Phase-Behavior Modeling of Hydrocarbon Fluids in Nanopores Using PR-EOS Coupled with a Modified Young–Laplace Equation

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ABSTRACT: The effect of capillary pressure on the vapor–liquid two-phase equilibrium calculation has been extensively studied for the past two decades. However, the calculation accuracy is often weakened by the false assumptions and inherent flaws present in the modeling process. In this work, a modified Young–Laplace equation proposed by Tan and Piri [Tan, S.; Piri, M. Equation-of-State Modeling of Confined-Fluid Phase Equilibria in Nanopores. Fluid Phase Equilib. 2015, 393, 48–63.] is coupled with volumetranslated Peng–Robinson equation of state to study the effect of capillary pressure on the two-phase equilibrium calculation in confined nanopores. In order to successfully apply the modified Young–Laplace equation during the vapor–liquid equilibrium calculation process, this study models the tuning parameter $\lambda$ in the modified Young–Laplace equation (as proposed by Tan and Piri for perturbed-chain statistical associating fluid theory equation of state) for several pure hydrocarbons and their mixtures by matching experimental data collected from the literature. The tuning parameter $\lambda$ can be expressed as a unique function for each pure substance or mixture. It is found that the tuning parameter $\lambda$ shows a quadratic polynomial relationship with temperature, and the value of $\lambda$ is always less than one. The $\lambda$ can become negative under certain circumstances, which adjusts the capillary pressure to a lower value. It increases with an increasing pore radius; this is different from the results obtained by Tan and Piri which showed that the tuning parameter $\lambda$ decreases with an increasing pore radius. The above rules apply to the tuning parameter $\lambda$ obtained for both pure substances and mixtures. Using the two-phase equilibrium calculation coupled with the modified Young–Laplace equation, the calculated vapor pressures for pure substances and two-phase boundaries for mixtures match very well with the experimental data. Implementation of the modified Young–Laplace equation greatly improves the accuracy of the two-phase equilibrium calculation considering the capillarity effect. Such a modeling strategy could be integrated into a reservoir simulator to conduct more accurate flow simulations for tight/shale reservoirs.

1. INTRODUCTION

Tight/shale reservoirs are featured with nanoscale pores. It is well-established that the confined space in those nanopores introduces large capillary pressure which can pose a significant impact on the phase behavior and flow dynamics of reservoir fluids.1−5 Experimental works and theoretical approaches to describe the vapor–liquid two-phase equilibrium in a confined space are thereby developed to grasp an understanding of the reservoir-fluid phase behavior inside nanopores.6−10

Saturation pressure curves of pure hydrocarbon components in confined nanopores are studied experimentally in many research studies.11−18 The saturation pressure curves can be determined by measuring the adsorption volume of hydrocarbons at different temperatures in a nanomaterial such as SBA-15 or MCM-41. It was found that the saturation pressures of hydrocarbons at given temperatures are reduced significantly inside nanomaterials.11−14 Saturation pressures of hydrocarbon mixtures inside a confined space have also been studied experimentally.8,9 Qiu et al.9 used a novel high-pressure differential scanning calorimeter19 to measure the dew point pressures at different temperatures for the $C_1$−$C_2$ mixture in the nanomaterial SBA-15. This apparatus is then later used to measure saturation pressures of $C_2$ in confined nanopores.17 It was found that saturation pressures of $C_2$ and the $C_1$−$C_2$ mixture significantly decreased because of the strong capillarity
effect in a confined space. Zheng et al. fabricated multiple nanochannels on a microfluidic device and measured the dew point pressures for the C1−C3 mixture at different temperatures inside the nanochannels. In the experiments, they all observed a dramatic reduction of the dew point pressures for hydrocarbon mixtures because of the capillarity effect. Critical points of some reservoir fluids are recently measured in nanopores to reveal the effect of confinement on critical property shifts. In their works, amicroDSC apparatus was used to measure the critical points of two pure components (CO2 and CH4) and one C1−C6 mixture in the nanomaterial SBA-15. They found that the critical pressures of the investigated fluids in nanopores are greatly reduced from their bulk critical pressures. On the basis of the measured data, they also developed a set of equations to calculate critical pressure/temperature shifts in the confined space. The critical-property-shift model they developed has a similar format as the model proposed by Zarragoicoechea and Kuz.

Experiments are costly and time-consuming. Theoretical works are thereby drawing more attention over the years. One of the earliest works that theoretically studied the capillarity effect on the vapor−liquid equilibria in a porous medium was conducted by Bruslovsky. The author proposed a new equation of state (EOS) to couple the effect of the capillary pressure into the two-phase equilibrium calculation for hydrocarbon mixtures. The modeling results show that the bubble point becomes lower than the bulk one, and the dew point pressure becomes higher than the bulk one when capillary pressure is considered in EOS calculations. In the following years, many research studies have also suggested that the vapor−liquid equilibria are greatly affected by the capillary pressure in nanopores. The deviation of the entire two-phase envelope from the bulk condition because of capillary pressure in nanopores was studied by Nojabaei et al., they found that the dew point pressure increases in the upper dew point branch (at pressures above the cricondentherm point), but decreases in the lower dew point branch (at pressures below the cricondentherm point). Moreover, the vapor−liquid equilibrium is not affected by confined nanoparticles at the critical point because the capillary pressure reaches zero at the critical point. The above findings concur with a later work by Sandoval et al. Rezavesh et al. performed multiple two-phase flash calculations coupled with capillary pressure and concluded that there exists a maximum capillary pressure at each temperature above which the two-phase equilibrium is not possible. Apart from simply coupling the capillary pressure into the vapor−liquid equilibrium calculation, other methods have also been developed to improve the accuracy of the two-phase equilibrium description in confined nanopores. Zarragoicoechea and Kuz developed an analytical model to calculate the critical property shifts because of the confinement effect in nanopores. This model assumes a neutral wall. The effect of adsorption on the critical property shifts is thereby not reflected in this model. They compared their modeling results against the experimental data of critical point shifts in nanopores for several pure substances. It was observed that this model offers a better fitting to the experimental data when the pore radius is relatively large. When the pore radius is relatively small, the multilayer adsorption may affect the shift of the critical properties significantly in experiments, while it was not considered in the proposed model. This results in a poor agreement between the modeling results and the experimental data when the pore radius is small. Nevertheless, this method is coupled in several research to study the combined effect of capillarity and confinement on the multiphase equilibrium in nanopores. Modified van der Waals EOS by adding an additional term, and they predicted a shift in the two-phase critical point because of the capillarity effect. The additional term is a function of pore radius, potential width, and potential energy between the pore wall and fluid molecules. The most significant advantage of this method is that the phase equilibrium predicted by this model in nanopores can be reduced to the bulk one when the pore radius approaches infinity. This is not featured in the model proposed by Zarragoicoechea and Kuz. Furthermore, the model proposed by Travalloni et al. can also be implemented in the most widely used Peng−Robinson EOS (PR-EOS). Pang et al. took the effect of porous media into account during the vapor−liquid equilibrium calculation in nanopores. They employed the Blake−Kozeny model to calculate the tortuosity factor of porous media and then calculated the pore radius using the tortuosity factor, permeability, and porosity. It was concluded that the effect of porous media on the two-phase equilibrium calculation is significant and cannot be neglected when the pore radius is less than 1000 nm. Jin and Firoozabadi coupled both capillary pressure and surface adsorption into the vapor−liquid equilibrium calculation. A deviation of the two-phase boundaries from its bulk condition due to capillary pressure and surface adsorption was observed in their study. They further concluded that the effect of surface adsorption on the vapor−liquid equilibrium in nanopores is insignificant, compared to the effect of the capillary pressure, when the pore radius is larger than 10 nm. More recently, another modified PR-EOS is proposed to account for the interaction between pore walls and fluid molecules in nanopores. In this model, the molar volume term in PR-EOS is modified to be a function of the effective molecule volume coefficient and the ratio of the fluid molecule radius to the confined nanopore radius. This model takes into account the fluid adsorption and effective molar volume of the confined nanopore. The critical-property-shifts for pure substances calculated by this model match the experimental data fairly well. It was seen in this study that the degree of the critical temperature shift due to the confined nanopore increases linearly with a decreasing pore radius, while the degree of the critical pressure shift due to the confined nanopore increases quadratically with a decreasing pore radius. Nevertheless, this method is computationally expensive. Recently, by introducing an empirical tuning parameter, λ, Tagipirsi modified the Young−Laplace equation for more accurate modeling of confined phase behavior. They developed correlations of the tuning parameter λ for several pure substances including nitrogen, carbon dioxide, argon, oxygen, krypton, pentane, and hexane. In their paper, they coupled the modified Young−Laplace equation with the perturbed-chain statistical associating fluid theory equation of state (PC-SAFT EOS) to study the phase behavior of certain fluids in confined nanopores. They also suggested a simple linear mixing rule to calculate λ for mixtures using the λ correlations obtained for pure substances. However, their innovative work still bears some issues. The λ correlations for pure substances in their work were developed specifically to couple with the PC-SAFT EOS, which is more computationally demanding.
compared to other EOSs such as PR-EOS. However, the $\lambda$ correlations for pure substances developed in their work were only applicable to subcritical temperatures. This can be sometimes troublesome when one applies the linear mixing rule to calculate $\lambda$ for mixtures because the critical temperature of mixtures often exceeds the critical temperature of some individual components. Taking the binary mixture methane—ethane (14.98 mol % methane and 85.02 mol % ethane) as an example, the critical temperature of this binary mixture is 295.9 K, while the critical temperature of pure methane is merely 190.6 K. In order to successfully utilizing the linear mixing rule to calculate $\lambda$ for mixtures such as methane—ethane, the $\lambda$ correlation of pure methane under supercritical temperatures must be developed. The $\lambda$ correlation under supercritical conditions exists as merely a parameter to adjust the vapor—liquid capillary pressure of mixtures; it does not necessarily have any physical meaning other than being a tuning constant.

This work aims to address the issue that the current cubic-EOS-based modeling method cannot well reproduce the results for the binary mixture $C_1$—$C_3$ calculated by the volume translated PR-EOS and measured in experiments. The solid line and the dashed line represent the dew point pressure curve calculated in bulk conditions and in the confined space, respectively. PR-EOS$^{33}$ coupled with capillary pressure tends to overpredict dew point pressures at higher temperatures and underestimate dew point pressures at lower temperatures. This work is thus devoted to improve the accuracy of the vapor—liquid equilibrium calculation in confined nanopores by developing a new two-phase flash calculation algorithm employing the commonly used PR-EOS$^{33}$ and a modified Young–Laplace equation.$^{36}$ This paper extends and improves the work of Tan and Piri$^{36}$ by developing the $\lambda$ correlations for pure substances and mixtures that can be coupled with a more-efficient EOS, namely, PR-EOS.$^{33}$ This study also calculates a correlation of the tuning parameter $\lambda$ for pure methane under supercritical conditions.

As mentioned previously, the implementation of the modified Young–Laplace equation relies on the modeling of the tuning parameter $\lambda$. To derive the $\lambda$ correlation for various hydrocarbons, experimental data are collected from the literature, including capillary condensation data for pure hydrocarbons and dew point pressure data for hydrocarbon mixtures. We first present the vapor—liquid equilibrium calculation algorithm that is coupled with the modified Young–Laplace equation. Then, the tuning parameter $\lambda$ for six pure substances and two mixtures is computed based on the collected experimental data. Finally, the measured vapor pressures for pure substances and phase boundaries for mixtures are compared against the calculated ones using the generalized tuning parameter $\lambda$. The novelty of this work is that this study employs PR-EOS$^{33}$ in confined two-phase equilibrium calculations instead of PC-SAFT$^{37}$ used in the work of Tan and Piri.$^{36}$ The motivation for doing so is that PR-EOS$^{33}$ is simpler and more straightforward than PC-SAFT,$^{37}$ making it still the most commonly used EOS in numerical simulations. Moreover, this work develops $\lambda$ correlations for two hydrocarbon mixtures to examine the application of the modified Young–Laplace equation$^{36}$ to hydrocarbon mixtures. This is not featured in the work of Tan and Piri.$^{36}$

The rest of this paper is divided into four main sections. First, the methodology is presented. All the main equations governing the two-phase equilibrium calculation and capillary pressure calculation are presented. Then, the numerical algorithm of the flash calculation is presented in detail. The next section presents all the two-phase equilibrium calculation results for pure substances and mixtures. Finally, all the major findings are summarized in the Conclusions section.

![Figure 1](image-url). Dew point pressures of the binary mixture $C_1$—$C_3$ measured using a nanofluidic device with nanochannels$^9$ and calculated from PR-EOS$^{33}$ coupled with capillary pressure (with the assumption of zero contact angle). The experimental data are retrieved from the study by Zhong et al. (2018).$^9$

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**Figure 1** gives an example of the dew-point-pressure curve for the binary mixture $C_1$—$C_3$ calculated by the volume translated PR-EOS and measured in experiments.$^9$ The black dots represent the dew point pressures measured at different temperatures.$^9$ The solid line and the dashed line represent the dew point pressure curve calculated in bulk conditions and in the confined space, respectively. PR-EOS$^{33}$ coupled with capillary pressure tends to overpredict dew point pressures at higher temperatures and underestimate dew point pressures at lower temperatures. This work is thus devoted to improve the accuracy of the vapor—liquid equilibrium calculation for pure substances and mixtures under supercritical conditions. As mentioned previously, the implementation of the modified Young–Laplace equation relies on the modeling of the tuning parameter $\lambda$. To derive the $\lambda$ correlation for various hydrocarbons, experimental data are collected from the literature, including capillary condensation data for pure hydrocarbons and dew point pressure data for hydrocarbon mixtures. We first present the vapor—liquid equilibrium calculation algorithm that is coupled with the modified Young–Laplace equation. Then, the tuning parameter $\lambda$ for six pure substances and two mixtures is computed based on the collected experimental data. Finally, the measured vapor pressures for pure substances and phase boundaries for mixtures are compared against the calculated ones using the generalized tuning parameter $\lambda$. The novelty of this work is that this study employs PR-EOS$^{33}$ in confined two-phase equilibrium calculations instead of PC-SAFT$^{37}$ used in the work of Tan and Piri.$^{36}$ The motivation for doing so is that PR-EOS$^{33}$ is simpler and more straightforward than PC-SAFT,$^{37}$ making it still the most commonly used EOS in numerical simulations. Moreover, this work develops $\lambda$ correlations for two hydrocarbon mixtures to examine the application of the modified Young–Laplace equation$^{36}$ to hydrocarbon mixtures. This is not featured in the work of Tan and Piri.$^{36}$

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### Table 1. Summary of Experimental Works Used to Develop Correlations of the Tuning Parameter Lambda for Different Fluids

| Fluid | Material | Pore Radii, nm | Temperature, K | References |
|-------|----------|----------------|----------------|------------|
| $C_1$ | SBA-15   | 1.704—3.281    | 262.15—300.15  | Qiu et al., 2019$^9$ |
| $C_1$ | MCM-41   | 1.291—3.030    | 279.55—323.95  | Qiu et al., 2020$^9$ |
| $n-C_4$ | MCM-41 | 1.291—3.030    | 279.55—323.65  | Barsotti et al., 2018$^{11}$ |
| $n-C_5$ | MCM-41, SBA-15 | 2.285, 3.935 | 258—298 | Barsotti et al., 2018$^{11}$ |
| $n-C_6$ | MCM-41 | 1.203—2.122    | 303—323        | Russo et al., 2012$^{12}$ |
| $n-C_7$ | SBA-15  | 2.3—3.9        | 299.15—309.15  | Qiao et al., 2004$^{13}$ |
| $C_1$—$C_2$ | SBA-15 | 1.704—3.281    | 242—273        | Vinh-Thanh et al., 2005$^{14}$ |
| $C_1$—$C_3$ | a nanofluidic device with nanochannels | 4, 40 | 282.15—301.15 | Qiu et al., 2018$^9$ |
| $C_1$—$C_3$ | a nanofluidic device with nanochannels | 4, 40 | 282.15—301.15 | Zhong et al., 2018$^9$ |
2. RESULTS AND DISCUSSION

This work employs a modified Young−Laplace equation\(^{36}\) in a two-phase flash calculation algorithm to study the vapor−liquid equilibrium in confined nanopores. The proposed algorithm is applied to calculate the vapor−liquid equilibrium in confined nanopores for seven examples of hydrocarbon fluids to examine the robustness of the proposed algorithm. The examples presented in this section include six pure substances and two binary mixtures. For each example, we first collected experimental saturation pressure data for hydrocarbons in confined nanopores from the literature. The collected experimental data are summarized in Table 1. Table 2 lists the properties of all hydrocarbon components that are involved in the example studies.

### 2.1. Examples of Pure Substances

The vapor−liquid equilibrium of six pure hydrocarbon substances in confined nanopores are studied in this work, including pure ethane (C\(_2\)), pure propane (C\(_3\)), pure n-butane (n-C\(_4\)), pure n-pentane (n-C\(_5\)), pure n-hexane (n-C\(_6\)), and pure n-heptane (n-C\(_7\)). The saturation pressures of these hydrocarbon fluids are calculated using the aforementioned methodology and compared with the experimental data. As for C\(_2\), C\(_3\), n-C\(_4\), n-C\(_5\), and n-C\(_6\), the saturation pressures calculated using PR-EOS\(^{33}\) and the original Young−Laplace equation\(^{39}\) are larger than the saturation pressures measured in experiments at all temperatures. As for n-C\(_7\), however, the saturation pressures calculated by using PR-EOS\(^{33}\) and the original Young−Laplace equation\(^{39}\) can become lower than the measured saturation pressure; this implies that negative values of the tuning parameter \(\lambda\) are required to match the measured results.

In order to adjust the calculated capillary pressure to match the real capillary pressure present in experiments, the tuning parameter \(\lambda\) is first computed using the aforementioned procedure for each pore radius. The computed tuning parameter \(\lambda\) for C\(_2\), C\(_3\), n-C\(_4\), n-C\(_5\), n-C\(_6\), and n-C\(_7\) at different temperatures and pore radii is given in Figures 2−7.

Based on the calculated \(\lambda\) shown in Figure 2, the following empirical correlation for \(\lambda\) can be developed for C\(_2\) (\(R^2 = 0.9902\)).

\[
\lambda = -63.8 + 0.4323T + 0.45240p - 0.00072T^2 \nonumber
- 0.00153Tr_p
\]  

(1)

Based on the results shown in Figure 3, the following empirical correlation for \(\lambda\) can be developed for C\(_3\) (\(R^2 = 0.9984\)).

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**Table 2. Physical Properties of Methane, Ethane, Propane, n-Butane, n-Pentane, n-Hexane, and n-Heptane Used in the PR-EOS Model\(^{38}\)**

| Substance | T\(_c\), K | P\(_c\), bar | \(\omega\) | MW, g/mol | P\(_{ch}\), bar |
|-----------|-----------|-------------|---------|----------|-------------|
| C\(_1\)    | 190.6     | 46          | 0.008   | 16.04    | 77.33       |
| C\(_2\)    | 305.4     | 48.84       | 0.098   | 30.07    | 108         |
| C\(_3\)    | 369.8     | 42.46       | 0.152   | 44.10    | 157.31      |
| n-C\(_4\)  | 425.2     | 38          | 0.192   | 58.12    | 189.9       |
| n-C\(_5\)  | 469.6     | 33.94       | 0.251   | 72.15    | 231.5       |
| n-C\(_6\)  | 507.4     | 29.69       | 0.296   | 86.17    | 271         |
| n-C\(_7\)  | 540.2     | 27.36       | 0.351   | 100.20   | 312.5       |

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**Figure 2.** Computed tuning parameter \(\lambda\) of C\(_2\) based on the experimental data.\(^{17,19}\) The solid lines are trend lines which are drawn for visual guide purpose.

**Figure 3.** Computed tuning parameter \(\lambda\) of C\(_3\) based on the experimental data.\(^{11}\) The solid lines are trend lines which are drawn for visual guide purpose.

**Figure 4.** Computed tuning parameter \(\lambda\) of pure n-C\(_7\) based on the experimental data.\(^{11}\) The solid lines are trend lines which are drawn for visual guide purpose.
Based on the regression of the experimental data shown in Figure 4, we can obtain the following $\lambda$ correlation for $n$-C$_4$ ($R^2 = 0.9474$).

$$
\lambda = -22.15 + 0.1353T + 1.3140r_p - 0.00020T^2
- 0.00396Tr_p
$$

(2)

Based on the regression of the experimental data shown in Figure 4, we can obtain the following $\lambda$ correlation for $n$-C$_4$ ($R^2 = 0.9973$) based on the results shown in Figure 5.

$$
\lambda = -27.75 + 0.17490T + 0.26790r_p - 0.00027T^2
- 0.00073Tr_p
$$

(3)

By using the curve fitting tool, we can obtain the following $\lambda$ correlation for $n$-C$_5$ ($R^2 = 0.9981$).

$$
\lambda = -33.19 + 0.22460T + 0.86970r_p - 0.00037T^2
- 0.00306Tr_p
$$

(4)

Based on the regression of the experimental data shown in Figure 6, we can readily develop the following $\lambda$ correlation for $n$-C$_6$ ($R^2 = 0.9916$).

$$
\lambda = -21.06 + 0.12160T + 1.6470r_p - 0.00017T^2
- 0.00501Tr_p
$$

(5)

At a temperature of 298.15 K, the tuning parameter $\lambda$ of pure $n$-heptane becomes negative for pore radii of 2.30 and 2.75 nm. This negative value of the tuning parameter $\lambda$ effectively reduces the calculated capillary pressure. Based on the results shown in Figure 7, we can develop the following $\lambda$ correlation for $n$-C$_7$ ($R^2 = 0.9916$).

$$
\lambda = -32.51 + 0.15330T + 2.01010r_p - 0.00016T^2
- 0.00615Tr_p
$$

(6)

To compare the tuning parameter $\lambda$ of different hydrocarbons, we calculate $\lambda$ of C$_2$ to $n$-C$_7$ over 295—310 K at a pore radius of 1 nm. Results are shown in Figure 8. Despite the fact that experimental saturation pressure data for C$_2$ to $n$-C$_7$ are collected from different research groups, it is interesting to observe from Figure 8 that, at a fixed temperature and pore
radius, \( \lambda \) shows a monotonic decreasing trend for hydrocarbons with an increasing carbon number.

In this work, when the modified Young–Laplace equation\(^{36} \) is coupled with PR-EOS, the calculated \( \lambda \) for \( C_2, C_3, n-C_4, n-C_5, n-C_6, \) and \( n-C_7 \) suggests a quadratic polynomial relationship between \( \lambda \) and temperature. Moreover, \( \lambda \) increases with increasing pore radii for all temperatures; this is different from the results obtained by Tan and Piri\(^{36} \) which showed that the tuning parameter \( \lambda \) decreases with an increasing pore radius. The tuning parameter \( \lambda \) for \( C_2, C_3, n-C_4, n-C_5, n-C_6, \) and \( n-C_7 \) can be empirically determined by using eqs 1–6, respectively, at a given temperature and a given pore radius. The calculated \( \lambda \) can then be fed into the modified Young–Laplace equation to adjust the calculated capillary pressure. Figures 9–14 present the saturation pressure curves of \( C_2, C_3, n-C_4, n-C_5, n-C_6, \) and \( n-C_7 \) measured from experiments and calculated from two-phase equilibrium calculations coupled with capillary pressure calculated by using the original Young–Laplace equation\(^{39} \) and the modified Young–Laplace equation\(^{36} \).

![Figure 9. Saturation pressures of \( C_2 \) measured in SBA-15\(^{17,19} \) and calculated from vapor–liquid equilibrium calculations coupled with the (a) original Young–Laplace equation\(^{39} \) and the (b) modified Young–Laplace equation.\(^{36} \) The experimental data are retrieved from the study by Qiu et al. (2019) and Qiu et al. (2020).\(^{17,19} \)](https://dx.doi.org/10.1021/acsomega.0c00963)

![Figure 10. Saturation pressures of \( C_3 \) measured in MCM-41\(^{11} \) and calculated from vapor–liquid equilibrium calculations coupled with the (a) original Young–Laplace equation\(^{39} \) and the (b) modified Young–Laplace equation.\(^{36} \) The experimental data are retrieved from the study by Barsotti et al. (2018).\(^{11} \)](https://dx.doi.org/10.1021/acsomega.0c00963)

In Figures 9–14, the solid curves represent the vapor–liquid equilibria of pure hydrocarbon fluids under bulk conditions. The black symbols represent experimental saturation pressure data, and the different dashed curves represent saturation pressure curves calculated by vapor–liquid equilibrium calculations coupled with the original Young–Laplace equation\(^{39} \) and the modified Young–Laplace equation.\(^{36} \) It is shown in Figures 9–14a that the saturation pressures of \( C_2, C_3, n-C_4, n-C_5, n-C_6, \) and \( n-C_7 \) in confined nanopores measured from experiments and calculated from vapor–liquid equilibria are all reduced compared to the bulk one. As for \( C_3, n-C_4, n-C_5, n-C_6, \) and \( n-C_7, \) the saturation pressures predicted from vapor–liquid equilibrium calculations coupled with the original Young–Laplace equation\(^{39} \) are larger than the saturation pressures obtained from experiments at all pore radii. Furthermore, as temperature rises, the deviation between the measured and calculated saturation pressures becomes larger. This suggests that the actual capillary pressure existing
in confined nanopores in the experiments is larger than the calculated capillary pressure. One of the major reasons that may cause this is that the surface adsorption reduces pore radius, which, in turn, increases capillary pressure dramatically.

As for n-C_7, the calculated saturation pressures of n-C_7 in confined nanopores are in better agreement with the experimental data. The calculated saturation pressures of n-C_7 are mostly larger than the experimental data. At a temperature of 298.15 K, for pore radii of 2.75 and 2.30 nm, the calculated saturation pressures become lower than the experimental data.

After the modified Young–Laplace equation and the λ correlations are applied, the calculated saturation pressures of C_2, C_3, n-C_4, n-C_5, n-C_6, and n-C_7 in confined nanopores match the experimental data with decent accuracy. The application of the modified Young–Laplace equation with the λ correlations is effective in increasing the capillary pressure for C_2, C_3, n-C_4, n-C_5, and n-C_6 resulting in a good agreement with the measured saturation pressure data. The λ correlation for n-C_7 reduces the capillary pressures at lower temperatures but increases the capillary pressures at higher temperatures. Overall, the implementation of the modified Young–Laplace equation with proper modeling of the tuning parameter λ greatly improves the accuracy of the vapor–liquid equilibrium calculations for C_2, C_3, n-C_4, n-C_5, n-C_6, and n-C_7 in confined nanopores.

2.2. Examples of Binary Mixtures. In the work of Tan and Piri, pure substances were studied to develop the correlations of the tuning parameter λ. A linear mixing rule is proposed in their work to calculate the mixture λ based on the pure-substance λ. This practice was then applied in subsequent studies. In their studies, λ for mixtures of acetone/ethanol, ethanol/water, and CO_2/n-C_5 are calculated using the mixing rule and λ for the constituting components.

Figure 11. Saturation pressures of pure n-C_4 measured in MCM-41 and calculated from vapor–liquid equilibrium calculations coupled with the (a) original Young–Laplace equation and the (b) modified Young–Laplace equation. The experimental data are retrieved from the study by Barsotti et al. (2018).

Figure 12. Saturation pressures of pure n-C_5 measured in MCM-41 and SBA-15 and calculated from vapor–liquid equilibrium calculations coupled with the (a) original Young–Laplace equation and the (b) modified Young–Laplace equation. The experimental data are retrieved from the study by Russo et al. (2012).
Results showed that the application of the linear mixing rule offers a satisfactory accuracy in calculating the mixture $\lambda$. To examine the dependence of $\lambda$ for hydrocarbon mixtures on temperature and pore radius, vapor–liquid equilibria of the binary mixture $C_1$–$C_2$ and the binary mixture $C_1$–$C_3$ in confined nanopores are studied in this section. The feed composition of the mixture $C_1$–$C_2$ is 14.98 mol % $C_1$ and 85.02 mol % $C_2$, while the feed composition of the mixture $C_1$–$C_3$ is 20 mol % $C_1$ and 80 mol % $C_3$. The experimental dew point pressures of the mixture $C_1$–$C_2$ in confined nanopores are collected from Qiu et al. The experimental dew point pressures of the mixture $C_1$–$C_3$ are collected from Zhong et al. The capillary pressure is coupled in a two-phase equilibrium calculation to compute the dew point pressures of the two tested mixtures in confined nanopores. The binary interaction parameters (BIP) for the mixture $C_1$–$C_2$ and the mixture $C_1$–$C_3$ used in the PR-EOS model are given in Tables 3 and 4, respectively.

The computed tuning parameter $\lambda$ for the mixture $C_1$–$C_2$ and $C_1$–$C_3$ are shown in Figures 15 and 16, respectively.

Based on the regression of the experimental data shown in Figure 15, the following $\lambda$ correlation for the binary mixture methane–ethane can be obtained ($R^2 = 0.9726$).
Based on the results shown in Figure 16, we developed the following $\lambda$ correlation for the binary mixture $C_1-C_3$ ($R^2 = 0.9313$).

$$\lambda = -58.12 + 0.31950T + 0.49150r_p - 0.00041T^2 - 0.00163Tr_p$$

(8)

The above correlations can then be applied in the modified Young–Laplace equation $^{36}$ to adjust the calculated capillary pressure to improve the accuracy of the two-phase equilibrium calculation in confined nanopores. Figures 17 and 18 show the dew point pressure curves of the mixture $C_1-C_2$ and the mixture $C_1-C_3$, respectively, obtained from the experiment and from two-phase equilibrium calculations coupled with the original Young–Laplace equation $^{39}$ and the modified Young–Laplace equation $^{36}$.

It can be found in Figures 17 and 18 that the calculated dew point pressures of the two mixtures $C_1-C_2$ and $C_1-C_3$ in confined nanopores greatly deviate from the experimental data. For the mixture $C_1-C_2$, the calculated dew point pressures are larger than the measured ones. This suggests that the capillary pressure calculated by using the original Young–Laplace equation $^{39}$ is not capable of accurately representing the actual capillary pressure. For the mixture $C_1-C_3$, at most of the tested temperatures, the calculated dew point pressures are larger than the experimental data. At temperatures of 282.15 and 285.15 K, however, the calculated dew point pressures are lower than the experimental data measured at a pore radius of 4 nm. This implies that negative values of $\lambda$ are needed in this case. Based on the measured dew point pressure data, the tuning parameter $\lambda$ for the binary mixtures $C_1-C_2$ and $C_1-C_3$ can be determined at different temperatures and different pore radii.

After the modified Young–Laplace equation $^{36}$ is coupled with PR-EOS $^{33}$, the dew point pressures of the binary mixture $C_1-C_2$ and $C_1-C_3$ in confined nanopores calculated using the proposed algorithm match the experimental data with good accuracy. The $\lambda$ correlations obtained for the two tested
mixtures is proved to be effective in adjusting the calculated capillary pressure to the true capillary pressure in experiments. Ideally, $\lambda$ for mixtures can be determined based on the $\lambda$ of individual components using a certain type of mixing rule. Tan and Piri$^{36}$ suggested using a simple linear mixing rule to calculate the mixture $\lambda$ based on the pure-substance $\lambda$:

$$\lambda_m = \sum_{i=1}^{N_c} x_i \lambda_i$$  \hspace{1cm} (9)

where $\lambda_m$ is the mixture $\lambda$, $N_c$ is the number of components in the mixture, $x_i$ is the mole fraction of the $i$th component in liquid phase, and $\lambda_i$ is the $\lambda$ of the $i$th component. It can be seen in previous examples that, under certain circumstances, the temperature interval of the $C_1-C_2$ mixture’s two-phase region is above the critical temperature of $C_1$ in the mixture. Therefore, the $\lambda$ correlation for $C_1$ under supercritical conditions needs to be determined before calculating the mixture $\lambda$ with the mixing rule (i.e., eq 9). In this following exercise, we first validate the application of the mixing rule on calculating the mixture $\lambda$ using $\lambda$ of pure substances. Then, we use the $\lambda$ correlations of the mixture $C_1-C_2$ and pure $C_2$ to back calculate the $\lambda$ correlation of $C_1$ under supercritical conditions. It is worth noting that the experimental saturation pressure data for the mixture $C_1-C_2$ and pure $C_2$ is collected from experiments conducted by the same research groups. They used exactly the same material when measuring the saturation pressures of the mixture $C_1-C_2$ and $C_2$ in confined nanopores. The purpose of this example calculation is to demonstrate that there exists a $\lambda$ correlation of $C_1$ under supercritical conditions.

To examine if the mixing rule is feasible for calculating the mixture $\lambda$, we calculate bubble points of the binary hydrocarbon mixture $n$-$C_5$-$n$-$C_7$ (50–50 mol %) at different temperatures and pore radii. The $\lambda$ of this mixture is calculated using the mixing rule (eq 9) and the fitted $\lambda$ for pure $n$-$C_5$ and $n$-$C_7$. The calculated results are then compared with the measured bubble point data reported by Alfi et al.$^{43}$ The BIP used for calculation is given in Table 5.

**Figure 18.** Dew point pressures of the binary mixture $C_1-C_2$ measured using a nanofluidic device with nanochannels$^9$ and calculated from vapor–liquid equilibrium calculations coupled with the (a) original Young–Laplace equation$^{39}$ and the (b) modified Young–Laplace equation.$^{36}$ The experimental data are retrieved from the study by Zhong et al. (2018).$^9$

| BIP  | $n$-$C_5$ | $n$-$C_7$ |
|------|---------|---------|
| $n$-$C_5$ | 0       | 0.0021  |
| $n$-$C_7$ | 0.0021  | 0       |

Experimental vapor–liquid interfacial tension (IFT) data for the $n$-$C_5$-$n$-$C_7$ system are collected from Mohsen-Nia et al.$^{44}$ to develop the $\phi_{ij}$ correlation. The $\phi_{ij}$ correlation developed for $n$-$C_5$-$n$-$C_7$ system is given in eq 10.

$$\phi_{ij} = -0.0060T + 1.0088$$  \hspace{1cm} (10)

**Figure 19** shows the comparison between the calculation results and measured ones. It is interesting to observe from Figure 19 that the bubble points yielded by PR-EOS$^{35}$ and the
\( \lambda \) correlations match fairly well with the measured ones at small pore radii. The match is surprisingly satisfactory because the experimental data used for developing the \( \lambda \) correlations are conducted on nanodevices that are different from the ones used to measure the bubble points of \( n\text{-C}_x-\text{n-C}_y \) mixtures.

The back calculated \( \lambda \) correlation of \( C_1 \) under supercritical conditions is given in eq 11.

\[
\lambda = -12.93 + 0.37890T + 0.29020r_p - 0.00938T^2 \\
- 0.01779Tr_p
\]

(11)

The result calculation suggests that there exist correlations of \( \lambda \) for \( C_1 \) under supercritical conditions, and the correlations are still quadratic polynomial functions with temperature. Moreover, the tuning parameter \( \lambda \) becomes larger with an increasing pore radius. Such an example calculation confirms the feasibility of utilizing a simple mixing rule in calculating the mixture \( \lambda \) using \( \lambda \) of pure components. In the practice of calculating the mixture \( \lambda \) using \( \lambda \) of constituting substances, certain precautions should be applied. The best way of validating the \( \lambda \) correlations developed for the constituting substances and the mixing rule is to conduct systematic phase behavior experiments for pure substances and their mixtures using the same nanofluidic device or DSC setup. However, such a comprehensive experimental dataset is lacking. Future experimental works are needed to fill this gap.

3. SUMMARY AND CONCLUSIONS

The vapor—liquid equilibria of pure substances and mixtures in confined nanopores are studied in this research. This work aims to improve the accuracy of vapor—liquid equilibrium calculation of hydrocarbons in confined nanopores by coupling a modified Young—Laplace equation \(^{36} \) in the PR-EOS model. We developed correlations of the tuning parameter \( \lambda \) for six pure hydrocarbon substances and two binary hydrocarbon mixtures and applied the modified Young—Laplace equation in vapor—liquid equilibrium calculations. The following conclusions can be drawn from this study:

- For both pure substance and mixture, the correlation of the tuning parameter \( \lambda \) can be expressed as a quadratic polynomial function with temperature when the modified Young—Laplace equation \(^{36} \) is coupled with the PR-EOS model.\(^ {33} \)
- The tuning parameter \( \lambda \) becomes larger with an increased pore radius. This trend is valid for pure hydrocarbons and their mixtures.
- \( \lambda \) generally becomes smaller for pure hydrocarbon substances with smaller carbon numbers.
- The value of \( \lambda \) is always less than one. The \( \lambda \) can become negative under certain circumstances, which adjusts the capillary pressure to a lower value.
- The \( \lambda \) for \( C_1 \) under supercritical conditions can be expressed as polynomial functions with temperature. We also demonstrated that the \( \lambda \) under supercritical conditions can be back-calculated using the mixing rule.
- The accuracy of the vapor—liquid equilibrium calculations in confined nanopores can be significantly improved by applying the modified Young—Laplace equation \(^{36} \) with the experimentally derived \( \lambda \) correlations.

One advantage of using PR-EOS in the modeling strategy is that this enables the proposed approach to be readily integrated into the existing reservoir simulators. However, it must be noted that the development of \( \lambda \) correlations highly hinges on the availability of phase transition experiments in nanopores. But these experimental data are hardly available because of the technical challenges associated with such nanoscale experiments.

4. METHODOLOGY

A two-phase equilibrium can be determined by satisfying the chemical potential equality relation at given pressure, temperature, and feed composition.\(^ {45} \) In a conventional two-phase equilibrium, the liquid phase has the same pressure as the vapor phase. In confined nanopores, because of the existence of capillary pressure, the pressure of the nonwetting phase (vapor phase) is larger than the pressure of the wetting phase (liquid phase). The chemical potential equality condition can thereby be modified as

\[
\mu_i(P_l, T, x = \{x_i\}) = \mu_y(P_v, T, y = \{y_j\}) \\
i = 1, \ldots, N_c
\]

(12)

where \( \mu_i \) is the chemical potential of the \( i \)th component in the liquid phase, \( \mu_y \) is the chemical potential of the \( i \)th component in the vapor phase, \( P_l \) is the pressure in the liquid phase, \( P_v \) is the pressure in the vapor phase, \( T \) is the system temperature, \( x \) is the liquid-phase composition, \( y \) is the vapor-phase composition, and \( N_c \) is the number of components. The chemical potential equality condition can then be readily translated into fugacity equality condition\(^ {45} \)

\[
f_i(P_l, T, x = \{x_i\}) = f_y(P_v, T, y = \{y_j\}) \\
i = 1, \ldots, N_c
\]

(13)

where \( f_i \) is the fugacity of the \( i \)th component in the liquid phase, and \( f_y \) is the fugacity of the \( i \)th component in the vapor phase. In this work, PR-EOS\(^ {33} \) is employed to calculate the fugacity of each component in each phase\(^ {33} \)

\[
\ln \frac{f_i}{x^P} = \ln \frac{\phi_i}{B} = \frac{A}{2\sqrt{2}B} \left( \frac{B}{B} - 2 \sum_{i=1}^{N_c} y_i A_i \right) \ln \left( \frac{Z + (1 + \sqrt{2}B)}{Z - (1 - \sqrt{2}B)} \right) \\
i = 1, \ldots, N_c
\]

(14)

where \( y_i \) is the mole fraction of the \( i \)th component in any phase, \( P \) is the phase pressure, \( \phi_i \) is the fugacity coefficient of the \( i \)th component in any phase, \( Z \) is the phase compressibility factor, and \( A \) and \( B \) are EOS constants. Provided that the pressures of the liquid phase and the vapor phase are different in confined nanopores, the relation between \( P_l \) and \( P_v \) is given as

\[
P_v = P_l - r_p \frac{2\sigma}{r_p}
\]

(15)

where \( P_v \) is the capillary pressure across the equilibrating phases, \( \sigma \) is the IFT, and \( r_p \) is the pore radius. Capillary pressure is calculated using the Young—Laplace equation \(^{36} \) with assumptions of equal principle curvature radii and zero contact angle. The IFT between the liquid phase and the vapor phase is calculated using the following Weinaug—Katz model\(^ {36} \)
\[ \sigma_{lg} = \left[ \sum_{i=1}^{N_c} \rho_l M_i \left( x_i \rho_l - y_i \rho_v M_i \right) \right]^{1/4} \quad \text{for } i = 1, ..., N_c \quad (16) \]

where \( \sigma_{lg} \) is the IFT between the liquid phase and the vapor phase, \( \rho_l \) is the Parachor constant of the \( i \)th component, and \( \sigma_{lg} \) and \( \sigma_{lv} \) are the density of the liquid phase and the vapor phase, respectively. Here, the phase densities are calculated by volume translated PR-EOS which adopts the volume translation method proposed by Abudour et al.\(^{47}\) and Abudour et al.\(^{48}\). \( M_i \) and \( M_g \) are the molecular weights of the liquid phase and the vapor phase, respectively; \( x_i \) and \( y_i \) are the mole fractions of the \( i \)th component in the liquid phase and the vapor phase, respectively. In order to achieve better accuracy in IFT predictions, an approach proposed by Hugill and van Welsenes\(^{49}\) is applied to calculate the mixture Parachor constant. This approach can be expressed in eq 17.

\[
\begin{align*}
\Phi_{ch} &= \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} x_i x_j P_{chij} \\
\Phi_{ch} &= \sum_{i=1}^{N_c} y_i y_j P_{chij} \\
\Phi_{ch} &= \Phi_{ch} (P_{ch} + P_{ch}) / 2
\end{align*}
\quad (17)
\]

where \( \Phi_{ch} \) and \( \Phi_{ch} \) are the Parachor of the liquid phase and the vapor phase, respectively; \( \Phi_{ch} \) is the interactive parameter which needs to be calculated using the experimental IFT data. It was shown in the work of Hugill and van Welsenes\(^{49}\) that the interactive parameter \( \Phi_{ch} \) tends to have a linear relationship with temperature. The vapor—liquid IFT can be calculated using eq 18.

\[ \sigma_{lg} = \left[ \Phi_{ch} \left( \sum_{i=1}^{N_c} x_i \frac{\rho_l}{M_i} \right) - \Phi_{ch} \left( \sum_{i=1}^{N_c} y_i \frac{\rho_v}{M_i} \right) \right]^{1/4} 
\quad (18) \]

The accuracy of predicting vapor—liquid IFT using eqs 6 and 7 is validated below. The IFT data for mixtures C\(_1\)−C\(_3\) and C\(_1\)−C\(_2\) are collected from Weinaug and Katz\(^{46}\) and Baidakov et al.\(^{50}\). Then, we calculate interactive parameters at different temperatures using the collected experimental data. If there are more than one data point for each temperature, the average values of the interactive parameter at each temperature are used to develop \( \Phi_{ch} \) correlations. Finally, vapor—liquid IFTs are calculated using the volume translated PR-EOS and eqs 6 and 7; the calculation results are compared with the measured data. The \( \Phi_{ch} \) correlation developed for C\(_1\)−C\(_3\) and C\(_1\)−C\(_2\) systems is given in eq 19.

\[
\begin{align*}
\Phi_{ch}(C_1-C_3) &= -0.0110T + 3.9728 \\
\Phi_{ch}(C_1-C_2) &= 0.0046T + 0.3694
\end{align*}
\quad (19) \]

Figure 20 shows parity charts of the calculated and experimental IFTs for C\(_1\)−C\(_3\) and C\(_1\)−C\(_2\). It is seen from Figure 20 that the volume-translated PR-EOS and eqs 16−19 offer acceptable accuracy in reproducing the vapor—liquid IFT for the hydrocarbon mixtures. A combination of the Young—Laplace equation\(^{59}\) and Weinaug—Katz model\(^{16}\) with proper prediction of the Parachor constant provides a simple and quick estimation of the capillary pressure present. However, the capillary pressure calculated using this method does not necessarily represent the true situation in confined nanopores. The assumption of zero contact angle greatly weakens the correctness of the calculation results due to the fact that it is difficult for any reservoir to reach a complete liquid-wet condition. This assumption could make the calculation results less reliable. Moreover, when this method is applied to study the two-phase equilibrium in confined nanopores that have a pore radius less than 10 nm, the adsorption effect can become significant, leading to the creation of an adsorption layer and hence a reduction in pore radius.\(^{3}\) Pore-radius reduction is not considered in the original Young—Laplace equation\(^{59}\) during the calculation of capillary pressure.

In order to improve the accuracy of two-phase equilibrium calculations in confined nanopores and to mitigate the deviation of modeling results from experimental results, this work employs a modified Young—Laplace equation proposed...
by Tan and Piri. 36 The modified Young–Laplace equation is
given below36

\[ P_c = \frac{2\sigma}{r_p(1 - \lambda)} \]  
(20)

This new Young–Laplace equation 36 modifies the original
one by adding another term, that is, the tuning parameter \( \lambda \).
This tuning parameter could take into account both contact angle
and the reduction in the pore radius because of the adsorption effect.
Correlation of the tuning parameter \( \lambda \) can be empirically developed by fitting the experimental capillary
condensation results. In this work, we first set the value of the
tuning parameter \( \lambda \) to be zero and calculate the saturation
pressure of a given fluid at given temperature and pore radius.
Then, we gradually change the value of the tuning parameter \( \lambda \)
until the calculated saturation pressure matches precisely with
the measured one. After we obtain the tuning parameter \( \lambda \) for
all the experiment data points, curve fitting is employed to
generate a \( \lambda \) correlation. It was previously suggested that the
tuning parameter \( \lambda \) tends to be a function of temperature and
radius. 36 The developed \( \lambda \) correlation can then be embedded
into the modified Young–Laplace equation 1 to improve the
capillary pressure prediction in nanopores.

5. NUMERICAL ALGORITHM

The two-phase equilibrium calculation algorithm coupled with a
modified Young–Laplace equation 36 is constructed with an
outer loop and an inner loop. The outer loop solves for the
fugacity-equality relation and updates the phase equilibrium
ratio \( (k_i) \), while the inner loop solves the Rachford–Rice equation51
which can be derived from the material balance equation. The Rachford–Rice equation is given as51

\[ \sum_{i=1}^{N_c} \beta_i y_i = \sum_{i=1}^{N_c} \left( \frac{z_i(k_i - 1)}{1 + \beta_i(k_i - 1)} \right) = 0 \]  
(21)

where \( \beta_i \) is the vapor mole fraction, and \( z_i \) is the mixture
feed composition.

To start the calculation procedure, the phase equilibrium
ratio must be initialized using the Wilson equation52

\[ k_i = \frac{P_{ci}}{P} \exp \left[ 5.37(1 + \omega_i \left( 1 - \frac{T_{ci}}{T} \right) ) \right] \]  
(22)

where \( P_{ci} \) is the critical pressure of the \( i \)th component, \( \omega_i \) is the
acentric factor of the \( i \)th component, \( T_{ci} \) is the critical
temperature of the \( i \)th component, and \( T \) is the system
temperature.

The phase equilibrium ratio is then fed into the inner loop
to solve the Rachford–Rice equation51 using the successive
substitution method. By solving the Rachford–Rice equation,51
the phase compositions \( (x_i, y_i) \) and phase mole fractions
\( (\beta_i, \omega_i) \) can be obtained. The obtained results are then used to
calculate the capillary pressure using the modified Young–Laplace equation56
and the developed \( \lambda \) correlations. Then, the component fugacities
\( (f_{iuc}, f_{ic}) \) are calculated to check for the fugacity-equality condition. If the fugacity-equality condition is
satisfied, then, the calculation is stopped, and the phase compositions and mole fractions are obtained. If the fugacity-
equality condition is not satisfied, the phase equilibrium ratio is
then updated using the calculated component fugacities with the following equation55

\[ k_{iy}^{n+1} = k_{iy}^{n} \left( \frac{f_{iuc}^n}{f_{ic}^n} \right) \]  
(23)

where \( n \) represents the current iteration, and \( n + 1 \) represents
the next iteration. The updated phase equilibrium ratio is then
used to solve the Rachford–Rice equation,51 and the entire
calculation procedure is repeated until the fugacity-equality
condition is satisfied. A flowchart is provided in Figure 21 to
depict the calculation procedure of the two-phase equilibrium
calculation coupled with the modified Young–Laplace equation.50

Figure 21. Calculation procedure of the vapor–liquid equilibrium
calculation coupled with the modified Young–Laplace equation.50

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NOMENCLATURE
A, equation of state constant
B, equation of state constant
EOS, equation of state
$f_i^L$, fugacity of component $i$ in liquid phase, bar
$f_i^V$, fugacity of component $i$ in vapor phase, bar
IPT, interfacial tension, mN/m
$k_i^v$, phase equilibrium ratio of component $i$
$M_i^0$, molecular weight of liquid phase, g/mol
$M_i^g$, molecular weight of vapor phase, g/mol
$N_i$, total number of components
$P$, bulk pressure, bar
$P_{\text{fix}}$, Parachor of component $i$
$P_{ci}$, critical pressure of component $i$
$P_{cv}$, vapor pressure, bar
$P_{li}$, liquid pressure, bar
$P_{lv}$, vapor–liquid capillary pressure, bar
$p_i$, pore radius, nm
$R$, universal gas constant, 83.14459848 cm$^3$ bar K$^{-1}$ mol$^{-1}$
$T$, bulk temperature, K
$T_c$, critical temperature, K
$T_r$, critical temperature of component $i$
$x_i$, mole fraction of component $i$ in liquid phase
$y_i$, mole fraction of component $i$ in vapor phase
$Z_i$, compressibility factor
$\rho_i^v$, vapor phase density, g/cm$^3$
$\rho_i^l$, liquid density, g/cm$^3$
$\phi_i^L$, fugacity coefficient of component $i$ in liquid phase
$\phi_i^v$, fugacity coefficient of component $i$ in vapor phase
$\mu_i^c$, chemical potential of component $i$ in liquid phase
$\mu_i^v$, chemical potential of component $i$ in vapor phase
$\lambda$, tuning parameter in the modified Yong–Laplace equation
$\lambda_i$, tuning parameter $\lambda$ of component $i$
$\lambda_{mix}$, tuning parameter $\lambda$ of mixture

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