Methane Adsorption in Model Mesoporous Material, SBA-15, Studied by Small-Angle Neutron Scattering

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*Supporting Information

ABSTRACT: The understanding of methane adsorption is important for many industrial applications, especially for the shale gas production, where it is critical to understand the adsorption/desorption of methane in pores even as small as a few nanometers. Using small-angle neutron scattering (SANS), we have studied the adsorption of deuterated methane (CD₄) into one model mesoporous material, SBA-15, with pore diameter approximately 6.8 nm at the temperature range from 20 to 295 K at low pressure (≈100 kPa). A new scattering model is developed to analyze the SANS patterns of gas adsorption in SBA-15. The surface roughness of the SBA-15 matrix is estimated. The gas adsorption behaviors on the surface regions are extracted from the fitting. The rough surface of the pores is found to retain a large amount of CD₄ at the temperature above the capillary condensation temperature (Tᵥ). At temperatures below Tᵥ, the confined liquid and solid methane are estimated to be less dense than the corresponding bulk liquid and solid methane. Detailed theoretical analysis and experimental verification also show that SANS patterns at temperatures higher than Tᵥ are much more sensitive to the change of the excess adsorption, ε_ads, rather than the average density of adsorbed layers commonly used in many studies. The model we establish can be used to analyze future SANS/SAXS data for gas confined in similar model porous materials.

1. INTRODUCTION

Shale gas provided the largest share of U.S. natural gas production in 2013.¹ Its production in the U.S. increased from approximately 9.6 billion cubic meters (bcm) in 2001 to 282 bcm in 2015.² The success in extracting hydrocarbons from shale reservoirs has stimulated the increase in research on the pore morphology of shale rocks.³−⁵ However, the understanding of many fundamental issues related with the shale gas storage and transportation is still lacking despite all the industrial successes. Recently, it has been shown that the gas storage within the shale rocks is predominately associated with the organic component, the so-called kerogen, in the rocks,⁶ which is found to be imbedded within the inorganic matrix and has pores and capillaries of characteristic length scale between 1 and 100 nm.⁷ For nanometer pores, the pore surface plays important roles both as a gas storage location and as a flow modulator. The total hydrocarbon reserve is the summation of hydrocarbon adsorbed on the pore surface and the free gas in the pore.⁷ In order to better understand the adsorption properties of natural gas in the shale rocks, it is crucial to investigate the interaction of the natural gas and the pore surface and understand the gas adsorption and transportation mechanisms in small pores at the nanometer size scale.

Ordered mesoporous silicas have drawn much attention since their discovery in the early 1990s for various applications such as gas storage, heterogeneous catalysis, and separation processes.⁸−¹² These materials have relatively high surface area and uniform pore size. Their pores can be tailored in a wide range of sizes from about 2 up to 30 nm,¹³ which cover the essential pore size scale in kerogen and rocks. These properties make the mesoporous silicas suitable model adsorbents to study the adsorption mechanism of natural gases confined in nanofibers.

The gas adsorption on these model porous materials is widely studied by isotherm measurements for gases such as N₂ and Ar.¹⁴,¹⁵ X-ray scattering has been used to investigate the structure change during gas adsorption for Ar,¹⁶,¹⁷ K₂,¹⁸ and C₆F₁₂,¹⁹ on SBA-15 and MCM-41. However, there are only a few isotherm adsorption data for the most common component in natural gas, methane, on these model porous materials.²⁰−²³ Knowledge of a
methane adsorption mechanism on these materials, especially the detailed structure information, is still missing.

Different scattering models have been developed to explain the pressure-dependent scattering patterns of gas adsorption in SBA-15 and MCM-41, both with cylindrical mesopores packing into ordered hexagonal structure. To reproduce the X-ray diffraction intensity of SBA-15 and MCM-41 with gas molecules adsorbed on the pore wall, multilevel densities were used to model the cylindrical pores. Following the direction from outside the pore toward the pore center, the different density levels consist of (1) a dense silica matrix, (2) a corona region surrounding the mesopores formed by lower density microporous silica filled or partially filled with gas molecules, (3) liquid-like film of adsorbed gas molecules, and (4) a vapor core with negligible density.\textsuperscript{16,18,19} The existence of liquid-like film depends on the pressure and temperature. The corona region has been described in the literature as a constant density film,\textsuperscript{19} linear ramp diffuse layer,\textsuperscript{16} and Gaussian diffuse layer.\textsuperscript{16}

In this study, we investigate the methane gas adsorption in SBA-15 as a function of temperature at ambient pressure using small-angle neutron scattering (SANS). It is worth noting that there are very few studies on temperature dependence as most investigations of gas adsorption in SBA-15 and other model materials were performed as a function of pressure at a given temperature. This is the first quantitative structure analysis of the effect of temperature on methane gas adsorption at a wide range of temperatures (20–295 K) using SANS. Our experimental results reveal the detailed structure change during methane adsorption in SBA-15. In addition, a new theoretical scattering model is developed in this study to interpret the temperature dependence of the scattering patterns as the commonly used models in the literature fail to reproduce our experimental data. We also show that before capillary condensation takes place SANS/SAXS scattering patterns are more sensitive to the excess adsorption rather than the average density of the adsorbed gas molecules on the surface.

2. EXPERIMENTAL SECTION

Material Preparation. Mesoporous silica SBA-15 was synthesized by hydrothermal treatment, following the approach originally reported by Zhao et al.\textsuperscript{24} A commercial triblock copolymer (Pluronic P123) and tetraethyl orthosilicate (TEOS) were used as the structure-directing agent and the silicon source, respectively. An amount of 6 g of P123 was dissolved in 45 mL of deionized water and 150 mL of 2 M hydrochloric acid at 35 °C, and the solution was stirred vigorously, where 1 M equals to 1000 mol/m\textsuperscript{3}. Then, 13.8 mL of TEOS was added dropwise to the solution. The synthesis gel was aged for 24 h and then transferred to a Teflon bottle to be hydrothermally treated at 80 °C for another 24 h. The precipitated product was centrifuged and washed with deionized water until the pH value of the washing solution became 7. The sample was dried overnight at 80 °C. The white powder was annealed at 550 °C for 4 h to remove the surfactant molecules. N\textsubscript{2} adsorption isotherm measurement of the final SBA-15 powder results in the specific surface area 781.15 m\textsuperscript{2}/g, pore volume 0.8198 cm\textsuperscript{3}/g, and pore width 47.6 Å. The adsorption isotherm for N\textsubscript{2} on the synthesized SBA-15 can be found in Figure S7 of the Supporting Information (SI).

Experimental Setup. Small-angle neutron scattering (SANS) measurements were performed at nSoft-10m SANS and NGB-30m SANS at the National Institute of Standards and Technology (NIST) Center of Neutron Research (NCNR). The incident neutron wavelength, $\lambda$, was chosen to be 5 or 6 Å. The sample-to-detector distances, SSDs, were selected to cover a scattering vector ($q$) range from 0.01 to 0.5 Å\textsuperscript{−1}. All SANS data were corrected for the sample transmission, the background scattering, and the detector sensitivity based on a standard procedure described elsewhere.\textsuperscript{25}

The SBA-15 sample was degassed at 120 °C for 1.5 h before the experiment. The sample was then loaded in an aluminum sample cell with 1 mm path length. The temperature of the sample was controlled by a closed cycle refrigerator (CCR). Deuterated methane (CD\textsubscript{4}) was chosen as the gas adsorbate and was purchased from Cambridge Isotope Laboratories, Inc.\textsuperscript{26} CD\textsubscript{4} was loaded by a gas loading line linked between the sample cell and a CD\textsubscript{4} gas cart mounted with a pressure sensor. SANS measurement was first conducted on SBA-15 under vacuum. CD\textsubscript{4} gas was then loaded in situ to the SBA-15 sample powder. The measurements were done at different temperatures ranging from 20 to 295 K. The amount of the SBA-15 sample was maintained the same during the experiments. CD\textsubscript{4} pressure was monitored and maintained at about 100 kPa by a CD\textsubscript{4} gas cart at temperature above 112 K. The slight change of CD\textsubscript{4} pressure with temperature above 112 K can be found in Figure S5 in the SI. At $T < 112$ K, the valve connecting the CD\textsubscript{4} gas cart and the sample cell was turned off to prevent the condensation of gas in the bulk phase.

3. THEORETICAL MODEL FOR SANS DATA ANALYSIS

The small-angle scattering intensity $I(q)$ of powder SBA-15 without gas and SBA-15 loaded with CD\textsubscript{4} (we refer to the latter one as CD\textsubscript{4}/SBA-15 in the remainder of the paper) can be written as $I(q) = n(P(q)S(q))$. $q$ is the magnitude of the scattering vector defined as $q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$ where $\lambda$ and $\theta$ are neutron wavelength and scattering angle, respectively. $n$ is a prefactor related to average number density of SBA-15 mesopores in the neutron beam. $P(q)$ is the form factor describing the detailed structure of SBA-15 cylindrical mesopores with or without adsorbed and free CD\textsubscript{4} confined inside. $S(q)$ is the structure factor characterizing the hexagonally packed cylindrical pores. Because a powder-like sample is used, $\langle \cdots \rangle$ represents the ensemble average over all possible orientations of the SBA-15 grains. For hexagonally packed cylindrical pores, $S(q)$ is the summation of the delta functions located at hexagonal lattice points in reciprocal space, $q_{hk}$, where $h$ and $k$ are the Miller indices of the 2D lattice. To model $P(q)$ of the cylindrical pores with adsorbed gas molecules on the pore wall and free gas in the pore center, we treat the pore structure as the core–shell cylinder with multilevel densities similar to what was described in the literature.\textsuperscript{16,18} The shell is the region where the dense CD\textsubscript{4} molecules are adsorbed on the rough surface, and it includes the microporous corona region of the solid matrix and liquid-like film region.\textsuperscript{16,18,19} The center of mesopores consists of free CD\textsubscript{4} vapor.

To analyze our data, we have developed a new SANS model to calculate $P(q)$ for the case that the interface between the SBA-15 matrix and the adsorbed CD\textsubscript{4} layer (Inads−ads) is a Gaussian diffuse interface, while the interface between the adsorbed CD\textsubscript{4} layer and CD\textsubscript{4} vapor core (Inads+) is a smooth and sharp interface. It should be noted that the proposed model can be easily extended to more complicated cases. However, the current model is sufficient to describe the present case. In a previous study,\textsuperscript{16} both interfaces of Inads−ads and Inads+ are assumed to have the same degree of roughness; however, this model is not able to reproduce the scattering intensity variation as a function of temperature in our
measurements. Therefore, the roughness of the Inm-ads and Inads-v should have different properties.

Figure 1a and Figure 1c illustrate the cross section of the empty SBA-15 pore with a Gaussian diffuse interface and that of SBA-15 with adsorbed CD4 gas molecules on the diffuse pore wall (CD4/SBA-15), respectively. We define \( R_v \) as the radius of the CD4 vapor core and \( R_m \) as the nominal radius of the matrix pore, and \( L \) is the length of the cylindrical pore. \( \rho_v, \rho_{ads}, \) and \( \rho_{SBA-15} \) are neutron scattering length densities (SLDs) of the CD4 vapor core, the shell of adsorbed CD4, and the SBA-15 matrix, respectively. \( \sigma \) is the diffusive parameter used to characterize the surface roughness of the SBA-15 pore wall. \( \rho_{ads} \) can be transferred to mass density of adsorbed CD4 through the formula

\[
\rho_{mass} = \frac{\rho_{ads} M_w}{N_A b}
\]

\( \rho_{SLD} \) and \( \rho_{mass} \) are SLD and mass density of CD4, respectively. \( M_w \) is the molecular weight of CD4 (= 20 g/mol). \( b \) is the total bound coherent scattering length of one CD4 molecule (= 3.33 \times 10^{-4} \text{ Å}). \( N_A \) is the Avogadro’s constant.

With the full comprehensive derivation being present in the SI, the equation of the theoretical SANS intensity after the orientation average is expressed as

\[
\text{(1)}
\]

Figure 1. (a) Cartoon of the cross section of an empty cylindrical mesopore in the SBA-15 matrix with a Gaussian diffuse surface. (b) Radial distribution of the volume fraction \( \phi_{SBA-15}(r) \) of the empty SBA-15 matrix. (c) Cartoon of the cross section of the core−shell cylinder with a Gaussian diffuse interface between the SBA-15 matrix and the adsorbed CD4 layer (Inm−ads) and a smooth and sharp interface between the adsorbed CD4 layer and the CD4 vapor core (Inads−v). (d) Radial distribution of the gas-accessible volume fraction \( \phi_{GA}(r) \) (blue curve) and \( \phi_{SBA-15}(r) \) (gray dashed curve). \( r \) is the radial distance to the pore center. \( R_m \) is the nominal matrix radius, and \( R_v \) is the vapor core radius.
\( m_{h,k} \) is the multiplicity. \( J_1 \) is the first-order Bessel function. \( C \) is a constant prefactor related only to the length and number density of the cylindrical mesopores and is independent of temperature if the amount of SBA-15 inside the neutron beam is the same during scattering measurements. The second term in the bracket of eq 1 is introduced to correct for the nonphysical situation of negative mass density of the adsorbed \( CD_4 \) layer, which has not been addressed in an earlier study.\(^ {16} \) In that study, the authors used a much simpler cylindrical model by assuming both \( I_{n,m} \) and \( I_{n,ads} \) interfaces have the same roughness.\(^ {16} \) With their assumption, their equation is different from eq 1 and can be expressed as

\[
\lim_{q \rightarrow \infty} I(q) = C \sum_{h,k} \frac{1}{q_{h,k}} m_{h,k} \exp \left(-\frac{(\sigma_{h,k})^2}{2}\right) \times \left[ \frac{2J_1(q_{h,k} R_m)}{q_{h,k} R_m} - \sigma_{h,k} R_m \right] \exp \left(-\frac{(\sigma_{h,k})^2}{2}\right)
\]

However, eq 2 is only correct when \( R_m \geq R_e \). At high temperature or low pressure where the amount of adsorption is small, \( R_e \) can be larger than \( R_m \) and this equation will lead to a nonphysical negative mass density of adsorbed \( CD_4 \). A correction is necessary for this situation, which leads us to develop a new scattering model as shown in eq 1. The details for the derivation of eq 1 and the issue arisen from eq 2 can be found in the SI.

It should be noted that there is no physical reason for the assumption that interfaces \( I_{n,m} \) and \( I_{n,ads} \) have the same roughness as the roughness of one interface is mainly determined by the solid matrix while another one is determined by the combined effects of the solid surface and the adsorption properties of gas molecules. It is worth noting that eq 1 is also valid for \( R_e > R_m \). This is different than a typical core–shell model where both \( I_{n,m} \) and \( I_{n,ads} \) interfaces are sharp and smooth interfaces. Equation 1 can be applied to both empty SBA-15 and \( CD_4/\text{SBA-15} \) if the length of the cylindrical pore is treated as infinite. For empty SBA-15, the pore is under vacuum and \( R_e = 0 \) and \( \rho_{ads} = 0 \). The theoretical equation for the empty SBA-15 can be expressed as

\[
\lim_{q \rightarrow \infty} I(q) = C \sum_{h,k} \frac{1}{q_{h,k}} m_{h,k} \exp \left(-\frac{(\sigma_{h,k})^2}{2}\right) \times \left[ \frac{2J_1(q_{h,k} R_m)}{q_{h,k} R_m} \right] \exp \left(-\frac{(\sigma_{h,k})^2}{2}\right)
\]

When a pore is fully filled with liquid or solid methane below the capillary condensation temperature, \( R_e = 0 \). Equation 1 reduces to

\[
\lim_{q \rightarrow \infty} I(q) = C \sum_{h,k} \frac{1}{q_{h,k}} m_{h,k} \times \left[ \frac{(\rho_{ads} - \rho_{SBA-15}) R_m^2}{q_{h,k} R_m} \right] \exp \left(-\frac{(\sigma_{h,k})^2}{2}\right)
\]

Here \( \rho_{ads} \) is the SLD of pores fully filled with \( CD_4 \). In this case, the peak intensity is solely determined by the SLD difference of the filling methane and the matrix. Therefore, the peak intensity can be used to estimate the mass density of the methane in the liquid or solid state under confinement.

To fit the experimental SANS data using the theoretical equations present above, the instrument resolution should be taken into account. The measured SANS intensity \( I(q) \) can be expressed as

\[
I(q) = \int \frac{I(q')}{(2\pi \sigma(q'))^2} \exp \left(-\frac{(q - q')^2}{2\sigma^2(q)}\right) dq'
\]

where \( I(q') \) is the theoretical intensity calculated through eq 1 with \( q' \) as a dummy variable. The instrument resolution is approximated to be a Gaussian function with the standard deviation \( \delta(q) \) and \( q \)-dependent parameter \( \sigma(q) \).

4. RESULTS

The stability of the SBA-15 structure as a function of temperature is first examined. Figure 2a shows the SANS data for SBA-15 without loaded deuterated methane at 15, 115, and 295 K. The scattering patterns show clearly the first-order diffraction peak along with overlapped second- and third-order peaks. The peak positions confirm the \( \text{pmm} \) hexagonal symmetry of the mesopores. The lack of change in the scattering patterns over this temperature range indicates that the SBA-15 microstructure is stable between 15 and 295 K. The inset of Figure 2a shows a schematic plot of the hexagonally packed cylindrical mesopores within the SBA-15 grain.

After loading \( CD_4 \) at about 100 kPa, scattering patterns of \( CD_4/\text{SBA-15} \) change significantly with temperature in all the \( q \) ranges as indicated in Figure 2b. The relative peak intensities for all the peaks vary with temperature, and the fourth-order peak even shows up at certain temperatures. The intensity variation with temperature is solely due to the adsorption of \( CD_4 \) molecules into the pores.

The pore structure information on the empty matrix can be obtained by fitting the SANS data of the SBA-15 sample without loading gas molecules using eq 3. The center-to-center distance of the cylindrical pores is determined by the first-order peak position \( q_{max} \) as \( \frac{4\pi}{\lambda q_{max}} = 100.4 \) Å. The three fitting parameters in eq 3 are the prefactor \( C \), matrix radius \( R_m \), and diffusive parameter \( \sigma \), of the pore wall. Once having these, their values are fixed when analyzing the scattering data of \( CD_4/\text{SBA-15} \). The model fitting gives structural parameters of \( R_m = (34.1 \pm 0.05) \) Å and \( \sigma = (7.5 \pm 0.09) \) Å for the empty SBA-15 pore with a Gaussian diffuse interface, where the confidence intervals for uncertainties represent one standard deviation. The extracted radial distribution of the SBA-15 matrix volume fraction \( q_{SBA-15}(r) \) is plotted in Figure 1b.

It is important to point out that the accuracy of the SLD of the solid \( \text{SiO}_2 \) matrix under vacuum is crucial to extract the liquid or
solid methane density in the paper. The SLD of the SBA-15 matrix \( \rho_{\text{SBA-15}} \) is accurately determined by a different SANS experiment using the contrast variation method. This is a difficult task that needs considerable efforts to correctly set up the experiments. The details are provided in the SI. Figure S1 indicates that the H\(_2\)O/D\(_2\)O mixture with (59 ± 0.1) mol % of D\(_2\)O can match the SiO\(_2\) matrix. This corresponds to SLD and mass density of the SBA-15 matrix as \((3.51 ± 0.008) \times 10^{10}\) cm\(^{-2}\) and \((2.23 ± 0.005)\) g/cm\(^3\), respectively.

When loading gas into the pores, the pore center is filled with CD\(_4\) vapor and has a gas pore radius of \( R_v \). Because the CD\(_4\) vapor has very small density compared with the density of the adsorbed CD\(_4\) layer in the temperature and pressure conditions being studied, it is reasonable to fix the SLD of the vapor inside the core, \( \rho_v \), to be 0. In addition, the interface between the adsorbed CD\(_4\) layer and CD\(_4\) vapor (\( \text{In}_{\text{ads-v}} \)) is assumed to be a sharp interface. Equation 1 is used to fit the SANS data of CD\(_4\)/SBA-15. \( C, R_{\text{mv}} \) and \( \sigma \) are fixed as the values found in empty SBA-15. The fitting parameters for CD\(_4\)/SBA-15 are \( R_c \) and \( \rho_{\text{ads}} \). The fitting parameters used to obtain the best fits are listed in Table S1 in SI.

For each data set of both empty SBA-15 and gas-loaded SBA-15, a linear background is added to the first-order peak region and the \( q \) range below it. When plotting the intensity in log–log scale, the second and third peaks are grown on top of a linear line, and this clearly suggests a power law background in this \( q \) range (see Figure 2). These backgrounds are used to account for the diffuse scattering of imperfect lattice order of hexagonally packed structure and effects from other defects. Different backgrounds are used because the baseline of scattering pattern changes with \( q \) and temperature. In addition, Porod scattering \( I_p(q) = \sigma_v \times q^{-4} \) is added to account for the low \( q \) upturn, and the Porod constant \( \sigma_v \) is also a fitting parameter for each data set. This low-\( q \) scattering is due to the contrast between the SLD of interparticle space (vacuum or CD\(_4\) vapor) and the average SLD of granular powder particles in the sample. The validation of the addition of Porod scattering is described in the Instrument Resolution and SANS Backgrounds section in SI.

Figure 3 shows the SANS experimental data and fitting curves for empty SBA-15 at 295 K (Figure 3a), CD\(_4\)/SBA-15 at 225 K (Figure 3b), and CD\(_4\)/SBA-15 at 90 K (Figure 3c). 225 and 90 K are chosen to represent the data at temperature above the capillary condensation temperature \( T_c \) and temperature below \( T_c \) respectively. \( T_c \) is 119 K, and it can be determined by the temperature where the sudden drop of \( R_v \) happens. It is also reflected in the dramatic decrease of first-order peak intensity. More details will be discussed later. For temperature below \( T_c, R_v \) is set to be zero. It should be noted that even if we allow \( R_v \) to be a fitting parameter, the fitted \( R_v \) below \( T_c \) is all very close to zero. This is reasonable because after capillary condensation happens, the cylindrical pores should all be filled with CD\(_4\) liquid or solid. Since the second and third peaks are weak and can be affected by the assigned background, the fitting has been focused on capturing the intensity of the first peak, but the fitting to the second and third peaks is also reasonably good.

Figure 4 shows the experimental data of first peak intensity as a function of the temperature (red solid circles). Using the extracted fitting parameters listed in Table S1 in the SI, the calculated intensity of the first peak is also plotted in Figure 4 (black solid squares). Since the parameters for the solid matrix are fixed during the fitting of the SANS patterns for CD\(_4\)/SBA-15, only two factors affect the peak intensity. One is the SLD of the adsorbed methane \( \rho_{\text{ads}} \), and the other one is the vapor core radius \( R_v \). Change of the intensity of the first peak as shown in Figure 4 is then closely related to the adsorbed gas density and the relative thickness of the adsorbed dense gas region. It should be noted that because the surface is so rough it is not possible to define a monolayer thickness through the fitting of the scattering data at the high-temperature region. When the temperature decreases from 295 K, CD\(_4\) molecules are gradually adsorbed on the rough pore surface. The adsorbed layer thickness is still very small. Therefore, the peak intensity increases when the average density of the adsorbed layer increases on the surfaces. When the temperature slowly approaches to the capillary condensation temperature \( T_c \) (≈119 K), the radius of the CD\(_4\) vapor core \( R_v \) decreases slowly at temperature above 119 K. The first-order peak intensity drops dramatically between 119 and 112 K as the temperature is lowered. This is because the pores are suddenly fully filled by CD\(_4\) liquid. The intensity gradually increases again with further cooling from 112 to 20 K because density of CD\(_4\) inside the pores increases. The scattering patterns are reversible for both cooling and heating processes through the whole temperature range except for the temperature between 119 and 112 K (see Figure S4 in SI). The reversibility of the SANS data at temperature below \( T_c \) eliminates the possibility of partial filling scenarios described in the previous literature. The model is able to account for the second and third peaks on top of a linear line. This is reasonable because the baseline of scattering pattern changes with \( q \) and temperature.
to reproduce the change of the first-order peak intensity very well.

Figure 5 shows the parameters $R_v$, normalized mass density of adsorbed CD$_4$ above $T_c$, the mass density below $T_c$, and absolute adsorption in a cylindrical pore per length $M_{ads}$ as a function of temperature extracted from the current Gaussian model described by eq 1. $R_v$ gradually decreases with temperature, $T$, at $T$ above 119 K (see Figure 5a), but its value mostly remains about 40 Å. If we define qualitatively the outside boundary of an empty pore to be $R_m + 2\sigma \approx 49.1$ Å, the thickness of the dense region then remains about 9 Å before $T$ gets close to $T_c$. The gas adsorption region on the surface has not changed too much and is mostly determined by the roughness of the empty matrix. Therefore, it is not possible to directly obtain the information on multilayer adsorption conclusively. $R_v$ suddenly decreases to almost zero at $T < 119$ K, indicating the rapid expansion of the adsorbed gas region due to the capillary condensation. The thickness of adsorbed dense gas regions does not change too much above $T_c$, and therefore above $T_c$, all adsorbed gas molecules go to similar surface regions and cause the increase of average density in this region. It should be noted that the absolute value of the mass density above $T_c$ depends on the model used to describe the diffuse layer of the solid matrix. Therefore, the results are model dependent. We will discuss later in this paper that the Gaussian diffuse layer model is very useful to capture the main feature of the solid matrix but is still not sufficient to capture the details of the density profile. As a result, we only show normalized density here to highlight the trend of the density change. When the temperature approaches $T_c$, $\rho_{CD4,mass}$ should be very close to liquid density. The normalized mass density of adsorbed CD$_4$, $\rho_{CD4,mass,norm}$, is therefore normalized in a way that the average value of $\rho_{CD4,mass}$ in the temperature range from 119 to 140 K equals to the liquid density at 112 K. $\rho_{CD4,mass,norm}$ above $T_c$ increases dramatically when temperature is decreased, as shown in Figure 5b. $\rho_{CD4,mass,norm}$ reaches a saturated value at about 140 K and remains roughly constant between 140 and 119 K. There is a drop of $\rho_{CD4,mass,norm}$ at 119 K, and it may be due to the partial condensation of CD$_4$ inside the pores.
To estimate the absolute value of the mass density of the liquid or solid methane below $T_c$, $R_v$ is fixed to zero. (Even if we allow $R_v$ to be a fitting parameter, its value is negligibly small.) The extracted mass density of the confined CD$_4$ increases with the decrease of temperature, as shown in Figure 5c. Eventually CD$_4$ solidifies, and its density reaches a constant value of approximately 0.57 g/cm$^3$. The sudden increase in mass density between 60 and 70 K may be due to the occurrence of liquid–solid transition. The liquid-to-solid transition for bulk methane at 101.3 kPa is at 90.7 K. The bulk density at 101.3 kPa of liquid CD$_4$ at 110 K and that of solid CD$_4$ at 70 K are 0.53 and 0.62 g/cm$^3$, respectively. The confined CD$_4$ density at 110 K (liquid state) and that at 20 K (solid state) extracted from our SANS results are 0.493 ± 0.0003 and 0.570 ± 0.0005 g/cm$^3$, respectively. Therefore, the confined liquid and solid methane density are smaller than the corresponding bulk methane density. The lower density is likely due to the lower packing density introduced by the rough surface of the pore wall.

Absolute adsorption per length, $M_{ads}$ is calculated from integrating the mass density of CD$_4$ over a mesopore with diffuse surface. It is expressed as

$$M_{ads} = \int_0^\infty \rho_{CD_4,\text{mass}} \varphi_{GA}(r) 2\pi r dr$$

$M_{ads}$ is a function of $R_v$ and $\rho_{CD_4,\text{mass}}$. $\varphi_{GA}(r)$ is the gas-accessible volume fraction, and it decreases to 0 when $r$ approaches the dense silica matrix region. An example of $\varphi_{GA}(r)$ is plotted in Figure 1b. Figure 5d shows that $M_{ads}$ continues to increase when lowering temperature from 295 K and enhances suddenly after capillary condensation at $T_c$ because the pore is abruptly filled by the liquid CD$_4$. The increase in $M_{ads}$ below $T_c$ is due to the increase in $\rho_{CD_4,\text{mass}}$ of the confined CD$_4$ when further cooling the temperature.

It is surprising to notice from Figure 5d that the absolute adsorption, $M_{ads}$ at $T_c \approx 119$ K, when only the diffuse layer region is covered by CD$_4$ is larger than half of $M_{ads}$ at 112 K when the pores are fully filled with liquid CD$_4$. The extracted result indicates $M_{ads}(T = 119 \text{ K})/M_{ads}(T = 112 \text{ K}) = 0.58$. This result is consistent with what is found in the adsorption isotherm for N$_2$ (see Figure S7). The ratio of N$_2$ adsorption amount when all surfaces are fully covered prior to capillary condensation (282.73 cc/g (STP) at $P/P_0 \sim 0.51$) to adsorption amount when all pores are fully filled right after capillary condensation (499.53 cc/g (STP) at $P/P_0 \sim 0.73$) is 0.57. This shows that the rough surface of SBA-15 pores can adsorb a very large amount of CD$_4$. If we assume the density of liquid methane is the same in the core and in the diffuse region of the pore, the available volume in the diffuse layer is quite significant and contributes to the significant portion of the total methane adsorption. The high degree of surface roughness comes from both surface corrugations and micropores of the pore walls.\cite{19,28} We can also get a hint from the high specific surface area 781 m$^2$/g obtained from N$_2$ isotherm (BET) measurement. If we assume that the cylindrical mesopores are perfect cylinders with smooth surface (no
roughness), the specific surface area and pore volume of these perfect cylinders having the pore radius the same as the nominal matrix pore radius $R_m$ can be estimated by 

$$\frac{2\pi R_m^2}{(2\pi^2 - xR_m^2)\rho} \approx 190$$

m$^2$/g and 

$$\frac{\pi R_m^2}{(2\pi^2 - xR_m^2)\rho} \approx 0.32 \text{ cm}^3$/g, respectively, which are much smaller than what is found in the N$_2$ isotherm results. It should be noted that SANS only detects the “good” pores, i.e., the mesopores arranged in ordered hexagonal packing, while the N$_2$ isotherm measurement includes all the surfaces which can adsorb gas molecules. However, we still need to consider the roughness of the pore surface to produce the high specific surface area of 781 m$^2$/g and pore volume of 0.8198 cm$^3$/g measured by the N$_2$ isotherm. It is worth noting that by fitting the high q range from 0.29 to 0.35 Å$^{-1}$ using the Porod’s law $I(q) = c_q \times q^{-4}$ the surface to volume ratio $(S/V)$ can be extracted.

$$c_q = 2\pi(\Delta \rho)^2 \frac{S}{V}$$

where $V$ is the total sample volume exposed to neutrons and $S$ is the total surface area inside the volume $V$, including all the “good” and “bad” pores. Knowing the total amount of SBA-15 inside the volume $V$, the specific surface area is calculated to be 882 m$^2$/g, which is close to the value obtained from isotherm measurement (781 m$^2$/g). The large adsorption amount for the rough surface compared with the smooth surface with similar nominal matrix radius is also found from GCMC simulations by Coane et al.29 and Tanaka et al.30 The fact that a rough surface exists around the SBA-15 mesopores, it is not surprising that in model (4) achieve similar fitting quality and replicate first-order peak intensity as a function of temperature. As an example, the extracted $R_v$ is compared with that obtained using eq 1 as shown in Figure 6a. The results are qualitatively comparable to each other. However, the use of different models affects both $R_v$ and $\rho_{adv}$. The parameters obtained from model (4) and the current model are therefore biased by the models we choose.

5. DISCUSSION

It should be noted that we have also tried other models to fit our SANS data: (1) monodisperse core−shell model with smooth and sharp interfaces for both the interface between the matrix and adsorbed CD$_4$ layer ($I_{m-adv}$) and the interface between the adsorbed CD$_4$ layer and CD$_4$ vapor core ($I_{adv-v}$);31 (2) monodisperse core−shell model with the same Gaussian diffuse parameter $\sigma$ for both $I_{m-adv}$ and $I_{adv-v}$ interfaces;30 (3) polydisperse core−shell model with sharp $I_{m-adv}$ and $I_{adv-v}$ interfaces;16 and (4) monodisperse core−shell model with the sharp $I_{adv-v}$ interface but linear ramp diffuse $I_{m-adv}$ interface. Some of these models are also used in the literature.16,31,32

As suggested by a previous study28 that a microporous corona exists around the SBA-15 mesopores, it is not surprising that model (1) cannot reproduce the scattering intensity. In model (2), the diffusive parameter $\sigma$ is assumed to be the same for $I_{m-adv}$ and $I_{adv-v}$ interfaces, as suggested by Muroyama et al.16 However, this model cannot reproduce the change of first-order peak intensity as a function of temperature featured in Figure 4. A careful analysis of the model shows that the diffusive parameters have to be different for different interfaces. In model (3), the adsorbed CD$_4$ layer thickness is assumed to be the same for all the pores with different size. Again, this model fails to describe the scattering intensity. Although the current model described in eq 1 does not include the polydispersity effect of the mesopores, we do not exclude the possibility that the mesopores have pore-size distribution. Equation 1 is able to reproduce the SANS intensity and indicates that the more prominent effect is the surface roughness, and it is sufficient for current model fitting. Adding more parameters slightly improves the fitting quality but largely increases the fitting error bars.

Model (4) is similar to the current one we describe in eq 1, with the only difference in the assumption of the density profile of the empty matrix. It assumes that the solid matrix density changes as a linear function, which was also adopted in previous literature to study Kr adsorption on SBA-15.15 The fitting results of model (4) achieve similar fitting quality and replicate first-order peak intensity as a function of temperature. As an example, the extracted $R_v$ is compared with that obtained using eq 1 as shown in Figure 6a. The results are qualitatively comparable to each other. However, the use of different models affects both $R_v$ and $\rho_{adv}$. The parameters obtained from model (4) and the current model are therefore biased by the models we choose.
We can further calculate excess adsorption $\varepsilon_{\text{ads}}$, which is defined as the integral over a pore of adsorbed CD$_4$ mass density subtracted by the bulk CD$_4$ mass density at the same temperature and pressure conditions.

$$\varepsilon_{\text{ads}} = \int_0^\infty [\rho_{\text{CD}_4, \text{mass}} - \rho_{\text{CD}_4, \text{bulk}}(T, P)] \varrho_{\text{CD}_4}(r) 2\pi r dr$$

where $\rho_{\text{CD}_4, \text{bulk}}(T, P)$ is the bulk CD$_4$ density at temperature $T$ and pressure $P$. Above $T_c$, $\varepsilon_{\text{ads}} \approx M_{\text{ads}}$ because the bulk CD$_4$ gas density is negligible compared with adsorbed CD$_4$ density. The Gaussian and linear diffuse models almost give the same values of $\varepsilon_{\text{ads}}$, as shown in Figure 6b.

Interestingly, it turns out that when the amount of gas adsorbed is small the change of the scattering patterns is more sensitive to the excess adsorption, $\varepsilon_{\text{ads}}$, than to $R_v$ and $\rho_{\text{ads}}$. This can be demonstrated by analytically deriving $\varepsilon_{\text{ads}}$ at the limit of small $\varepsilon_{\text{ads}}$. For the simplest case of the core–shell cylinder where both $R_{\text{in,ads}}$ and $R_{\text{out,ads}}$ are sharp interfaces, the derivation of $\varepsilon_{\text{ads}}$ is given in the Calculation of Excess Adsorption section in the SI. For the complicated cases of Gaussian and linear diffuse models, the numerical calculation of $\varepsilon_{\text{ads}}$ is given and shown in Figure S6a and Figure S6b in the SI. Figure S6 indicates that the more complicated cases lead to the same conclusion that $\varepsilon_{\text{ads}}$ is a more reliable parameter than $R_v$ and $\rho_{\text{ads}}$ when gas adsorption amount is low, i.e., at high temperature.

Both Gaussian and linear models are used to fit the SANS data shown in Figure 2b. Even though $R_v$ and $\rho_{\text{ads}}$ obtained from the model fitting are different (see Figure 6a), $\varepsilon_{\text{ads}}$, extracted by the two models are very similar (see Figure 6b). This confirms that $\varepsilon_{\text{ads}}$ is a more model-independent parameter than $R_v$ and $\rho_{\text{ads}}$ and it is less sensitive to the used model. This is the exact reason why the error bars for $R_v$ and $\rho_{\text{ads}}$ are larger at higher temperatures when $\varepsilon_{\text{ads}}$ is small. The inclusion of additional higher-order peaks is very useful to more accurately determine $R_v$ and $\rho_{\text{ads}}$. In previous studies, the accuracy of fitting parameters highly depends on the number of diffraction peaks present in the scattering pattern. However, it should be noted that even with several higher-order peaks the intensity of the higher-order diffraction peaks is usually very small and is very sensitive to the background being subtracted.

Because the scattering patterns are more sensitive to the excess adsorption $\varepsilon_{\text{ads}}$, especially at high temperature, this in turn helps us to evaluate the density profile models we have tested. Even though both Gaussian and linear density models were used in the literature, it seems that both models are insufficient to address our data perfectly. The absolute mass density at $T > T_c$ obtained by the fitting is much larger than what we expect, and it is even larger than the liquid methane density at some temperatures (see Table S1 in SI). Even though we do not think this affects the trend that the average density in the adsorbed gas regions increases with the decrease of temperature (so we use “normalized” mass density instead of the absolute mass density at $T > T_c$). It is useful to investigate the possible reasons for the unusually high density in the adsorbed gas regions. Since $\varepsilon_{\text{ads}}$ is the most model-independent parameter, if we assume different models give similar values of $\varepsilon_{\text{ads}}$, the higher density means that both Gaussian and linear models of density profile underestimate the gas-accessible volume at the diffuse layers when $\varepsilon_{\text{ads}}$ is small. A more complex function can certainly make the fitting better. However, since we only have one clear first-order peak together with blurred second- and third-order peaks, we do not have enough information to reliably extract the fine difference of the density profile. Further work is needed to characterize this.

It should be noted that the mesopores of SBA-15 are fully filled after capillary condensation, and the mass density of the CD$_4$ confined in the pores is not coupled with $R_v$ anymore ($R_v = 0$ below $T_c$). The mass density can be accurately determined and is plotted in Figure 5c.

6. CONCLUSION

In this study, methane adsorption is investigated for a model silica porous material, SBA-15, which has cylindrical pores packed in a hexagonal pattern. SANS is used to study in situ gas adsorption into SBA-15 and determine the structural details of methane adsorption for a wide range of temperatures at ambient pressure. A new and better SANS model is developed in order to satisfactorily explain our data. The empty SBA-15 matrix is found to have a very rough surface, which determines the thickness of the adsorbed dense gas regions. The rough surface has significant contribution to the total gas adsorption. Below the capillary condensation temperature $T_c$, the pore is filled by CD$_4$ liquid. The density of the liquid methane inside the mesopores is accurately determined. The results show that decreasing temperature increases the density of liquid methane. Eventually liquid—solid phase transition happens, and the density of CD$_4$ solid remains about constant when further lowering the temperature. It is found that above $T_c$ the scattering patterns are more sensitive to the excess adsorption $\varepsilon_{\text{ads}}$ rather than the vapor core radius $R_v$ and SLD of the adsorbed CD$_4$ $\rho_{\text{ads}}$ which were commonly used in many studies. After applying different models to study the gas adsorption, $\varepsilon_{\text{ads}}$ is found to be less model biased. The rough surface of the pore wall is shown to be able to retain lots of gas molecules above $T_c$. Our results indicate that it is important to study the roughness of the shale rocks as it potentially plays an important role in the gas storage capacity and affects the overall gas permeability. The theoretical scattering model we develop in this study is also very useful to analyze SAXS/SANS data of other different types of gas molecules in model porous materials to characterize the gas adsorption in confined spaces.
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(26) Identification of a Commercial Product Does Not Imply Recommendation or Endorsement by the National Institute of Standards and Technology, nor Does It Imply That the Product Is Necessarily the Best for the Stated Purpose.