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Quasi-Two-Dimensional Phase Transition of Methane Adsorbed in Cylindrical Silica Mesopores[†]

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Abstract

Using Monte Carlo and molecular dynamics simulations, we examine the adsorption of methane in cylindrical silica mesopores in an effort to understand a possible phase transition of adsorbed methane in MCM-41 and SBA-15 silica that was previously identified by an unexpected increase in the adsorbed fluid density following capillary condensation, as measured by small-angle neutron scattering (SANS) [Chiang, W-S., et al., *Langmuir* **2016**, 32, 8849]. Our initial simulation results identify a roughly 10 % increase in the density of the liquidlike adsorbed phase for either an isotherm with increasing pressure or an isobar with decreasing temperature and that this densification is associated with a local maximum in the isosteric enthalpy of adsorption. Subsequent analysis of the simulated fluid, via computation of bond-orientational order parameters of specific annular layers of the adsorbed fluid, showed that the layers undergo an ordering transition from a disordered, amorphous state to one with two-dimensional hexagonal structure. Furthermore, this two-dimensional restructuring of the fluid occurs at the same thermodynamic state points as the aforementioned densification and local maximum in the isosteric enthalpy of adsorption. We thus conclude that the densification of the fluid is the result of structural reorganization, which is signaled by the maximum in the isosteric enthalpy. Owing to the qualitative similarity of the structural transitions in the simulated and experimental methane fluids, we propose this hexagonal reorganization as a plausible explanation of the densification observed in SANS measurements. Lastly, we speculate how this structural transition may impact the transport properties of the adsorbed fluid.

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Supporting Information Available

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b03406.

I. SANS intensity measurements used to generate Figure 1; II. Description of the fluid-fluid and fluid-solid interaction models used in GC-TMMC and MD molecular simulations; III. Description of the procedure for identifying layers of the adsorbed fluid, unwrapping and projecting those layers into a 2D surface, and calculation of the bond-orientational order parameters (including Q_6) for the 2D projections; IV. Supplementary figures of adsorption isotherms and Q_6 order parameters for pore sizes $R/\sigma = 3.0, 4.0, 6.0$, and 8.0 at temperatures $k_B T/\epsilon = 0.73, 0.85$, and 1.50 . (PDF) This material is available free of charge via the Internet at <http://pubs.acs.org/>.

Graphical abstract

Introduction

In recent years, the rapid growth in hydrocarbon extraction from shale formations^{1–3} has led to a renewed interest in the thermodynamics of fluids confined in nanoporous materials,^{4–6} particularly for gases that are or resemble the light alkanes that compose natural gas.^{7,8} Additionally, spent shale formations may prove useful in storage and sequestration applications.^{9,10} From an engineering point of view, the exploitation of fluids in nanoporous confinement presents a unique challenge. For example, since shale contains many pores in the length scale from 1 nm to 100 nm,^{11,12} the thermophysical properties of a fluid adsorbed in shale are altered drastically from that of the macroscopic, bulk-scale fluid and consequently, extraction or storage modeling cannot rely on bulk-fluid properties alone. A simple example is the existence of long-lived metastable states and the paired capillary evaporation and condensation transitions of a confined fluid below its bulk critical temperature, leading to adsorption-desorption hysteresis and a new, apparent “phase diagram” of the confined fluid.¹³ Gas extraction under conditions favorable to hysteresis would be required to consider that effect in process design and planning. Beyond thermodynamics, it is known that the dynamics of fluids in nanoporous confinement cannot be modeled with conventional macroscopic approaches alone.^{14–17} The molecular length scale leads to adsorbate-adsorbent interactions that extend through most if not all of the pore, which implies that the confined fluid dynamics cannot be decomposed into an interior fluid following macroscopic continuum dynamics and an interfacial (e.g., surface tension) effect at the pore wall.¹⁷ Furthermore, recent work by some of the present authors^{18,19} has shown that self-diffusion, which may be used as a proxy for Fickian transport diffusion, is deeply connected to the details of adsorption thermodynamics (e.g., the pore-averaged self-diffusion is roughly constant for gaslike state points following monolayer formation). Clearly, an understanding of the unique thermodynamics of fluid adsorption in the nanopores of shale is beneficial for engineering exploitation of those rock formations.

Shale rock, at least as an adsorbent, is a challenge to study if only for (1) the diversity of shale types worldwide and (2) the nonuniform matrix of organic (e.g., kerogen) and inorganic components that actually compose shale.²⁰ Ordered mesoporous silica materials can be used as a stand-in for actual shale in experiments and modeling of light alkanes in shale as they allow for better control and understanding of the experimental material, can be synthesized at pore sizes similar to those in actual shale, and possess chemically similar inorganic components.^{21–23} Additionally, mesoporous silica in various forms has also been studied via molecular simulations and statistical mechanical density functional theory, using

well-tuned models of silica that concomitantly lead to relatively good agreement between molecular models and experiments.^{24–26} Consequently, while it is not expected that adsorption studies of silica adsorbents perfectly characterize adsorption in shale, mesoporous silica is a good platform for approximating shale formations and limiting the set of experimental variables and conditions. Adsorption in mesoporous silica will likely be a rich, fruitful area of study that will enable better modeling and engineering use of shale formations.

Since their introduction nearly 30 years ago, mesoporous silica adsorbents have found applications in many areas related to or exploiting adsorption, such as separations, heterogeneous catalysis, and as pharmaceutical delivery.^{27–31} Additionally, gas adsorption as a technique for characterizing the pore structure of mesoporous silicas has become practically de rigeur, due to well-proven adsorption kernels for silica based on both molecular simulation and density functional theory,^{26,32–35} even including an approximation of surface roughness.³⁶ Studies of silica, especially those based on theory and simulation, have provided excellent insight into the thermodynamic mechanisms of adsorption, including a molecular understanding of the adsorption-desorption hysteresis effect,^{37,38} in-pore fluid cavitation,^{39,40} and the details of dynamic adsorption (desorption) processes.^{41–44} However, while studies of silica adsorbents have been widespread and successful, the adsorbate species is usually an inert characterization gas such as argon or nitrogen; studies with alkanes (whether experiment or simulation) have been done,^{45–48} but are fewer in number. So, while adsorption mechanisms of these light gases in mesoporous silicas is well understood, an understanding of alkane behavior in shale would benefit from additional study of alkane adsorption in silicas.

The relative lack of experiments and simulations of methane (CH_4) adsorption in mesoporous silicas prompted recent work by some of the present authors^{49,50} in which a small-angle neutron scattering (SANS) technique was introduced and used for that exact purpose. SANS can directly measure the density of fluid inside the pores with defined pore size without being influenced by the defects in the materials and, thus, is sensitive enough to detect slight changes in the pore (cf. Section I of the Supporting Information). In ref⁴⁹, the SANS experiments were used to study the adsorption of deuterated methane (CD_4) in mesoporous silica as a model system for natural gas in shale. The experiments were done using MCM-41 and SBA-15, two silica adsorbents with similar cylindrical pore geometry but different pore radii, 1.65 nm and 3.41 nm, respectively, and different surface roughnesses. The adsorption isobars (derived from the intensity of SANS measurements, not direct volumetric or gravimetric adsorption measurements), exhibit an interesting feature: densification of the liquidlike phase with decreasing temperature. (As noted in ref⁵⁰, Figure 1 is not strictly an isobar for temperatures below capillary condensation, but it serves the purpose of an isobar for the present discussion.) This feature is visible in the upper left quadrant of Figure 1 (a recreation of Figure 3d in ref⁴⁹); for both adsorbents there is a discontinuity in the isobar near 120 K to 125 K, which corresponds to capillary condensation,⁴⁹ but the density of the adsorbed phase continues to increase, by approximately 10 % as the temperature decreases from 100 K to 20 K. Furthermore, this densification appears as a shoulder in the isobar (sign change in the concavity), with the fastest rise in density appearing in the middle of the densification. To our knowledge, this

shoulder has not been previously observed in measurements of CH₄ adsorption in mesoporous silica. Typically, a high-density adsorbed phase (e.g., state points following capillary condensation) is similar to a bulk liquid phase in that it is mostly incompressible.¹³ For example, in our previous work⁵¹ studying the adsorption of argon in carbon nanotubes, the liquid phase density increases slowly and monotonically with pressure, with a total increase of less than 5 % for pores of comparable size (cf. Figure 5 of Ref⁵¹). The larger and more rapid increase in density exhibited by CD₄ adsorption in the silica pores in Figure 1 might then be associated with some other phenomena, such as a speculated liquid-solid transition.⁴⁹ Investigation of this density rise in adsorbed CH₄ and a proposed explanation is the subject of the following work.

This paper is organized as follows. First, we briefly describe the molecular simulation techniques used to study CH₄ adsorption in mesoporous silica; additional details regarding our molecular models and structural characterization metrics are described in the Supporting Information. We then present and discuss our simulations results, including adsorption isotherms and isobars, structural metrics of adsorbate ordering in the model cylindrical silica pores, and graphical snapshots of molecular structuring in the pores. Finally, we summarize our main findings, and discuss possible engineering implications.

Molecular Simulation Methods

To better understand the densification effect seen in SANS-derived isotherms, we turned to molecular simulations of model CH₄ in cylindrical pores that mimic SBA-15 and MCM-41 adsorbents. In our model CH₄ was represented by a single-site cut and linear force shifted 12-6 Lennard-Jones (LJ) molecule, with energy parameter ϵ and diameter parameter σ . The silica adsorbents were modeled by a cylindrical pore with a 10-4 (integrated) LJ potential, with pore radius parameter R . The fluid-fluid and fluid-solid potentials, along with their parameters, are described in full in Section II of the Supporting Information. We treat CD₄ and CH₄ as identical in our (classical) simulations, as the interaction potentials should not differ greatly despite the difference in molecular weight. We used two forms of molecular simulation to examine the structural characteristics of CH₄ adsorption in cylindrical silica. Monte Carlo simulation was used to compute equilibrium adsorption isotherms while molecular dynamics simulation was used to calculate structural order parameters. The particular methods are described as follows.

First, we used Grand Canonical Transition-matrix Monte Carlo (GC-TMMC)^{52,53} to compute adsorption isotherms and the isosteric enthalpy of adsorption, in an implementation identical to our previous work^{51,54} though with initialization of the simulation using the Wang-Landau algorithm.^{54–56} The main output of our GC-TMMC simulations was the particle-number macrostate probability distribution, $\Pi(N; \mu, V, T)$, in which N is the number of adsorbate molecules, μ is the chemical potential, V is the system volume, and T is the temperature. The resultant $\Pi(N; \mu, V, T)$ was then processed according to the analysis technique described in ref⁵¹ to compute the adsorption isotherm and isosteric enthalpies of adsorption via histogram reweighting of $\Pi(N; \mu, V, T)$ from the original μ to other values. As in our previous work,^{51,54} the thermodynamic bulk pressure, p_b , associated with the imposed μ and T was obtained from simulations of the bulk fluid using the GC-TMMC

technique, the results of which are available online in ref⁵⁷. Each GC-TMMC simulation performed in this work was run for 2×10^{10} trial moves, with a 4:3:3 ratio of displacement, insertion, and deletion moves, respectively. Lastly, μ was selected for each $k_B T/\epsilon$ to correspond to a liquidlike, high-density state.

Second, we utilized molecular dynamics (MD) simulations to examine the structural characteristics of CH₄ adsorption in the same cylindrical silica pores. We employ the same simulation techniques as in refs¹⁸ and ¹⁹ and thus do not restate the full details here. In short, molecular dynamics (MD) simulations were performed in the canonical ensemble (fixed N , V , and T), with $N = 4000$ particles. The axial length of the pore, L_z , was varied to achieve a desired average pore density $\rho\sigma^3 \equiv N/(\pi R^2 L_z)$. The fluid-fluid and fluid-solid interaction parameters were identical to those used for GC-TMMC. Configurational snapshots from the MD simulations were stored for analysis following completion of the simulation. The main metric used for describing the structure of adsorbed CH₄ is a calculated bond-order parameter, which we discuss in full in Section III of the Supporting Information.

Simulations were run at temperatures ranging from LJ-reduced temperatures $k_B T/\epsilon = 0.73$ to 2.00 (corresponding to 109 K to 450 K) to span fluid conditions above and below the critical temperature ($k_B T/\epsilon = 1.207$) of the model fluid.⁵⁷ The pore size was set to inner radii of $R = 4\sigma$ and 6σ (1.49 nm and 2.24 nm) and axial length of $10\sigma = 3.73$ nm for GC-TMMC and the aforementioned varying length for MD. Additionally, we simulated two other pore sizes, $R = 3\sigma$ and 8σ , but present those results in the Supporting Information as they were qualitatively similar to those for $R = 4\sigma$ and 6σ and changed none of the conclusions. To simplify comparison of the current results with our previous works, we will present all results in units reduced by the appropriate combination of LJ parameters σ and ϵ . For example, density is presented as $\rho\sigma^3$. We convert our results to real units when necessary. Furthermore, we will present all measurements of adsorbate loading in absolute terms to avoid unnecessary definition of either the available pore volume or a dividing surface.⁵⁸

Results and Discussion

To preface a full discussion of structural transitions of CH₄ during adsorption in mesoporous silica, we first present some simulation results that clearly display behavior similar to the hypothesized structural transition seen in SANS measurements. In Figure 2, we plot the adsorption isotherms ($\rho\sigma^3$) and associated isosteric enthalpies (q_{st}/ϵ) of adsorption for CH₄ in cylindrical silica with pore radii $R = 4\sigma$ and 6σ (1.49 nm and 2.24 nm), at $k_B T/\epsilon = 0.73$ (109 K). In panel a, the isotherms are both type IVa, with H1 adsorption-desorption hysteresis,⁵⁹ indicative of subcritical adsorption in mesopores. Consistent with usual type IV behavior, the isotherms exhibit sharp shoulders at low pressure, which identifies the regime of film/monolayer formation, followed by multilayer adsorption, and, finally, porefilling adsorption following capillary condensation.¹⁸ In both cases, the local maxima in q_{st}/ϵ at low loading ($\rho\sigma^3 \approx 0.15$ to 0.25) identify the completion of monolayer formation. Up to this point, the isotherms are broadly similar to adsorption in strongly adsorbing mesopores.^{18,19,51} Following capillary condensation, however, the CH₄-silica isotherms show a less-seen behavior: further densification of the liquidlike phase. This is visible near $p_b/p_0 = 0.25$ for $R = 4\sigma$ and $p_b/p_0 = 0.5$ for $R = 6\sigma$. Typically, for pressures above capillary condensation,

the adsorbed phase behaves like a bulk liquid with low compressibility and minimally-varying density. Both isotherms in Figure 2 exhibit a nearly 10 % increase in the density of the liquidlike phase following capillary condensation and a distinct shoulder. This is particularly evident in the $R = 4\sigma$ isotherm at $p_b/p_0 = 0.24$ and $\rho\sigma^3 = 0.67$, but also appears in the $R = 6\sigma$ isotherm at $p_b/p_0 = 0.50$ and $\rho\sigma^3 = 0.73$. In both cases, the plot of the isosteric enthalpy exhibits corresponding local maxima at $\rho\sigma^3 = 0.67$ for $R = 4\sigma$ and at $\rho\sigma^3 = 0.73$ for 6σ . Therefore, these local maxima in q_{st} are associated with the densification of the liquidlike adsorbed phase in a manner similar to the correspondence of the low-density local maxima to the completion of monolayer formation.

The densification shown by the two isotherms in Figure 2 shows some similarities to that in Figure 1 in that the density of a liquidlike phase increases, though we draw this initial comparison with caution as the data in Figure 2 is an isotherm plotted vs pressure whereas Figure 1 is an isobar plotted vs temperature. The shoulder in the $R = 4\sigma$ isotherm data is the feature of most interest, as the SANS-derived adsorption results for both SBA-15 and MCM-41 also show a shoulder shape (in temperature series) with an approximate 10 % increase in density. Due to the absence of a discontinuity in the density (and isosteric heat) at or near this densification, the densification is obviously not a capillary phase transition akin to capillary condensation (or capillary evaporation for the reverse). A more likely hypothesis is that this densification is the result of some structural transition of the adsorbed, liquidlike phase, particularly since it is associated with a local maximum in the isosteric enthalpy of adsorption. Historically, the first local maximum in the isosteric enthalpy, as a function of adsorbate loading, is interpreted as indicating a structural transition of the first layer of adsorbate molecules.^{13,33,60} This is particularly evident for adsorption in a smooth adsorbent (as in our model), as the adsorbate forms a well-defined, but amorphous, film at low pressure that transforms to a highly-structured, nearly crystalline monolayer^{61,62} when that layer reaches its maximum capacity. The densification we observe in Figure 2 from our CH₄-silica simulations may be a similar phase transition, though it occurs at a higher pressure and at densities that more closely resemble a liquid state.

In the following subsections, we will examine the densification of CH₄ adsorbed in cylindrical silica through adsorption isotherms spanning a broad temperature range and bond-orientational order parameters for particular state points on those isotherms. One objective is to mimic the SANS-derived results in Figure 1 via construction of an adsorption isobar for a particular pressure and thus more closely tie our molecular simulations of adsorption to the experimental measurements that motivated this work. Additionally, we ran multiple TMMC and MD simulations with different initial configurations to confirm the consistency of our results across repeated simulations. We found that our isotherms were faithfully reproduced by separate simulations and that the uncertainty in bond-order parameter calculations was smaller than the symbol size in our figures. Therefore, for clarity we omit error bars in the figures that follow.

Adsorption Isotherms and Adsorption Isobars

Figure 3 displays adsorption isotherms for $R = 4\sigma$ and 6σ and temperatures in the range of $k_B T/\epsilon = 0.73$ to 2.00. We note that the pressure scale has been changed from units reduced

by the respective saturation pressure (p_b/p_0) to standard LJ-reduced units ($p_b\sigma^3/\epsilon$) since some simulations were done above the bulk-fluid critical temperature. Also, the pressure axis is plotted on a logarithmic scale to display isotherm features more clearly at low-pressure. The isotherms from Figure 2 are the coldest (purple) isotherms given in Figure 3. The key feature to note is the continuing densification of the adsorbed CH_4 phase with increasing pressure, particularly for temperatures below $k_B T/\epsilon \approx 1.10$, confirming that the densification of the high-density phase is not restricted to the single-temperature results in Figure 2. (We also ran simulations at $R = 8\sigma$ for the same range of temperatures, which also exhibit qualitatively identical results.) Furthermore, this densification produces the distinctive isotherm shoulder seen in Fig 2 for $R = 4\sigma$ over a range of temperatures. The same feature is present for $R = 6\sigma$, but less prominently.

For more straightforward comparison with the previous SANS experiments, we constructed adsorption isobars ($\rho\sigma^3$ vs T) by selecting points from separate adsorption isotherms in Figure 3, for fixed values of pressure. The results of this isotherm→isobar conversion are shown in Figure 4. The essential shape of the isobars is exactly as expected: adsorption decreases with increasing temperature for a particular pressure and there is an obvious transition from liquidlike to gaslike densities for certain isobars in the temperature range $k_B T/\epsilon = 0.73$ to 1.00. The main feature of note relevant to the present work echoes the densification feature seen in Figure 1: for the high pressures shown in the plot, a trace of the isobar beginning at high temperature/low adsorption shows, first, the formation of a high-density, liquidlike phase (roughly, the vertical or near vertical rise of $\rho\sigma^3$) and, later, a further densification indicated by a step in the isobar before $\rho\sigma^3$ effectively plateaus. This additional densification increases the adsorbed fluid's density by approximately 10 % and is the identical behavior to that observed in the SANS-derived adsorption isobars in Figure 1. Furthermore, the thermodynamic state points that correspond to this secondary densification in the isobar correlate with state points in the isotherms of Figure 3 that show the shoulder in the isotherm associated with the liquid-phase densification. The results in Figure 4 therefore show that the simulation model system, LJ- CH_4 confined in a cylindrical silica mesopore, qualitatively reproduces the same adsorption isobar behavior as found via SANS experiments. As discussed earlier, however, the adsorption isobars do not provide any insight into any molecular phenomena associated with this densification.

Lastly, we again turn to calculations of the isosteric heat of adsorption to better understand the densification effect. Figure 5 displays q_{st} calculations associated with the isotherms in Figure 3 for the cold temperatures ($k_B T/\epsilon = 0.73$ to 0.8). As noted previously in the discussion of Figure 2b, the major features of interest in both subplots are the local maxima in q_{st} at a pressure above the capillary condensation point (i.e., for a liquidlike state). The appearance of a maximum in q_{st} at a pressure above the capillary condensation transition is uncommon; in recent work¹⁹ where we simulated adsorption in systems ranging from “weakly” to “strongly” attractive adsorbents, no system exhibited such a local maximum in q_{st} . Thus, this local maximum in the CH_4 -silica system is an interesting feature on its own. What provokes further interest is that the high-density local maxima align with the densification evident in both Figures 3 and 4, in that it is encountered by either (1) following an isotherm with increasing density or (2) following an isostere (which is a rough proxy for pressure) with decreasing temperature. Furthermore, correlation of the adsorption isotherm

with the isosteric heat confirms that the high-density local maxima are associated with the densification or shoulder in the isotherm noted previously. Figure 6 (panels a, b, e, and f) display the regions of densification noted in Figure 2 for $R/\sigma = 4.0$ and 6.0 for $k_B T/\epsilon = 0.73$, with visual correlation of certain points on the isosteric heat trace with the corresponding points on the isotherms. The maximum in q_{st}/ϵ is located at the midpoint of the densification of the adsorbed liquidlike phase. Given that the expected low-density maxima correspond to completion/reorganization of the first adsorbed monolayer,^{13,33,60} it is likely that the high-density maxima in q_{st} reflect some further change in the structure of the adsorbed fluid. Thus, the next area of investigation is an effort to describe the observed densification effect in the adsorbed-fluid structure itself, through the use of structural metrics.

Adsorbate Fluid Structure

Our early investigation of the origin of this densification effect focused on a commonly used metric to examine the structure of a confined fluid: the fluid (radial) density profile $\rho(r)$. Examples of these density profiles at certain points along the adsorption isotherms are shown in Figure 6 (panels c and g), with each individual density profile corresponding to a noted point on both the isotherm and isosteric heat traces. Unfortunately, our examination of plotted density profiles, and others not shown in this manuscript, did not yield any particular insight into the densification effect; the local maxima in $\rho(r)$ increase with ρ (equivalently, with p_b) as expected (and as required due to the increase in density), but there is no relative change in the peaks in $\rho(r)$ or a shift of those peaks that might indicate a nontrivial change in the adsorbate structure. This lack of notable change in $\rho(r)$ is present in, for example, panels c and g of Figure 6. Therefore, we turned to a visual examination of the fluid structure for better insight.

To visualize the fluid structure, we found it necessary to extract certain regions of the pore volume for individual analysis. This decision is motivated by the fairly obvious observation that a fluid confined in a cylindrical (or, more generally, a non-Cartesian) geometry is unlikely to form an isotropically ordered structure. In contrast, for sufficiently large pore diameter the fluid forms distinct annular layers, with structure appearing in a quasi-2D manner in each annular layer, which is shown in Figure 7a. The quasi-two-dimensional (2D) structuring of fluids in cylindrical confinement was noted by Do et al.,^{61,62} specifically in the context of layer-specific fluid compressibility and changes in isosteric heat that correlate with layering. Our procedure for extracting individual adsorbed layers is described in Section III of the Supporting Information. In short, for each configurational snapshot saved from an MD simulation, a specific annular monolayer is identified and extracted from the snapshot and then “unwrapped” into a periodic, 2D planar projection of the configuration.

In Figure 6 (panels d and h), we show close-ups of the film (i.e., the first layer) and second layer structure, in 2D projection, at the three isotherm points that we have already discussed. For the lowest density point, prior to densification of the liquid, the film layer appears to be somewhat ordered while the second layer is more or less random. At the highest density points, postdensification, both layers include obvious hexagonal ordering. These snapshots correspond to intuition concerning q_{st} : the high-density local maximum is suggestive of some structural transition in the fluid and the snapshots seem to indicate that the transition is

a 2D structural transition. Figures SI.5 and SI.6 of the Supporting Information show additional points along the $k_B T/\epsilon = 0.73$ isotherms, which further highlights the appearance of hexagonal ordering while following points along the isotherms. Furthermore, this 2D hexagonal ordering is not isolated, but extends through the entire layer. Figure 7 shows different views of a single configuration taken from an MD simulation for $R/\sigma = 4.0$, $k_B T/\epsilon = 0.73$, and absolute density $\rho\sigma^3 = 0.7$ (though with $N = 1000$ to allow the figure to show the full axial length). Figures 7 (panels b and c) shows the film and second layers unwrapped into 2D projections of their actual annular structure, with periodic images along the boundaries of the 2D projection. The hexagonal ordering suggested by the small snapshots in Figure 6d is undeniable here. The film layer shows a highly-ordered hexagonal molecular arrangement spanning the entire 2D projection, with only small defects or lattice faults. The second layer also shows hexagonal ordering, less so than the film and with more defects. These snapshots show that the densified state at $\rho\sigma^3 = 0.7$ has clearly changed to an ordered adsorbate structure, which aligns with intuition based on the observed local maximum in q_{st} . To quantify this structural transition in a more objective manner, we turn to bond-order metrics to examine the densifying fluid in closer detail.

The metric we selected to quantify adsorbate fluid structure in the cylindrical silica pores is bond-orientational order parameter Q_6 ,^{63,64} as measured for the 2D projections of adsorbed annular layers. Our selection of this metric is based on the structural snapshots that suggest hexagonal ordering, which can be quantified well by Q_6 . The procedure for calculating Q_6 is fully described in Section III of the Supporting Information. In short, Q_6 was computed for the 2D unwrapped and projected snapshots described earlier and then averaged over the entire set of snapshots. This yields averages of those order metrics as a function of ρ , which can be converted to a function of p_b via interpolation of TMMC-derived adsorption isotherm. For the following discussion, we focus on the average Q_6 metric as it provided the clearest signal of a change in the structural properties of the adsorbed fluid layers. For reference, we note that $Q_6 = 0.575$ for a fully periodic face-centered cubic (FCC) lattice and the 100, 110, and 111 facets of the FCC lattice yield $Q_6 = 0.586, 1.00$, and 0.741 , respectively.^{63,65} We also note that the 111 FCC facet corresponds to a perfect 2D hexagonal lattice.

Figure 8 plots both the adsorption isotherm and Q_6 vs fractional pressure (actual pressure divided by the bulk saturation pressure) for the CH_4 -silica system at $k_B T/\epsilon = 0.73$. Additionally, the figure includes visual guidelines that identify three state points in the region of liquid densification that are identical to the specific state points identified in Figure 6 (panels a-d). We note that Q_6 is plotted separately for different annular layers; in this figure and those that follow we plot only the film (first) layer and the second layer, as subsequent layers contain too few molecules to obtain good statistical averages of Q_6 . For low pressure, the traces of Q_6 for the film and second layer are indistinguishable. In Figure 8, Q_6 is virtually unchanged up to a fractional pressure of 0.2, holding a value of ≈ 0.3 , after which there is a rapid rise in its value for both layers shown. For comparison, we calculated Q_6 for a random 2D hard sphere system (see Section III of the Supporting Information) and found its value to be approximately 0.31. Thus, below $p_b/p_0 = 0.2$, both the film and second layers structurally resemble amorphous 2D layers. For higher pressures, however, Q_6 roughly doubles in value, indicating the formation of quasi-crystalline order in those annular

layers. Q_6 for the film layer exceeds 0.6 at a fractional pressure of 0.3, which is between the values of the 100 and 111 FCC facets. The second layer is less structured, with $Q_6 \rightarrow 0.55$ for $p_b/p_0 = 0.3$. Both layers are approaching Q_6 values that indicate a near-hexagonal ordering. The rapid rise in Q_6 for both layers coincides with the region of densification, in this case with the prominent shoulder in the isotherm. Furthermore, by recalling that the three state points identified in Figure 8 are the same as those in Figure 6 (panels a-d), we can make the joint observation that, for the CH_4 -silica system with $R/\sigma = 4.0$ and $k_B T/\epsilon = 0.73$, the densification corresponds to both a local maximum in the isosteric heat and a hexagonal ordering of the first two adsorbed layers. Finally, we can visually confirm the appearance of hexagonal ordering in Figure 6d. For the lowest density, 0.65, prior to densification of the liquid, the film layer appears to be somewhat ordered while the second layer is more or less random. At the highest density, 0.7, postdensification, both layers include obvious hexagonal ordering.

In Figure 9, we plot the isotherm and Q_6 for $R/\sigma = 6.0$ and $k_B T/\epsilon = 0.73$ in the same manner as done for $R/\sigma = 4.0$ in Figure 8. As stated earlier, the densification is less sharp than for the smaller pore. The trends noted in the previous paragraph for the smaller pore are present here, only shifted to slightly higher pressure (and adsorbed density). Q_6 rises from 0.3, indicating little fluid ordering, to nearly 0.6 for the film layer and 0.55 for the second layer. Visually, the appearance of hexagonal ordering is evident in Figure 6 h. Thus, the larger pore results confirm the coincidence of (1) densification of the adsorbed methane that is already in a liquidlike state, (2) a local maximum in the isosteric heat, and (3) hexagonal restructuring of the individual adsorbed layers as indicated by a rise in Q_6 to a value near that of the 111 FCC facet.

To examine temperature-dependent densification, similar to the isobaric SANS measurements of ref⁴⁹, Figure 10 is the analogue of Figure 8 for $k_B T/\epsilon = 0.85$, which according to the isobars in Figure 4 should not exhibit the densified liquidlike state as seen for $k_B T/\epsilon = 0.73$. As expected, the Q_6 metric indicates that there is no 2D hexagonal structuring of the first two adsorbed layers for this pore size and temperature. Thus, in temperature space the densification of the high-density, liquidlike phase occurs between temperatures 0.85 and 0.73, depending on the chosen pressure, if at all. We find the same results for $R/\sigma = 6.0$ as shown in Figures SI.13-SI.14. Furthermore, results for $R/\sigma = 3.0$, shown in Figures SI.7-SI.9, identify the same densification trend, though with hexagonal ordering persisting at $k_B T/\epsilon = 0.85$ but not at $k_B T/\epsilon = 1.50$. For $R/\sigma = 8.0$, shown in Figures SI.16-SI.18, ordering of the adsorbed layers is present at $k_B T/\epsilon = 0.73$ but with lower Q_6 values than for the smaller pore sizes. In Figure SI.19, we take the isothermal results for $R/\sigma = 4.0$ in Figures SI.10-SI.12 along with data from simulations at other temperatures to construct a plot of Q_6 vs $k_B T/\epsilon$ for select isobars. As expected from our already-presented results, we see in Figure SI.19 that Q_6 rises rapidly from 0.31 to approximately 0.6 for a range of temperatures $k_B T/\epsilon < 0.85$, depending on the isobar pressure, indicating an ordering transition along the temperature axis. The summary of the results in these figures is that densification of the adsorbed fluid at liquidlike conditions occurs concurrently with an increase in (hexagonal) ordering of individual layers of adsorbed fluid, either with an increase in pressure at fixed temperature or a decrease in temperature at fixed pressure.

Summary and Conclusions

The key observations obtained from the results of our molecular simulations of CH₄ adsorption in cylindrical silica mesopores may be summarized as follows. First, adsorption isotherms exhibit an approximately 10 % rise in the adsorbed density of the liquidlike phase that is manifested as a distinct shoulder in the isotherm, dependent on the pore size and pressure. Second, plots of the isosteric enthalpy of adsorption contain a local maximum at a liquidlike density, secondary to one at low density. Visual examination of the adsorbed fluid finds evident hexagonal ordering of the film and second adsorbed layers, which is quantitatively confirmed via the rise from ≈ 0.3 to > 0.55 of the Q_6 bond-orientational order parameter of 2D projections of those layers. Lastly, isobars show a sharp transition in the isobar density, at temperatures below the gaslike $\rightarrow$ liquidlike transition, at state points that correspond to the 10 % rise in the isotherm density. Furthermore, the results shown in Figures 6-10 indicate that these key observations coincide, in that the rise in ρ , the local maximum in q_{sb} and the rise in Q_6 occur in the same band of densities, with visual confirmation of molecular ordering via configurational snapshots. We are thus led to propose that the densification of liquidlike CH₄ in cylindrical silica mesopores is the result of a molecular rearrangement of the adsorbed, liquidlike phase from a (relatively) disordered, amorphous state to one with 2D hexagonal ordering in individual annular layers. To our knowledge, no such structural transition has been previously reported for CH₄ adsorption in cylindrical silica pores, and past simulations of adsorption in cylindrical silica mesopores with other adsorbate species (e.g., N₂ and Ar in buckytube models of MCM-41⁶⁶⁻⁶⁹) showed no densification of the liquid phase that would prompt an investigation like ours. Lastly, we can further propose that the 2D reordering transition is also present in adsorption isobars, since the relevant thermodynamic state points are identical.

The summation of these observations is that simulated LJ-CH₄ adsorbed in cylindrical silica pores undergoes a structural transition of the liquidlike phase from amorphous layers to 2D hexagonally-ordered layers as a function of either temperature or pressure, which may be identified by a 10 % rise in the density of the liquidlike phase. Since this same feature is present in the analogous experimental system, we can propose that a similar structural transition is plausibly responsible for the densification seen in adsorption isobars of CD₄ in SBA-15 (as a sharp transition) and MCM-41 (as smooth densification). Additionally, this proposition does not negate the suggestion in the original work that the experimentally-observed densification could be a liquid-solid transition;⁵⁰ for confined fluids, it is often difficult to distinguish between liquid and solid adsorbed phases.¹³ The hexagonal ordering seen in the film and second layers is more similar to a solid than to an amorphous liquid and, thus, could be considered a “solidification” of those portions of the adsorbed methane. That the solidification of the first layers of CH₄ occurs via hexagonal ordering is not surprising, as the hexatic structure of frozen LJ molecules in porous materials was described previously.^{70,71} Thus, while our present work has not attempted to rigorously identify a liquid-to-solid transition temperature for LJ-CH₄ in cylindrical mesoporous silica, the 2D structural reorganization of the first two layers of adsorbed fluid is consistent with the expectation of hexatic ordering of the final crystal structure.

Three additional questions arise from our results. The first concerns the nature of the 2D hexagonal structural transition, whether, for example, it may be classified as a first- or second-order phase transition. For the simulated CH₄ fluid, the reordering transition most closely resembles a second-order phase transition in that it is not associated with a discontinuity in either the density or a heat metric (e.g., q_{sp}),⁷² in contrast to the analogy between a first-order phase transition and capillary condensation. (We note, for completeness, that traditional descriptors of phase transitions must be applied with caution to confined systems; for example, authors elsewhere^{13,73} have discussed how true critical points do not exist for cylindrical confinement since the correlation length can grow to infinity in only one Cartesian direction, the pore axis.) Thus, while the heat characteristics of the adsorption process do change at the 2D hexagonal structural transition (e.g., passing through a local maximum), there would be no analogue to a latent heat effect associated with the transition. A second question concerns the specificity of this 2D transition to the CH₄-silica system, as opposed to Ar-carbon nanotube (CNT) and Ar-solid CO₂ systems that we have examined elsewhere.^{18,19,51} While this question requires an in-depth examination of its own, we speculate that the densification effect follows from the relative strength of the fluid-solid interaction. Comparison of the fluid-solid potential of the CH₄-silica system shows that it falls between the extremes of the strongly adsorbing Ar-CNT systems and the weakly adsorbing Ar-CO₂ systems and thus, the resultant thermodynamic characteristics also fall between the two. Initially, the weaker fluid-solid interaction leads to a less structured film, as compared to the Ar-CNT system. The film is, however, better defined than that for the Ar-CO₂ system. Then, the second layer begins building up before that film is highly structured. Finally, because the distinct layers are still amorphous, even after capillary condensation raises the density to near-liquid conditions, further densification cannot proceed without a structural reorganization that increases the free volume of each layer. The third open question is the role of surface roughness in the real materials.^{74,75} The SANS experiments indicated significant roughness,⁴⁹ while our model silica is perfectly smooth, which could either promote or retard 2D ordering of the adsorbed methane depending on the exact nature of that roughness.

The existence of the 2D structural transition of CH₄ adsorbed in cylindrical silica pores may have some important consequences on dynamic considerations for use of such materials. As we have shown previously,^{18,19} the self-diffusion dynamics of gases adsorbed in cylindrical confinement are closely tied to adsorption thermodynamics. The important conclusion from that previous work is that different diffusion regimes are associated with different structural motifs (e.g., the relatively constant diffusion regime that coincides with multilayer adsorption, after film formation but prior to pore filling) and the rapidly dropping self-diffusion during the pore filling part of the isotherm. In the case of CH₄ adsorbed in cylindrical silica, the 2D structural transition is qualitatively similar to the boundary between film formation and multilayer adsorption and hence, the self-diffusion behavior associated with it may be intriguing. The likely situation is that the self-diffusion dynamics slow even further due to increased molecular frustration in the now well-ordered layers. This in turn may be manifested as slow transport diffusion, an engineering limitation on the use of similar materials, perhaps even shale. We intend to study the self-diffusion of CH₄ in cylindrical silica in future work.

In summary, we presented results from molecular simulations that indicate that CH₄ adsorbed in cylindrical silica pores at liquidlike conditions undergoes a structural transition in which individual adsorbed layers become hexagonally ordered. This effect is suggested by plots of the isosteric heat of adsorption that exhibit a high-density local maximum unlike most adsorptive systems and confirmed through calculations of the Q_6 bond-orientational order parameter that show that the adsorbed layers, when projected onto 2D surfaces, numerically approach the Q_6 value for the 111 FCC facet. We proposed that this structural transition is responsible for the roughly 10 % increase in the density of the liquidlike adsorbed phase. Finally, the increase in density seen in simulations is qualitatively similar to a density increase seen in adsorption of CD₄ in both SBA-15 and MCM-15 and may be a plausible explanation of that otherwise unexplained effect.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Experimental (absolute) adsorption isobars of CD₄ in cylindrical SBA-15 (blue) and MCM-41 (orange) at ≈ 100 kPa, from Figure 3d of ref⁴⁹, as measured via small-angle neutron scattering (SANS). (We note that the pressure was not strictly held constant at 100 kPa; as discussed in ref⁵⁰, the pressure gradually decreased with decreasing temperature.) The inset is an enlargement of the isobar in the region where an unexpected densification is observed. Error bars identify the standard deviation of the isotherm derived from SANS measurements. The pore radii are noted in the legend.

Figure 2.

Example GC-TMMC simulation results for CH_4 adsorption in cylindrical silica pores at $k_B T/\epsilon = 0.73$ for pore radii 4σ (blue) and 6σ (orange). (a) Absolute adsorption-desorption isotherm, $\rho\sigma^3$, plotted vs fractional pressure of the bulk adsorptive fluid, p_b/p_0 where p_0 is the bulk saturation pressure at the stated temperature. (b) Isotheric enthalpy of adsorption, q_{st}/ϵ , plotted vs adsorbate loading. The plot of q_{st} for $R = 6\sigma$ has been shifted by 5ϵ . In both subfigures, the dotted lines identify the capillary condensation (increasing ρ) and evaporation (decreasing ρ).

Figure 3.

Adsorption isotherm (absolute) of CH_4 adsorption in cylindrical silica pores for temperatures ranging from $k_B T/\epsilon = 0.73$ to 2.0, plotted as the reduced density vs the (log-scale) reduced pressure. (a) Isotherms for pore size $R/\sigma = 4.0$. (b) Isotherms for pore size $R/\sigma = 6.0$. In both subfigures, the temperature ($k_B T/\epsilon$) is identified by the color scale bar, ranging from purple for the coldest temperature ($k_B T/\epsilon = 0.73$) to red for the hottest ($k_B T/\epsilon = 2.0$). Adsorption-desorption hysteresis is present for some low temperatures, as shown by the vertical lines at the capillary phase transitions.

Figure 4.

Adsorption isobars (absolute) of CH₄ adsorption in cylindrical silica pores for reduced pressures ranging from $p_b\sigma^3/\epsilon = 10^{-4}$ to 3×10^{-3} , plotted as the reduced density vs the reduced temperature. (a) Isobars for pore size $R/\sigma = 4.0$. (b) Isobars for pore size $R/\sigma = 6.0$. In both subfigures, the reduced pressure is identified from the color scale bar, ranging from red for the lowest pressure to purple for the highest. For clarity, the isobars were constructed from the “desorption” branches of the isotherms that showed hysteresis (i.e., isotherm points for all liquidlike states and those gaslike states for pressures below capillary evaporation). In a and b, the insets are enlargements of the portions of the isobars that show the postcondensation densification.

Figure 5.

Isosteric heat of adsorption, q_{st}/ϵ , for CH_4 adsorption in cylindrical silica pores plotted vs absolute adsorption, for the isotherms at temperatures $k_B T/\epsilon = 0.73$ to 0.80 in Figure 3. (a) Calculations of q_{st}/ϵ for pore size $R/\sigma = 4.0$. (b) Calculations of q_{st}/ϵ for pore size $R/\sigma = 6.0$. All traces of q_{st}/ϵ save that of $k_B T/\epsilon = 0.73$ have been shifted by multiples of $+3$. The reduced temperature of the confined fluid is noted along each curve.

Figure 6.

Properties of CH_4 -silica adsorption at $k_B T/e = 0.73$, focusing on three thermodynamic states that are color-coded: red, green, and blue. (a) Closeup of the adsorption isotherm on the region of liquid-phase densification for $R/\sigma = 4.0$. (b) Closeup of the isosteric heat of adsorption for the same region. (c) Radial density profiles of the same at the noted reduced densities. (d) Configuration snapshots of the film (first) and second annular adsorbed layers in projected and unwrapped coordinates (see Section III of the Supporting Information) at the noted reduced densities. The color codes are consistent in panels a, b, c, and d (i.e., the red points, density profiles, and snapshots are all for $\rho\sigma^3 = 0.65$). Panels e, f, g, and h: as for a, b, c, and d, respectively, but for $R/\sigma = 6.0$ and the noted reduced densities.

Figure 7.

Visual representation of a configuration of LJ CH_4 in a cylindrical silica pore of inner diameter $R/\sigma = 4.0$ at $k_B T/\epsilon = 0.73$, for (absolute) adsorbed density $\rho\sigma^3 = 0.7$. This configuration corresponds to the state color-coded blue in Figures 6 (panels a-d) and 8 (i.e., after densification of the already high-density adsorbed phase and after the high-density local maximum in the isosteric enthalpy of adsorption). (a) Axial view, with molecules in the film layer colored blue, orange in the second layer, and gray for all others. The cylindrical silica wall is shown by the gray annulus. (b) 2D Projection of the film layer, with the actual molecules in dark color and periodic images in light. (c) As for b, for the second layer.

Figure 8.

Simulation results for CH₄ adsorption in a cylindrical silica pore of radius $R/\sigma = 4.0$ at $k_B T/\epsilon = 0.73$. (a) Adsorption isotherm (absolute) plotted vs (log-scale) fractional pressure, where p_0 is the bulk fluid saturation pressure for the same temperature. (b) Q_6 bond orientational order parameter as a function of fractional pressure for the film (the first layer of adsorbate molecules, adjacent to the adsorbent surface) and second layers. The three vertical lines are visual guides that identify specific states points in the region where the liquidlike phase densifies, with adsorbed density associated with each line identified in the legend of panel a. The three state points are the same three identified in Figure 6. In panel b, the symbols for the film and second layers overlap for $p_b/p_0 < 2 \times 10^{-1}$.

Figure 9.
As Figure 8, for $R/\sigma = 6.0$.

Figure 10.
As Figure 8, for $k_B T/\epsilon = 0.85$.