Measuring and modelling supercritical adsorption of CO₂ and CH₄ on montmorillonite source clay

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ABSTRACT

The porosity of clay minerals is dominated by nanoscale pores that provide a large surface area for physical and chemical interactions with the surrounding fluids, including gas adsorption. Measuring gas adsorption at subsurface conditions is difficult, because elevated pressures are required and the interactions between the supercritical gas and the clay are relatively weak. Here, we report on the measurement of adsorption isotherms of CO₂ and CH₄ on the source clay Na-montmorillonite (SWy-2) at different temperatures (25–115°C) over a wide range of pressures (0.02–25 MPa). The experimental observations are thoroughly analysed by considering both net and excess adsorbed amounts, and by extracting adsorption metrics, such as the Henry’s constants and enthalpy of adsorption. The results consistently indicate that SWy-2 favours adsorption of CO₂ over CH₄ with selectivity, S ≈ 5.5. The experimental data are successfully described using a Lattice Density Functional Theory (LDFT) model. The adsorption energetics estimated by the model compare well with the experimentally obtained enthalpy of adsorption. It is further shown that even at the highest pressure the pore space of the clay is only partially filled and that the degree of saturation increases upon approaching the critical temperature of the gas. The ability of the LDFT model to reveal pore-dependent adsorption behaviours demonstrates its potential against empirical models, such as the Langmuir equation, which fail at capturing the complexities of supercritical gas adsorption at subsurface conditions.

1. Introduction

Clays are ubiquitous in the subsurface and are receiving increasing attention in the context of geo-energy technologies, such as the geological storage of CO₂ in sedimentary rock formations or the production of natural gas from so-called unconventional shale plays. These minerals appear in a wide range of concentrations in sandstone reservoirs (up to 50 vol% [1]) and in the seals above them (typically, thick layers of mudstones or shales with clay mass fractions in the range of 30–80% [2]), and are major constituents of organic-rich shale formations that are being exploited for hydrocarbon recovery (e.g. Barnett: 3 to 40 vol %, Haynesville: 20 to 40 vol% and Eagleford: 6 to 20 vol% [3]). Clays (and clay-rich systems in general) can be considered as “geosorbents”, because most of their porosity is dominated by nanoscale pores (width less than 100 nm), which produce a large specific surface area (SSA) available for physical interactions with reservoir fluids, including gas adsorption. The latter results in the creation of a high-density, liquid-like phase on the pore walls, which has important implications on the storage of gas [4,5] and on its transport through the microporous matrix of the rock [6–8]. While geosorbents are weakly sorbing when compared to known industrial microporous adsorbents, such as zeolites or carbons, the large bulk density of rocks (∼ 2.5 g/cm³) and the large spatial footprint of geologic formations suggest that the actual contribution of gas adsorption in these systems may still be significant. The extent of CO₂ trapping by sorption on clays in a typical sandstone reservoir with 20% porosity and 10 vol% of clays has been estimated to be of the same order as trapping by CO₂ dissolution in reservoir brines [5]. In organic-rich shales, gas sorption on both the organics and clay minerals can account for up to 60–70% of the total Gas-In-Place (GIP) [4]. To increase hydrocarbon recovery from the shale, the use of supercritical CO₂ as a fracturing fluid has also been proposed. Such an operation would benefit from an increased production by exploiting an in situ adsorption (CO₂)/desorption (CH₄) process [9], as previously attempted for deep coal seams reservoirs [10]. Therefore, from a practical perspective, gas adsorption on clays creates potential for (i) significant storage of gas in reservoirs having larger clay contents, (ii) enhanced gas production from clay-rich shale formations, and (iii) increased storage security by limiting gas diffusion through the seals above potential CO₂ sequestration sites.

In clays, nanopores are found in the so-called interlayer space

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between basal surfaces (referred to as the internal SSA) and in the interparticle voids that are created when clay minerals form aggregates (contributing to the so-called external and edge SSA) [11]. While the resulting SSA (700–1000 m²/g) is the highest known among major natural minerals [11], experimental observations suggest that its accessibility depends on several factors, including the properties of the exchanged cation [12,13], the probing adsorptive [14], and the hydration state of the interlayer spacing [15]. Most significantly, while gas adsorption can always occur on the external surface of a (dry) swelling clay, such as montmorillonite (external SSA = 30 m²/g as measured by N₂ [15]), experimental evidence now exists that some fluids, such as supercritical CO₂, can penetrate the interlayer spacing and adsorb also onto the internal surface of the clay [13,16,17]. However, the total extent of adsorption of CO₂ (or other gases, such as CH₄) on clays under subsurface conditions, where water is likely to be present, remains uncertain. The adsorption capacity of clay minerals for CO₂ and CH₄ in the presence of water has been investigated both experimentally [18,19] and through simulations [20,21]. These studies demonstrate that water may either decrease the adsorption capacity by competitively occupying sorption sites or increase it by providing more accessible micropore volume. In this context, because they are derived from large and reasonably homogenised stocks [22], source clays are regarded as an excellent class of reference materials to develop experimental protocols for the study of supercritical gas adsorption on geosorbents with large clay contents.

Supercritical gas adsorption studies on montmorillonite and other source clays (e.g. kaolinite and illite) are found in the literature [18,19,23–28], but the data set is far from being complete and some of the reported observations remain controversial. While all these studies consistently show that the extent of gas adsorption varies depending on the type of clay, less agreement is found on the actual order among the various clays (e.g. Fan et al. [25] v. Ji et al. [23] for the adsorption of CH₄). Some authors have observed significant hysteresis between adsorption and desorption isotherms [27], a phenomenon that is unexpected at supercritical conditions. Studies with CO₂ as an adsorptive report negative excess adsorption values at elevated pressures and invoke mechanisms, such as interfacial fluid dilution, to interpret the results [29,30]. While the definition of excess adsorption does not preclude a priori the existence of negative values [31], we contend that these observations should also be interpreted by considering the intrinsic difficulty of estimating the skeletal volume of a microporous solid that leads to measurement uncertainties at elevated bulk densities [32]. The available data set for supercritical gas adsorption on clays is also quite scattered. Studies are often limited to one gas (CO₂ or CH₄) and to one temperature (or to a fairly narrow range), which precludes the observed behavior in two independent measurements reported by Kulda and Prasad [33], and aimed at removing the strongly bound water within the clay to attain a dehydrated (0 W) state.

The pure gases used in this study were obtained from BOC (Surrey, UK) at purities of 99.9992% for N₂, 99.995% for CO₂, 99.5% for CH₄, and 99.999% for He. The critical properties of the pure adsorbates are as follows: Tc(CO₂) = 304.1 K, Pc(CO₂) = 73.8 bar, ρc(CO₂) = 10.63 mol/L; Tc(CH₄) = 190.6 K, Pc(CH₄) = 46.0 bar, ρc(CH₄) = 10.14 mol/L; Tc(N₂) = 126.2 K, Pc(N₂) = 34.0 bar, ρc(N₂) = 11.18 mol/L.

3. Experiments

3.1. Material charactisation

The microscopic structural properties of SWy-2 were determined via low-pressure physisorption analysis, which was conducted using N₂ at 77.4 K in the pressure range of 8 × 10⁻⁵ to 1 × 10⁻¹ MPa in a 3Flex Surface Characteriser Analyzer (Micromeritics, Georgia, USA). The pore volume and the pore-size distribution of meso- and macro-pores (widths larger than 2 nm) were evaluated by the application of the BJH theory that accounts for the volume desorbed via both capillary evaporation (described by the Kelvin equation) and thinning of multilayers of adsorbed molecules in cylindrical pores [34]. To account for the characteristic geometry of pores formed by the arrangement of the platy clay particles, a modified version of this theory was applied in this study that assumes the formation of hemicylindrical menisci in slit-pores [35]. Its derivation is described in the Supplementary Materials - Section 1; the obtained equations were applied to the desorption branch of the measured isotherm and by computing the thickness of adsorbed layers from the Harkins-Jura equation [36]. The micropore volume (pore widths smaller than 2 nm) was quantified from the linearisation of the Dubinin-Radushkevich (DR) equation, which describes the degree of micropore filling by the ratio between the volume of adsorbed phase, V_a, and the maximum micropore adsorption capacity, V_m, at STP conditions (P_{STP} = 10^5 Pa and T_{STP} = 273.15 K). The latter is converted to liquid conditions (hence to the micropore volume) with a suitable estimate of the molar density of the adsorbate, which in this study is taken as the liquid density of N₂ at 77 K and 10^6 Pa (µ_a = 28.8 mol/L).

The obtained estimate was compared to the total micropore volume obtained by the Horvath-Kawakoe (HK) method for slit-like pore geometry [37]. Lastly, the specific surface area (SSA) of the sample was estimated using the linear form of the BET equation [38], which is used to derive the value of the monolayer capacity, Q_m, formed by evenly...
distributed adsorbed molecules with a given value of the molecular area, \( A_m (0.162 \text{ nm}^2 \text{ for N}_2) \).

3.2. High-pressure adsorption experiment

The high-pressure measurements have been conducted using the experimental set-up shown in Fig. 1 that involves a magnetic suspension balance from Rubotherm (Bochum, Germany). The experimental set-up also includes (i) a liquid thermostat (Julabo F25, Seelbach, Germany) to control the temperature (± 0.01°C) inside the sorption chamber that is measured by a resistance temperature detector located just below the sample basket, and (ii) a syringe pump (Model 500D from Teledyne ISCO, California, USA) to compress the adsorbing gases and maintain a constant pressure in the system. The pressure of the system is measured by two pressure sensors (Keller PAA-33X, Winterthur, Switzerland) located inside the control unit (see Fig. 1); one measures pressure up to 40 bar and the other measures up to 700 bar both with 0.01% full-scale accuracy. A detailed description of the working principle of the balance can be readily found in the literature [39] and only the main operating equations are summarised below.

The measured quantity is the excess adsorbed amount, which is defined as the difference between the absolute amount of adsorption, \( m_a \), and the product of the bulk density, \( \rho_b \), and the adsorbed phase volume, \( V_a \). The excess amount of adsorption can be directly obtained from the balance using the following equation:

\[
\text{MP}_{\text{ex}}(P, T) = m_a - \rho_b V_a = \text{MP}_{1}(P, T) - \text{MP}_{1,0} + \rho_b V_0
\]

where \( V_0 \) is the sum of the skeletal volume of the sample material and the suspended metal parts (including the sample holder). The term \( \text{MP}_{1}(P, T) \) is the measured weight (sample and the suspended metal parts) under the experimental conditions, while \( \text{MP}_{1,0} \) is that measured under vacuum. The value of \( \rho_b \) is determined in situ from the buoyancy experienced by a titanium sinker with a known volume (\( V_{sk} = 4.364 \pm 0.002 \text{ cm}^3 \)):

\[
\rho_{sk} = \frac{m_{sk,0} - m_{sk}}{V_{sk}} = \frac{(\text{MP}_{2,0} - \text{MP}_{1,0}) - (\text{MP}_{1}(P, T) - \text{MP}_{1}(P, T))}{V_{sk}}
\]

where \( m_{sk,0} \) and \( m_{sk} \) are the measured weights of the titanium sinker under vacuum and the experimental conditions, respectively; \( \text{MP}_{1}(P, T) \) is the combined measured weight of \( \text{MP}_{1}(P, T) \) and the sinker under the experimental conditions, and \( \text{MP}_{1,0} \) is that measured under vacuum. The amount of excess adsorption at each bulk fluid density is then finally reported on a specific molar basis (\( \mu \text{mol/g} \)) in the following format:

\[
\text{MP}_{\text{ex}}(P, T) = \frac{\text{MP}_{1}(P, T) - \text{MP}_{1,0} + \rho_{sk} V_0}{M_m n_s}
\]

where \( M \) is the fluid molar mass and \( n_s \) is the weight of the adsorbent material. Experimental data are presented also in terms of net amount of adsorption, \( n_{\text{net}} \), which is obtained by simply replacing the term \( V_0 \) in Equation (3) with the volume of the suspended metal parts, \( V_{\text{met}} \). As described in recent studies [31,40,41], the use of net adsorption removes the ambiguities associated with the definition of the adsorbent's skeletal volume. Additional details on the estimation of the value of \( V_0 \), \( m_s \), and \( V_{\text{met}} \) are provided in Section 3.2.1.

The adsorption measurements have been carried out in the pressure range 0.02 MPa < \( P < 25 \text{ MPa} \) and at four different temperatures (\( T = 25, 50, 80 \) and \( 115 \text{ C} \)); at each pressure step, the system was allowed to reach adsorption equilibrium for approximately 120–180 min and the average of the readings over the last 10–20 min was taken as the equilibrium point (corresponding to approximately 20–40 points and a standard deviation between 1 \( \times 10^{-3} \text{ g} \) and 2 \( \times 10^{-4} \text{ g} \)). Equations (2) and (3) are used to estimate the uncertainty values associated with each measurement of the bulk fluid density and adsorption amount (both net and excess) using the general formula of error propagation, as described in the Supplementary Materials - Section 2. For a weakly adsorbing material, such as clays, the uncertainty values were found to be non-

Fig. 1. Schematic diagram of the experimental set-up used for the measurement of gas adsorption isotherms at supercritical conditions.
negligible, particularly at high-pressures (> 130 bar) with values ranging between ± 7–14 μmol/g and ± 4–8 μmol/g for excess adsorption of CO2 and CH4, respectively, and ± 3–5 μmol/g and ± 3–6 μmol/g for net adsorption of CO2 and CH4, respectively. To examine the presence of hysteresis, the experiments have been performed in both adsorption and desorption modes for CO2, while CH4 isotherms were measured only in desorption mode.

3.2.1. High-pressure helium gravimetry
The term \( V_0 \) in Equation (1) is the sum of the skeletal volume of the adsorbent material (\( V_0 \)) and that of the suspended metal parts (\( V_{\text{susp}} \)). This parameter represents a key correction factor and, potentially, a major source of uncertainty when measuring supercritical gas adsorption on weakly adsorbing materials [31,32]. The value of \( V_0 \) is determined by introducing helium into the sorption chamber. The lack of adsorption leads to the following mass balance:

\[
\text{MP}_{l,10}(P, T) = \text{MP}_{l,0} - \rho_{\text{Hel}} V_0 \tag{4}
\]

The fluid density of helium, \( \rho_{\text{Hel}} \), is calculated using Equation (2). A linear fit to a plot of \( \text{MP}_{l,10} \) against \( \rho_{\text{Hel}} \) gives a slope equal to \(- V_0 \) and an intercept equal to \( \text{MP}_{l,0} = m_l + m_{\text{met}}, \) where \( m_{\text{met}} \) is the mass of the suspended metal parts. In this study, several pressure (or density) points were taken and the linear fits were applied using the method of weighted linear regression that takes into account the individual uncertainty values associated with each measured helium point (see Supplementary Materials - Section 3). Measurements were performed at 115 °C, so as to minimise the possibility of helium adsorption reported in previous studies [32,43], and in the pressure range from vacuum to 130 bar (thus reaching a bulk gas density, \( \rho_b = 0.017 \) g/cm³). The measurements were taken at every 10–20 bar interval prior to the high-pressure CO2 adsorption experiment, and six additional measurements were performed following the CO2 experiment (prior to the CH4 experiment) to examine whether the adsorbent material experienced any structural change.

An additional set of measurements was carried out without an adsorbent in the measuring cell to obtain estimates of the mass and volume of the suspended metal parts. These experiments were conducted using CO2 at \( T = 60 \) °C and up to \( P = 20 \) MPa, thus covering a wide range of bulk density values from vacuum to \( \rho_b \approx 0.7 \) g/cm³. The following estimates were obtained: \( m_{\text{met}} = 5.285 \) g and \( V_{\text{susp}} = 0.667 \) cm³ (the uncertainty values are not given as they are smaller than the decimal places in which these quantities are reported). The mass and volume of the adsorbent material are readily obtained as \( m_l = \text{MP}_{l,0} - m_{\text{met}} \) and \( V_l = V_0 - V_{\text{susp}}, \) and their uncertainties are estimated following the standard rules of error propagation, as described in the Supplementary Materials - Section 2 and 3.

4. Modelling

4.1. Henry’s constant and enthalpy of adsorption
The Henry’s constant is commonly regarded as one of the fundamental parameters that describes an adsorbate-adsorbent pair. Its accurate determination is required in the calculation of other relevant thermodynamic properties (e.g. enthalpy of adsorption) and provides a useful basis for assessing adsorption selectivity of a gas mixture. Accurate values of Henry’s constants are difficult to obtain from adsorption isotherms measured via a gravimetric technique due to the minuscule weight change produced by adsorption of gas at very low pressures [44]. The treatment of the adsorption isotherms with the virial equation represents a reliable approach to circumvent this challenge [35]. The virial equation can be recast into the following form:

\[
\ln(n^a/P) = K_0 + K_0 n^a + K_1(n^a)^2 + K_2(n^a)^3 + \cdots \tag{5}
\]

where \( n^a \) is the absolute amount adsorbed, \( P \) is the pressure and \( K_0 \) to \( K_3 \) are the virial coefficients that are characteristic of the gas-solid system and temperature under consideration. We note that pressure has not been replaced by the fugacity in Equation (5), as the latter is applied only up to moderate pressures in this study (i.e. up to \( 2–5 \) MPa for CO2 and \( 5–8 \) MPa for CH4 depending on the temperature). In this pressure regime, it is also safe to assume that \( n^{u} = n^a. \) The Henry's constant, \( K_0 = \exp(K_n), \) can be obtained from the zeroth-order virial coefficient, which can be conveniently estimated from the extrapolation to zero loadings of the linear portion of the virial isotherm when plotted as \( \ln(n^a/P) \) versus \( n^a \) [45].

The differential enthalpy of adsorption for a pure, perfect gas is defined by the following thermodynamic equation [46]:

\[
\Delta h = R \left[ \frac{\delta \ln(P)}{\delta (1/T)} \right]_n \tag{6}
\]

In the limit of zero coverage, \( n^{u} = n = K_0 P \) and the differential enthalpy of adsorption can thus be directly found from the temperature dependence of the Henry's constant:

\[
\Delta h_0 = \lim_{P \to 0} \Delta h = -R \left[ \frac{\delta \ln(K_0)}{\delta (1/T)} \right]_n \tag{7}
\]

If the zero-coverage enthalpy, \( \Delta h_0 \), is assumed to be independent of temperature [45], Equation (7) can be integrated to yield:

\[
K_0 = \frac{3}{RT} \exp(-\Delta h_0/RT) \tag{8}
\]

Accordingly, \( \Delta h_0 \) is the negative value of the slope of the linear fit obtained from plotting \( \ln(K_0) \) against \( 1/T \) multiplied by the ideal gas constant, \( R. \) The value of \( \Delta h_0 \) is negative due to the exothermic nature of adsorption, and it is common to refer to its absolute value as the isosteric heat [46].

4.2. LDFT model for single-component adsorption

The model used in this study to describe the adsorption of CO2 and CH4 on clay is based on the lattice density functional theory (LDFT). The equations at the basis of this theory have been derived by Ono and Kondo [47], and were later formalised by Aronovich and Donohue [48] for supercritical fluids in three dimensional pores. The LDFT model has been successfully applied to reproduce measurements of subcritical and supercritical adsorption on various porous materials, including commercial sorbents (e.g. zeolites, silica and carbons [49–51]) and geosorbents, such as coal [52,53] and shale [54]. One of the distinctive features of this approach is that information on the microscopic structural properties of materials, such as the pore sizes and pore volume, are direct inputs to the model. Moreover, by accounting for the interaction energies between each pair of components in the system (fluid-fluid and surface-fluid), the LDFT model provides a more realistic picture of the adsorption process, thereby representing a significant departure from semi-empirical isotherm equations. With reference to Ottiger et al. [52], the working equations for single-component adsorption in a slit pore with J lattice layers are defined as follows:

\[
0 = \epsilon_d + \epsilon_{zd}(z_2 \delta_{j+1} + z_1 \delta_j - z_0 \delta_{j-1}) + kT \ln \left( \frac{\delta_j(1-\delta_{j-1})}{\delta_{j-1}(1-\delta_j)} \right) \quad \text{For } j = 1 \tag{9}
\]

\[
0 = \epsilon_d(z_2 \delta_{j-1} + z_2 \delta_{j+1} + z_1 \delta_j - z_0 \delta_{j-1}) + kT \ln \left( \frac{\delta_j(1-\delta_{j-1})}{\delta_{j-1}(1-\delta_j)} \right) \quad \text{For } 1 < j < J \tag{10}
\]

\[
0 = \epsilon_d + \epsilon_{zd}(z_2 \delta_{j-1} + z_2 \delta_{j+1} - z_0 \delta_{j-1} + kT \ln \left( \frac{\delta_j(1-\delta_{j-1})}{\delta_{j-1}(1-\delta_j)} \right) \quad \text{For } j = J \tag{11}
\]

where \( \delta_j \) is the probability of having a fluid molecule on site \( j \) and \( \delta_{j-1} \) is the probability of having a fluid molecule in the bulk. The probability can be referred to as a degree of occupancy, which can be converted
into physical units (e.g., density values of the adsorbed and bulk fluid), as described in the next section. In the equations, $c_\ell$ and $c_\ell'$ denote the surface-fluid interaction energy and fluid-fluid interaction energy, respectively; $z_0$ is the bulk coordination number, $z_1$ is the monolayer coordination number, and $z_2$ is the adjacent layer coordination number expressed as $(c_\ell - c_\ell')/2$; $K$ is the Boltzmann's constant and $T$ is the temperature. The walls of the slit pore are located at $j = 1$ and $j = J$. In this formalism, we note that (i) fluid-fluid pair interactions are restricted to those between the nearest neighbouring molecules only and (ii) only the molecules that are near the wall interact with the surface. This set of non-linear equations can be solved simultaneously for $\delta_j$ for given values of $\delta_a$, $\delta_x$, and $T$ with a chosen lattice packing pattern that defines the values of the coordination numbers: $z_0$, $z_1$, and $z_2$. We also note that in this work the same set of lattice equations is used to model isotherms at both sub- and super-critical conditions, creating a unique and consistent framework to study gas adsorption on clay mineral surfaces. This is in contrast to previous studies in which the equations were modified to consider the long-range interactions between the solid wall and fluid molecules under subcritical conditions [54,55].

The LDFT model can reproduce a variety of adsorption isotherms, including the Langmuir model [56], which has been widely applied to describe adsorption on clays. The Langmuir model assumes monolayer adsorption ($\delta_j = \delta_a$ for $j \geq 2$ in the LDFT formulation) and no interactions between fluid molecules ($\delta_{\ell} = 0$). Under these conditions Equation (9) ($i = 1$) reduces to:

$$\delta_1 = \frac{\bar{K}_{\ell} \delta_b}{1 + (\bar{K}_{\ell} - 1)\delta_b} \approx \frac{\bar{K}_{\ell} \delta_b}{1 + \bar{K}_{\ell} \delta_b}$$  \hspace{1cm} (12)

where $\bar{K}_{\ell} = \exp(-\varepsilon_{\ell}/kT)$ is a dimensionless Henry's constant. The right-hand side of the equation holds as the term $(-\varepsilon_{\ell}/kT) \approx 2 - 3$ in this study and therefore $\delta_1 \rightarrow 1$. It also follows that the LDFT model approaches the correct limiting behaviour at low concentrations ($\delta_a \rightarrow 0$ and $\delta_1 < < 1$ in the LDFT formulation), which is described by Henry's law:

For $\delta_a \rightarrow 0$: $\delta_1 = \bar{K}_{\ell} \delta_b$  \hspace{1cm} (13)

With reference to the analysis carried out in Section 4.1, it can be readily seen that:

$$\bar{K}_{\ell} = \exp(-\varepsilon_{\ell}/N_0/RT) = \exp(-\Delta u_{\ell}/RT)$$  \hspace{1cm} (14)

where $\Delta u_{\ell} (< 0)$ is the change in internal energy due to adsorption, $R = kT$, and $N_0$ is the Avogadro's number. Therefore, the surface-fluid interaction energy parameter, $\varepsilon_{\ell}$, provides another means to estimate the limiting differential enthalpy of adsorption from the following relation: $-\Delta h_{\ell} = -\Delta u_{\ell} + RT$.

4.2.1. Translation to physical units

The lattice occupancy, $\delta_j$, obtained from solving the lattice equations is translated to density values, $\rho$, using the following correlation proposed by Hocker et al. [51]:

$$\rho = \frac{\rho_{\max} \delta}{\rho_{\max}(1 - \delta) - \rho_{\max}(1 - 2\delta)}$$  \hspace{1cm} (15)

This function fulfills the following physical constraints: (i) the lattice occupancy is zero at zero density, (ii) the critical density of the fluid, $\rho_c$, corresponds to the lattice occupancy value of 0.5 [57], and (iii) the maximum density, $\rho_{\max}$, must correspond to completely filled lattice occupancy (i.e. $\delta = 1$). The same equation is used in this study for describing the experiment at subcritical conditions ($T < T_c$), where the phase transition between the gas and liquid states corresponds to a lattice occupancy value of 0.5. To achieve this, $\rho_c$ is set to $\rho_{\max}$ for $\delta_1 < 0.5$, while $\rho_c$ is set equal to $\rho_{\max}$ for $\delta_1 \geq 0.5$, as in this state the gas molecules are considered to have experienced condensation (i.e. $\rho = \rho_{\max}$, irrespective of the value of $\theta$).

The excess amount of adsorption can thus be computed from the density profile in each pore, i.e.

$$n_{\text{ex}} = \sum_{k=1}^{K} \frac{\rho_{\text{pore},k}}{J_k} \sum_{j=1}^{h_j} (\rho_j - \rho_h)$$  \hspace{1cm} (16)

where $\rho_h$ is the density corresponding to the $j^{th}$ lattice site in a pore with $J_k$ lattice sites. The pore-size distribution of the adsorbent is discretised into $K$ number of pores of different sizes, each with a specific pore volume, $v_{\text{pore},k}$, thus fulfilling the physical constraint:

$$v_{\text{pore},k} = \sum_{j=1}^{h_j} v_{\text{pore},j}$$  \hspace{1cm} (17)

where $v_{\text{pore}}$ is the specific total pore volume of the adsorbent, which has been estimated from $N_2$ physisorption analysis. The resulting molar excess adsorption, $n_{\text{ex}}$, is plotted against the bulk density to report adsorption graphically as isotherms.

4.2.2. LDFT parameters determination

The following parameters are required to solve the LDFT model and to translate the results into physical units: the fluid-fluid ($c_\ell$) and surface-fluid ($c_\ell'$) interaction energies, the maximum fluid density (saturated lattice), $\rho_{\max}$, and a suitable choice of pore sizes. The number of lattice layers $J$ of the given slit pore is expressed as the ratio of the size of the pore (described by its width, w) and of the fluid molecule (described by the kinetic diameter, see below) rounded to the nearest integer value. Because the lattice fluid is assumed to behave as a regular solution, $c_{\ell}$ can be estimated from the critical temperature of the fluid [51], i.e. $c_{\ell} = 4kT_c/c_\ell'$, where $c_\ell = 12$ is the bulk coordination number of the closest hexagonal packing lattice pattern. The values of $c_\ell'/k$ were found to be 101.4, 63.5 and 42.1 K for CO2, CH4, and N2, respectively. The pore sizes are obtained from the analysis of the subcritical $N_2$ isotherm.

The remaining parameters (c_\ell and $\rho_{\max}$) were fitted to obtain the best agreement between the LDFT simulations and experimental data. For the value of $\rho_{\max}$ the saturated liquid density at the experimental conditions was used for adsorption isotherms computed below the critical temperature of the fluid, as it is the case for $N_2$ at 77 K ($\rho_{\max} = 28.8$ mol/L). For the calculations at supercritical conditions, which applies to the experiments with CO2 and CH4 in this study, the adsorption process is no longer controlled by the vapour-liquid transition, and $\rho_{\max}$ is thus treated as an additional fitting parameter in the model, independent of temperature. To this aim, bounds were given to constrain the values of $\rho_{\max}$ within physical limits. The upper limit was set by the number density of close-packed spheres, i.e. $\rho_{\max} = \sqrt{2}/(\pi N_0)$, where $\rho$ is the molecule’s kinetic diameter, which takes a value of 4.0 Å (CO2) and 3.8 Å (CH4) giving $\rho_{\max} = 36.7$ mol/L (CO2) and $\rho_{\max} = 42.8$ mol/L (CH4). The lower limit for $\rho_{\max}$ was calculated from the reciprocal of the van der Waals co-volume, i.e. $b' = b/RT_c$ [58], corresponding to 23.3 mol/L (CO2) and 23.2 mol/L (CH4). Due to the inapplicability of a supercritical adsorbed phase to fill the entire pore space, the right-hand side of Equation (16) is multiplied by a temperature-dependent saturation factor, $c_{sat}$, which is defined as the ratio of the maximum volume occupied by the adsorbed fluid and the volume of the pore. Thus, the specific volume of the supercritical adsorbed phase at “saturation” is defined as $c_{sat} v_{\text{pore}}$, where the $v_{\text{pore}}$ is the measured specific total pore volume of the adsorbent from $N_2$ physisorption analysis as in Equation (17).

4.3. Solution procedure

The set of non-linear equations of the LDFT model was solved using the function fsolve in MATLAB. In this study, a hexagonal lattice packing pattern was used for supercritical fluids ($z_0 = 12$, $z_1 = 6$, and $z_2 = 3$), while the cubic configuration was adopted for $N_2$ adsorption at 77 K ($z_0 = 6$, $z_1 = 4$, and $z_2 = 1$). The maximum number of iterations
and the termination tolerance were set to their default values (400 and $1 \times 10^{-6}$, respectively). The experimental data were used to fit the parameters of the LDFT model by minimising the sum of the squared residuals, defined as:

$$
\Phi = \sum_{i} \sum_{j} (n_{\text{exp}}(i, j) - n_{\text{calc}}(i, j))^2
$$

(18)

where $T$ is the total number of temperature conditions (isotherms), $N$ is the number of experimental points in the given isotherm, and $n_{\text{exp}}$ and $n_{\text{calc}}$ are the measured and calculated amounts of excess adsorption for each data point, respectively. The error minimisation was done using the fmincon and fminsearch functions in MATLAB. These functions were allowed to run for a maximum of 200 iterations to find the error-minimising parameters with the default value of termination tolerance equal to $1 \times 10^{-4}$. The set of fitted parameters are the surface-fluid interaction energy ($\Sigma \varepsilon_{\text{fl}}$, fluid-dependent), the maximum fluid density ($\rho_{\text{m}}$, fluid dependent), and the saturation factor ($c_{\text{sat}}$, temperature-dependent).

5. Results

In this section, the results of the adsorption experiments of $N_2$, $CO_2$, and $CH_4$ on SWy-2 are presented together with the LDFT model fits to these isotherms (Sections 5.2 and 5.3). The construction of the experimental isotherms and the LDFT model simulations relies heavily on the structural properties of SWy-2, such as its skeletal and pore-size distribution. These properties are discussed first (Section 5.1) and have been determined from the analysis of $N_2$ physisorption and helium gravimetry experiments (results summarised in Table 1). Thermodynamic parameters (Henry’s constants and isosteric heat) that characterise the supercritical adsorption systems under study are presented in Section 5.4 using the virial equation of state and the van’t Hoff equation.

5.1. Material characterisation

5.1.1. $N_2$ physisorption isotherm

The $N_2$ adsorption isotherm acquired at 77.4 K up to $P/P^0 = 0.99$ is shown in Fig. 2a. The isotherm is of type II with a hysteresis loop of type H3 according to the classification by Thommes et al. [60].

This hysteresis loop is indicative of slit-like pores of clay minerals formed by their non-rigid platy particles [35]. The increasing adsorbed amount as $P/P^0$ reaches unity without a plateau indicates that SWy-2 contains both meso- and macropores [33]. In addition, the sharp increase in the adsorbed amount in the low-relative pressure range ($P/P^0 < 0.01$) suggests that SWy-2 has a noticeable level of micropore filling as shown in the inset of Fig. 2a. The micropore volume has been estimated using the linear form of the DR equation ($1.5 \times 10^{-4} < P/P^0 < 0.05$), which gave a specific micropore volume of 0.0138 cm$^3$/g. This value agrees well with the micropore volume estimated by the HK method (0.0134 cm$^3$/g). As discussed in Section 3.1, the pore volume and pore-size distribution of meso- and macropores of SWy-2 have been obtained by applying the BJHT technique for slit-like pore geometry. The results are presented in Fig. 3, in which each incremental pore volume associated with each interval reduction of $P/P^0$ is plotted against the average pore width, $\bar{\sigma}$.

Fig. 3 shows a major peak for small mesopores with a size between 2 and 3 nm, and an appreciable pore volume associated with larger meso- and macropores (2 nm $< \bar{\sigma} < 80$ nm). The latter amounts to 0.0766 cm$^3$/g; the sum of the micropore volume and the meso-/macropore volume is $\tau_{\text{mp}} = 0.0904$ cm$^3$/g. The BET plot of the $N_2$ physisorption isotherm exhibited a linear region between $3.4 \times 10^{-2} < P/P^0 < 0.23$. The slope and the intercept of this linear region as well as their uncertainty values were estimated through the method of simple linear regression as described in the Supplementary Materials - Section 3. The obtained SSA of SWy-2 was 32.02 ± 0.19 m$^2$/g, which shows a good agreement with the value reported by the Clay Minerals Society (31.82 ± 0.22 m$^2$/g) and estimates found in the literature, as shown in Table 1.

The LDFT model was applied to describe the $N_2$ adsorption isotherm as shown in Fig. 2a. The modelling parameters were obtained by fitting the experimental desorption data to the LDFT model and are summarised in Table 2. As discussed in Section 4.2, the LDFT model simulates adsorption inside pores of different sizes separately. To do so, the pore-size distribution and pore volumes of SWy-2 obtained from the BJHT theory and the DR equation were discretised into pores with corresponding lattice pore widths each with its respective pore volume as shown in Fig. 3. In particular, the micropores have been represented by a pore with 4 layers (i.e. $J = 4$); the characteristic peak (2 nm $< \bar{\sigma} < 3$ nm) in Fig. 3 was associated to a mesopore with 7 layers, while mesopores in the range of 3 nm $< \bar{\sigma} < 10$ nm were grouped into a single pore with $J = 17$. The remaining mesopores and macropores were given a number of layers equal to the following: $J = 34, 46, 65, 100, and 180$. These model pores were equally applied to $N_2$, $CO_2$, and $CH_4$ because of their similar molecular diameters: 3.7 Å ($N_2$), 4.0 Å ($CO_2$), and 3.8 Å ($CH_4$) [61,62]. It can be seen that the model captures the general shape of the $N_2$ isotherm; the characteristic stair-like shape of the model isotherm is the direct manifestation of the condensation process in a lattice structure characterised by a discrete number of layers. Nevertheless, the model predicts the occurrence of condensation below the saturation pressure inside confined spaces, in agreement with other models that describe such fluid behaviours (e.g. the Kelvin equation). In particular, it can be seen in Fig. 2b that the micropores are filled, or the maximum adsorbed amount is reached, at $P/P^0 \approx 0.4$, while larger pressures are needed to reach saturation in the mesopores ($P/P^0 \approx 0.9$). The mesopores also demonstrate a gradual increase towards the saturation pressure showing a shape that is analogous to type IV isotherm [60]. The macropores show almost no adsorption until $P/P^0$ approaches the saturation pressure, where condensation results in a sharp increase in the adsorbed amount. The obtained estimate of $\Delta h_{\text{LDFT}} = c_{\text{fl}}N_2 = -3.4$ kJ/mol is expectedly smaller than estimates for $N_2$ adsorption on zeolite 5 A beads ($\Delta h_{\text{LDFT}} = -21$ kJ/mol) reported by Ruthven and Xu [63], and much closer to the latent heat of vapourisation of $N_2$ at 77 K, i.e. $-\Delta h_{\text{Vap}} = -\Delta h_{\text{LDFT}} + RT = 4$ kJ/mol $\approx -\Delta h_{\text{Vap}} = 5.6$ kJ/mol [64].

5.1.2. Skeletal volume

As discussed in Section 3.2.1, the skeletal volume and weight of the sample material are obtained from the helium measurements in the gravimetric high-pressure apparatus. Fig. 4 shows the values of $M_H$ plotted against the helium mass fraction.
density for two sets of measurements: a set taken prior to the CO₂ measurements and another taken after the CO₂ measurements (prior to the CH₄ measurements). These two sets of helium measurements showed a slight shift in the values of $M_P^1$, which may be attributed to a small amount of CO₂ molecules that were not completely removed during the intermediate degassing step. Despite this shift, the slopes of the linear fits to these sets differed only by 0.3%, which is within the uncertainty values of each slope. Therefore, all of the experimental data from two sets of measurements were taken into account to determine the skeletal volume and sample weight of SWy-2 with a weight correction to the second set of measurements to account for the shift in $M_P^1$.

The resulting values of $V_0$ and $m_0$ of SWy-2 are $1.304 \pm 0.001$ cm³ and $1.727$ g, respectively. The skeletal density of SWy-2 was then calculated to be $2.709 \pm 0.005$ g/cm³ from the known value of $V_{met} = 0.667$ cm³ obtained from the measurements with CO₂ and an empty sample holder (see Section 3.2.1). This value of the skeletal density compares well with the apparent density of $2.694$ g/cm³ reported for sodium Wyoming bentonite determined via pycnometry with hydrocarbon liquids [59]. Notably, both values are well below the crystallography density of montmorillonite (~2.8 g/cm³ [59]), suggesting that a fraction of the void space (including the interlayer space) is inaccessible to helium. This result is consistent with observations from cryogenic physisorption analysis (Section 5.1.1), where an apparent SSA ($\sim 30$ m²/g) was found that is significantly smaller than its counterpart.

---

**Table 2**

LDFT model parameters for the description of CO₂, CH₄ and N₂ adsorption on SWy-2 at sub- and super-critical conditions.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$\sigma$ [Å]</th>
<th>$\varepsilon/k$ [K]</th>
<th>$\varepsilon_d/k$ [K]</th>
<th>$\rho_{max}$ [mol/L]</th>
<th>$\tau_{pore}$ [cm³/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>4.0</td>
<td>-101.4</td>
<td>-1151.4</td>
<td>26.8</td>
<td>0.0904</td>
</tr>
<tr>
<td>CH₄</td>
<td>3.8</td>
<td>-63.5</td>
<td>-841.7</td>
<td>24.8</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>3.7</td>
<td>-42.1</td>
<td>-407.5</td>
<td>28.6</td>
<td></td>
</tr>
</tbody>
</table>

---

**Fig. 2.** (a) N₂ physisorption isotherm taken at 77.4 K: experimental data (symbols) and LDFT simulations (solid line). The upward facing arrow indicates the adsorption branch while the downward facing arrow indicates the desorption branch. The inset plot shows the adsorption points for which $P/P^0 \leq 0.001$. (b) Contribution to total amount of N₂ adsorption by pores of different sizes simulated by the LDFT: micropores ($J = 4$, solid line), small mesopores ($J = 7$, dashed line), and large mesopores ($J = 100$, dash-dot line).

**Fig. 3.** Incremental (symbols) and discretised (bars) pore volume, $\Delta V$, plotted against the average pore width, $w_p$. Discretised pore-size distribution used for the LDFT model is labelled with the respective pore volume percentage for each pore. The average pore widths are translated to lattice model pores with given numbers of layers ($J = 4, 7, 13, 46, 100$, and $180$).

**Fig. 4.** $M_{P,He}$ values plotted against the helium density at multiple pressures up to 130 bar taken prior to the high-pressure CO₂ adsorption experiment (dark-coloured symbols) and taken after the CO₂ experiment (light-coloured symbols). The slopes of the linear regression lines (dashed lines) are used to estimate $V_0 = V_{met} + V_c$. 

---

obtained from crystallographic considerations (~800 m$^2$/g [15]). The agreement between the value of $V_0$ obtained from the helium measurements and that determined from independent pycnometric density measurements supports the reliability of the skeletal volume estimated via this method. This is key, because this parameter affects considerably the estimation of the excess adsorbed amount at elevated bulk densities. For example, an increase in the value of $V_0$ by 1% in this study would increase the amount of CO$_2$ excess adsorption at 50°C by 5% at 40 bar and by 139% at 250 bar. The importance and limitations of determining the correct value of $V_0$ using helium has been discussed in previous studies [65-67]. However, its effect on the measurement uncertainty at high-pressure for weakly adsorbing materials and the associated error bars are rarely presented in the literature. The experimental approach adopted in this study that utilises repeated sets of multiple helium measurements within a wide range of pressure proved to be an apt method, as it introduces an acceptable uncertainty in the measured excess adsorbed amount.

5.2. Supercritical adsorption of CO$_2$ and CH$_4$ experiments

The adsorption of CO$_2$ and CH$_4$ was measured at 25, 50, 80 and 115°C up to 250 bar. As described by Equation (1), the values of $\rho_s$ of CO$_2$ and CH$_4$ are required to quantify the excess amount of adsorption. These values were measured in situ by the balance and are compared here to values predicted by a suitable equation of state for each fluid (the Span & Wagner equation of state [68] for CO$_2$ and the Setzmann & Wagner equation of state [69] for CH$_4$) to validate the accuracy of the measurements. Fig. 5 shows an excellent agreement between the experimental data and the densities calculated using the equations of state for both CO$_2$ and CH$_4$ showing deviations less than 0.5% for CO$_2$ and 0.4% for CH$_4$ on average above 5 bar. Below 5 bar, the difference between the experimental and calculated densities is larger, as a result of uncertainties in the measured weights. However, the computed excess adsorbed amount is largely unaffected by this error, because the buoyancy correction term is negligible at these conditions.

Fig. 6 shows the measured net adsorption of CO$_2$ and CH$_4$ as a function of the bulk density at each temperature investigated. It can be seen that this measure of adsorption is negative for a large portion of the isotherm and that positive values are observed only up to small values of the bulk density (<0.7 mol/L for CO$_2$ and <0.03 mol/L for CH$_4$, as shown in the inset of the figure). Negative values of the net adsorbed amount are expected when the loss in storage volume introduced by the presence of the solid material is no longer compensated by the gain in storage capacity produced by gas adsorption. In dry SWy-2, this point is reached at low bulk density values relative to those observed for measurements with commercial adsorbent, such as 13X zeolite (10–11 mol/L) [41], reflecting the modest adsorption capacity of clays per unit mass of solid. As shown in the inset of the figure, the crossing point moves to larger bulk density values as temperature is increased, due to corresponding increase in adsorption. As an additional verification, dashed lines are also shown in the figure with a slope corresponding to the independently measured specific skeletal volume of the clay sample (~$V_0/m_s$). We observe that the experimental isotherms outline a linear region at large densities with a slope that is at least as large as the value computed from the skeletal volume, highlighting the small contribution introduced by the volume occupied by the adsorbed phase (the slope of the isotherm should approach the value $- (V_0 + V_s)/m_s$ at saturation).

Fig. 7, where the excess adsorbed amount is plotted against the bulk fluid density together with the LDFT simulation results. To confine the comparison between the experimental results and the LDFT simulations by the gain in storage capacity produced by gas adsorption. In dry SWy-2, this point is reached at low bulk density values relative to those observed for measurements with commercial adsorbent, such as 13X zeolite (10–11 mol/L) [41], reflecting the modest adsorption capacity of clays per unit mass of solid. As shown in the inset of the figure, the crossing point moves to larger bulk density values as temperature is increased, due to corresponding increase in adsorption. As an additional verification, dashed lines are also shown in the figure with a slope corresponding to the independently measured specific skeletal volume of the clay sample (~$V_0/m_s$). We observe that the experimental isotherms outline a linear region at large densities with a slope that is at least as large as the value computed from the skeletal volume, highlighting the small contribution introduced by the volume occupied by the adsorbed phase (the slope of the isotherm should approach the value $- (V_0 + V_s)/m_s$ at saturation).

The experimental excess adsorption isotherms are shown in Fig. 7, where the excess adsorbed amount is plotted against the bulk fluid density together with the LDFT simulation results. To confine the comparison between the experimental results and the LDFT simulations...
to supercritical adsorption, the adsorption data of CO\textsubscript{2} at 25 °C have been excluded from Fig. 7. Moreover, no distinction is made in the figure among data measured in adsorption and desorption mode, due to the lack of observation of any hysteresis effect. The experimental data of CO\textsubscript{2} and CH\textsubscript{4} adsorption are tabulated in the Supplementary Materials - Section 4. Both CO\textsubscript{2} and CH\textsubscript{4} isotherms show the amount of excess adsorption increasing monotonically with pressure before reaching a maximum value. After passing through the maximum points, the isotherms gradually decrease with increasing pressure. The maxima occur around $\rho_0 \approx 5$ mol/L for CO\textsubscript{2} at all temperatures, which corresponds to a sharp increase in the bulk density; the sharper increase in the bulk density at 50 °C ($T/T_T = 1.06$) leads to a more pronounced maximum peak at the same temperature. Interestingly, the shape of the CO\textsubscript{2} isotherms at elevated densities ($\rho_0 > 10$ mol/L) differs from the characteristic linear decrease observed with microporous solids [41] and is more reminiscent of the curved behaviour observed with mesoporous materials [39]. Similar features are observed for the isotherms measured with CH\textsubscript{4}; however, the effects are much weaker in this case, as the experimental temperatures of CH\textsubscript{4} in this study are farther from its critical temperature ($T/T_T = 1.5 - 2.0$).

### 5.3. Supercritical adsorption of CO\textsubscript{2} and CH\textsubscript{4} modelling

The LDFT model results are also shown in Fig. 7, where it can be seen that this model captures the experimental observations very well over the entire pressure range and at each temperature (the values of the objective function are $\Phi = 1.13 \times 10^4$ $\mu\text{mol}^2/\text{g}^2$ and $\Phi = 1.71 \times 10^3$ $\mu\text{mol}^2/\text{g}^2$ for CO\textsubscript{2} and CH\textsubscript{4}, respectively). The parameters used in the model are summarised in Table 2. Among them, the surface-fluid interaction energy ($e_{sf}$) and the density of the saturated lattice ($\rho_{max}$) were fitted to obtain the best agreement between the LDFT model and the experimental data. We note that for a given gas, both parameters are independent of temperature. From the values of the parameter $e_{sf}$ for CO\textsubscript{2} (−1151.8 K) and CH\textsubscript{4} (−841.7 K), estimates for the zero coverage differential enthalpy of adsorption are obtained that take values of $\Delta h_{i,\text{LDFT}}$ ≈ −12.5 kJ/mol (CO\textsubscript{2}) and $\Delta h_{i,\text{LDFT}}$ ≈ −9.8 kJ/mol (CH\textsubscript{4}). These values are just above the latent heat of vapourisation of the two gases (i.e. $\Delta h_{\text{vap}}$ = −10.3 kJ/mol for CO\textsubscript{2} at 273.15 K and $\Delta h_{\text{vap}}$ = −8.2 kJ/mol for CH\textsubscript{4} at 112 K [64]), in agreement with the common perception that for physisorption, $\Delta h_{i}/\Delta h_{\text{vap}} < 1.5 - 2$ [70]. The fact that the values obtained here are at the lower end of the expected range is not surprising given that clays are weakly sorbing materials and that the parameter $e_{sf}$ describes solely the interactions between the surface and the first adsorbed layer. Notably, the stronger affinity observed in the adsorbed amounts towards CO\textsubscript{2} as compared to CH\textsubscript{4} is also reflected in the relative values of the surface-fluid interaction energy $\epsilon_{SF,\text{CO}_2}/\epsilon_{SF,\text{CH}_4} \approx 1.4$.

The resulting values of $\rho_{max}$ are 26.8 mol/L for CO\textsubscript{2} ($\rho_{max}/\rho_0 = 2.52$) and 24.8 mol/L for CH\textsubscript{4} ($\rho_{max}/\rho_0 = 2.45$). These estimates are closer to the inverse of the van der Waals co-volume than the number density of close-packed spheres (see Section 4.2). In particular, both values are comparable to results obtained on a mesoporous silica ($\rho_{max}/\rho_0 = 2.5$) and significantly smaller than those obtained on microporous zeolite ($\rho_{max}/\rho_0 = 3.45$) with CO\textsubscript{2} [51], confirming that the degree of packing of the adsorbed molecules is strongly affected by the pore structure of the adsorbent material. The similarity of the values obtained for CO\textsubscript{2} and CH\textsubscript{4} supports this observation, because the two molecules share comparable kinetic diameters. We also note that a constant value of $\rho_{max}$ has been used for each gas, which corresponds to a complete filling of the lattice, irrespective of temperature. Accordingly, all isotherms in Fig. 7 for a given gas converge to a single value, corresponding to the point where the density of the adsorbed phase is equal to that of the bulk phase. This characteristic behaviour of excess adsorption isotherms is also seen for other fluids adsorbing onto various porous materials, such as silica gel, HKUST-1, and activated carbon [39,71–73].

### 5.4. Henry’s constants and isosteric heat

The Henry’s constants, $K_{max}$ of CO\textsubscript{2} and CH\textsubscript{4} on SWy-2 were obtained from the zeroth-order coefficient, $K_0 = \ln(K_{max})$, of the virial equation, Equation (5), which was fitted to the excess adsorption data, as shown in Fig. 8a. Only the zeroth and first-order virial coefficients were needed in the parameter estimation, as the coefficients of higher order all tended to zero. Also, the adsorption data considered for fitting were the points measured at bulk density values below 10% of the liquid densities of CO\textsubscript{2} and CH\textsubscript{4} (21.1 and 26.0 mol/L, respectively) to keep the difference between absolute and excess adsorption sufficiently small ($n^{\text{abs}} \approx n^{\text{ex}}$). These correspond to adsorption points below 50 bar for CO\textsubscript{2} and 80 bar for CH\textsubscript{4} as shown in Fig. 8a. The advantage of using the virial treatment to obtain the Henry’s constant can be appreciated from the analysis of Fig. 8b, where the same data are represented as $\ln(n^{\text{ex}}/P)$ plotted against $n^{\text{ex}}$. In the plot, a linear region appears well beyond the Henry’s Law limit that can be conveniently used to estimate the Henry’s constants from the $y$-intercepts of the linear fit at $n^{\text{ex}} = 0$ [45]. In this study, however, the virial equation was used to fit the experimental data directly to reduce subjectivity of back-extrapolation. Moreover, to account for uncertainties on the measured adsorption values in the determination of the Henry’s constants, 1000 realisations of the
parameter estimation have been carried out by randomly varying the experimental data within the estimated error bars. The standard deviation of the zeroth virial coefficient was used to estimate the corresponding uncertainty value of the Henry's constant (see Supplementary Materials - Section 2).

The obtained coefficients are summarised in Table 3 for both CO₂ and CH₄ as a function of temperature. The selectivity at the limit of zero pressure is also reported that has been calculated as the ratio of the Henry's constants, i.e. \( S = \frac{K_{H,CO₂}}{K_{H,CH₄}} \), with an average value \( S \approx 5.5 \) for the range of temperature investigated in this study. The stronger adsorption affinity towards CO₂ as compared to CH₄ for this clay is in agreement with the LDFT model results discussed above in terms of the surface-fluid interaction parameter, \( \varepsilon/\sigma \).

When plotted as a function of the inverse of temperature (Fig. 9), the obtained Henry’s constant follow a linear behaviour suggesting that a correlation of the form of Equation (8) applies. The corresponding values of the zero coverage deviation of the distribution of the zeroth virial coefficient, \( \Delta v \), have been calculated to be \(-18.4 \pm 0.6 \text{kJ/mol}\) and \(-14.2 \pm 0.7 \text{kJ/mol}\), respectively. The uncertainty values of \( \Delta h_0 \) have been obtained using the same method adopted to estimate the uncertainty values of the Henry’s constant. Notably, the ratio between these values is in excellent agreement with that predicted by the LDFT model, i.e. \( \frac{\Delta h_{0,CO₂}}{\Delta h_{0,CH₄}} \approx \frac{H_{L,DFT,CO₂}}{H_{L,DFT,CH₄}} \approx 1.3 \). Yet, the absolute values obtained from the experiments are approximately 1.5 times larger than their numerical counterparts, as shown by the solid lines plotted in Fig. 9 that represent the LDFT model predictions. We also note that the latter have been corrected upon introducing a pre-factor \( \gamma_0 \) in Equation (14), which would otherwise take a value of one. In this study, the pre-factor has been obtained by minimising the difference between model prediction and experimental data in the \( \ln(K_{H,fi}) \) vs. \( 1/T \) plot (\( \gamma_0 = 0.40 \mu \text{mol/g-bar} \) for CO₂ and \( \gamma_0 = 0.19 \mu \text{mol/g-bar} \) for CH₄). The corresponding values obtained from the linear fit to the experimental are significantly lower, i.e. \( K_{H,CO₂} = 0.650 \mu \text{mol/g-bar} \) for CO₂ and \( K_{H,CH₄} = 0.041 \mu \text{mol/g-bar} \) for CH₄. Discrepancies of similar order have been reported between experimental and theoretical values of the pre-factor in Equation (8), including data for CO₂ and N₂ [45]. We also argue that the required calibration of the LDFT model against the experimental values of the Henry’s constant reflects the lack of measurements in this study at sufficiently low bulk density values.

### Table 3

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>CO₂</th>
<th>CH₄</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_i \times 10^3 )</td>
<td>( K_i \times 10^3 )</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>853 ± 8.0</td>
<td>6.02 ± 0.29</td>
<td>11.6 ± 1.2</td>
</tr>
<tr>
<td>50</td>
<td>43.3 ± 1.1</td>
<td>6.01 ± 0.08</td>
<td>8.05 ± 0.5</td>
</tr>
<tr>
<td>80</td>
<td>25.3 ± 0.9</td>
<td>7.01 ± 0.15</td>
<td>5.45 ± 0.4</td>
</tr>
<tr>
<td>115</td>
<td>15.1 ± 0.7</td>
<td>8.14 ± 0.31</td>
<td>3.00 ± 0.1</td>
</tr>
</tbody>
</table>

6. **Discussion**

As presented in Section 5.3, the LDFT model has successfully described the adsorption of CO₂ and CH₄ on SWy-2 under various experimental conditions. However, the benefits of the LDFT model need to be evaluated by considering the underlying assumptions of this approach; these include (i) the adoption of a specific structure and shape of the pores (a slit in this study); (ii) the discretisation of the pore into an integer number of layers; (iii) the use of the same lattice spacing for different adsorbates. These limitations can be overcome through the use of approaches that are more rigorous (and computationally more intensive), such as Density Functional Theory (DFT) and Grand Canonical Monte Carlo (GCMC) simulations [47]. However, the ability to account for a distribution of pore sizes, which is achieved by applying the LDFT model, enables revealing adsorption behaviours that are pore-size specific and that become particularly evident at near-critical conditions. The LDFT model represents therefore a step forward compared to conventional approaches, such as semi-empirical isotherm equations that provide only a macroscopic description of the adsorption equilibrium. These underlying features of the LDFT model and its comparison to the Langmuir model, the most commonly used empirical equation, are discussed in the following section.

#### 6.1. CO₂ and CH₄ adsorption on SWy-2: comparison with literature data

The measurement of supercritical gas adsorption on clays is a technical and scientific challenge. The main reason for this is the intrinsic difficulty in performing the experiments and in their description, because the interactions between a supercritical gas and the clay are complex. The requirement of conducting the experiments at elevated pressures, together with the weakly sorbing nature of geomaterials sets very high demands on measurement accuracy, as demonstrated by a recent inter-laboratory comparison on carbonaceous shales, which has been only partly successful [75]. In this context, source clays represent an excellent class of reference materials for comparing experimental data and to develop suitable protocols for supercritical adsorption experiments on geosorbents and their interpretation.

In Fig. 10, the CO₂ and CH₄ adsorption isotherms obtained in this study are compared to adsorption isotherms reported in the literature, which were measured under similar conditions (see Table 4 for details). The samples studied by Liu et al. [24] and Ji et al. [23] are montmorillonite and montmorillonite-dominated rocks (~80 % wt.) sourced from Inner Mongolia and China, respectively, while all other samples have been sourced from the Source Clays Repository and used as-received Na-rich [18,25,28] or by re-saturating the sample with sodium ions [29].

It can be seen that the reported isotherms disagree considerably with the adsorbed amount ranging between 250 and 650 μmol/g (CO₂), and 150 and 550 μmol/g (CH₄) near a bulk density value of 5 mol/L (corresponding to 80 bar and 120 bar for CO₂ and CH₄ at 50°C, respectively).
suggest that the pores are far from being fully saturated was introduced in this study and de
obtained in this study are plotted in Fig. 11 as a
and
are
cv
v
represents
montomorillonite-rich sample [23] at 5°C. Data from the present study combine measurements on two distinct SWy-2 samples using di

values of SSA are reported by these studies using clay samples with
saturated STx-1 [29]. The nature of the interlayer cation (e.g. Na v. Ca) a
‡
Sourced from Inner Mongolia.
†
Montmorillonite dominated rock sourced from Sichuan Province in China.

Table 4
Experimental details of literature adsorption studies on Montmorillonite.

<table>
<thead>
<tr>
<th>Author</th>
<th>T [°C]</th>
<th>Fluid</th>
<th>Cation</th>
<th>Source clay</th>
<th>Degas condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Busch et al. [18]</td>
<td>45</td>
<td>CO₂</td>
<td>Na</td>
<td>SWy-2</td>
<td>105 °C under vacuum</td>
</tr>
<tr>
<td>Schaef et al. [28]</td>
<td>50</td>
<td>CO₂/CH₄</td>
<td>Na</td>
<td>SWy-2</td>
<td></td>
</tr>
<tr>
<td>Rother et al. [29]</td>
<td>50</td>
<td>CO₂</td>
<td>Na</td>
<td>STx-1</td>
<td></td>
</tr>
<tr>
<td>Fan et al. [25]</td>
<td>60</td>
<td>CH₄</td>
<td>Na</td>
<td>SWy-2</td>
<td>70 °C under vacuum</td>
</tr>
<tr>
<td>Ji et al. [23]</td>
<td>50</td>
<td>CH₄</td>
<td>Ca</td>
<td>Montmorillonite⁺</td>
<td>250 °C with He as carrier gas</td>
</tr>
<tr>
<td>Liu et al. [24]</td>
<td>60</td>
<td>CH₄</td>
<td>Ca</td>
<td>Montmorillonite⁺</td>
<td></td>
</tr>
</tbody>
</table>

respecively). The nature of the interlayer cation (e.g. Na v. Ca) affects the available micropore volume [12] and may explain the trend observed among the isotherms measured with CH₄ [23,24]. In fact, higher values of SSA are reported by these studies using clay samples with oppositely larger interlayer cations (> 70 m²/g for Ji et al. [23] and > 50 m²/g for Liu et al. [24]), as compared to the value obtained in this study (32.02 m²/g). While the adsorption isotherms reported by Busch et al. [18], Schaef et al. [28], and Fan et al. [25] were all measured on montmorillonite SWy-2, only the results reported by Fan et al. [25] agree with those measured there. On the one hand, inaccuracies in the estimation of the skeletal volume may be the origin of some of the discrepancies observed at elevated pressures (see Section 5.1.2), including the appearance of negative excess adsorption values. On the other hand, the spread of the values that is observed at su
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accuracy due to the intercalation of adsorbing gases as seen in the case of supercritical CO₂, leading to larger sorption capacities [16,17,78]. Laboratory studies that systematically investigate the effect of exchanged cations and the hydration states on adsorption at elevated pressures are not sufficient in the literature and so are the analyses of measurement uncertainties associated with supercritical adsorption experiments on clays. This makes it challenging to ascertain the reliability of the reported literature data and to make inter-laboratory comparisons.

6.2. The adsorbed phase in clay nanopores

As anticipated in Section 4.2, a temperature-dependent saturation factor cₙₐₜ is introduced in this study and defined as the ratio of the maximum volume occupied by the adsorbed fluid and the total pore volume. While this expedient was required to achieve a good agreement between experiments and LDFT simulations, it also possesses a physical basis, as explained in the following. The achievement of ρₘₜₐₓ represents a theoretical limit imposed by the regular lattice; in practice, the adsorbed molecules are likely to experience packing inefficiencies in the confined pore space of the adsorbent material [31]. Furthermore, the absence of a vapour-liquid transition at supercritical conditions precludes a complete filling of the pore space by the supercritical adsorbed phase, even at extremely large pressures [42]. Both effects are expected to depend on the experimental temperature and to be molecule-specific. Accordingly, in our modelling approach the values of ρₘₜₐₓ and ρₚₒₑₑ are kept constant (as these represent physical limits imposed by the chosen model and the material, respectively), while the specific volume of the supercritical adsorbed phase can vary, reaching a value at “saturation" (= cₙₐₜρₚₒₑₑ) that is temperature- and fluid-dependent. This definition of the saturation factor is somewhat analogous to earlier attempts introduced to capture this variability in the LDFT adsorption model, such as the temperature-dependent pore-filling capacity (ϕₘₜₐₓρₚₒₑₑ) [51] or to the so-called “isotherm pre-factor" that accounts for a variable density of active pores with temperature [49,79].

The values of cₙₐₜ obtained in this study are plotted in Fig. 11 as a function of the temperature and for each gas. For both CO₂ and CH₄, the values of cₙₐₜ suggest that the pores are far from being fully saturated
with adsorbed fluid (c_	ext{sat} < 0.7 for CO₂ and c_	ext{sat} < 0.5 for CH₄). Interestingly, the value of this parameter (i) increases with decreasing temperature and (ii) is larger for CO₂ (c_	ext{sat} = 0.55 – 0.7) as compared to CH₄ (c_	ext{sat} = 0.4 – 0.45) at equivalent temperature. Upon normalisation of the experiment temperature with the critical temperature of the gas, the data delineate a common curve (shown in the inset of the figure), where the volume occupied by the adsorbed phase increases with decreasing temperature with a gradient that becomes steeper as the critical temperature is approached. This behaviour is reminiscent of early observations of critical adsorption on porous solids [80] and suggests that complete saturation of the pore space in clays may be achieved at near-critical conditions. Additional experimental data on different substrates are required to corroborate this interesting finding.

6.3. Modelling supercritical adsorption on geosorbents

The successful application of the LDFT model to describe supercritical gas adsorption on SWy-2 leads to the question of whether simpler, semi-empirical adsorption models would be equally suitable. The Langmuir model is a widely used example of such models and has been previously applied to clays [23–26]. As described in Section 4.2, the LDFT model reduces to the Langmuir equation (Equation (12)) when adsorption coverage is limited to a monolayer and the interaction energy between fluid molecules is neglected. The obtained equation can be dimensionnalised and combined with the definition of the excess amount of adsorption to yield the following expression:

\[ n^\text{ex} = n^\text{m} k_i f \left( \frac{1 - \frac{\rho}{\rho_i}}{1 + k_i f} \right) \]  

(19)

where \( n^\text{m} \) is the monolayer capacity, \( k_i \) is the Langmuir equilibrium constant, \( f \) is the fugacity, and \( \rho_i \) is the adsorbed phase density. To describe adsorption in the high-pressure range, the latter is often assumed to take a certain value, usually the liquid density at specific conditions [41]. In the following, two scenarios are investigated, namely where this density is taken as the maximum value predicted by the LDFT model (\( \rho_{\text{max}} = 26.8 \text{ mol/L for CO}_2 \) and \( \rho_{\text{max}} = 24.9 \text{ mol/L for CH}_4 \)) or where it is used as a fitting parameter (in addition to \( n^\text{m} \) and \( k_i \), parameter values given in the caption of Fig. 12). The results from this parameter estimation are presented in Fig. 12a (CO₂) and b (CH₄) for the excess adsorption isotherms measured on SWy-2 at 50°C, where the relative percentage error between experiment and models (Langmuir and LDFT) is plotted as a function of the bulk density. For the sake of clearer representation, only one Langmuir scenario is shown where the adsorbed phase density was used as fitting parameter (light-coloured symbols). It can be seen that both models perform equally well on the CH₄ data; deviations are generally less than 5% and the values of the minimised function normalised by the maximum excess adsorbed amount (\( \Phi = \Phi n_{\text{ex max}}^\text{m} \)) are small (\( \Phi = 2.7 \text{ µmol/g} \) and \( \Phi = 1.2 \text{ µmol/g} \) for the LDFT and Langmuir model, respectively). On the contrary, the two models differ considerably in the description of the CO₂ isotherm, where the LDFT model (\( \Phi = 11 \text{ µmol/g} \)) now outperforms the Langmuir model (\( \Phi = 22 \text{ µmol/g} \)). We note that statistical significance is implied here, because both models use the same number of adjustable parameters to find the optimum match to the experimental data.

Fig. 12c compares excess adsorption isotherms on SWy-2 at 50°C obtained upon application of the LDFT and Langmuir models. For the latter, two sets of curves are shown to represent the results obtained for different (constant) values of the adsorbed phase density. In agreement with the considerations above, both models produce similar isotherms for CH₄, which therefore both agree with the experimental data. Deviations are observed only for \( \rho_i > 10 \text{ mol/L} \), but the validation of the model predictions at these elevated bulk densities is precluded by the lack of experimental observations above 250 bar. The CO₂ isotherms produced by the two models are quite different; as shown in the figure, only the LDFT model matches the experimental data well, while both Langmuir fits result in significantly larger values of the minimised objective function (\( \Phi = 22 \text{ µmol/g} \) for \( \rho_i = 23.1 \text{ mol/L} \) and \( \Phi = 35 \text{ µmol/g} \) for \( \rho_i = 26.8 \text{ mol/L} \)). Notably, the Langmuir model misplaces systematically the maximum excess adsorbed amount and fails at capturing the characteristic non-linear descending part of the isotherm for both scenarios considered. As anticipated above, the ability to validate these models at elevated bulk densities is only limited by the scarcity of experimental data. In the figure, fresh data are shown that have been measured in this study between 200 and 650 bar on SWy-2 using a different Rubotherm balance that is able to achieve these extreme conditions (\( \rho_i > 20 \text{ mol/L} \)). The agreement between these data and the LDFT prediction is satisfactory considering the small values of the excess adsorbed amount at these elevated pressures (\( \sim 100 \text{ µmol/g} \)) and the associated measurement uncertainties (shown by the error bars). In particular, we note that in agreement with the predictions by the LDFT model and contrary to the Langmuir model, the experiments outline a convex isotherm shape with increasing bulk density.

The richer (and more complex) behaviour of the CO₂ isotherm can be traced back to the temperature of the experiment, which is closer to the critical temperature of the gas (\( T/T_c = 1.06 \)) as compared to CH₄ (\( T/T_c = 1.7 \)). The vicinity to the critical point is such that concurring temperature effects in pores become more pronounced and the isotherm shape reflects features that can be associated with a specific distribution of pore sizes [51]. In SWy-2, these features are typical of a material that possesses a large fraction of mesopores for which the isotherm maximum occurs at higher density (\( \rho_i > 5 \text{ mol/L} \)) and the bending behaviour of the isotherm becomes more pronounced, as observed in commercial mesoporous adsorbents [39,81]. The LDFT model can be used to reveal these patterns, because it produces individual, pore-specific isotherms and pore-density profiles, as shown in Fig. 13. In the figure, (a) excess isotherms and (b)-(c) pore occupancy profiles are presented in lattice units and refer to CO₂ adsorption data computed at 50 °C in micro- and meso-pores with 4 and 17 layers, respectively (corresponding to 1.6 nm and 6.8 nm). In the micropore, adsorption at low coverages increases steeply reaching a maximum at approximately \( \delta_i = 0.2 \) followed by a fairly linear decrease. On the contrary, in the mesopore the increase in the adsorbed amount is more gentle, the maximum is reached only at \( \delta_i = 0.4 \) and the descending part is characterised by a pronounced curvature. It is the combination of these features that gives rise to the behaviour observed experimentally and shown in Fig. 12c. Accordingly, the greater value of lattice adsorption in the micropores as compared to the mesopores is the manifestation of the lattice occupancy profiles.
observed in these pores and shown in Fig. 13b and c. Although the fluid-solid interaction parameter, $\varepsilon_{sf}$, is the same for both pores, the close proximity of the parallel pore walls inside the micropores causes the values of lattice occupancy of all layers to be above their corresponding values of bulk occupancy. In contrast, fluid densification in the mesopores is reached only near the walls, while in the centre of the pores the lattice occupancy profiles plateau to the bulk values.

7. Concluding remarks

Understanding the adsorption mechanisms of CO$_2$ and CH$_4$ on clay minerals has relevance to many applications, including the geological storage of CO$_2$ and the recovery of shale gas. In this study, the adsorption of CO$_2$ and CH$_4$ on dry Na-montmorillonite (SWy-2) has been measured over a wide range of temperature and pressure conditions using a gravimetric technique. The experimental data have been evaluated using both net and excess adsorption formalisms. The results indicate that CO$_2$ adsors more strongly than CH$_4$ on SWy-2, as quantified by the selectivity, $S = K_{CO_2}/K_{CH_4} \approx 5.5$, and the adsorption energetics, $\Delta h_{R,CO_2}/\Delta h_{R,CH_4} \approx 1.3$. The adsorption isotherms have been successfully described by the LDFT model, which proves to be more rigorous and accurate than semi-empirical approaches based on the Langmuir isotherm (or variations thereof). The model uses the pore-size distribution of the material as input parameter and provides estimates of the isosteric heat that compare favourably with results obtained experimentally. Most significantly, the LDFT model reveals adsorption behaviours that are pore-size specific; these effects become particularly evident for isotherms that are measured at slightly supercritical temperatures (CO$_2$ in this study) in materials that possess a significant amount of mesoporosity, such as the clay investigated here. We contend that this observation is not limited to CO$_2$ and SWy-2, but that these phenomena are likely to be observed in other clay-rich rocks and with other relevant geo-fluids, such as light hydrocarbons or their mixtures that attain near-critical conditions at subsurface conditions.

Fig. 12. Relative deviations between experiment and model (LDFT - squares and Langmuir model - circles) as a function of the bulk density for the isotherms measured at 50°C on SWy-2 with (a) CO$_2$ and (b) CH$_4$. (c) The corresponding experimental excess adsorption isotherms (symbols) are compared to predictions by the LDFT (solid lines) and Langmuir model (dashed lines - two scenarios). The filled symbols are the same data reported in Fig. 7, while the empty symbols are measurements carried out in a different Rubotherm balance up to 65 MPa. The following Langmuir parameters are obtained [n$^\infty$ [ = ] \(\mu\)mol/g, kL [ = ] bar$^{-1}$, and $\rho_a$ [ = ] mol/L]: [606, 0.036, 26.8] and [888, 0.018, 23.2] for CO$_2$, and [243, 0.023, 24.9] and [256, 0.021, 23.1] for CH$_4$.

Fig. 13. (a) Lattice excess adsorption isotherms computed for CO$_2$ at 50°C in two pores, namely 4 (micropores) and 17 layers (mesopores). The corresponding lattice occupancy profiles in (b) 4 layer pore and (c) 17 layer pore. The dashed lines represent the values of $\theta$: 0.25, 0.5, and 0.75.