

Molecular Simulation Study of Vapor–Liquid Critical Properties of a Simple Fluid in Attractive Slit Pores: Crossover from 3D to 2D

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We present the effect of surface attraction on the vapor–liquid equilibria of square well (SW) fluids in slit pores of varying slit width from quasi 3D to 2D regime using molecular simulation methodologies. Four to five distinct linear regimes are found for shift in the critical temperature with inverse slit width, which is more prominent at higher surface fluid interaction strength. On the other hand, shift in the critical density and the critical pressure does not show any specific trend. Nevertheless, critical density and pressure show the sign of approaching toward the 3D bulk value with increase in the slit pore width, H , beyond 40 molecular diameters. The crossover from 3D to 2D behavior for attractive pores is observed around 14–16 molecular diameters, which is significantly different from the crossover behavior in the hydrophobic slit pore. Critical properties for $H \leq 2$ molecular diameters are indifferent to the surface characteristics. Corresponding state plot displays fluctuating positive deviation of spreading pressure for large pores and negative deviation for small pores from the bulk saturation value. Such behavior is more accentuated at stronger surface–fluid interaction strength. We also present vapor–liquid surface tensions of the SW fluid for different attractive planar slit-pores of variable slit-widths. Vapor–liquid surface tension or interfacial width values are insensitive to the surface–fluid interaction strength for slit width, $H \leq 2$ molecular diameters. At a given slit width and temperature, vapor–liquid interfacial width is found to decrease with increasing wall–fluid interaction for $H > 2$. However, interfacial properties approaches to the bulk value with increasing slit width. On the other hand, surface tension at a reduced temperature displays a nonmonotonic behavior with the change in H , which is in good agreement with the nature of the corresponding scaled interfacial width.

1. Introduction

It has been observed that confined fluids in micro- to nanometer pore sizes, regardless of geometry, exhibit minimal to significant deviations from bulk thermophysical and structural properties.^{1–3} These differences have generated great interest, as confined fluids feature conspicuously in both technology and nature. Recent investigations^{4–8} suggest that dimensionality of the system largely determines the behavior of materials under confinements. Several studies by theory, molecular simulations, and experiments have been performed to understand various changes in the equilibrium and the dynamical properties of the confined fluid.^{9–22} However, some inherent limitations are always associated with different approaches, which limit its applicability. For example, experimental approach is not feasible to capture the fluid properties in ultra nanopores or if it does it may give only very approximate information on molecular level details from the existing techniques. On the other hand, elegance of molecular simulation accompanied with modern day computing power and new efficient algorithms have been useful in investigating the properties of fluids confined in nanopores of few molecular diameters, which can be used to bridge the theory and the experimental outcomes. Moreover, molecular simulation methods can provide a microscopic picture of a fluid in the interaction field of the confined space and enable one to examine the underlying physics.

Detailed knowledge of the phase coexistence properties of confined fluids is of crucial importance for the interpretation of experimental data on fluids in nanopores. This further can be

helpful to optimize the various industrial processes.^{23–30} Burgess et al.,³¹ Keizer et al.,³² Machin,³³ and others^{34,35} observed that vapor–liquid critical temperature is suppressed under confinement. This decrease in the critical temperature increases as pore size decreases. However, due to wide pore size distribution and irregular pore geometry, it has not been possible to establish a quantitative relation between critical point shift and pore size. In recent years with the discovery of well-defined geometry of mesoporous materials, such as MCM-41,³⁶ MCM-48, and SBA-15,³⁷ allowed direct experimental measurements of critical points with some quantitative linear trends. For example, Thommes et al.³⁸ and Morishige et al.³⁹ observed experimentally that the shift in the critical temperature has linear dependence on the inverse pore width. Further, Vishnyakov et al.⁴⁰ performed Monte Carlo simulations on carbon slit pore and obtain the similar results as seen experimentally in former investigations; however, the simulations were limited to five molecular diameters. On the other hand, later investigations of Vortler⁴¹ suggest nonlinear dependence of shift in critical temperature as a more generic behavior in nanopores. In another investigation pertaining to square well fluid, Zhang and Wang⁴² studied the shift in the critical temperature in a cylindrical pore for various wall–fluid and fluid–fluid interaction strengths, using DFT calculations, and found a nonmonotonic behavior; additionally, Zhang and Wang's study⁴² on critical density in cylindrical pore indicates monotonic behavior with wall–fluid interactions. In a subsequent work, Singh et al.⁴³ reported similar observation of shift in critical temperature for square well fluids in slit pores; critical temperature first increase with the increase in the wall–fluid interaction strength and decrease subsequently on

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further increase in the wall–fluid interaction strength. In a recent investigation with variable square-well fluids under hard slit-pore confinements, Jana et al.⁴⁴ observed two different linear regimes in the shift in critical temperature with inverse slit width; whereas, investigations on critical density revealed fluctuations with local maxima and minima. However, in all the above studies, a comprehensive study of the effect of surface–fluid interaction on the crossover from 3D to 2D in terms of critical properties is missing. This is our main objective of the current investigation. In addition, this work will also provide insight to the effect of pore size and surface attraction on the approach of various properties toward the bulk values.

In the current work, using the SW potential model,^{45–49} we have explored the effect of wall–fluid interaction on the critical, structural, and vapor–liquid interfacial properties in slit pore with varying slit-width from 1 to 40 molecular diameters. The paper is organized as follows. Section 2 outlines the potential models and simulation details. In section 3, we present the results of our investigation, and section 4 concludes the study.

2. Simulation Details

In this work, we have employed grand-canonical transition matrix Monte Carlo (GC-TMMC) to calculate vapor–liquid phase diagram and surface tension. The method is described in detail elsewhere.^{43,50} GC-TMMC has been applied recently for variety of systems^{51–57} mainly due to ease of utilizing the parallel processors and efficiency over GEMC.⁵⁸ GC-TMMC along with finite size scaling (FSS) analysis of Binder⁵⁹ can also be used to find the surface tension of vapor–liquid under confinement as shown in our earlier work.⁴³

In this work, fluid–fluid and wall–fluid interactions are represented by the following square-well potentials:

$$u_{\text{ff}}(r) = \begin{cases} \infty, & 0 < r < \sigma_{\text{ff}} \\ -\varepsilon_{\text{ff}}, & \sigma_{\text{ff}} \leq r < \lambda_{\text{ff}}\sigma_{\text{ff}} \\ 0, & \lambda_{\text{ff}}\sigma_{\text{ff}} \leq r \end{cases}$$

$$u_{\text{wf}}(z) = \begin{cases} \infty, & 0 < z < \sigma_{\text{ff}}/2 \\ -\varepsilon_{\text{wf}}, & \sigma_{\text{ff}}/2 \leq z < \lambda_{\text{wf}}\sigma_{\text{ff}} \\ 0, & \lambda_{\text{wf}}\sigma_{\text{ff}} \leq z \end{cases} \quad (1)$$

where r is the interparticle separation distance, z is separation distance of the particle from the surface, $\lambda_{\text{ff}}\sigma_{\text{ff}}$ is the fluid–fluid potential well diameter, ε_{ff} is the depth of the fluid–fluid potential well, σ_{ff} is the diameter of the fluid–fluid hard core, $\lambda_{\text{wf}}\sigma_{\text{ff}}$ is the fluid–wall potential well diameter, and ε_{wf} is the depth of the fluid–wall potential. All quantities reported in the rest of the article are made adimensional using characteristic energy, ε_{ff} , and length scale, σ_{ff} . For example, temperature, pressure, and surface tension are scaled by $\varepsilon_{\text{ff}}/k$, $\varepsilon_{\text{ff}}/\sigma_{\text{ff}}^3$, and $\varepsilon_{\text{ff}}/\sigma_{\text{ff}}^2$, respectively. In this work, λ_{ff} , λ_{wf} , and ε_{ff} are kept 1.5, 1.0, and 1.0, respectively, and ε_{wf} is varied discretely from 2 to 6.

Critical parameters are estimated by using the coexistence data obtained via GC-TMMC and the least-squares fit of the following scaling law:⁶⁰

$$\rho_l - \rho_v = C \left(1 - \frac{T}{T_c}\right)^\beta \quad (2)$$

where, ρ_l , ρ_v , and T_c are coexistence liquid and vapor number densities and critical temperature, respectively; C and β are fitting parameters. The parameter β is also known as order parameter critical exponent. The critical temperature, T_c , estimated from eq 2, is used to calculate the critical density, ρ_c , from the least-squares fit of the following equation:

$$\frac{\rho_l + \rho_v}{2} = \rho_c + D(T - T_c) \quad (3)$$

where D is a fitting parameter.

Critical pressure, P_c , is calculated using the least-squares fitting of the saturation pressure data obtained from the GC-TMMC simulations to the following expression, which has similar form as the Antoine equation:

$$\ln P_c = A - \frac{B}{T_c} \quad (4)$$

where A and B are fitting parameters. The above empirical form is also utilized to obtain the critical pressure for confined fluids as shown earlier for square-well fluids⁴³ and alkanes.⁶¹

The saturated z -density profiles (profiles perpendicular to the slit surface), ρ_z , are obtained by recording $\rho(N, z)$ for each particle number sampled during GC-TMMC simulations. Coexistence density profiles are finally calculated using the following expression below:

$$\rho(z)_{\text{vapor/liquid}} = \frac{\sum_{i \in \text{vapor/liquid}} \Pi_C(i) \rho(i, z)}{\sum_{i \in \text{vapor/liquid}} \Pi_C(i)} \quad (5)$$

where Π_C is the coexistence probability density distribution obtained from the application of histogram reweighting technique⁶² on the transition matrix generated from the GC-TMMC simulation.

The interfacial free energy of a two-dimensional surface can be expressed with the system size according to the Binder's formalism,⁵⁹ and is given by

$$\beta\gamma_L = \frac{\beta F_L}{2A} = C_1 \frac{1}{A} + C_2 \frac{\ln L}{A} + \beta\gamma_\infty \quad (6)$$

where γ_L is an apparent system-size-dependent surface tension, γ_∞ is the true infinite-system ($L \rightarrow \infty$) interfacial tension, and C_1 and C_2 are constants. The method enables one to evaluate the infinite-system size interfacial tension by extrapolating a series of finite-system interfacial free energies.

Grand-canonical simulations are conducted with 30% displacement and 70% insertion/deletion moves. Although, periodic boundary conditions were implemented in the unconfined directions but to reduce any significant finite-size effect⁶³ of simulation cell size, on the coexistence properties, the maximum numbers of particles in the simulation cell were varied from 800 to 38000, depending on the slit-width studied in this work. To calculate the surface tension using GC-TMMC and finite size scaling, we performed simulations for different box lengths varying from $L \sim 12$ to 55 depending on the slit-width. Four independent runs are conducted to obtain the statistical error in critical properties and vapor–liquid surface tension. The errors

in pore critical temperature (T_{cp}), critical density (ρ_{cp}), and critical pressure (P_{cp}) for the quasi-2D and 2D regime, $1 \leq H \leq 2$, are less than 0.04, 0.6, and 0.2%, respectively; whereas, for the $H > 2$ corresponding errors are less than 0.1, 0.05, and 0.16%, respectively. On the other hand, statistical errors in surface tension for the studied slit-widths at two different reduced temperatures, T_R ($T_R = T/T_{cp}$), 0.91 and 0.935 are less than 6.7 and 2.3%, respectively.

Vapor–liquid interfacial width is calculated using molecular dynamics (MD) simulation.⁴³ The slab-based molecular simulation technique is used to determine the density profile of the coexisting vapor and liquid phases. We start with the simulation box filled with molecules placed on a FCC lattice such that density is slightly higher than the coexistence liquid density. In the next step, we create a slab by expanding the box in one direction perpendicular to the confined axis. Periodic boundary conditions are applied to the nonconfined directions. MD simulations are conducted in the canonical ensemble (NVT) with $N = 2500$ particles, where the liquid phase is present as a slab of the simulation box in coexistence with the vapor phase filling up the rest of the simulation cell. The trajectories of the particles are obtained by integration of Newton's equation of motions (EOM). The EOM for each particle is integrated with the velocity-Verlet⁶⁴ algorithm with a time step Δt . The reduced time step Δt (in units of $\sigma\sqrt{m/\epsilon}$) is fixed at 0.04. We have taken 2×10^5 time steps as the equilibration period and equal number for the production period. Density profiles obtained from NVT-MD simulations is fitted to the following expression to evaluate the interfacial width:⁶⁵

$$\rho(z) = \frac{1}{2}(\rho_l + \rho_v) - \frac{1}{2}(\rho_l - \rho_v) \tanh\left(\frac{2(z - z_0)}{\delta}\right) \quad (7)$$

where δ is the interfacial width and z_0 is the position for Gibbs dividing surface.

3. Results and Discussion

3.1. Effect of Slit Width and Surface Attraction on Vapor–Liquid Phase Equilibria.

We start our discussion with the effect of confinement and surface attraction on the vapor–liquid phase diagram of the SW fluid. Figure 1a,b presents the vapor liquid phase diagram of SW fluid confined in slit pore for two typical wall–fluid interactions, $\epsilon_{wf} = 2$ and 4, and slit widths, H , ranging from 40 molecular diameter (quasi-3D) to the 1 molecular diameter (2D). Bulk vapor–liquid phase diagram is included in Figure 1a,b to see the comparative behavior of coexistence densities of the confined fluid. Figure 1a,b clearly depicts the significant effect of surface attraction and slit width on coexistence densities and, in turn, on critical properties. Our investigations indicate that vapor phase densities for $H = 40$ and $\epsilon_{wf} = 2$ are much closer to that of bulk vapor phase compared to that for $\epsilon_{wf} = 4$. On the other hand, corresponding liquid density branch, at both the surface attractions, almost coincide with bulk phase liquid densities. Increase in surface attraction shift the vapor density branch toward higher value as seen for $\epsilon_{wf} = 4$, which resulted in increased critical density relative to that of bulk or lower attractive surface, $\epsilon_{wf} = 2$, for the same $H = 40$. Moreover, at $H = 40$, critical temperatures with either of the surface attractions are extremely close to the bulk critical temperature. On the other hand, decrease in the pore size decreases the critical temperature monotonically until $H < 2$ (quasi-2D region), where T_{cp} becomes

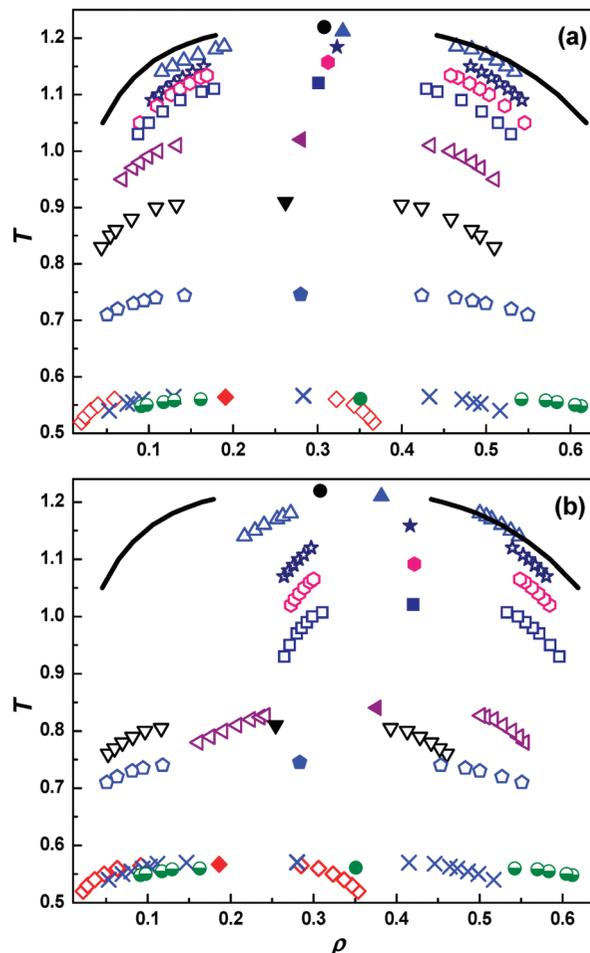


Figure 1. Temperature–density vapor–liquid coexistence curve for the square-well fluid in the slit pore confinement of pore width, H , varying from 40 to 1 for two different wall–fluid interactions, $\epsilon_{wf} = 2$ and 4 are shown in (a) and (b), respectively. Solid curves represent the bulk coexistence densities with filled black circle as the bulk critical points. Open and filled symbols represent the coexistence densities and critical points, respectively. In (a) and (b), from top, symbols triangle, star, hexagon, square, left triangle, inverted triangle, pentagon, diamond, cross, and half-filled circles represent $H = 40, 12, 8, 6, 4, 3, 2, 1.9, 1.25$, and 1, respectively. The thick cross symbol represents critical point for $H = 1.25$.

constant irrespective of the surface attraction. However, pore critical density fluctuates and goes through different local maxima and minima as H decreases from 40 to 1. This behavior is seen for $\epsilon_{wf} = 2$ and 4, as shown in Figure 1a,b.

Interestingly, it is observed that vapor–liquid coexistence densities and critical properties remain indifferent for $H \leq 2$, irrespective of the wall–fluid interactions studied in the current investigation. This insensitiveness behavior is depicted in Figure 2a for a typical case of $H = 1.7$ for three different wall–fluid interactions. Similar insensitiveness is also observed in local z -density profiles of the coexisting vapor and liquid cases as shown in Figure 2b for two typical wall–fluid interactions. On the major reason for the insensitiveness behavior is that the layering near the wall, which is the main cause for the difference in higher pore width for different surface field, is missing for $H \leq 2$ as the maximum number of layers possible is limited to 2 for $H = 2$, for example. Hence, there is no additional effect of wall attraction to increase the layering near the wall for $H \leq 2$. Thus, critical properties is insensitive to the surface field for $H \leq 2$.

In Figure 3a, we present the shift in pore critical temperature, $[(T_{cb} - T_{cp})/T_{cb}]$, versus inverse H for four different wall–fluid

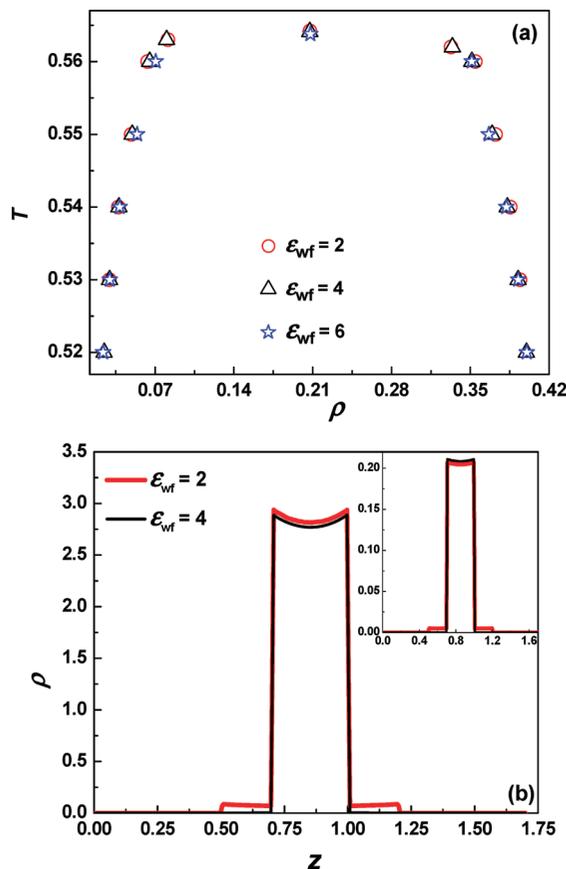


Figure 2. Comparison of temperature–density vapor–liquid coexistence curve for the square-well fluid in the slit pore confinement of $H = 1.7$ for three different wall–fluid interactions are shown in (a). In (b), a typical local z -density profile of coexisting vapor and liquid phases are shown at a fixed $T = 0.53$ for two different wall–fluid interactions. Inset shows the vapor density profiles.

interactions, $\epsilon_{wf} = 2, 3, 4,$ and 6 studied in the current work, and also include $\epsilon_{wf} = 0$ results from our previous work.⁴⁴ Here, T_{cb} is the bulk critical temperature. Interestingly, various different linear regimes are being observed for the shift in pore critical temperature. It is apparent from Figure 3a that for $H \leq 2$ and $H > 20$ shift in the pore critical temperature is insensitive to the surface–fluid attraction strength. On the other hand, for $2 < H \leq 20$, a shift in T_{cp} is sensitive to the wall–fluid interaction strength and becomes more prominent with increasing wall–fluid interaction strength. This behavior primarily indicates significant differences in structural properties of vapor and liquid like phases in various regimes of slit widths. These linear regimes have different slopes, which suggest that the rate of shift in T_{cp} is not constant across the slit width range. These distinct linear regimes, which were missing in the hard slit pore, generated a great interest for this investigation. For example, with $\epsilon_{wf} = 4$, a change in H from 5 to 4 leads to a higher shift in T_{cp} compared to the change in H from 4 to 3, which in view of the scaling law⁶⁰ indicates that a change in the difference of the average coexistence vapor and liquid densities, $(\rho_l - \rho_v)$ is larger for the change in H from 5 to 4 as compared to that for 4 to 3. Similarly, a shift in T_{cp} is found to be lower for the change in H from 3 to 2 compared to that for the change in H from 2 to 1.9, which in turn indicates a relatively less change in $(\rho_l - \rho_v)$ for the former case.

To get the physical insight for the different linear regimes of shift in T_{cp} observed in Figure 3a, a closer look of fluid phase density profiles under these confinements needs to be considered.

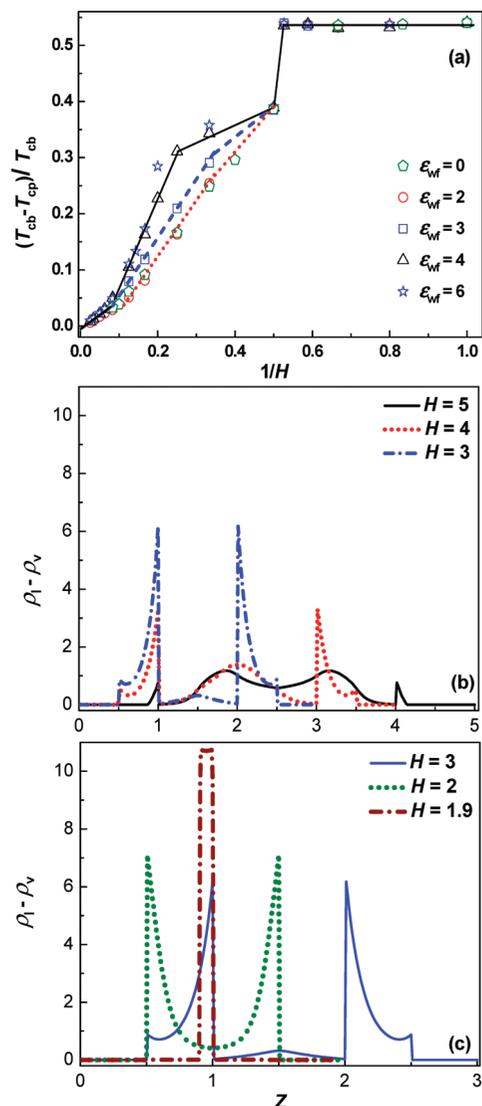


Figure 3. Shift in the pore critical temperature vs inverse H is shown in (a) for different wall–fluid interactions. Lines serve as a guide to the eye. In (b) and (c), local z -density profile differences of coexisting liquid and vapor phases are shown for different H with a typical wall–fluid interaction, $\epsilon_{wf} = 4$. All profiles in (b) and (c) are at the same reduced temperature, $T_R = 0.94$.

Figure 3b displays the local z -density profiles of coexisting vapor and liquid phases for $H = 5, 4,$ and 3 at a fixed reduced temperature, $T_R = T/T_{cp} = 0.94$, for a typical case of wall fluid interaction strength $\epsilon_{wf} = 4$. It is observed that, with a fixed wall–fluid interaction, distribution of fluid particles under confinement changes significantly with the degree of confinement. For example, change in H from 5 to 4, changes the difference of average coexistence vapor–liquid density by 18%. On the other hand, a change in H from 4 to 3 changes $(\rho_l - \rho_v)$ only by 9%. This indicates that, even though change in the extent of confinement of the two cases is the same, the change in the difference of the average coexistence vapor–liquid density is doubled. This indicates that structural changes in fluid phase with degree of confinement play a significant role in their respective average coexistence densities and, hence, on the critical temperature. This explains the observation of Figure 3a, where we noticed a larger slope for the shift in T_{cp} for $H = 8-4$ regime as compared to that for $H = 2-4$ regime. Here, it is also important to point out another aspect of the coexistence density profile observed with stronger surface–fluid attraction. It is observed that, with higher surface attractions, $\epsilon_{wf} = 4$ and

6 and $H > 4$, two coexistence phases are difficult to distinguish near the slit surfaces. Liquid profile dominates over vapor throughout the slit width, except near the surface, where due to the stronger field, even the vapor phase is seen to have significant layering. This is also evident from a typical vapor–liquid density profile shown in Figure 7b for $\epsilon_{wf} = 4$ and $H = 8$.

To explain the shift in T_{cp} for regimes, $H = 4$ to 2 and 2 to 1.9, we have investigated the local z -density profiles of the coexisting vapor and liquid phases in the above-mentioned slit pores at a fixed reduced temperature, $T_R = 0.94$ for $\epsilon_{wf} = 4$ and is shown in Figure 3c. We observed that, for a change in the H from 3 to 2, change in the difference of average coexistence vapor–liquid density is around 22%, whereas, for a change in H from 2 to 1.9, the average coexistence density difference is found to alter by around 40%, which is dramatically large with respect to the change in the extent of confinement. This abrupt change in coexistence density difference resulted in a sharp change in the slope of shift in T_{cp} , as seen in Figure 3a.

3.2. Critical Properties in Attractive Pores: Crossover from 3D to 2D. In this work, critical temperature is calculated by rectilinear diameter approach, as mentioned in section 2. We have also verified the correctness of the critical temperature due to the rectilinear diameter approach with that predicted from the extrapolation of the temperature vs surface tension curve for which surface tension approaches zero. A typical comparison with $\epsilon_{wf} = 4$ is done for two cases of slit widths, $H = 2$ and 8. The value of vapor–liquid surface tension, γ , obtained from the extrapolation for slit widths, $H = 2$ and 8, are practically zero, as $T \rightarrow T_{cp}$. For example, in the vicinity of T_{cp} (estimated from rectilinear diameter approach), γ for $H = 2$ and 8 is around 2.56×10^{-21} and 3.87×10^{-26} , respectively, estimated from the fit of GC-TMMC+FSS data. This shows that rectilinear diameter approach provides a reasonable good estimate of T_{cp} .

In a recent investigation, Vortler et al.⁶³ reported the system size effect on phase equilibria in two- (2D) and three-dimensional (3D, bulk) square-well fluids. In that investigation, it has been reported that the influence of the system size on the coexistence properties of the bulk (3D) fluid is weak. On the other hand, the author suggested that with 2D (monolayer) fluid, 800–1000 particles are sufficient to predict the reasonably accurate coexistence properties. However, the authors did not study the effect of system size on critical properties of quasi-3D and quasi-2D square-well fluid. In the current investigation, we studied the effect of system size on the critical properties for some typical cases of quasi-3D and quasi-2D square-well fluid. We have investigated system size effect for the three typical cases of $H = 8, 2$, and 1.9, with $\epsilon_{wf} = 4$. The same set of temperatures is used to estimate the critical properties for different system size. We observed that for $H = 8$ by increasing N_{max} from 1000 to 3500 particles, T_{cp} decreases and ρ_{cp} increases by 0.7 and 0.04%, respectively. Similarly, for $H = 2$, by increasing N_{max} from around 810 to 4100 particles T_{cp} decreases and ρ_{cp} increases by 0.8 and 0.3%, respectively. On the other hand, for $H = 1.9$, by increasing N_{max} from around 640 to 2440 particles, T_{cp} and ρ_{cp} decreases by around 1 and 2%, respectively. This suggests that the system size has a significant effect on the critical properties for N_{max} , in the GCMC simulations, less than some threshold value, which depends upon pore size of the system. In this investigation, N_{max} varied from 800 (for $H = 1$) to 38000 ($H = 40$) particles. Considering a reasonable accuracy in the evaluated critical properties, we now present a

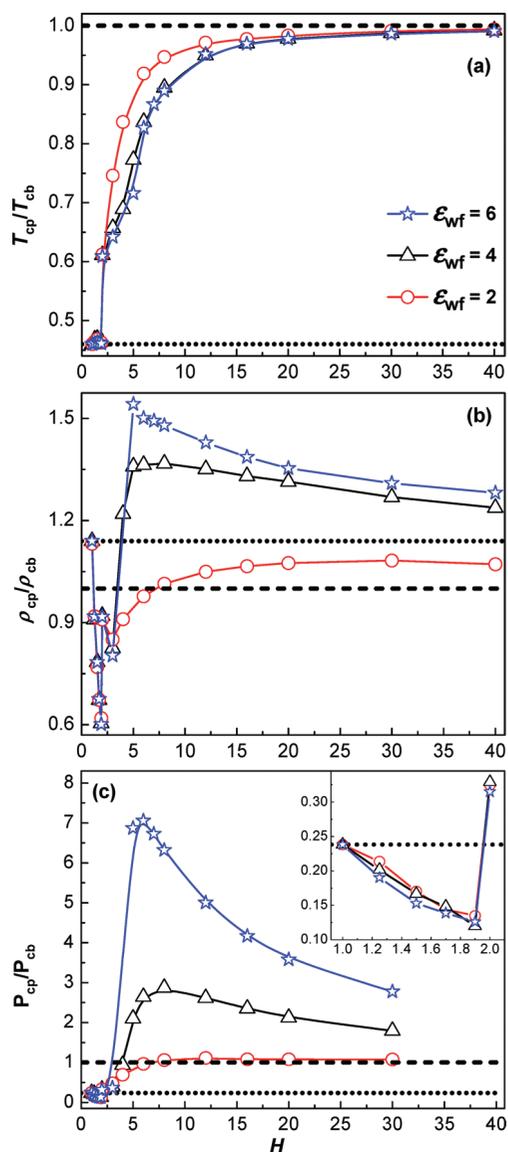


Figure 4. Dependence of pore critical temperatures, critical density, and critical pressure (all reduced by the corresponding bulk values) on slit width, H , varying between the 3D (represented by dash line) to 2D (represented by dotted line) geometry are shown in (a), (b), and (c), respectively, for three different wall–fluid interactions. In the inset of (c), critical pressure data for $H < 3$ is shown. Symbols represent the simulation data. Lines serve as a guide to the eye.

systematic analysis of the effect of confinement on various critical properties.

Figure 4a presents a rigorous comparison of variation of the pore critical temperature, reduced by 3D bulk value, T_{cp}/T_{cb} (where $T_{cb} = 1.219(1)$ is the bulk critical temperature obtained in this investigation and also predicted in earlier investigations^{66–68}), of square-well fluid versus slit width, H , for three typical wall–fluid interactions, $\epsilon_{wf} = 2, 4$, and 6. It is clearly seen that for $H \leq 2$ or $H > 20$ surface attraction does not play any significant role on the critical temperature. On the other hand, for $2 < H < 20$, T_{cp}/T_{cb} is sensitive to the surface field. T_{cp}/T_{cb} changes monotonically with H and slowly approaches 1 for H much larger than 40. Nevertheless, for $H = 40$ and $\epsilon_{wf} = 2, 4$, and 6, T_{cp}/T_{cb} is 0.994, 0.992, and 0.991, respectively, which is close to the prediction from the mean field theory.⁶⁹

Critical density is found to increase in the quasi-2D regime ($H < 2$), with decrease in the pore size, even though T_{cp} remains almost constant, similar to the case of hard slit pore.⁴⁴ This is

due to the shifting of vapor and liquid density branch toward higher value. This shifting is resulted in the increase of coexistence density diameters, $[(\rho_l + \rho_v)/2]$; as a result, critical density increases. For example, for a typical case of $\varepsilon_{wf} = 4$ and $T_R = 0.94$, change in H from 1.9 to 1.25 increases coexistence density diameter around 51% that in turn resulted in around a 50% increase in critical density.

Figure 4b,c presents the comparison of variation in the ρ_{cp}/ρ_{cb} and P_{cp}/P_{cb} versus H for three different wall–fluid interactions, $\varepsilon_{wf} = 2, 4,$ and 6 . Similar to other properties, these two critical properties remains unaffected by the strength of surface–fluid interaction for $H \leq 2$; however, these properties are significantly affected by the value of ε_{wf} for $H > 2$. Figure 4b shows that ρ_{cp}/ρ_{cb} follows a nonmonotonic path contrary to T_{cp}/T_{cb} ; however, it shows a sign of approaching toward 3D bulk value, $\rho_{c,R}(3D)$ as $H \rightarrow \infty$. These investigations also indicate that, for $H > 3$, the rate of change in ρ_{cp}/ρ_{cb} is comparatively lower for the case of weaker wall–fluid attraction as compared to that seen for the stronger one. Similar nonmonotonic behavior is also observed for P_{cp}/P_{cb} , as shown in Figure 4c. With these investigations it is apparent that, in the extremely small slit pores, $H \leq 2$, all three of the critical properties are independent of the surface attraction. For larger pores, unlike the critical temperature, the critical density and critical pressure approach toward the bulk value are significantly affected by the wall–fluid interaction strength. Though, at $H = 40$, for $\varepsilon_{wf} = 2, 4,$ and 6 , $\rho_{cp}/\rho_{cb} = 1.07, 1.24,$ and 1.28 , respectively; on the other hand, at $H = 30$, P_{cp}/P_{cb} is $1.07, 1.8,$ and 2.77 , respectively, for the studied interactions. Clearly, with higher surface attractions, $\varepsilon_{wf} = 4$ and 6 , critical density and critical pressure are comparatively more away from the bulk value for the highest slit width studied in this work. This indicates that pore critical temperature approaches to bulk 3D value with relatively quicker compared to the critical density and critical pressure. Moreover, the rate of approach of pore critical temperature toward bulk value slows down significantly at higher slit widths. This work clearly indicates that threshold pore size above which fluid is expected to behave as bulk is strongly dependent on the surface–fluid interaction strength. For a weak attractive pore, $\varepsilon_{wf} < 2$, $H = 40$ is a reasonable large pore size, where critical properties are within 5% of the bulk critical values.

3.3. Critical Exponents and Crossover from 3D to 2D.

3.3.1. Correlation Length Critical Exponent. Fisher and Nakanishi⁶⁹ with the help of scaling arguments showed that the decrease in the critical temperature in larger pores should obey the relation $(T_{cb} - T_{cp})/T_{cb} = kH^{-1/\nu}$, where ν is the critical exponent for the correlation length and k is a proportionality constant. To account for the strong adsorbed layer on pore walls it is necessary to replace the true pore width H , by a modified pore width, H_{eff} , which accounts for the adsorbed layers that form prior to capillary condensation. In an earlier work by Brovchenko et al.,⁷⁰ for water in hydrophobic slit pores, it was shown that the crossover from 3D to 2D behavior occurs roughly around 8 molecular diameters. However, the largest pore studied in that work was limited to only 10 molecular diameters. In the current work we have investigated the crossover behavior of the square-well fluid in three different surface attractions. Using Ising 3D (bulk) correlation length critical exponent⁷¹ $\nu(3D) = 0.63$ and Ising 2D correlation length critical exponent^{72,73} $\nu = 1$, we have evaluated the effective layering thickness, t , of the adsorbed layer in the slit pore by fitting the logarithmic form of the relation $(T_{cb} - T_{cp})/T_{cb} = k(H - t)^{-1/\nu}$. We observed that for larger pore width the layering thickness, t , is insignificant irrespective of the surface attraction. However, for smaller pores

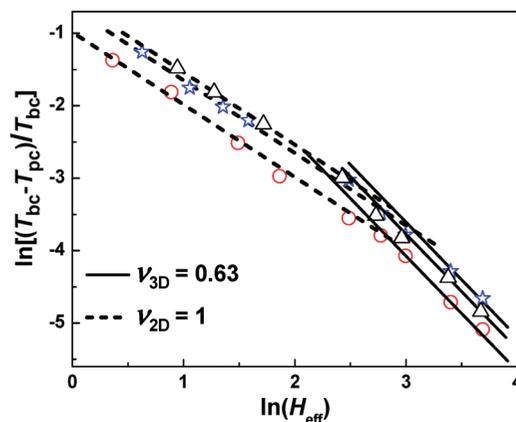


Figure 5. Crossover from 3D to 2D of square-well fluid for three different surface attractions, $\varepsilon_{wf} = 2, 4,$ and 6 are shown. Correlation length critical exponent, ν , is represented by solid and dashed lines for 3D and 2D regimes, respectively. Symbols have the same meaning as in Figure 4.

it is appreciable and cannot be neglected. Layering thickness is observed to be around 1.5, 2.4, and 3.1 for the surface attractions $\varepsilon_{wf} = 2, 4,$ and 6 , respectively, in the smaller pore regime. However, in the larger pore regime the layering thickness of around $6.2 \times 10^{-13}, 2.8 \times 10^{-9},$ and 8.1×10^{-9} are observed for $\varepsilon_{wf} = 2-6$, which are negligibly small. In Figure 5, shift in critical temperature, $(T_{cb} - T_{cp})/T_{cb}$, is plotted as a function of effective slit width, H_{eff} (i.e., $H - t$), on a log–log scale for three typical wall–fluid interactions, $\varepsilon_{wf} = 2, 4,$ and 6 . It is evident from Figure 5 that the crossover from 3D to 2D is observed at around $H \sim 14-16$ for the studied surface attractions in this work. However, based on our previous work on *n*-alkane⁶¹ in graphite and mica slit pore, it would be fair to conclude that crossover from 3D to 2D is dependent also on the fluid structure along with the surface field.

3.3.2. Critical Exponent of the Order Parameter. Coexistence envelope shape is characterized by the relation of the order parameter, $\Delta\rho = (\rho_l - \rho_v)/2$, with temperature. Below T_{cp} , $\Delta\rho$, should follow a universal scaling law:^{74,75} $\Delta\rho \sim [(T_{cp} - T)/T_{cp}]^\beta$. In Figure 6a, $\Delta\rho$ is shown as a function of reduced temperature, $(T_{cp} - T)/T_{cp}$, on a log–log scale for $\varepsilon_{wf} = 2$, and H varying from 40 to 1. Slope of the lines represents the β value for the respective slit widths. Interestingly, for $H = 8-40$, the order parameters falls very close to each other perhaps due to the similar shape of the coexistence envelopes as seen in Figure 1. The critical exponents obtained for different surface field are plotted against inverse H and is shown in Figure 6b. It is evident that β approaches 2D Ising value⁷⁶ of 0.125 with decreasing H . However, at larger slit widths, β value is overestimated from the Ising 3D value. For example, for $H = 40$, β is overestimated from the Ising 3D value by 20, 24, and 29% for $\varepsilon_{wf} = 2, 4,$ and 6 , respectively. The value of β observed for 3D bulk square-well fluid, on the other hand, in this investigation from a least-squares fit is 0.33 ± 0.01 , which is very close to the Ising 3D value of 0.326. Overestimation of β under confinement for larger pores ($H \sim 30-40$) generated an interest to see if there is any effect of system size on the β . To this end, we studied the effect of system size on the critical exponent, β , for some typical cases of slit width, $H = 8, 2,$ and 1.9 , with $\varepsilon_{wf} = 4$. We observed that, for $H = 8$, increasing N_{max} from around 1000 to 3500 particles with the same range of temperatures for the critical point calculation in both the cases decreases β by 10%. Similarly, for $H = 2$, increasing N_{max} from around 810 to 4100 particles decreases β by 14%. On the other hand, in the quasi-2D regime, for $H = 1.9$, increasing N_{max} from around 640 to

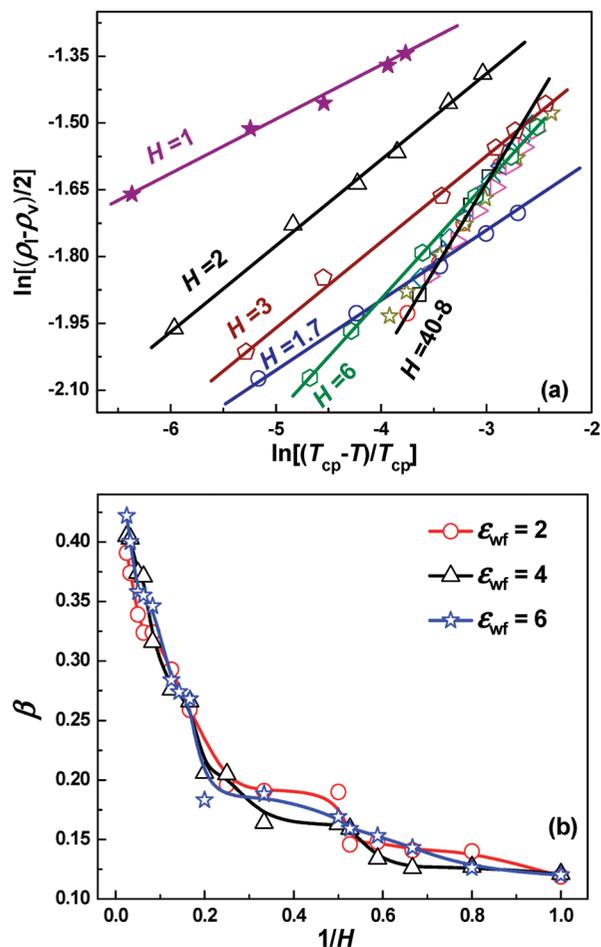


Figure 6. Variation of order parameter, $\Delta\rho$, from pore averaged densities with reduced temperature, $(T_{cp} - T)/T_{cp}$, is shown on a log–log scale for a typical surface attraction, $\epsilon_{wf} = 2$, in (a). The pore widths H are indicated. Slope of the lines represent the order parameter critical exponent, β . In (b), variation in β is shown as a function of inverse H for three different values of ϵ_{wf} . Error in β (1–3%) is of the order of symbol size.

2440 particles decreases β by 5% only. Moreover, for $H = 40$, the largest slit width studied in this work, even $N_{max} = 38000$ led to an overestimation of β value by around 29%. These investigations indicate that β does show a significant effect from the system size, as opposed to what is seen for the critical properties. This probably suggests that system size should be considered for obtaining a good estimate of β . For any accurate estimation of critical exponents, finite system size scaling approach is more appropriate.⁷⁷ Nevertheless, with the range of system size considered in this work, we did not notice any significant change on the critical properties of the vapor–liquid phase equilibria as also discussed in the previous subsection.

3.4. Corresponding State Analysis of Vapor–Liquid Phase Equilibria. Figure 7a and b present the corresponding state plot of the phase diagram and density profile, respectively, of the SW fluid confined in an attractive slit pore with $H = 8$. Figure 7a shows that at a higher slit width, $H = 8$, nature of surfaces plays a significant role on the coexistence phase diagram. It is observed that, at a given reduced temperature T_R , stronger wall–fluid interaction tends to increase the reduced vapor density and lowers the reduced liquid density. To understand this behavior of coexistence phase diagram, we evaluated the local z -density profiles of coexisting phases at a typical reduced temperature, $T_R = 0.94$, for the two typical attractive surfaces, $\epsilon_{wf} = 2$ and 4. Figure 7b shows the typical z -density profiles of

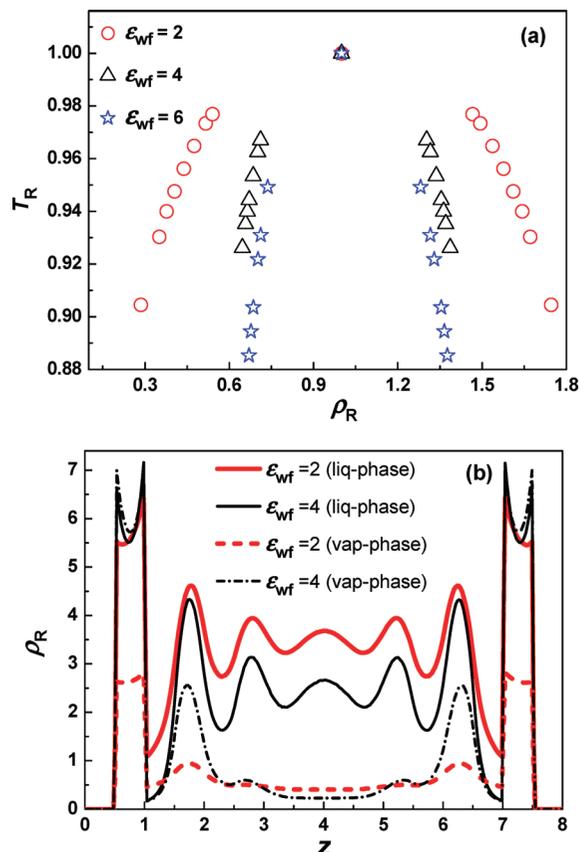


Figure 7. Corresponding state plots of vapor–liquid coexistence envelopes at $H = 8$ for three different ϵ_{wf} are shown in (a). Typical z -density profiles of coexisting vapor and liquid phases are shown in (b) at $T_R = 0.94$.

the two coexisting phases, which clearly indicates the denser vapor layer for stronger surface attraction; hence, average vapor density with stronger surface attraction is higher compared to that for the case of lower surface attraction. On the other hand, peak density of the liquid layer near the surface is not much different for different surface interaction strengths; however, the reduced density of the layer away from the surface decreases with an increase in the surface–fluid interaction strength. The dominance of liquid density peaks in the region away from surfaces of the slit width does in fact result in higher average reduced liquid density for the pore with $\epsilon_{wf} = 2$, as observed in Figure 7a.

Figure 8 shows the corresponding state plot of spreading pressure (spreading pressure is the pressure component parallel to the confining surfaces, which in this work is the same as the vapor–liquid equilibrium pressure), P_R ($P_R = P/P_{cp}$), versus T_R , for the confined fluid with various slit widths for a typical wall–fluid interaction, $\epsilon_{wf} = 4$. In addition, bulk value is also included in Figure 8 for comparison. Chen et al.⁷⁸ earlier predicted that nanocapillary pressure of a fluid oscillates with inverse of capillary size, as it approaches to few molecular diameters, which suggests that the behavior of fluids in a nanosize capillary deviates from that of Kelvin’s equation. In this work, specific calculations to check the behavior of Kelvin’s equation in small pores have not been performed; however, a certain indication of the deviation from Kelvin equation is probably reflected in the spreading pressures, under confinement, as shown in Figure 8. Similar observations of fluctuating positive and negative deviations were observed for the confined n-alkanes in mica and graphite slit pores reported in our earlier work.⁶¹ At a reduced temperature, spreading pressure at the largest slit

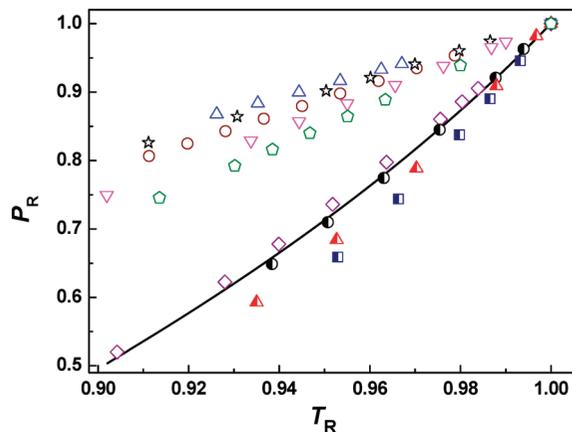


Figure 8. Reduced spreading pressure, P_R , vs reduced temperature, T_R , is shown for the bulk (3D) and the slit pore confined square-well fluid with a typical wall-attraction $\epsilon_{wf} = 4$. The solid curve represents the bulk value and the open symbols, pentagon, circle, triangle, star and diamond represent $H = 30, 16, 8, 6, 5$, and 4 , respectively; half-filled circle, square, and triangle represent $H = 3, 2$, and 1.9 , respectively. Half-filled symbols represent the data of negative deviation from the bulk.

width studied in this work is higher than the bulk saturation pressure and it increases with decrease in H until $H \sim 8$; subsequent reduction in H leads to decrease in the value and eventually coincide with the bulk saturation pressure at around $H = 4-3$. Further reduction in the H decreases the spreading pressure below the bulk saturation pressure and reaches to a minima at around $H = 2$. Below $H = 2$, spreading pressure again increases but remain below the bulk line. Interestingly, maximum negative deviation from the bulk saturation value is observed with $H = 2$, irrespective of the surface attraction studied in this work.

3.5. Vapor-Liquid Interfacial Tension under Confinement. The anomalous confined phase equilibria properties of a square well fluid discussed in the earlier section suggests that there might also be an interesting behavior of the vapor-liquid surface tension, γ , for various slit widths and wall-fluid interactions. Figure 9a shows the variation of γ versus inverse H for the two typical wall-fluid interactions. It is observed that for $H \leq 2$, γ remains almost unaffected with the change in the wall-fluid interaction strength as also suggested by the plot of phase diagrams as shown in Figure 2a. At larger slit widths, $H > 2$, the effect of wall-fluid interaction on surface tension is significant, which is akin to the behavior seen in the phase coexistence properties. It is observed that for $H > 2$, at the same T_R , vapor-liquid surface tension is larger for less attractive surface. This indicates that dissimilarity between vapor and liquid phases becomes more prominent for weaker wall-fluid interaction as compared to that for the stronger one. It is obvious from Figure 9a that for a fixed surface attraction and slit width, γ decreases with increasing temperature, as expected. It is apparent from Figure 9a that γ has a maxima at $H = 2$ for all the studied cases in this investigation and the surface tension value is extremely close to the respective bulk values. This indicates that at $H = 2$, dissimilarity is highest between the two coexisting phases. To see this dissimilarity of the two coexisting phases, we have evaluated the difference of liquid and vapor phases average densities for a typical case, $\epsilon_{wf} = 4$ and $T_R = 0.91$ and 0.935 , at $H = 1.5, 2$, and 3 . The difference in coexisting average vapor and liquid phase densities at the aforementioned slit widths for $T_R = 0.91$ and 0.935 are around $0.435, 0.569, 0.441$ and $0.408, 0.533, 0.411$, respectively. Clearly, at either temperature, the difference in the average

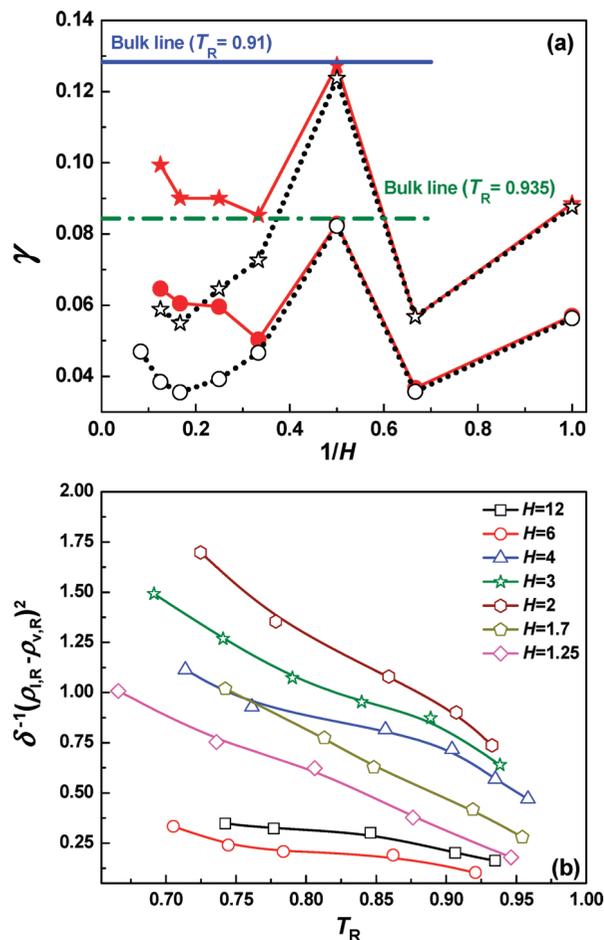


Figure 9. Vapor-liquid surface tension, γ vs inverse H of a square well fluid is shown in (a) at two different reduced temperatures, $T_R = 0.91$ and 0.935 , for $\epsilon_{wf} = 2$ and 4 . The two horizontal lines represent the corresponding bulk values. Filled symbols represent the case of $\epsilon_{wf} = 2$ and open symbols represent $\epsilon_{wf} = 4$. Symbols star and circle represent the case of $T_R = 0.91$ and 0.935 , respectively. In (b), $\delta^{-1}(\rho_{l,R} - \rho_{v,R})^2$ vs T_R is shown for various H , with a typical wall-fluid attraction, $\epsilon_{wf} = 4$. Error bars are of the order of symbol size.

coexistence densities is comparatively larger at $H = 2$ as compared to the neighboring slit widths. This comparatively larger dissimilarity in the two coexisting phases average densities are also reflected at the vapor-liquid interface in terms of a maxima of γ at $H = 2$. Moreover, with increasing H vapor-liquid surface tension is seen to approach toward the respective bulk values. It is noted that, for the bulk fluid, simulation box size can lead to oscillatory behavior in the γ from slab-based methodologies.^{79,80} In the current work, γ is calculated using GC-TMMC+FSS approach, which is not an explicit interface based method. There is no fluctuation seen in the finite size surface tension using the GC-TMMC technique. On the contrary, it gradually approaches to the infinite size surface tension.

Surface tension is related to interfacial width, δ , or thermal fluctuation of the interface.⁸¹ In this work, we investigate the vapor-liquid interfacial width by fitting the tan-hyperbolic function to the vapor-liquid density profile obtained from NVT-MD simulations. Interfacial width found to increase nonlinearly with temperature (figure not shown) for square-well fluids under attractive slit pore confinements, which is similar to the behavior seen for SW fluids confined in hard slit-pore.⁴⁴ Further, according to density functional theory of liquid-gas interface,⁸² γ is proportional to $\delta^{-1}(\rho_l - \rho_v)^2$. However, to put a proper perspective, we have used the densities in the reduced form. In

Figure 9b, $\delta^{-1}(\rho_{l,R} - \rho_{v,R})^2$ is plotted against reduced temperatures, T_R , for various slit width and a typical wall attraction case of $\varepsilon_{wf} = 4$. The nonmonotonic behavior shown in Figure 9b resembles the nonmonotonic behavior of γ at a fixed T_R and varying H , as shown in Figure 9a. The behavior change in the γ in the reduced form is similar hence not reported separately. Similar to Figure 9a, Figure 9b shows that the value of $\delta^{-1}(\rho_{l,R} - \rho_{v,R})^2$ at $H = 2$ is the maximum and the least for $H = 6$ for the studied range of T_R . Figure 9b clearly indicates that the γ values are directly related to the $\delta^{-1}(\rho_{l,R} - \rho_{v,R})^2$, as suggested by the DFT.⁸²

4. Conclusions

We investigated, in this work, the influence of pore size, ranging from 40 to 1 molecular diameter, on the phase coexistence envelope and various critical properties of a square-well fluid under confinement with attractive slit-pore surfaces. In contrast to the previous estimation, the dependence of shift in critical temperature versus inverse H is found to follow more than two linear regimes and this becomes more prominent as the surface–fluid attraction increases. In this investigation, with $\varepsilon_{wf} = 4$ and 6, around 4–5 linear regimes differing with each other in their slopes are observed. Interestingly, the change in slope is of nonmonotonic nature, as the degree of confinement ranges from quasi 3D to 2D geometry. On the other hand, the critical temperature under confinement is found to vary monotonically between 2D and 3D geometry and approaches slowly to the 3D value with increasing slit width. We observed that, for $H = 40$ and $\varepsilon_{wf} = 2, 4$ and 6, T_{cp}/T_{cb} is 0.994, 0.992, and 0.991, respectively. On the contrary, corresponding critical density and critical pressure are found to vary nonmonotonically with some fluctuations before it actually approaches the 3D value for infinitely large slit width. In general, the stronger the surface–fluid attraction, the slower the rate of approach toward the bulk value. Our current investigations indicate that crossover from 3D to 2D behavior for the square-well fluid occurs at around a 14–16 molecular diameter for attractive pores with $\varepsilon_{wf} = 2$ –6. Moreover, based on our earlier work on n -alkanes confined in graphite and mica slit pores, we can conclude that the crossover behavior is strongly dependent on the molecular structure of the fluid and the confining surfaces. This work also indicates that spreading pressure under attractive slit pore confinements fluctuates around the bulk saturation pressure. The role of different attractive surfaces on the critical and vapor–liquid interfacial properties is found to be insignificant for $H \leq 2$. However, the vapor–liquid interfacial tension under confinement is found to oscillate for $H < 8$. Similar oscillatory behavior is shown by the scaled interfacial width, $\delta^{-1}(\rho_{l,R} - \rho_{v,R})^2$, at fixed reduced temperature with varying slit width.

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