Modeling High-Pressure Methane Adsorption on Shales with a Simplified Local Density Model

Ke Hu* and Helmut Mischo

ABSTRACT: Shale gas has attracted increasing attention as a potential alternative gas in recent years. Because a large fraction of gas in shale formation is in an adsorbed state, knowledge of the supercritical methane adsorption behavior on shales is fundamental for gas-in-place predictions and optimum gas recovery. A practical model with rigorous physical significance is necessary to describe the methane adsorption behavior at high pressures and high temperatures on shales. In this study, methane adsorption experiments were carried out on three Lower Silurian Longmaxi shale samples from the Sichuan Basin, South China, at pressures of up to 30 MPa and temperatures of 40, 60, 80, and 100 °C. The simplified local density/Elliott−Suresh−Donohue model was adopted to fit the experimental data in this study and the published methane adsorption data. The results demonstrate that this model is suitable to represent the adsorption data from the experiments and literature for a wide range of temperatures and pressures, and the average absolute deviation is within 10%. The methane adsorption capacity of the Longmaxi shale exhibited a strong linear positive correlation with the total organic carbon content and a linear negative correlation with increasing temperature. The rate of decrease in the methane adsorption capacity with swing temperature increased with the total organic carbon content, indicating that the organic matter is sensitive to temperature.

INTRODUCTION

In recent years, interest in shale gas has grown because of the advances in horizontal drilling and hydraulic fracturing techniques. In 2015, shale gas development accounted for 50% of natural gas production in the United States, and this is estimated to increase to nearly 70% in 2040. To meet the domestic energy demands, China started shale gas exploration and production in the Sichuan Basin in 2009. It is predicted that shale gas may account for nearly 50% of China’s natural gas production by 2040.

Unlike conventional reservoirs, shale gas itself is both the source and the reservoir. Generally, under practical stratum conditions, there are three types of stored shale gas: free gas in interparticle pores and microfractures, adsorbed gas on the surfaces of organic matter and clay minerals, and dissolved gas in kerogen and bitumen. Ambrose et al. indicated that the percentage of adsorbed gas to the total gas in shales was between 20 and 80%. Montgomery et al. pointed out that the percentage of adsorbed gas to the total gas in place could be as high as 50–60% in some cases. Therefore, adsorbed gas is a large fraction in shale gas reservoirs. Consequently, it is critical to investigate the adsorption capacity on shale for gas-in-place assessments and gas production predictions. Additionally, knowing the specific ratio of adsorbed gas and free gas is vital to identify gas migration mechanisms within shale reservoirs.

In recent years, many methane isothermal adsorption experiments have been performed on shale samples. Chalmers and Bustin and Ross and Bustin examined the methane adsorption capacities in shales in British Columbia, Canada, at 6 MPa at 30 °C. Rexer et al. measured the methane adsorption capacity on Alum shale under practical geological conditions up to 14 MPa and between 27 and 200 °C. Heller and Zoback measured the adsorption capacities and induced the swelling of methane and carbon dioxide on U.S. shales and pure minerals up to 10 MPa at 40 °C. Zhang et al. observed methane adsorption at 35, 50, and 65 °C and pressures of up to 15 MPa on Eocene Green River Formation, Devonian–Mississippian Woodford Shale, and isolated kerogen. Gasparik et al. examined methane sorption on organic-rich shales from Europe and the United States at pressures up to 25 MPa and...
temperatures up to 150 °C on dry samples and up to 38 °C on moisture-equilibrated samples. Merkel et al.\textsuperscript{15} performed methane sorption experiments on lacustrine shale from Scotland that was dry or had one of four different moisture contents at 45 °C and up to 25 MPa. Shabani et al.\textsuperscript{16} inspected 19 dry and moisture-equilibrated shale samples between 45 and 130 °C at pressures up to 25 MPa. The samples were collected from the Jurassic Sargelu and the Cretaceous Garau formations in Lurestan province, southwest Iran.

With the increasing interest in shale gas in China, Chinese shales have been analyzed. Tan et al.\textsuperscript{17} collected marine black shale samples from the Upper Yangtze Platform, South China, and tested the adsorption capabilities at pressures up to 25 MPa at 46 °C. Pan et al.\textsuperscript{18} applied the supercritical Dubinin–Radushkevich (sD–R) model to fit the methane adsorption data recorded at pressures up to 35 MPa for Longmaxi shales collected from southeast Chongqing, South China. Tian et al.\textsuperscript{19} studied methane adsorption at 35.4, 50.6, and 65.4 °C and pressures up to 15 MPa for eight overmature Lower Silurian–Upper Ordovician shale samples collected from the Sichuan Basin. Yang et al.\textsuperscript{20} used the modified supercritical Dubinin–Astakhov (sD–A) model to describe methane adsorption on Paleozoic shales from the Sichuan Basin at temperatures ranging from 30 to 120 °C and pressures up to 25 MPa. Wang et al.\textsuperscript{21} discussed the influence of pore characterization on methane adsorption of shale samples from the Upper Yangtze Platform, South China. Li et al.\textsuperscript{22} examined methane adsorption on Niutitang Shale (Lower Cambrian) collected from northeast Guizhou Province, southwest China, at various temperatures (40–120 °C) and pressures (up to 35 MPa). Zhou et al.\textsuperscript{23} discussed the density of the adsorbed phase using the sD–R model for eight Longmaxi shale samples from the Sichuan Basin, China, at 60 °C and up to 30 MPa.

However, some of the above investigations were carried out under moderate pressures (≤15 MPa)\textsuperscript{9–11,13,19} or quite low temperatures (≤60 °C)\textsuperscript{9,10,12,15,17,23} compared with the actual shale reservoir conditions. Unlike coalbed methane, which is usually deposited in shallow coal seams at depths of less than 1000 m, shale reservoirs are generally much deeper and under very different pressure and temperature conditions. Taking the Lower Silurian and Lower Cambrian shales in the Sichuan Basin, southwest China, as examples, the burial depth for industrial shale gas production ranges from 2000 to 4000 m.\textsuperscript{24} Theoretically, the temperature and pressure ranges of practical shale reservoirs are 60–120 °C and 20–40 MPa, respectively, assuming that the hydrostatic pressure gradient is 0.01 MPa/m and the normal geothermal gradient is 3 °C/100 m. Obviously, these values are much higher than the critical pressure (4.64 MPa) and critical temperature (–82.5 °C).\textsuperscript{25} Therefore, methane adsorption is supercritical under shale reservoir conditions. At relatively low pressures, the conventional adsorption model can fit the isotherms very well because the adsorption quantity is quite low and the volume of the adsorbed phase is negligible. However, excess adsorption will greatly deviate from the absolute adsorption (i.e., the actual adsorption) under high pressures,\textsuperscript{12,25} and this may result in substantial underestimation in gas-in-place and gas production calculations. Consequently, adsorption at relatively low pressures or low temperatures cannot represent the actual stratum conditions of shale formations.

Most previous studies have applied the modified Langmuir model, sD–R model, or sD–A model to match the experimental data. The Langmuir model is an ideal model and assumes that the adsorbate is adsorbed on a homogeneous surface in a monolayer and ignores the interactions between the adsorbed molecules.\textsuperscript{26} The sD–R model and its variant, the sD–A model, are based on pore filling theory for pore diameters smaller than 2 nm,\textsuperscript{29} but numerous previous studies have revealed that pore sizes in shale formations cover a wide range from micro to macro.\textsuperscript{30–39} Zhou et al.\textsuperscript{30} indicated that methane adsorption on shale involves synchronized pore filling and monolayer adsorption. Furthermore, for supercritical liquids, the saturated vapor pressure, which is an important parameter in the sD–R and sD–A models, is no longer defined.\textsuperscript{31} However, the model parameters acquired from the modified Langmuir model, sD–R model, and sD–A model are temperature-dependent. Consequently, they can only be used to obtain adsorption isotherms at specific temperatures and cannot be used to calculate the adsorption capacities at other temperatures. Furthermore, the density of the adsorption phase, which is set as a constant during model matching, is always higher than the upper limit of the liquid-phase methane density (424 g/m\textsuperscript{3}).\textsuperscript{22,23} A recent molecular simulation indicated that the density of the adsorption phase was position-dependent in slit pores.\textsuperscript{42} These phenomena indicate that the modified Langmuir model, sD–R model, and sD–A model may be physically unreasonable and limited to the representation of methane adsorption on shales. Therefore, a robust model with temperature-independent parameters is needed for promoting the understanding of supercritical methane adsorption of shales.

At this point, the simplified local density (SLD) model,\textsuperscript{43} which superimposes the fluid–solid potential on a fluid equation of state (EOS) to represent the adsorption of supercritical fluids in a slit, was successfully applied to describe the adsorption behaviors of pure and mixed gases in shales, coals, and active carbons\textsuperscript{44,45} over wide ranges of pressure and temperature. The SLD model is a thermodynamic method with only two temperature-independent undetermined parameters.\textsuperscript{46} Furthermore, Pan and Connell\textsuperscript{47} proposed the SLD model with a swelling model to predict the adsorption-induced swelling of coals. The Elliott–Suresh–Donohue (ESD) EOS\textsuperscript{48} is a simple model consisting of attractive and repulsive terms and takes shape factors into consideration. Consequently, the ESD equation can more accurately represent interactions than the Peng–Robinson equation.\textsuperscript{49} Therefore, the SLD model with the ESD equation provides specific advantages for a wide range of adsorption-related phenomena for adsorption and formation on organic rocks.

The aim of the present research was to perform methane adsorption on Longmaxi shales under high pressures (up to 30 MPa) and high temperatures (up to 100 °C). Experimental data were acquired using a magnetic suspension balance (gravimetric method). In addition, we attempted to use the SLD/ESD model to fit the adsorption isotherms. Furthermore, methane adsorption data on shales in the literature were selected to test the viability of the SLD/ESD model to represent the adsorption behavior on different shales.

### MATERIALS AND METHODS

**Samples and Geological Details.** Three samples were collected from the Longmaxi Formation in the Sichuan Basin, southwest China. The lower Silurian Longmaxi marine shale formation in the Weiyuan–Changning area is dominated by black carbonaceous shales with a stable thickness of 26–50 m. The total organic carbon (TOC) content ranges from 1.9 to
7.3% and the vitrinite reflectance ranges from 2.3 to 2.8%.\textsuperscript{50} Fresh samples were collected and sealed for preservation in the laboratory. Samples NY09 and NY21 were drilled from wells and Sample NY17 was drilled from an outcrop. The well location is not disclosed because of confidentiality reasons.

**Mineralogy and Organic Petrography.** To determine the TOC contents, the samples were crushed to 60–80 mesh. A sample (10 g) of each powder was immersed in dilute hydrochloric acid to remove carbonates. After the acid was drained from the samples, the samples were dried overnight at 65 °C. Subsequently, the TOC contents were measured using a carbon/sulfur analyzer (CS-244; Leco, St. Joseph, MI, USA).

Maturity is generally estimated by vitrinite reflectance. Because of the lack of vitrinite in marine shales, we took \( T_{\text{max}} \) from Rock-Eval pyrolysis using the equation \( R_0 = 0.0149 \times T_{\text{max}} - 5.85 \) to approximate the vitrinite reflectance.\textsuperscript{54}

X-ray diffraction was used to determine the relative mineral percentages of the shale samples. Powdered samples with the same grain size as for the TOC measurements were inspected using a Bruker D8 ADVANCE diffractometer with Cu Kα X-rays (1.5406 Å) at 40 kV and 40 mA. The 2θ scan range was 3–45° with a step size of 0.02° and an increased rate of 2°/min.

**Low-Pressure \( \text{N}_2 \) Adsorption/Desorption.** To investigate the pore structure and pore size distributions of the samples, low-pressure \( \text{N}_2 \) adsorption/desorption at −196.15 °C with a relative pressure \( (P/P_0) \) between 0.01 and 0.995 was conducted on a porosimetry system (ASAP 2020, Micromeritics Instruments). Each sample was crushed and sieved to a mesh size of 60–80 and then outgassed at 110 °C for 24 h to remove bound water and residual gases. The \( \text{N}_2 \) adsorption data between \( P/P_0 = 0.05 \) and 0.35 were selected to calculate the Brunauer–Emmett–Teller (BET) specific surface area, \( S_{\text{BET}} \), and the total pore volume was obtained at a relative pressure of 0.995. The average pore diameter was derived from 4 \( V/S_{\text{BET}} \), and the micropore volume (<2 nm) was calculated by the \( t \)-plot method.\textsuperscript{53}

**High-Pressure Methane Adsorption.** Methane excess adsorption isotherms were run on dry samples with a gravimetric adsorption/desorption setup (ISOSORP-HP, Rubotherm, Germany) at pressures up to 30 MPa and temperatures of 40, 60, 80, and 100 °C. The core unit was a magnetic suspension balance with a precision of 0.01 bar for the pressure, and 0.01 mg for the mass. The maximum test temperature and pressure were 150 °C and 35 MPa, respectively. To measure the adsorption isotherms, high-purity methane (99.99%) was injected by an ISCO pump into the pressure chamber, and the change in mass in the chamber was determined directly by the magnetic suspension balance.

The methane excess adsorption experiments were performed on crushed samples with grain sizes between 60 and 80 mesh. Crushing of samples can minimize the time required to reach equilibrium in a tight rock with extremely low permeability.\textsuperscript{54} Approximately 5 g of the crushed sample was used for each test. To remove the residual gas and moisture, the crushed samples were placed in the sample chamber before adsorption at 110 °C under approximately 0.01 atmospheric pressure until a constant mass was achieved. The equilibrium time for each pressure was set to 2 h. To evaluate the experimental repeatability, the isothermal measurement was repeated at 60 °C for each sample.

Briefly, the experimental system employs the conservation of mass as follows

\[
m = m_{\text{abs}} + m_i + m_s - (V_c + V_i + V_r) \times \rho_g
\]

where \( m \) is the mass recorded by the magnetic suspension balance, \( m_{\text{abs}} \) is the mass of the adsorbed phase, \( m_i \) is the mass of the sample container, \( m_s \) is the mass of the shale powder, \( V_c \) is the volume of the sample container, \( V_i \) is the volume of the shale powder, \( V_r \) is the volume of the adsorbed phase, and \( \rho_g \) is the density of the bulk phase. Currently, both \( m_{\text{abs}} \) and \( V_r \) are immeasurable in eq 1. According to the definition of Gibbs excess adsorption,\textsuperscript{55} the excess adsorption amount \( (m_a) \) can be calculated at a given temperature and pressure using the following equation

\[
m_a = m_{\text{abs}} - V_s \times \rho_s = V_s \times (\rho_i - \rho_s) \quad (2)
\]

where \( \rho_s \) is the density of the adsorbed phase.

Combination of eqs 1 and 2 gives the following equation

\[
m_a = m_{\text{ex}} - m_i - m_s + (V_i + V_r) \times \rho_g
\]

Obviously, all the parameters on the right side of eq 3 can be measured experimentally or calculated directly from the EOS. If either the density of the adsorbed phase \( (\rho_s) \) or the volume of the adsorbed phase \( (V_r) \) is known, the absolute adsorption can be written as follows

\[
m_{\text{abs}} = m_{\text{ex}} + V_s \times \rho_s = m_{\text{ex}}/\left(1 - \rho_i/\rho_s\right) \quad (4)
\]

**Theory of the SLD/ESD Model.** The SLD model can describe the adsorption and desorption of pure and mixed gases over a large pressure range. It assumes that the adsorbate molecules reside in a rectangular shaped slit and are located between the two surfaces of the slit (Figure 1).

![Figure 1. Schematic diagram of the slit geometry.](https://dx.doi.org/10.1021/acsomega.9b03978)

The width between the two surfaces is \( L_s \) and the perpendicular distance between the adsorbate and the surface is \( z \). The adsorbate interacts with the two surfaces of the slit and the molecules in the bulk phase. At equilibrium, the SLD model assumes that the chemical potential of the bulk phase \( (u_{\text{bulk}}) \) equal to the chemical potential of the adsorbate molecule \( (u(z)) \) at any point \( z \) is expressed as the sum of the fluid–fluid potential and fluid–solid potential as follows

\[
u(z) = u_{\text{bulk}} = u_{\text{ff}}(z) + u_{\text{fs}}(z)
\]

where the subscript “bulk” means the bulk phase, and “ff” and “fs” signify fluid–fluid and fluid–solid interactions, respectively. The chemical potential of the bulk phase can also be written in terms of fugacity as follows

\[
u_{\text{bulk}} = u_0(T) + RT \ln \left( f_{\text{bulk}} / f_0 \right)
\]
where $u_n(T)$ designates the chemical potential of an arbitrary reference state, and $f_\alpha$ represents the fugacity of the reference state.

For the fluid—fluid interaction, the chemical potential can be derived using a similar equation

$$u_f(z) = u_f(T) + RT \ln(f_{\text{fl}(z)}/f_\alpha)$$

(7)

where $f_{\text{fl}}(z)$ is the fugacity of the fluid at an arbitrary position $z$.

For the interaction between the fluid and the slit wall, the chemical potential can be written as

$$u_{\text{fl}}(z) = N_A\left[\psi^{\ell}(z) + \psi^{s}(L-z)\right]$$

(8)

where $N_A$ is Avogadro’s number, and $\psi^{\ell}(z)$ and $\psi^{s}(L-z)$ are the interaction potentials for a single fluid molecule with the two surfaces of a slit with width $L$.

Substituting eqs 6–8 into eq 5 provides the fugacity of the fluid—fluid interaction at an arbitrary position $(z)$ under equilibrium

$$f_{\text{fl}}(z) = f_{\text{bulk}} \exp\left(-\frac{\psi^{\ell}(z) + \psi^{s}(L-z)}{kT}\right)$$

(9)

where $k$ is the Boltzmann constant. The fluid—solid interaction is an attractive force, which means $\psi^{\ell}(z)$ and $\psi^{s}(L-z)$ are negative, and the fugacity of the adsorbed phase is higher than the fugacity of the bulk phase.\(^{43,44}\)

The fluid—solid interaction for a single methane molecule, $\psi^{s}(z)$, is described by the Lennard-Jones 10–4 potential.\(^{50}\)

$$\psi^{s}(z) = 4\pi\rho_0\sigma_0^2\left[\frac{\sigma_0^{10}}{5(z + \sigma_0/2)^{10}} - \frac{1}{2}\sum_{i=1}^{4}\left(z + \sigma_0/2 + (i - 1)\sigma_0\right)^{10}\right]$$

(10)

$$\varepsilon_0 = \sqrt{\varepsilon_\ell \times \varepsilon_\text{ss}}$$

(11)

where $\rho$ is the number of molecules per unit area of the slit, which is given by $\rho = 0.382 \text{ atoms}/\AA^2$; $\varepsilon_0$ and $\varepsilon_\ell$ are the fluid—solid and solid—solid interaction energy parameters, respectively; and $\sigma_0$ and $\sigma_\ell$ represent the molecular diameter of the adsorbate and the carbon interplanar distance of the organic matter, respectively. We set $\sigma_0$ to 0.335 nm as this is the value of graphite.\(^{57}\) and obtained the values of $\sigma_\ell$ and $\varepsilon_\ell$ from the literature.\(^{56}\) The fluid—solid molecular diameter $\sigma_\ell$ and the fictitious coordinate $z'$ for the following numerical integration are defined as

$$\sigma_\ell = \frac{\sigma_\ell + \sigma_\text{ss}}{2}$$

(12)

$$z' = z + \sigma_\ell/2$$

(13)

The fugacity of the bulk phase, $f_{\text{bulk}}$, is calculated by the EOS.

The fugacity of the bulk fluid can be represented in the ESD EOS

$$Z = 1 + Z_{\text{rep}} + Z_{\text{attr}}$$

(14)

$$Z_{\text{rep}} = \frac{4\eta}{1 - 1.9\eta}$$

(15)

$$Z_{\text{attr}} = \frac{9.5\eta Y}{1 + 1.7745(\eta Y)}$$

(16)

where $Z$ is the compressibility factor for the nonideal gas; $Z_{\text{rep}}$ and $Z_{\text{attr}}$ represent the compressibility factor of the repulsive term and attractive term, respectively; $\varepsilon$ is the shape factor of the repulsive term; $q$ is the shape factor of the attractive term; $\eta$ is the reduced density given by $\eta = b\rho_\ell(z)$, where $b$ is the component’s size parameter and $\rho_\ell(z)$ is the molar local density; and $Y$ is the temperature-dependent attractive energy parameter given by eq 17.

$$Y = \exp(e/kT) - 1.0617$$

(17)

Then, the fugacity of the bulk fluid $f_{\text{fl}(z)}$ can be represented as follows\(^{59}\)

$$\ln f_{\text{fl}(z)} = -\frac{4}{1.9}e \ln(1 - 1.9\eta) + \frac{4\eta}{1 - 1.9\eta} - \frac{9.5q}{1.7745}\eta Y$$

$$- \ln \frac{V}{RT}$$

(18)

where $V$ is the molar volume, $T$ is the temperature, and $R$ is the ideal gas constant.

As shown in Figure 1, the methane molecules are adsorbed close to the inner surface of the slit wall, and the intermolecular stress potential and the assembled shape of the pores are related to the pore positions. A previous study\(^{50}\) gave a lower limit in the integration of $3/8\sigma_0$ and an upper limit of $L - 3/8\sigma_0$. The local density is treated as zero for distances less than $3/8\sigma_0$ from the wall. The value $3/8\sigma_0$ is chosen to account for most of the adsorbed gas. The excess adsorption is defined as the excess number of moles per unit mass of the adsorbent

$$n_{\text{ex}} = \frac{A}{2} \int_{3/8\sigma_0}^{L - 3/8\sigma_0} [\rho(z) - \rho_{\text{bulk}}] dz$$

(19)

where $\rho_{\text{ex}}$ is the molar density of the fluid at distance $z$ perpendicular from the surface of the wall, $\rho_{\text{bulk}}$ is the bulk density of the fluid, which is far from the wall; and the fluid—solid potential is zero. At a given temperature and pressure, we can only obtain the fugacity and density distribution in the slit. Consequently, there are no multiple solutions for the excess adsorption from the SLD model. Subsequently, the absolute adsorption can be derived by the Gibbs definition

$$m_{\text{abs}} = \frac{A}{2} \int_{3/8\sigma_0}^{L - 3/8\sigma_0} \rho_{\text{ex}} \eta_{\text{sf}}$$

(20)

In this SLD model, there are two regression parameters: the width of the slit $L$ and the fluid—solid interaction energy parameter $e_{\ell}$.

The density distribution of the adsorbed phase and the excess adsorption in the slit during the equilibrium can be calculated by the following steps:\(^{53}\)

(1) At a given bulk pressure $(P)$ and temperature $(T)$, the density of the bulk phase $\rho_{\text{bulk}}$ and the fugacity of the bulk phase $f_{\text{bulk}}$ can be obtained from the EOS.

(2) By using the Lennard-Jones 10–4 potential (eq 10), $\psi(z)$ is calculated, and the chemical potential $u_\ell(z)$ will be obtained from eq 8. From eq 6, we can get the chemical potential of the bulk phase $u_{\text{bulk}}$, then, by
solving eq 5, the fluid–fluid potential \( u_{ff}(z) \) will be calculated.

(4) Eq 9 will be used to evaluate the fugacity of the fluid–fluid \( f_{ff}(z) \).

(5) When solving eq 18, we can get the local density \( \rho_f(z) \) which is equal to the density of the adsorption phase \( \rho(z) \).

(6) The adsorbed density distribution and the excess adsorption in eq 19 can be easily calculated.

## RESULTS AND DISCUSSION

Mineralogy and Organic Petrography. The three samples in this study displayed a TOC range of 1.54−6.13% (Table 1). During the burial and maturation of organic matter, myriad organic pores are generated, and these are the most important sites for gas adsorption. The XRD results showed the mineral composition of the Longmaxi Formation in the Sichuan Basin that was dominated by siliceous minerals (quartz, K-feldspar, and plagioclase), clay minerals (kaolinite, chlorite, illite, and illite−smectite mixture), and carbonatite (calcite and dolomite). The percentage of siliceous minerals ranged from 46.5 to 62.8%. The most abundant siliceous mineral was quartz, with the content range from 35.0 to 57.6%. The carbonatite content of the samples ranged from 6.5 to 38.7%. All the samples contained a minor pyrite with the content between 1.5 and 6.7%, indicating a reducing depositional environment. The equivalent vitrinite reflectance of the Longmaxi Formation shales varied from 1.3 to 2.3%. This illustrates that the thermal maturities of sample NY09 and sample NY21 are at the overmature stage (\( R_0 > 2.0\% \)) and sample NY17 is at the mature stage. The thermal maturity parameters suggest that the Longmaxi Formation in the study area is in the gas generation window (1.0% < \( R_0 < 3.0\% \)).

Quantitative Analyses of Pore Morphology. The isotherms of low-pressure \( \text{N}_2 \) adsorption and desorption at −196.15 °C for the Longmaxi shales are presented in Figure 2. According to the International Union of Pure and Applied Chemistry classification system, all the low-pressure nitrogen adsorption and desorption isotherms of the samples are type II isotherms.\(^6\) These types of isotherms are typical for mesoporous materials and indicate pore filling of micropores at low relative pressures and multilayer adsorption at moderate pressures.\(^3\) All the isotherms show H3-type adsorption hysteresis, which suggests that slit-shaped pores are the predominant pore types.\(^4\) When the relative pressure is close to 1, the sharp increase in the amount adsorbed implies the presence of macropores. The pore parameters for \( \text{N}_2 \) adsorption and desorption are illustrated in Table 2. The BET specific surface areas of all three samples were in the range 14.07−23.61 m\(^2\)/g; the total pore volume range was 20.246−29.816 cm\(^3\)/kg; and the average pore diameters were in the mesopore range and between 4.995 and 5.755 nm.

| sample | \( S_{BET} \) \( (m^2/g) \) | \( V_{total} \) \( (cm^3/kg) \) | average diameter \( (nm) \) | \( V_{mic} \) \( (cm^3/kg) \) |
|---|---|---|---|---|
| NY09 | 21.18 | 29.816 | 5.630 | 6.422 |
| NY17 | 14.07 | 20.246 | 5.755 | 4.535 |
| NY21 | 23.61 | 29.476 | 4.995 | 6.846 |

The pore diameter distribution was derived from the desorption branch of the \( \text{N}_2 \) isotherms using the nonlocal density functional theory (NLDFT).\(^3\) All the samples exhibited broad pore diameter ranges, with the majority of pores between 1 and 100 nm Figure 3.

Methane Adsorption Isotherms and Data Fitting. Excess methane adsorption measurements for the three shale samples collected from the Sichuan Basin, southwest China, were conducted using a magnetic suspension balance and the

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Table 1. Mineral Composition and Organic Petrographic Characteristics\(^a\)

| relative content of clay minerals \( (wt\%) \) | quantitative analysis of whole-rock minerals \( (wt\%) \) |
| sample | K | C | I | I/S | C/S | quartz | K-feldspar | plagioclase | calcite | dolomite | pyrite | total clay | \( R_0 \) (%) | TOC (wt %) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NY09 | 1 | 5 | 17 | 69 | 8 | 35.0 | 3.3 | 11.9 | 5.3 | 1.2 | 1.5 | 41.8 | 2.2 | 1.54 |
| NY17 | 0 | 0 | 39 | 61 | 0 | 42.5 | 0.4 | 3.6 | 25.8 | 12.9 | 3.8 | 11.0 | 1.3 | 2.92 |
| NY21 | 1 | 4 | 26 | 59 | 10 | 57.6 | 5.2 | 5.0 | 2.5 | 3.9 | 6.7 | 21.0 | 2.3 | 6.13 |

\(^a\)K = Kaolinite, C = chloride, I = illite, I/S = illite−smectite mixed mineral, and C/S = chlorite/smectite mixed mineral.

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gravimetric method. Good repeatability of the adsorption measurements was observed with agreement between the two runs performed for each sample at 60 °C (Figure 4), indicating that the experimental process is precise and there is no change in the pore size distribution. In Figure 5, the dots represent the experimental data, and the curves give the fitting results of the SLD/ESD model. All of the excess adsorption isotherms measured in this study increased rapidly with increasing pressure up to a maximum and then showed a slight decline in the excess adsorbed amount at higher pressures. This phenomenon has been widely observed by other authors in both experiments and molecular simulations. It is clear that the absolute adsorption, $m_{\text{abs}}$, is a monotonic increasing function of pressure. However, because of the differences between $m_{\text{abs}}$ and $V_{\text{ads}}$, $V_{\text{ads}}$ may increase faster than $m_{\text{abs}}$ at high pressures.

In the pressure ranges used in this study, the isotherms did not intersect, but the differences between the isotherms at high pressures were not distinct in all cases. They may intersect with each other at higher pressures, which is a characteristic of high excess adsorption at high temperatures. The pressure ranges corresponding to the maximum value of the excess amount were 10.5–12.3 MPa at 40 °C, 10.5–14 MPa at 60 °C, and 12.3–16 MPa at both 80 and 100 °C. All fitting was conducted by the synchronized optimization of the fit for all the experimental data for a given sample at different temperatures through the adjustment of two parameters, $L$ and $\varepsilon_{fs}$. The adjustable parameters used in this study to fit the isotherms are summarized in Table 3. It should be noted that all the specific surface areas, $A$, in this study and in the literature were directly determined using the BET equation based on the N$_2$ adsorption/desorption method. By contrast, some authors have taken the specific surface area as a regressed parameter depending on the adsorbed gas. The model shows good consistency for the representation of the temperature dependence of the adsorption isotherms without any temperature-dependent parameter. Here, we used the average absolute deviation (% AAD, eq 21) to evaluate the model and experimental data.

$$\text{% AAD} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{n_{\text{cal}} - n_{\text{ex}}}{n_{\text{ex}}} \right| \times 100$$

(21)

where $n_{\text{cal}}$ is the adsorption calculated by the SLD/ESD model and $N$ is the number of data points used.

Figure 4. Repeatability tests for the three shale samples at 60 °C.

Figure 5. Measured and fitted methane excess adsorption isotherms for sample NY09 (a), sample NY17 (b), and sample NY21 (c) at different temperatures.

Literature Data. We complied an adsorption database (Table 3) for gas adsorption measurements on shales using data from previous publications with different pressures, temperatures, BET specific surface areas, and TOC contents. The data were collected from a number of sources. Table 3 also shows the slit length ($L$), solid–solid interaction energy ($\varepsilon_{fs}$), and % AAD. Selected isotherms and model fitting are shown in Figures 6–9. From the information in Table 3 and Figures 6–9, it is obvious that the SLD/ESD model can describe the excess adsorption data from the experiments in this study and the literature within experimental uncertainties. In this study, the SLD/ESD model can represent the experimental isotherm data with a % AAD lower than 5%.
The regression parameter $L$ in the SLD model ranges from 1.29 to 1.63 nm, which shows good consistency on the same order as that of low-pressure N$_2$ adsorption examination and an imaging method. For the regression parameter $\varepsilon_{fs}$, which represents the solid−gas interaction, there is a wide range from 53 K (NY09, this study) to 145 K (FC-49, Li et al. 2017). It shows a large deviation for the value (70.61 K) estimated by the Lorentz−Berthelot combination rule

$$\varepsilon_{fs} = \sqrt{\varepsilon_{ss} \varepsilon_{ff}}/k,$$

where $\varepsilon_{ss}/k$ is the solid−solid interaction parameter (using 28 K for carbon atoms and 178.082 K for methane). The Lorentz−Berthelot combination rule can only describe the interaction roughly and is best suited to gas molecules with simple structures. In the SLD model, the fluid−solid energy parameter, $\varepsilon_{fs}/k$, is a geometric mean of $\varepsilon_{ss}/k$ and $\varepsilon_{ff}/k$. As the fluid−fluid interaction energy parameter for methane is fixed (178.082 K) and independent of the adsorbent, higher values of $\varepsilon_{ss}/k$ signify stronger fluid−solid interactions. Additionally, the deviation between $\varepsilon_{fs}$ and the value from the Lorentz−Berthelot combination rule may reveal that organic matter is not the only contributor to the

### Table 3. SLD Model Representations for Methane Adsorption for Shale Samples

| sample | temperature (°C) | pressure (MPa) | $S_{BET}$ (m$^2$/g) | TOC (%) | $L$ (nm) | $\varepsilon_{fs}$ (K) | % AAD | source |
|--------|----------------|----------------|---------------------|---------|---------|-----------------------|-------|-------|
| NY09   | 40/60/80/100    | 30             | 21.18               | 1.54    | 1.29    | 53                    | 7.07/4.89/3.10/4.06 | this study |
| NY17   | 40/60/80/100    | 30             | 14.07               | 2.92    | 1.47    | 74                    | 4.58/2.31/3.91/7.5  | this study |
| NY21   | 40/60/80/100    | 30             | 23.61               | 6.13    | 1.29    | 74                    | 8.19/4.84/4.24/5.13 | this study |
| FC-37  | 60             | 35             | 11.1                | 1.3     | 83      | 7.4                   | 4.58/3.91/7.5       | Li et al. 2017 |
| FC-45  | 60             | 35             | 16.4                | 1.4     | 104     | 6.4                   | 4.58/3.91/7.5       | Li et al. 2017 |
| FC-47  | 60/80/100/120   | 35             | 12.1                | 3.5     | 1.3     | 98                    | 7.9/8.5/6.7/9.5/12.9 | Li et al. 2017 |
| FC-49  | 60             | 35             | 13.3                | 4.7     | 1.58    | 145                   | 5.0               | Li et al. 2017 |
| FC-53  | 60             | 35             | 26.2                | 10.7    | 1.4     | 104                   | 5.7               | Li et al. 2017 |
| FC-55  | 60             | 35             | 19.9                | 8.6     | 1.6     | 118                   | 7.7               | Li et al. 2017 |
| FC-59  | 60             | 35             | 18.3                | 9.2     | 1.56    | 127                   | 5.3               | Li et al. 2017 |
| FC-62  | 60             | 35             | 15.2                | 6.8     | 1.31    | 114                   | 10.9              | Li et al. 2017 |
| FC-66  | 40/60/80/100/120 | 35           | 18.4                | 7.3     | 1.53    | 101                   | 5.6/5.6/4.1/5.0/8.5 | Li et al. 2017 |
| FC-72  | 40/60/80/100/120 | 35           | 23.6                | 11.3    | 1.53    | 113                   | 4.2/4.7/6.2/7.9/7.0 | Li et al. 2017 |
| HAD-7090 | 45/55/85       | 13             | 25.1                | 7.41    | 1.4     | 68                    | 2.3/4.2/4.7        | Li et al. 2017 |
| HAD-7119 | 45/55/85       | 14             | 21                  | 7.15    | 1.53    | 65                    | 2.4/3.6/4.4        | Li et al. 2017 |
| 4−04   | 35/50/65        | 15             | 12.5                | 1.87    | 1.28    | 70                    | 5.7/6.3/7.1        | Tian et al. 2017 |
| 4−08   | 35/50/65        | 14             | 16.9                | 2.45    | 1.33    | 69                    | 4.4/4.2/5         | Tian et al. 2017 |
| 4−33   | 35/50/65        | 14             | 14.2                | 1.99    | 1.42    | 72                    | 4.2/8.3/6         | Tian et al. 2017 |
| 4−47   | 35/50/65        | 15             | 18.5                | 3.34    | 1.38    | 73                    | 4.9/2.6/2.3       | Tian et al. 2017 |
| 4−54   | 35/50/65        | 12             | 20.2                | 4.52    | 1.43    | 80                    | 2.8/2.7/0.1       | Tian et al. 2017 |
| 4−61   | 35/50/65        | 14             | 19.3                | 5.44    | 1.47    | 90                    | 5.2/4.2/4.1       | Tian et al. 2017 |
| 4−64   | 35/50/65        | 15             | 17.8                | 4.07    | 1.48    | 88                    | 6.0/4.8/5.3       | Tian et al. 2017 |
| 4−65   | 35/50/65        | 14             | 20.6                | 5.74    | 1.42    | 85                    | 4.7/5.1/4.8       | Tian et al. 2017 |
| CN_11  | 30/50/80/100/120 | 24           | 28.75               | 4.83    | 1.41    | 61                    | 3.6/3.6/8.8/9/13.3 | Yang et al. 2017 |
| CN_22  | 39/50/80/100    | 24             | 14.96               | 2.87    | 1.44    | 75                    | 2.5/4.9/6.5/6.1   | Yang et al. 2017 |
| CN_23  | 30/50/80/100/120 | 22           | 14.19               | 2.92    | 1.26    | 60                    | 5.5/3.2/3.6/4.9/2.7 | Yang et al. 2017 |
| CN_32  | 39/50/80/100    | 24             | 14.95               | 0.89    | 1.63    | 61                    | 3.3/4.2/2.6/4.1   | Yang et al. 2017 |

Figure 6. Plots of measured and SLD model-fitted excess adsorption for samples FC-37, FC-45, FC-49, FC-53, FC-55, and FC-59 at 60 °C. Reproduced with permission from [Li, T.; Tian, H.; Xiao, X.; Cheng, P.; Zhou, Q.; Wei, Q. Geochemical Characterization and Methane Adsorption Capacity of Overmature Organic-Rich Lower Cambrian Shales in Northeast Guizhou Region, Southwest China. Mar. Pet. Geol. 2017. https://doi.org/10.1016/j.marpetgeo.2017.06.043]. Copyright 2017 Elsevier Ltd.

Figure 7. Plots of measured and SLD model-fitted excess adsorption for samples S4-08, S4-47, and S4-61 at different temperatures. Reproduced with permission from [Tian, H.; Li, T.; Zhang, T.; Xiao, X. Characterization of Methane Adsorption on Overmature Lower Silurian-Upper Ordovician Shales in Sichuan Basin, Southwest China: Experimental Results and Geological Implications. Int. J. Coal Geol. 2016, 156, 36−49. https://doi.org/10.1016/j.coal.2016.01.013]. Copyright 2016 Elsevier B.V.
adsorption process, but other minerals can also provide adsorption sites for methane.

**Influence of the TOC Content and Specific Surface Area on the Adsorption Capacities.** As illustrated in Figure 10, all the maximum excess adsorbed amounts for the samples in this study and the samples from the literature showed large linear positive correlations with the TOC content, indicating that organic matter is the main carrier of adsorbed methane molecules. This can be elucidated from two aspects. First, abundant micro- and mesopores are widely observed in organic matter by field emission scanning electron microscopy (FE-SEM), focused ion beam SEM (FIB-SEM), low-pressure N₂ adsorption/desorption tests, and small-angle neutron scattering. Abundant micro- and mesopores provide large specific surface areas and numerous sorption sites for methane molecules. Because of the higher density of the adsorbed phase, micropores and fine mesopores have much higher adsorption potentials than large mesopores and macropores. At the beginning of the adsorption process, the methane molecules occupy sites with higher potentials. Second, as a nonpolar gas, methane molecules are preferentially attracted by hydrophobic organic matter rather than hydrophilic minerals. All the intercepts of the regression lines in Figure 10 are nonzero, demonstrating that the minerals, especially montmorillonite and the illite–smectite mixed mineral, can adsorb methane.

Excess adsorption capacities from the literature show good linear positive correlations with the specific surface area. Generally, the specific surface areas of shales are mainly determined by micropores, and a high specific surface area means that the organic matter contains a substantial number of nanopores. Therefore, shale samples exhibit similar tendencies to the TOC contents, and their adsorption capacities increase with increasing specific surface area. However, the data in this study did not show good linear correlations ($R^2 = 0.47$), and...
this was mainly because the number of samples was limited \((n = 3)\); Figure 11.

**Influence of Temperature on the Methane Adsorption Capacity.** To examine the temperature dependence of the methane adsorption capacity on shale samples, the isotherms were measured at different temperatures for all the samples. The entire shale samples showed that the adsorption capacity decreased at high temperatures under isobaric conditions as adsorption was an exothermic process. The maximum adsorption showed a strong linear correlation \((R^2 > 0.99)\) with the reciprocal of the absolute temperature. Similar phenomena have been observed by many other authors.\(^{11,18,22,72}\) The correlations between the gas adsorption capacity and the rate of decrease were in the following order: sample NY21 > NY17 > sample NY09 (Figure 12). The slope of the fitted straight line, which could be considered as the rate of decrease of the methane adsorption capacity with increasing temperature, increased with the TOC content of the shale sample. A plot of the rate of decrease versus the TOC content (%) showed good linear correlations, which indicated that the TOC content was sensitive to the increasing temperature (Figure 13).

Numerous publications have already demonstrated that when organic matter is warmed to the glass-transition temperature \((T_g)\), its molecules have abundant freedom of motion to reorganize.\(^{73}\) Consequently, high temperatures may change the structure of the organic matter. By contrast, the isosteric heat of adsorption is believed to be independent of temperature\(^{74}\) when only taking the interaction between the gas and the sample matrix into consideration. Additionally, when methane is adsorbed on the shale surface, there are two kinds of molecular interactions affecting the adsorption capacity. Namely, there is the adsorbent/adsorbate interaction and the adsorbate/adsorbate interaction. The adsorbate/adsorbate interaction has been ignored in all previous investigations. Theoretically, the isosteric heat of methane adsorption will remain constant with increasing temperature if only the adsorbent/adsorbate interaction is considered.\(^{75}\) The discrepancy with the experimental data indicates that the adsorbate/adsorbate interaction, including the adsorbed phase and bulk phase, may greatly affect the adsorption capacity of methane. Otherwise, increasing the temperature can enhance the process of adsorption—desorption of methane and lead to a greater ratio of free gas molecules. Notably, adsorption is a dynamic equilibrium process, and the residence time for an adsorbed molecule on the surface is shorter at higher temperatures than at lower temperatures because of higher kinetic energy. Ye et al. pointed out that some weak adsorption sites may lose the methane molecules when increasing the temperature because of the heterogeneity distribution of the shale surface.\(^{76}\) The grand canonical Monte Carlo simulation revealed that the density of adsorbed methane decreased with increasing temperature.\(^{77}\) Subsequently, the macroscopic measurement of excess adsorption at high temperatures decreases.

**Deviation Analysis of the ESD-SLD Model and Experimental Data.** Figure 14 presents the percentage deviations for adsorption data from selected samples. Figure 14a shows the deviations calculated for adsorption data from the three samples in this study, and Figure 14b,c shows the percentage deviations for adsorption data from the studies of Li et al.\(^{22}\) at 60 °C, Rexer et al.,\(^{11}\) 2013, and Tian et al.,\(^{19}\) 2016 and that for the sample CN22 from Yang et al.\(^{20}\) Overall, 89.3% of all the adsorption data were predicted with deviations of less than 10%. Obviously, no matter the temperature, at relatively low pressures, the percentage deviations were much higher (e.g., up to 38.4% for the sample FC-72, from Li et al.,
Figure 14. Percentage deviations of the SLD model and experimental data: (a) data from this study; (b) literature data at 60 °C. Reproduced with permission from [Li, T.; Tian, H.; Xiao, X.; Cheng, P.; Zhou, Q.; Wei, Q. Geochemical Characterization and Methane Adsorption Capacity of Overmature Organic-Rich Lower Cambrian Shales in Northeast Guizhou Region, Southwest China. *Mar. Pet. Geol.* 2017, [https://doi.org/10.1016/j.marpetgeo.2017.06.043](https://doi.org/10.1016/j.marpetgeo.2017.06.043)]. Copyright 2017 Elsevier Ltd. (c) Data for samples HAD 7090 and HAD 7119; samples S4-04, S4-08, S4-44, S4-47, S4-54, S4-61, S4-64, and S4-65; and sample CN22. Reproduced with permission from [Rexer, T. F. T.; Benham, M. J.; Aplin, A. C.; Thomas, K. M. Methane and S4-65; and sample CN22. Reproduced with permission from *HAD 7119; samples S4-04, S4-08, S4-44, S4-47, S4-54, S4-61, S4-64, S4-61, S4-64, and S4-65; and sample CN22. Reproduced with permission from [Rexer, T. F. T.; Benham, M. J.; Aplin, A. C.; Thomas, K. M. Methane Adsorption on Shale under Simulated Geological Temperature and Pressure Conditions. *Energy and Fuels* 2013, [https://doi.org/10.1021/ef400381v](https://doi.org/10.1021/ef400381v)]. Copyright 2013 American Chemical Society. Reproduced with permission from [Tian, H.; Li, T.; Zhang, T.; Xiao, X. Characterization of Methane Adsorption on Overmature Lower Silurian-Upper Ordovician Shales in Sichuan Basin, Southwest China: Experimental Results and Geological Implications. *Int. J. Coal Geol.* 2016, 156, 36–49. [https://doi.org/10.1016/j.coal.2016.01.013](https://doi.org/10.1016/j.coal.2016.01.013)]. Copyright 2016 Elsevier B.V.

As a direct method, the gravimetric method appears to be reliable, and it may show a relatively high deviation at high pressures. Otherwise, the buoyancy effect of the adsorbed phase is always neglected, which may underestimate the adsorbed quantities for the gravimetric methods. The SLD model supposes that the adsorbed phase and bulk phase obey the same EOS and calculates the density of the adsorbed phase. It should be noted that even the adsorbed gas appears in a compressed state, which cannot be accurately described by the EOS. The ESD model is weaker for predicting the adsorption phase with liquidlike densities. Another possibility is that the specific surface area derived by the BET theory is not capable of characterizing the specific surface area in reality, especially for shale samples containing micropores. The BET theory was derived from the Langmuir model with an additional hypothesis. For shale samples containing wide pores, pore filling may occur at pressures close to the pressure range where a monolayer–multilayer forms on the pore walls, which will lead to a considerable overestimation of the monolayer capacity. Furthermore, to simplify the computational process, the assumed geometry in the SLD model is a rectangular prism. This is because of the low quantity of excess adsorption at relatively low pressures, and any small deviation in the predicted data may lead to a large deviation. Therefore, methane molecules are adsorbed at active sites with a high adsorption potential; so, the adsorption data at low pressures are more sensitive to the potential distribution of the adsorbent. Because pores are the main adsorption sites for methane molecules, the pore size distribution of the organic matter is critical to the adsorption potential. As mentioned above, the pore size distributions for shale samples were wide (1–100 nm) in this study and showed multimodal distributions in the NLDFT pore size distribution and other studies. By contrast, in the SLD model, there is only one parameter for the slit length, \( L \), to represent the pore size distribution. Consequently, the SLD model cannot predict the adsorption data accurately at relatively low pressures. Some authors have proposed an adjustable parameter as a coefficient for the pore size distribution. This may not only increase the accuracy of the model but also greatly increase the calculation effort.
However, as widely observed by FE-SEM and FIB-SEM, the pores in shales are mostly cylindrical in reality. This discrepancy in the geometry between the actual shale and the SLD model may engender a deviation between the experimental and calculated data.

CONCLUSIONS AND SUMMARY

High-pressure methane adsorption isotherms were determined at different temperatures for shale samples collected from the Longmaxi Formations in the Sichuan Basin, southwest China. The SLD/ESD model was used to accurately describe supercritical methane adsorption on the tested shales and published gas adsorption data from the literature. The conclusions from this study are as follows.

The three samples investigated here display a TOC content range of 1.54–6.13%. The samples are dominated by siliceous minerals (46.5–62.8%), clay minerals (11–41.8%), and carbonatite (6.5–38.7%). Their BET specific surface areas range from 14.07 to 23.61 m²/g. The equivalent vitrinite reflectance varies from 1.3 to 2.3% and reaches the level for gas generation.

The methane adsorption capacity is primarily positively correlated with the TOC content, which indicates that the TOC content is a major factor controlling the adsorption capacity. The correlation between excess methane adsorption and BET specific surface area is not significant. As the temperature increases, the excess adsorption decreases, and the rate of decrease shows a good linear correlation with the TOC content, which demonstrates that the TOC content is sensitive to temperature.

The SLD/ESD model with only two temperature-independent regression parameters shows good consistency for the representation of adsorption isotherms within an AAD of less than 5. This model is also capable of describing excess adsorption data from the literature.

AUTHOR INFORMATION

Corresponding Author
Ke Hu — Institute of Mining and Special Civil Engineering, TU Freiberg, Freiberg, Sachsen 09599, Germany; orcid.org/0000-0003-2494-9061; Email: ke.hu@student.tu-freiberg.de

Author
Helmut Mischo — Institute of Mining and Special Civil Engineering, TU Freiberg, Freiberg, Sachsen 09599, Germany

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b03978

Notes
The authors declare no competing financial interest.

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