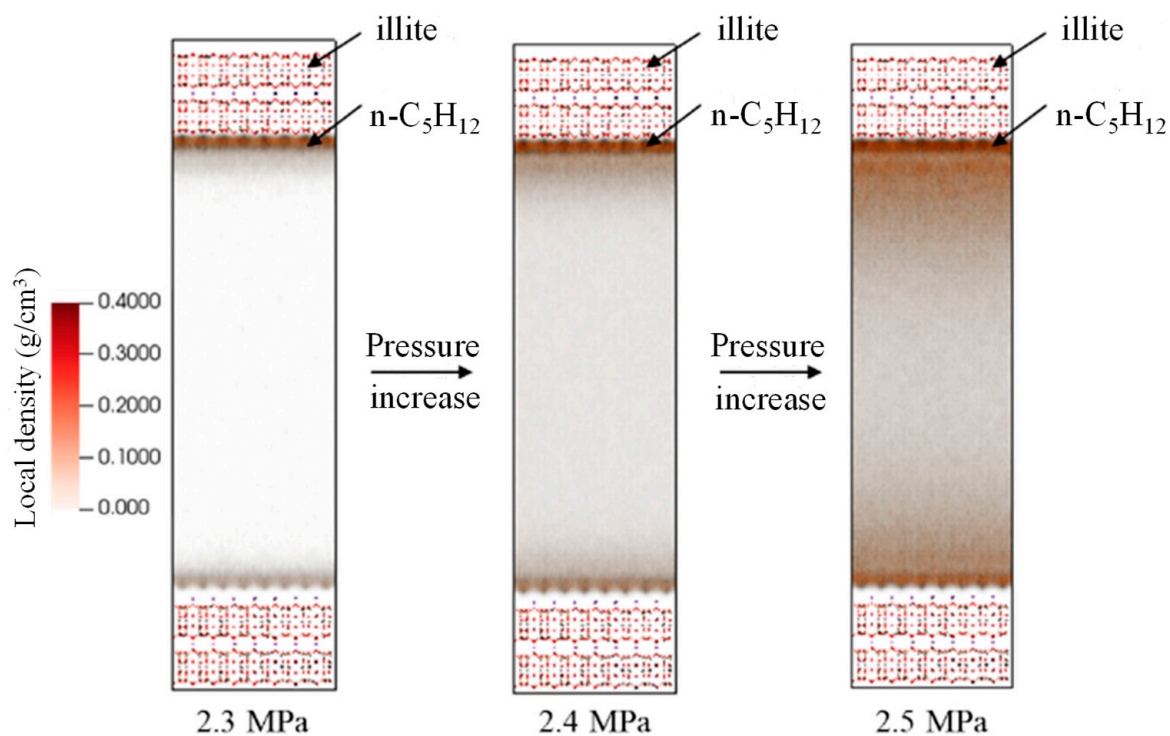


Figure 6. Representative simulation snapshots and corresponding local density of n-pentane confined in a 10 nm illite nanopore at $T = 445$ K.

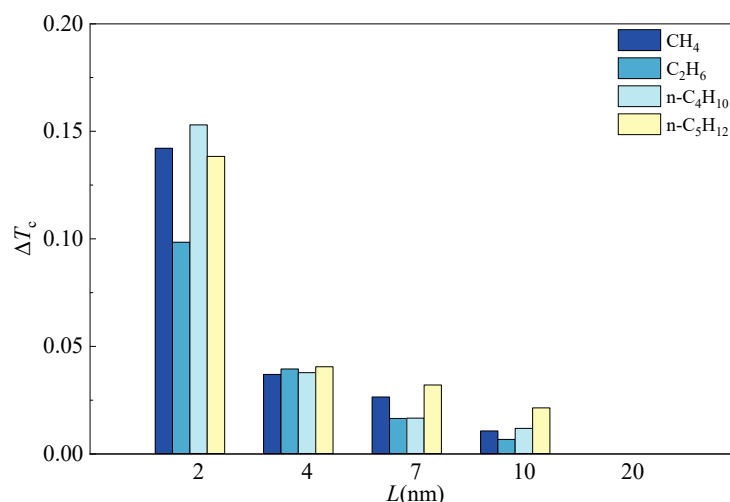


Figure 7. The critical temperature shift in different hydrocarbons in 2–20 nm illite nanopores. ΔT_c represents the relative shift in critical temperature.

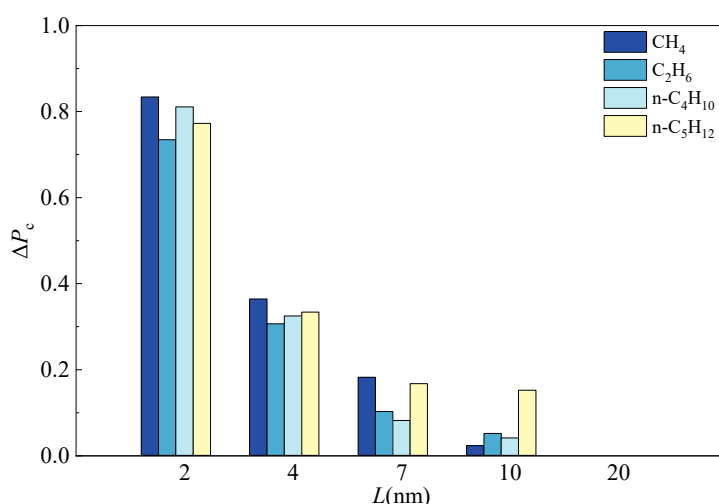


Figure 8. The critical pressure shift in different hydrocarbons in 2–20 nm illite nanopores. ΔP_c represents the relative shift in critical pressure.

3.2. Effect of Fluid-Wall Interaction on Phase Behavior of Hydrocarbons

We compared our GCMC simulation results with those from Jin et al. [37,43], as shown in Figure 9. Jin et al. [37,43] investigated the phase equilibrium of methane confined within graphite-based nanopores. As illustrated in Figure 9, the equilibrium gas density declines as the pore size increases, whereas the liquid density exhibits an upward trend. The equilibrium gas density in nanopores exceeds the bulk density, whereas the equilibrium density of the liquid is less than the bulk value. Specifically, in a 10 nm illite pore, the gas and liquid densities of methane at 160 K are 0.090 g/cm³ and 0.332 g/cm³, respectively. These values deviate from their corresponding bulk densities of 0.025 g/cm³ and 0.335 g/cm³, respectively. This can be explained by the formation of high-density adsorption layers within the pores, which increases the overall gas phase density within the confined space [27]. Moreover, the confinement-induced suppression of capillary condensation pressure reduces the density of both the central free phase and the resultant liquid phase [44]. As the nanopore size increases, the expanding pore volume gradually outweighs the influence of the adsorbed phase on the overall gas density, resulting in an overall decrease in gas density [45]. As the nanopore size approaches 20 nm, the confine-

ment effect diminishes, and the gas and liquid densities approach their respective bulk values [45].

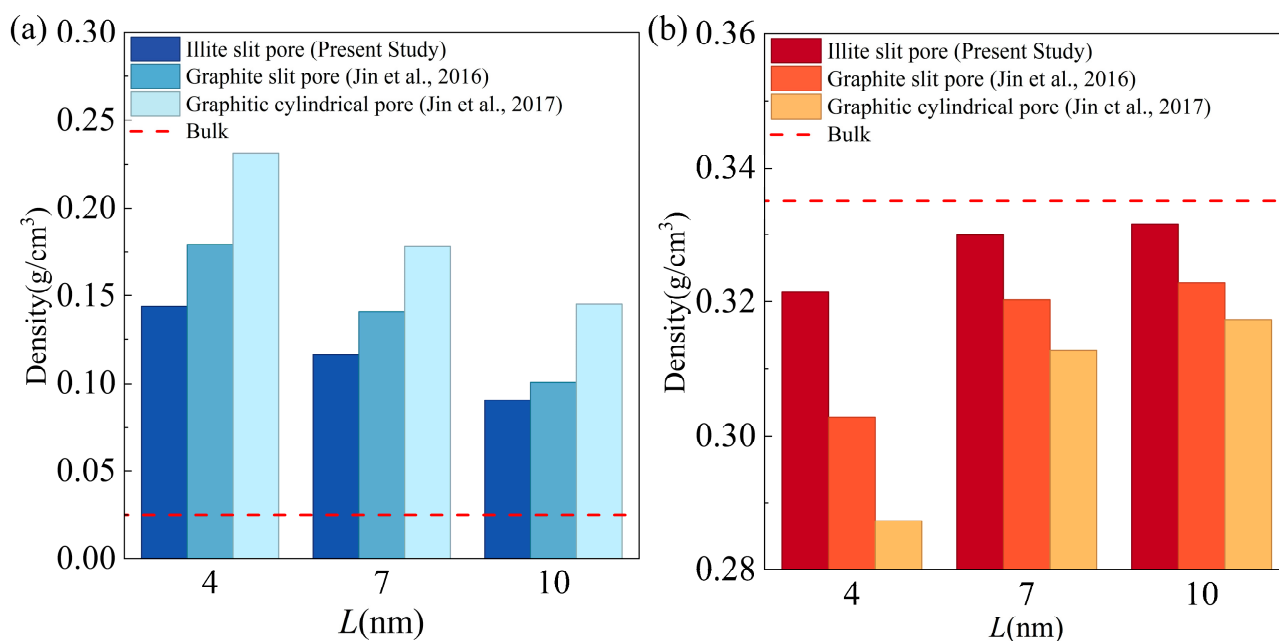


Figure 9. Equilibrium gas and liquid phase densities of methane in nanopores as a function of pore size at 160 K: (a) gas density; (b) liquid density. The results for graphite slit and cylindrical pores are obtained from Jin et al. [37,43].

In addition, the confinement effect varies in different pore materials. Compared with illite slit pores, graphite slit pores exhibit a stronger confinement effect, leading to greater shifts in the phase equilibrium density of methane. Specifically, at a nanopore size of 7 nm and a temperature of 160 K, the gas density and liquid density of methane are 0.117 g/cm^3 and 0.33 g/cm^3 in illite slit pores, respectively. In contrast, these values shift to 0.141 g/cm^3 and 0.32 g/cm^3 in graphite slit pores, respectively. This difference is associated with stronger methane-wall interactions in graphite pores than in illite pores. The zero-coverage isosteric heat of adsorption provides a quantitative measure of fluid-wall interaction strength. Reported values are approximately 12.6–13.7 kJ/mol for methane adsorption on graphite [46], compared with approximately 3.5–9.24 kJ/mol for methane adsorption in illite pores [47,48]. These energetic parameters are consistent with the more pronounced confinement effects observed in the graphite slit pores.

Figure 10 shows the shift in the T_c of methane confined within graphite and illite nanopores. The critical temperature shift is more significant in graphite nanopores than in illite ones. This is because graphite exerts stronger fluid–solid interactions than illite, increasing confinement and resulting in more pronounced critical property shifts [49–51]. Furthermore, the highly ordered atomic structure of graphite amplifies the fluid-wall interactions, in contrast to the relatively disordered and complex surface morphology of illite [25]. Figure 10 also shows that the critical temperature shift is more significant in graphite cylindrical nanopores than in slit ones. This is because cylindrical pores possess a larger specific surface area than slit pores at an identical pore size, thereby intensifying the confinement effect and leading to a more substantial shift in critical temperature [27,52].

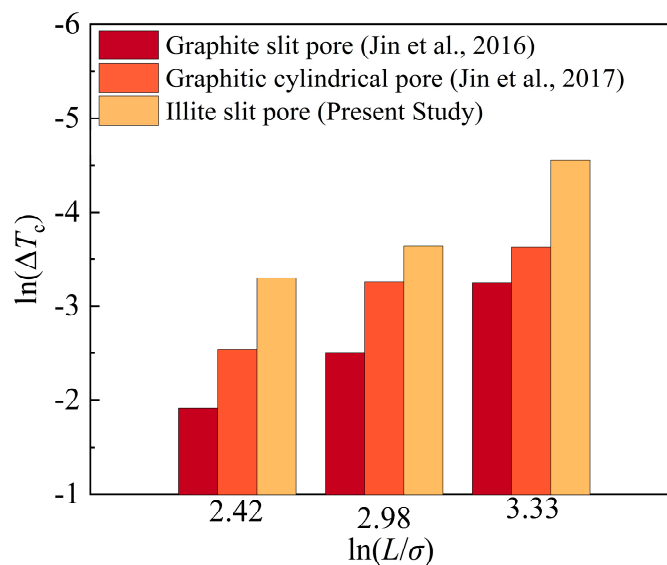


Figure 10. Comparison of critical temperature shifts for confined methane: effects of pore geometry and surface chemistry. The results for graphite slit and cylindrical pores are obtained from Jin et al. [37,43].

3.3. Critical Properties Shift Correlations

Critical temperature and pressure exhibit significant shifts within nanopores. To quantify these deviations, various correlations have been developed to predict the shift in critical properties [31,53,54]. Most of them are derived from molecular simulation data obtained in carbonaceous nanoporous media, such as graphite slit pores and carbon nanotubes [24,28,55]. However, these correlation equations may not be applicable to clay nanopores.

Figure 11 shows the critical-property shifts as functions of the ratio of molecular diameter to pore size, σ/L . The ΔT_c data exhibit an approximately parabolic dependence on σ/L , whereas the ΔP_c data display an S-shaped trend. Accordingly, the ΔT_c and ΔP_c data were fitted using a quadratic equation and a logistic-type function, respectively. As shown in Figure 11, both models provide good fits to the simulation data. The quadratic- and logistic-type models had R^2 values of 0.92 and 0.95, respectively, and corresponding RMSE values of 0.014 and 0.061. The resulting correlations are expressed as follows:

$$\Delta T_c = 1.5009 \times \left(\frac{\sigma}{L}\right)^2 + 0.2591 \times \left(\frac{\sigma}{L}\right) \quad (2)$$

$$\Delta P_c = \frac{0.8492 \times [1 - \exp(-46.9355 \times \frac{\sigma}{L})]}{1 + \exp[-27.8544 \times (\frac{\sigma}{L} - 0.1212)]} \quad (3)$$

$$\Delta T_c = \frac{T_{cb} - T_{cp}}{T_{cb}} \quad (4)$$

$$\Delta P_c = \frac{P_{cb} - P_{cp}}{P_{cb}} \quad (5)$$

where ΔT_c and ΔP_c are the relative shift in critical temperature and critical pressure, T_{cp} and P_{cp} are the critical temperature and critical pressure of hydrocarbons in nanopores, T_{cb} and P_{cb} are the critical properties of hydrocarbons in bulk conditions. L is the pore size (nm), σ denotes the molecular size (nm), with values of 0.3565, 0.3775, 0.4687, and 0.5029 nm for methane, ethane, n-butane, and n-pentane, respectively [40,55]. According to Equations (2) and (3), as L approaches infinity and σ/L tends to zero, both ΔT_c and ΔP_c approach zero, meaning the confinement effect is eliminated, which is physically consistent.

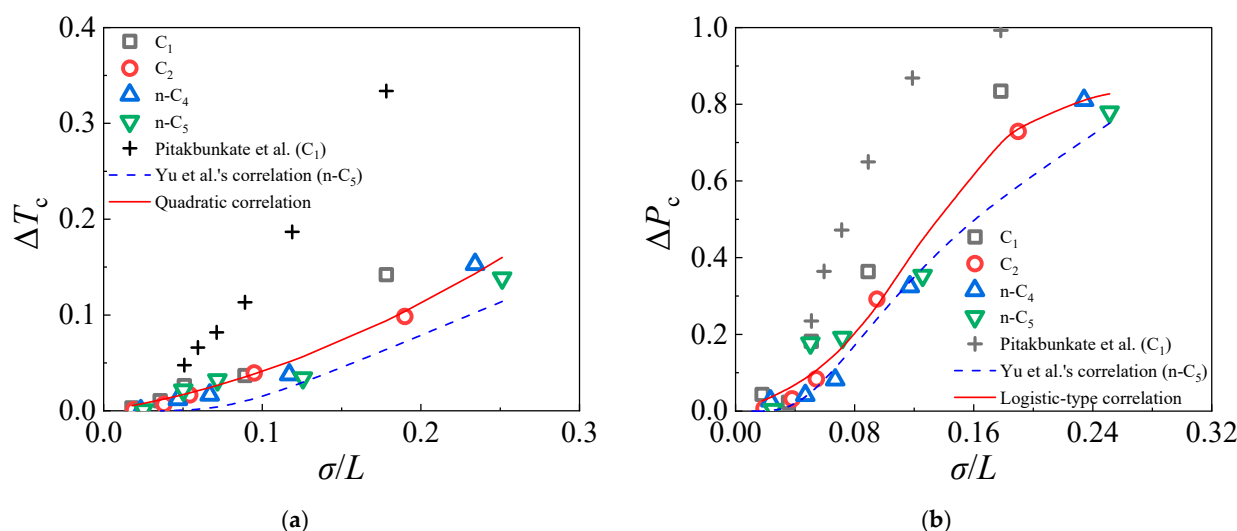


Figure 11. Critical property shifts as functions of σ/L (a) ΔT_c and (b) ΔP_c .

Because direct experimental measurement of hydrocarbon critical properties in clay nanopores remains challenging, we compared our results with independent molecular simulation data from the literature. These data were included in Figure 11 but were not used in the regression. Specifically, the critical-property shifts in methane confined in graphite slit pores reported by Pitakbunkate et al. [24] and the correlation developed by Yu et al. [41] for n-pentane confined in quartz slit pores were compared with the present correlations. At comparable values of σ/L , the critical-property shifts in graphite slit pores are generally larger than those predicted by the present correlations, whereas Yu et al.'s correlation predicts smaller shifts. Consequently, the predictions for illite nanopores generally fall between the graphite- and quartz-pore results. The critical-property shifts follow the order graphite > illite > quartz. This trend is consistent with the molecular simulation results of Chen et al. [56], who compared the isosteric heats of methane adsorption in graphite, illite, and quartz slit pores. They reported the following order: graphite > illite > quartz, with higher isosteric heats indicating stronger fluid–solid interactions. This supports the physical consistency of the present correlations and suggests that stronger fluid–solid interactions produce more pronounced confinement-induced shifts in critical properties.

The present correlations were developed at the pore scale for illite pores. For reservoir-scale numerical simulations, an upscaling workflow is therefore required. First, core-scale measurements, such as XRD and low-pressure N_2 adsorption, are used to characterize the mineralogical composition and pore-size distribution. Second, the present correlations for illite pores are combined with existing correlations for organic pores and other inorganic pores. As a first-order approximation, the shifts in critical properties can be calculated using pore-volume weighting and then incorporated into an equation-of-state model for PVT calculations in reservoir simulations, thereby enabling the consideration of nanoconfinement effects in compositional reservoir simulations of shale formations.

4. Conclusions

This study provides a quantitative assessment of the nanoconfinement-induced shifts in hydrocarbon critical properties within illite nanopores. The major conclusions are as follows:

- (1) Nanoconfinement reduces T_c and P_c relative to their bulk values. For the investigated hydrocarbons in 2–20 nm illite slit pores, the relative shifts in T_c and P_c are approximately 0–15% and 0–84%, respectively. These shifts decrease with increasing pore size and become negligible at 20 nm.

- (2) The shifts in critical properties are jointly governed by pore size, pore-wall material, and pore geometry. Smaller pores enhance the overlap of wall-potential fields, while stronger fluid–solid interactions and larger specific surface areas intensify the confinement effect, leading to more pronounced shifts in the critical properties.
- (3) Two new correlations were established to characterize the critical property shifts within illite nanopores. These correlations are anticipated to be useful in simulations of shale oil and gas production.

These conclusions are limited to pure alkanes confined in idealized illite slit pores under the molecular models and simulation conditions adopted in this study. Factors such as pore-surface heterogeneity, irregular pore geometry, mixed mineral compositions, and multicomponent fluids were not considered and require further investigation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr14162534/s1>, Figure S1: Density-pressure isotherms of ethane in illite nanopore: (a) 20 nm; (b) 10 nm; (c) 7 nm; (d) 4 nm; (e) 2 nm; Figure S2: Density-pressure isotherms of n-butane in illite nanopore: (a) 20 nm; (b) 10 nm; (c) 7 nm; (d) 4 nm; (e) 2 nm.

Author Contributions: Conceptualization, S.Z., N.L., Z.H. and W.R.; Methodology, K.Y., W.R., N.L. and K.W.; Software, K.Y. and F.H.; Writing—original draft, K.Y. and S.Z.; Writing—review and editing, N.L., S.X. and W.R.; Funding acquisition, W.R. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding author.

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