

**MULTISCALE ADSORPTION AND DIFFUSION STUDIES
IN UNCONVENTIONAL SHALE GAS RESERVOIRS**

BY

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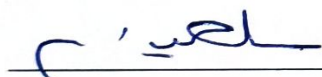
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I dedicate this thesis my creator, the Almighty God, who is my source of inspiration, wisdom, knowledge and understanding, and then to my lovely wife Success for her morale support during my Ph.D. and finally to my Parents Isioma & Azunne for their prayers and encouragement.

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LIST OF ABBREVIATIONS

AFM	:	Atomic Force Microscopy
APM	:	Areal Porosity Method
BET	:	Brunauer, Emmett and Teller
BJH	:	Barrett, Joyner and Halenda
BSE	:	Backscatter Electron
DRIFTS	:	Diffuse reflectance Fourier transform infrared spectroscopy
EBSD	:	Electron Backscatter Diffraction
EDX	:	Energy-Dispersive X-Ray Spectroscopy
EGME	:	Ethylene Glycol Monoethyl Ether
HCPC	:	Hierarchical Clustering of Principal Components
IUPAC	:	International Union of Pure and Applied Chemistry
LEED	:	Low Energy Electron Diffraction
LOD	:	Limit of Detection
MIP	:	Mercury Injection Porosimetry
NDIR	:	Non-Destructive InfraRed
NMR	:	Nuclei magnetic resonance

QEMSCAN	:	Quantitative Evaluation of Minerals by Scanning Electron Microscopy
SANS	:	Small Angle Neutron Scattering
SAXS	:	Small Angle X-ray Scattering
SEM	:	Scanning Electron Microscopy
SSA	:	Specific Surface Area
SSM	:	Solid Sample Measurements
STP	:	Standard Temperature and Pressure
3D-SIMS	:	Three-Dimensional Secondary Ion Mass Spectroscopy
TEM	:	Transmission Electron Microscopy
TOC	:	Total Organic Content
XRD	:	X-ray diffraction
μXRF	:	Micro- X-ray fluorescence

ABSTRACT

Full Name : [Clement Chekwube Afagwu]
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[Dissolved molecules in the cylindrical pores and adsorbed molecules in the microcracks diffuse through the kerogen microstructure to the inorganic shale matrix. SEM reconstructed shale pore structures bypass micropores and the preservation of the associated organic matter heterogeneity is uncertain during pyrolysis which results in erroneous modeling of the reservoir transport mechanisms. In this study, a comprehensive molecular simulation workflow was utilized to develop a new self-diffusion and shale apparent permeability model for realistic kerogen structures and complex geometry, after a robust validation with both experimental and computational datasets. The results revealed that the impact of organic matter heterogeneity in the form of diffusion tortuosity, sorbed gas interaction, and effective confining pressure on transport phenomena is higher in micropores when reservoir pressure depletion reaches below 2,000 psi. Furthermore, the results were extended to formulate a novel simulation framework based on Gaussian Pressure Transients that coupled these multiscale physics models to describe flow in hydraulic fractured shale gas reservoirs. Results are sensitive to the essential reservoir parameters of pressure depletion, matrix permeability, organic content, and local heterogeneity. The simultaneous solution of molecular and pressure diffusivity equations reveals their interdependencies. The flux of the sorbed phase contributes to the production

rate by some factor that is determined by the organic matter sorption capacity. The methodology provided in this study can be utilized to simulate mass transport in shale reservoirs and predict hydrocarbon production rates, which may greatly aid asset management decisions and maximization of the ultimate recovery.

|

ملخص الرسالة

الاسم الكامل: كليمنت تشيكوبي افاغوو

عنوان الرسالة: دراسات الامتزاز والانتشار متعدد النطاقات في خزانات الغاز الصخري غير التقليدية

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نماذج النفاذية الظاهرة من الصخر الزيتي في الأدبيات لوصف تدفقات الانتشار في المسام النانوية للمادة العضوية ، يتم إجراؤها التي تعطي تمثيلاً غير واقعي SEM بشكل أساسي باستخدام الأنابيب النانوية الكربونية ، وشقوق الكربون ، والجرافيت ، وصور لعدم تجانس المادة العضوية في الصخر الزيتي من حيث بنية المسام وتكوينها ، والتي يؤدي إلى نمذجة خاطئة لآليات نقل الخزان. في هذه الدراسة ، تم استخدام سير عمل محاكاة جزيئية شامل لتطوير نموذج جديد للنفاذية الواضحة للانتشار الذاتي والصخر الزيتي لهياكل الكروجين الواقعية والهندسة المعقدة ، بعد التحقق من صحة قوية مع كل من مجموعات البيانات التجريبية والحسابية. كشفت النتائج أن تأثير عدم تجانس المادة العضوية في شكل بداية نظام الانتشار الانتقالي المتأخر ، وتعرج الانتشار ، وتفاعل الغاز الممتص وضغط الحصر الفعال يكون أعلى في المسام الدقيقة عندما يصل استنفاد ضغط المسام إلى أقل من 2000 رطل لكل بوصة مربعة. علاوة على ذلك ، تم تمديد النتائج لتشكيل إطار محاكاة جديد يعتمد على عابرات الضغط الغاوسي التي اقترن هذه النماذج الفيزيائية متعددة النطاقات لوصف التدفق في خزانات الغاز الصخري المكسور الهيدروليكي. النتائج حساسة لمعايير المكنن الأساسية لاستنفاد الضغط ونفاذية مادة الأساس والمحتوى العضوي وعدم التجانس المحلي. يكشف الحل المتزامن لمعادلات الانتشار الجزيئي والضغط عن الترابط بينهما. يساهم تدفق المرحلة الممتصة في معدل الإنتاج ببعض العوامل التي تحددها قدرة امتصاص المادة العضوية. يمكن استخدام المنهجية الواردة في هذه الدراسة لمحاكاة النقل الجماعي في الخزانات الصخرية والتنبؤ بمعدلات إنتاج الهيدروكربونات ، والتي قد تساعد بشكل كبير في اتخاذ قرارات إدارة الأصول وتعظيم الانتعاش النهائي.

CHAPTER 1

INTRODUCTION

The production of hydrocarbons from unconventional reservoirs has increased significantly in recent times, especially in the United States [1]. Technological breakthroughs in fracturing techniques and horizontal well drilling are keys to the improved exploitation of hydrocarbons in these types of assets. Unconventional reservoirs refer to hydrocarbon-bearing rock types that require well stimulation and enhancement to produce oil and gas in commercial quantities. Examples of such rocks include tight gas sandstone, gas hydrates, oil shale formations, heavy oil sandstone, and shale gas rocks, among others. Shale gas is a type of unconventional formation, that is formed through an abiogenic and biogenic process at a great burial depth and certain temperature condition, exists as a source and reservoir rock [2,3], and commonly exploited in the fossil fuel industry. Tight sand and shale gas constitute over 60% of natural gas production in the United States. By 2050, it could make up over 90% of total U.S gas production [4] (**Figure 1**). Interestingly, organic-rich shale has the greatest potential among these unconventional resources [5]. The organic matter (OM) present is dispersed; a major component of these scattered compounds in potentially lucrative shale formations is known as kerogen [6]. Kerogen is an insoluble organic compound present in shale reservoirs with its elemental composition varying based on its origin and maturation [7]. Scanning electron microscopy (SEM) images of shale samples have revealed evidence of kerogen distribution within

inorganic matrix minerals, though this high resolution imaging technique may be inadequate to resolve OM with pore sizes below five nanometers [2, 5–10].

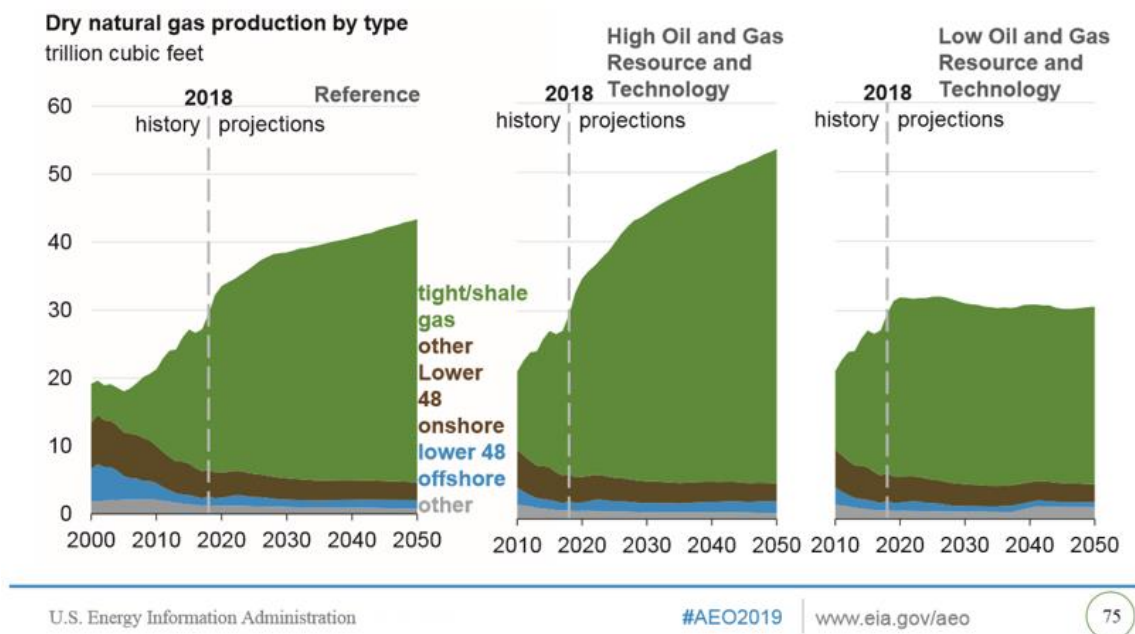


Figure 1 U.S. dry natural gas production increase due to development of tight and shale resources (U.S. Energy Information Agency [4])

The primary component of shale gas is methane, in addition to small quantities of carbon dioxide, nitrogen, water, ethane, and propane [15]. Methane is stored as bulk gas, adsorbed and dissolved gas; and are located in shale pores, phase-transitioning near organic walls and within OM, respectively. Some of the gas is stored in bulk near the adsorbed phase regions [16]. The quantity of gas stored varies significantly by pore size, surface chemistry, depth, temperature, pressure, organic content and variable water saturation [17–20]. The multiple pores that exist in mud rocks are subdivided into three basic categories, based on the International Union of Pure and Applied Chemistry, micropores (<2 nm), meso-pores (2 to 50 nm), and macro-pores (> 50 nm) [18,19,21]. The IUPAC grouping will be used

for all material pore size characterization throughout this study. While some organic shale samples may have a small fraction of micropores, there are a number of shale formations with over 30% micropores [22,23]. Gou et al. [23] imaged the Longmaxi organic-rich shale using a combination of high-resolution scanning and gas adsorption technique, and observed 2–98.5 μm sized microfracture, which accounted for 16% of total pore volume, while micropores (0.305–2 nm), mesopores (2–50 nm), and macropores (50 nm – 2 μm) accounted for 33%, 36%, 14% of pore volume respectively. Researchers use the term micro-porosity to describe pores with 0.5 to 5.0 nm radii [24]. The physics of porous media vary by pore scale.

Much effort has been made in the literature to explain that the detailed mass transport mechanisms responsible for the well rate when producing from shale formations differ from simulation models used in conventional reservoir engineering [25]. For instance, the Darcy flow is valid for macro-pores, but will produce erroneous results if employed solely to model gas transport in micro- and meso-porous materials [26–29]. The sedimentation processes responsible for shale formation in a quiet marine environment reduces the petrophysical quality of the reservoir (i.e. porosity and permeability), while the presence of quartz induces brittleness that renders shales subject to abundant natural fractures upon deep burial [30,31]. The presence of organic matter adds more complexity, as the hydrocarbon accumulation in the formation is self-sourced, with a significant amount of gas trapped in the nano- and micropores associated with the organic matter [10,32–38]. Analysis of the transport modes revealed the self-diffusion as the primary transport mechanism in these micropores [39–42]. Self-diffusion is governed by the pressure and the effective size. During typical span, the pressure drops which influences the sorption profile,

the net overburden stress on the pores, and the mean free path altering the magnitude of self-diffusivity. The ability to couple the multiscale physics, especially the transport physics in nanopores to simulate large scale flow in hydraulic fractured reservoirs still require more attention.

The remainder of this work is organized as follows. The chapter 2 will provide a detailed literature review to clay chemistry, kerogen chemical structure, kerogen adsorption, diffusion and a survey of diffusion tortuosity, which is the pore structure parameters that controls the self-diffusion mechanism. Consequently, survey the shale gas analytical and numerical transport models and compare their limitations and strengths in order to provide research gaps. Afterwards, the traditional simulation workflow that couples these transport physics to simulate flow in hydraulic-fractured shale gas reservoirs will be reviewed in the same chapter in order to identify research problem statements and formulate objectives accordingly in chapter 3. In chapter 4, the pore volume characteristics of clay-rich shale will be studied using a low-temperature adsorption experiment and the relationship to their chemical composition will be established. The main self-diffusion controlling pore structure characteristics of a realistic kerogen will be unraveled for the first time in literature, considering the impact of adsorption using adsorption-diffusion-tortuosity relationship in chapter 5. The insights obtained from decoupling the pore structure, sorption and self-diffusivity of natural gas was used in chapter 6 to propose an effective diffusion model that is validated with molecular simulation data to describe transport mechanisms in complex organic matter structures. Thereafter, the self-diffusivity model was utilized to update apparent permeability models for shale containing realistic kerogen of both circular and square geometry in chapter 7, and a new simulation framework based on Gaussian

Pressure Transients was introduced modeling production in hydraulic fractured shale gas reservoirs in chapter 8. Finally, conclusions and recommendations for follow up studies such as considering phase behavior in a condensate or a system of liquid and methane gas hosting in a microporous kerogen structure, and other trending studies will be provided in chapter 9. |

CHAPTER 2

LITERATURE REVIEW

Figure 2 shows some SEM images of shale samples containing both organic and inorganic matter nanopores [7]. Besides the organics, clay mineral is one of the constituents of shale matrix with significant adsorption capacity due to its unique inter-layer and external surface charges [43,44], and will be reviewed based on previous studies in section 2.1 of this chapter. Furthermore, discuss the characterization techniques of the pore systems in the same section 2.1.

The definition of kerogen has previously been provided as a type of insoluble organic matter and could vary with type and maturity which depends on the environment of deposition. In order to provide a better background of kerogen heterogeneity, the different kerogen types and chemical structures proposed in the literature will be reviewed in section 2.2. A literature survey of pore diffusion models for straight nanopores, sorbed gas and effective diffusion of sorbed gas studies will be provided in section 2.3. Afterwards, we will review the kerogen effective diffusion tortuosity, an important pore structural parameter in the discussion of gas transport in the same section, with more emphasis on diffusion tortuosity models as it relates effective diffusion of sorbed gases in kerogen.

Finally, based on the established understanding of clay and organic matter pore structures, which constitute the main components that hosts natural gas in shale especially in sorbed phase (sections 2.1 to 2.3), some common shale apparent permeability models and transport

simulators are highlighted in section 2.4 and 2.5 respectively. Next, the overall research gap and ultimate research objectives will be given in chapter 3.

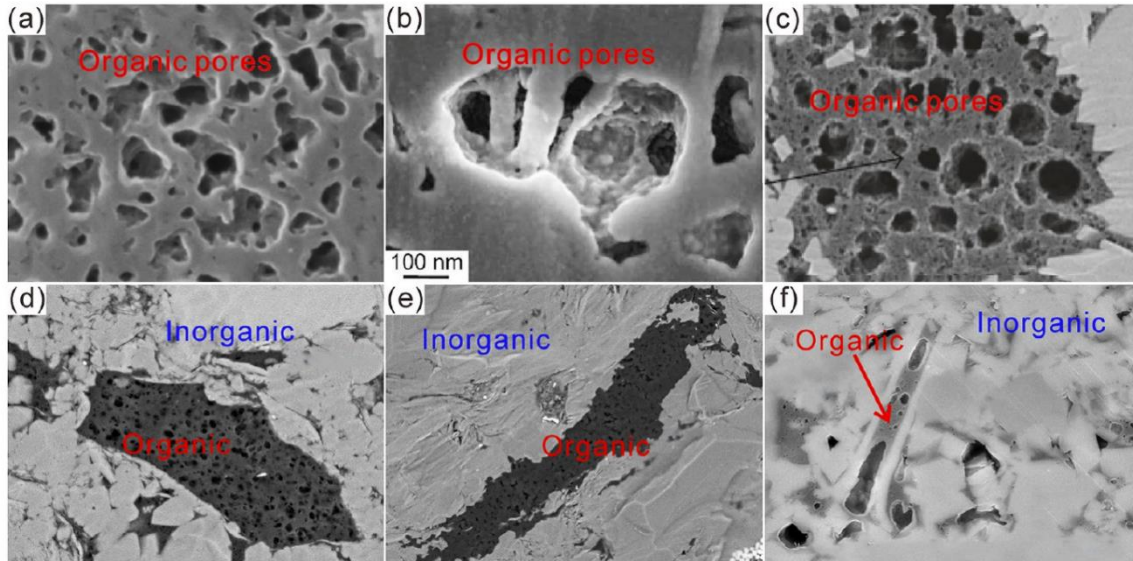


Figure 2 SEM images showing the nanostructure of the organic matter and inorganic minerals in shale matrix obtained from different sources. (a) Sichuan, (b) Green River (c) Green River, (d and e) Longmaxi, and (f) Eagle Ford [7].

2.1 Clay chemistry

Clay minerals can exist in both a free state and as components of inorganic minerals present in shale reservoirs [10,25,45]. Clay minerals are phyllosilicate and layered structures with net negatively charged internal surface layers and a charged edge. A clay crystal cell is an aggregation of an octahedral sheet of Brucite and/or Gibbsite and tetrahedral sheet of silicates [46,47]. The unit cell in a silica tetrahedral sheet contains a cation and four anionic oxygen atoms, and forms a continuous tetrahedral sheet, by sharing three out of its four corners with other tetrahedrons. Meanwhile, the unit cell in an alumina octahedral sheet has a cation and six oxygen anions and forms an octahedral sheet by adjoining with other

octahedron cells. The most common cations in the octahedral are Fe^{2+} , Fe^{3+} , Mg^{2+} , and/or Al^{3+} , while those in the tetrahedral sheets are Si^{4+} , and/or Al^{3+} respectively [48,49]. The different arrangements of the sheets and cations through isomorphous substitution phenomenon, gave rise to the variety of clay minerals that exist in nature [50]. The relative amount of tetrahedral (T) and octahedral (O) sheets in clay is generally described by T-O and T-O-T nomenclature, in 1:1 and 2:1 respectively [51].

The structural cations in clay sheets undergo isomorphous substitution, to create a net negative or positive charged surface. For instance, Al^{3+} and/or Fe^{3+} could substitute some Si^{4+} in the silicate sheet to result in a deficit charge of negative one on the clay surface. Similarly, Fe^{2+} and/or Mg^{2+} substitutes some Al^{3+} in the tetrahedral sheet of silicates to create a net negative charge. Cation exchange capacity (CEC) is the degree of negativity of a clay face charge. Depending on the environment of deposition, diagenetic processes, and one or both processes in isomorphous substitution occur to form the various types of clay minerals in nature [52]. More so, the degree of CEC is sensitive to the type of interlayer bonding that exists during its formation. Weak interlayer bonding like Vander Waal forces breaks easily, while strong intermolecular bonding like hydrogen bond yields more layers of tetrahedral and octahedral sheets per clay mineral. In other words, the latter will possess larger particle sizes and lower specific surface area. This process explains why kaolinite with hydrogen interlayer bonds have large particle sizes and consequently possess a small specific surface and lesser sites for isomorphous substitution. Conversely, montmorillonite, with weak Vander Waal forces, has a small particle size, a high specific surface and possesses more sites for isomorphous substitution and cation exchange [47].

Table 1 summarizes the properties of montmorillonite, alongside other clay types such as Illite, Chlorite and Kaolinite.

Table 1 Selected properties of some clay minerals [47]

Clay minerals	Layer arrangement	CEC (meq/100 mg)	Surface area (m ² /g)	Density (g/cm ³)	Layer thickness (nm)
Smectite	2:1	60-100	700	2-2.7	1.2-1.4
Illite	2:1	20-40	100	2.6-2.9	1.0
Chlorite	2:1	10-30	100	2.6-2.8	1.4
Kaolinite	1:1	3-15	20	2.5-2.7	0.7

The properties in Table 1 only represent typical values of CEC, surface area, density, and layer thickness. Still, there will be slight variation for computing the same attributes for different samples of clay minerals and measurement conditions.

These phyllosilicate materials possess sufficient surface area and void spaces for fluid storage in compressed and sorbed phases depending on their chemical composition and structures [53,54]. A mini review of clay swelling phenomenon, and the characterization of the chemical structures of four main clay types will be considered in section 2.1.1 and

2.1.2 respectively, followed by the survey of clay pore systems in section 2.1.3 and finally, clay adsorption studies in the literature will be provided in section 2.1.4.

2.1.1 Clay welling

Mechanisms for water absorption in clay minerals are hydrogen bonding, cation hydration, and osmosis and dipole attraction. More so, clay minerals have edge charges, strongly controlled by the solution pH or hydrogen ion concentration. For water of high PH (above 7.0 PH) in a clay sheet with hydroxide ions, dissociation of hydroxide in clay may occur to produce hydrogen ions for the solution to attain equilibrium of hydrogen concentration, leaving a negatively charged edge surface. Conversely, for a low PH water (below 7.0 PH), some of the excess hydrogen ion from water migrates to form positive hydroxyl ions at clay edges.

Clay swelling is an important phenomenon that occurs due to cation exchange capacity of these minerals when the negatively charged minerals meet cations in solution. Interestingly, the surface negative charges seek to be balanced through a process known as cation exchange, and, by the positive charged ions in the interlayer and solution [47]. This reversible process follows stoichiometry rules, and depends on the rate of cation diffusion, selectivity of cation based on its position in electrochemical series, valence and size of exchangeable cations. Clay swelling will be of utmost concern, if the mineral has a high specific surface area to cause an increase in rate of cation diffusion, where all other factors remain constant. For this reason, 2:1 clay layered structure, such as smectite, is more susceptible to swelling due to its high CEC. Further, this explains the reason for several wellbore instability problems when drilling with water-based mud.

2.1.2 Chemical composition and structure

X-ray Powder Diffraction (XRD) and X-ray Fluorescence (XRF) techniques are widely used to identify the bulk phase minerals composition in a material [55,56]. Srodon [57] employed XRD and XRF analyses to identify and quantify clay minerals in pure and clay-containing rocks. Similarly, Mattioli et al. [58] studied the 15 mixed and rich samples of illite, chlorite, smectite and kaolinite clay with the same techniques to understand the suitability of its mineralogy and chemical composition for cosmetic applications. Nevertheless, the semi-quantitative data from such methods do not discriminate between the main phases of the identified minerals at a much higher resolution. Further insights into the chemical constituents and physical features of clay are generally possible by using other methods based on the principles of radiation and penetrating-fluids.

There are many applications for some common radiation-driven methods such as Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), nano- and micro-CT scanning, Nuclear Magnetic Resonance (NMR), Small-Angle Neutron Scattering (SANS), and Small-Angle X-ray Scattering (SAXS) for pore size characterization [59–61] and fluid transport monitoring [62].

Some examples of the lattice structures and parameters of different clay chemical structures from the American mineralogy crystal database [63] and informed from X-ray powder diffraction (XRPD) analysis are represented in **Figure 3** and **Table 2** respectively. The four main clay types, chemical structure according to the American mineralogy crystal database [63], which is visualized using Vesta software, is presented in Figure 3. The different

minerals can be identified using the peak positions from XRPD patterns [64–69]. Thus, there will be a description of the minerals in clay and how they can be recognized in pure state from XRPD analysis.

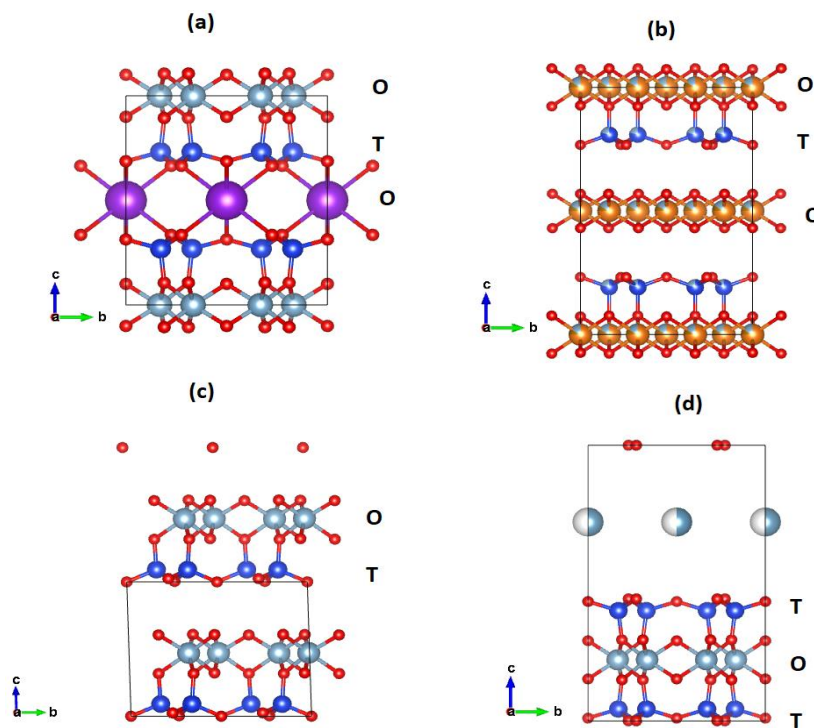


Figure 3 Snapshot of Clay layers with the following color scheme. O, red; Si, blue; Al, grey; K, purple. Clay layers depicted with bond structures. (a) Illite (a unit cell with two-half layers) (b) chlorite (a unit cell with two-half layers and the extra octahedral layer is rich in Mg^{2+} and Fe^{2+}) (c) kaolinite (two complete units) (d) montmorillonite, with only one complete layer of clay sheet

Table 2 Summary of lattice parameters and angles of clay minerals from the American mineralogist crystal database

Clay minerals	Chemical formula	Lattice parameters	Lattice angles (degree, °)	Space group
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		A (nm)	B (nm)	C (nm)	Volum e (nm ³)	α	β	γ	
Chlorite	$\text{Mg}_{2.292}\text{Fe}_{0.255}$ $\text{Al}_{0.865}\text{Si}_{1.585}$ O_9H_4	0.5336	0.924	1.437	0.703	90	96.93	90	C 2/m (#12-1)
Illite	$\text{KAl}_2\text{Si}_4\text{O}_{12}$ H_2	0.5202	0.898	1.023	0.468	90	101.5 7	90	C 2/m (#12-1)
Montmorillonite	$\text{Al}_2\text{Si}_4\text{O}_{12}\text{Ca}_{0.5}$	0.5180	0.898	1.500	0.698	90	90	90	P 1 (#1-1)
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_9\text{H}_4$	0.5155	0.894	0.741	0.330	91. 7	104.8 6	89. 8	C 1 (#1-4)

Here is a more detailed description of how the four types of clay minerals can be identified and differentiated based on their peaks and XRPD patterns.

Montmorillonite

Montmorillonite is a 2:1, T-O-T clay layered structure that forms the main composition of smectite. There are several chemical formulae for the minerals depending on its source and

purity, calcium and magnesium-rich smectite for instance is $(\text{Na}, \text{Ca})_{0.3}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ [70]. Some of the Ca^{2+} and Al^{3+} in the octahedral sheet undergo isomorphous substitution with Na^+ and Mg^{2+} respectively to form a negatively charged clay. On the other hand, chemical formula for iron-rich smectite is $\text{Na}_{0.3}\text{Fe}_2^{\text{III}}(\text{SiAl})_4\text{O}_{10}(\text{OH})_2 \cdot n(\text{H}_2\text{O})$ [66]. In XRD analysis, glycol is first added to the minerals, and then smectite is linked with a basal spacing of 1.7 nm. In the process of post-treatment with heat up to 300 °C, the spacing reduces to 1 nm [64] (**Figure 4**). It is worthy to note that peak heights are not completely appropriate to quantify the peak intensities of clay minerals due to the large variation that naturally occurs in clay basal width and shape. Rather, integrated peak intensities like peak area are suggested, because they are unaffected by wide variation in particle size, stacking faults and so-called order-disorder [64].

Recall that smectite inter-layer surfaces are negatively charged. For this reason, it undergoes reaction with the positive charges that exist in water, a type of cation exchange interactions through different possible mechanisms such as cation hydration, hydrogen bonding and osmosis.

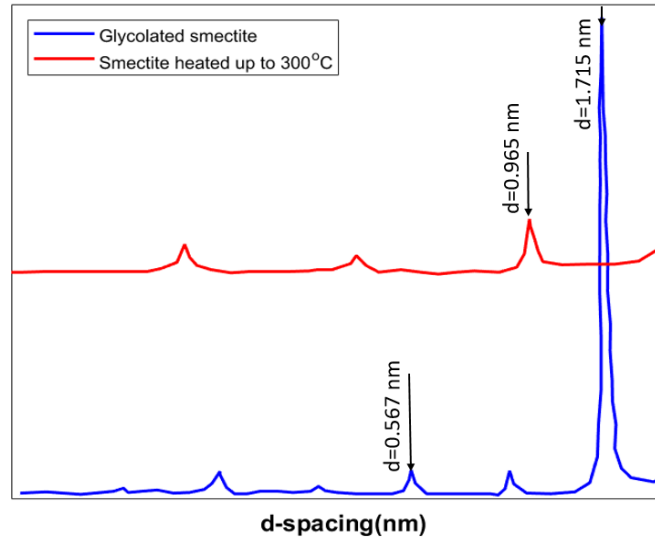


Figure 4 Pure smectite oriented XRPD patterns. Note sharpness of peak at 1.7 nm in the glycolated trace [64]

The dominant mechanism depends on the cations and anions concentration in water and the CEC of smectite. The interaction phenomenon results in more basal spacing and, consequently, a volume change, otherwise regarded as clay swelling. Sodium rich montmorillonite (Na^+ -rich smectite) swells more than Ca^{2+} rich smectite because of higher electro-positivity. Sodium ion rich clay will require more H^+ from water to balance the negatively charged clay if the edge charges are the same due to their valence difference, thereby resulting in more absorption of water. The swelling phenomenon can be reduced by replacing the Na^+ and Ca^{2+} by adding K^+ or cationic ammonium ions containing solvent or solute [70], since K^+ is highly electropositive than both cations.

Illite

Chemical formula is $(\text{K}, \text{H}_3\text{O}) \text{Al}_2(\text{Si}_3\text{Al}) \text{O}_{10}(\text{H}_2\text{O}, \text{OH})_2$, and it is naturally occurring in shale formation and claystone formation [70]. Illite contains an octahedral alumina sheet

sandwich between two tetrahedral silica sheets. The oxygen atoms, O^{2-} from the silicate form strong interlayer bonding with the hydrogen atoms, H^+ in the aluminum hydroxide sheet and undergo other possible isomorphous substitution to produce a negative net charge.

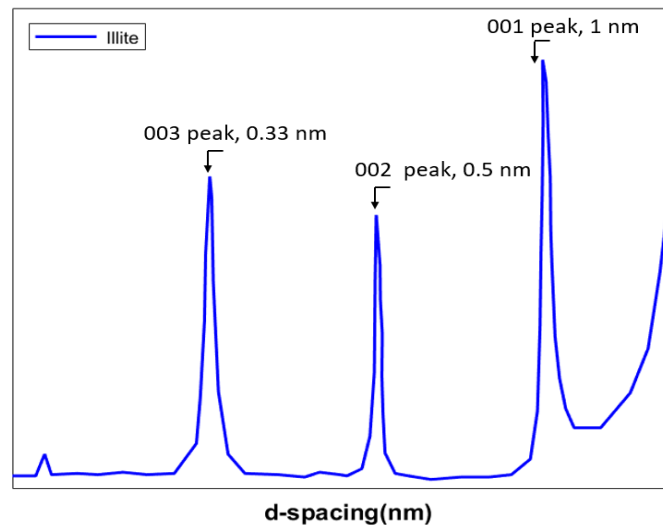


Figure 5 XRPD patterns (oriented and air dry) of Illite showing differences in relative intensities [64]

Furthermore, potassium ion balances the net negative charge in the T-O-T layer surface, thus, prevents the possibility of cation hydration of H^+ ion in water by the negative charge and inhibits clay swelling. XRPD analysis (**Figure 5**) identifies Illite by a series of intensity peaks at about 1.0, 0.5, and 0.33 nm when the clay is treated with glycol and heated up to 500°C; the peak positions and shape remain the same.

Chlorite

Chlorite consists of a group of phyllosilicate minerals commonly classified as Ninite, Chamosites (iron-rich), Pennantite, and Clinochlores (magnesium-rich). The mineral can exist either as a single grain, part of a lithic fragment or fine grain matrix (detrital chlorite)

[70]. On the other hand, authigenic chlorites could occur, as either grain coating, or pore filling, to serve as a good reservoir seal in sandstone, or bad reservoir quality respectively. The simplest unit of the clay is a T-O-T structure with an additional octahedral coordinated Al-O, Fe-O or Mg-O layers, which makes it a T-O-T-O di-octahedral species. The extra octahedral layer bonds weakly to Si-O in the T-O-T layer, thereby creating more hydrogen ions per unit cell in chlorite compared to other clay minerals. Other examples of di-octahedral species are Donbassite [67], Glagolevite (sodium-rich) [69], and some Franklinfurnaceite (calcium-rich) [65], Sudoite [67] and so on. For this reason, it gives a very high neutron log signal because of the high amount of H^+ ions. Worden et al. [49] present the generic chemical formula $(X, Y)_{4-6}(Si, Al)_4O_{10}(OH, O)_8$, where X and Y could be either a divalent or trivalent ions like Fe^{2+} , Fe^{3+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+} , Al^{3+} , Li^+ , or Ti^{4+} . In addition, some chlorite minerals species are tri-octahedral, and more common than the di-octahedral analogues [64]. Examples of a trioctahedral chlorite species are Baileychlore (zinc-rich) [68], some Cookeites and Sudoite [67]. Several ideal chlorite minerals and chemical composition are summarized in **Table 3**.

Table 3 Summary of some chlorite minerals

Minerals	Chemical composition	Reference
Chamosites	$(Fe_5^{II}Al_1)(Si_3Al_1)O_{10}(OH)_8$	[66]
Clinochlore	$(Mg_5Al)(Si_3Al_1)O_{10}(OH)_8$	[66]
Baileychlore	$(Zn_{2.5}Fe_{1.2}^{2+}Al_{1.17}Mg_{0.76}Mn_{0.01}^{2+} \quad 0.36)(Si_{3.55}Al_{0.45})O_{10}(OH)_8$	[68]
Cookeites	$Al_2(Si_3Al)O_{10}(OH)_2 \cdot (Al_2Li)(OH)_6$	[67]

Sudoite	$Al_2(Si_3Al)O_{10}(OH)_2 \cdot (Mg_2Al)(OH)_6$	[67]
Glagolevite	$Na(Mg, Al)_6[Si_3AlO_{10}](OH, O)_{10}$	[69]
Donbasites	$Al_2(Si_3Al)O_{10}(OH)_2 \cdot Al_{2.33}(OH)_6$	[67]
Franklinfurn aceite	$Ca_2Fe^{3+}Mn_3^{2+}Mn^{3+}Zn_2Si_2O_{10}(OH)_8$	[65]

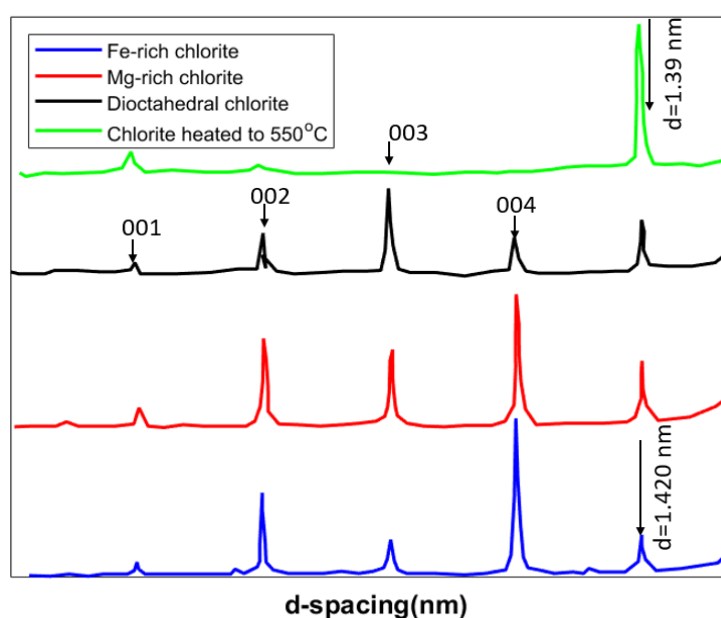


Figure 6 XRPD patterns (oriented, air dried) of Chamosites (Fe-rich chlorite), Clinocllore (Mg-rich chlorite), di-octahedral chlorite (Al-rich chlorite), and chlorite after heating to 550 °C [64]

From XRPD patterns and unusual relative intensities, the minerals present in a rock are identified. For instance, a di-octahedral chlorite is matched to a 003 peak that is greater than 002 and 004 peaks (**Figure 6**). If otherwise, then, it is a tri-octahedral species. All tri-octahedral species are soluble in hydrochloric acid. The figure showed that there could be an inter-stratification of Chamosites in rocks with 0.7 nm spacing. More so, all peaks in

Clinochlores (Mg-rich chlorite) have nearly equal intensities. When glycolated chlorites are heated, there is a peak contraction from 1.42 nm to 1.39 nm at 550 °C.

Kaolinite

Kaolinite is a 1:1 structure of aluminum octahedral and silica tetrahedral sheets. It is white in color and formed from chemical weathering of feldspar. The chemical formula is $Al_2Si_2O_5(OH)_4$ [47,66]. A hydrogen bond exists between the negative oxygen ions in the silicon oxide sheet and the positive hydrogen ion in the hydrolyzed aluminum hydroxide sheet. Due to the strong interaction between the sheets of clay, there will be more layers per unit clay cell and the particle size will be larger compared to other weakly bonded clay sheets like Montmorillonite. Ultimately, kaolinite clay experiences less swelling tendency because of the lesser surface area per volume ratio available for hydration and other mechanisms for ions exchange (that is, low cation exchange capacity) [70]. **Figure 7** showed that two peaks at 0.715 nm and 0.358 nm pinpoint the Kaolinite mineral.

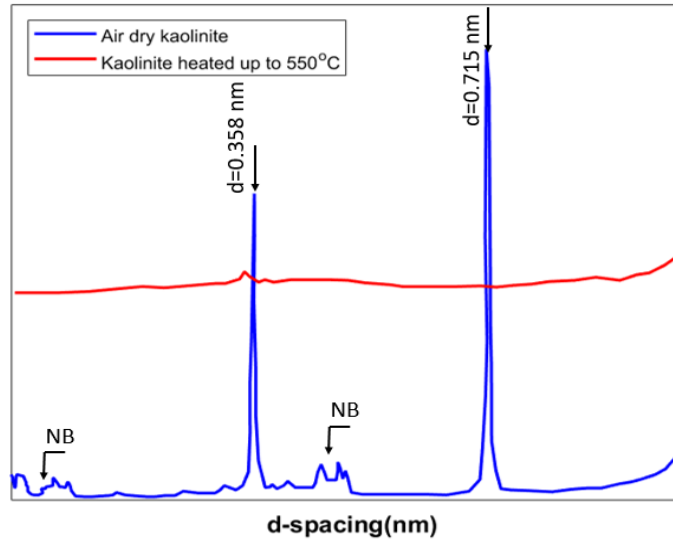


Figure 7 XRPD patterns (oriented) of kaolinite before and after heating to 550 °C, NB =non-basal (hkl) peaks from kaolinite [64]

2.1.3 Pore systems

Some sets of techniques, based on the principle of penetrating fluid have been successfully applied to track pore distribution, specific surface area (SSA), and pore spaces. Examples of methods are Mercury Injection Porosimetry (MIP) and low temperature adsorption approaches that could use carbon dioxide (CO₂), nitrogen (N₂), and argon gas as penetrating fluids [54,71–74]. Low-temperature adsorption techniques refer to methods obtained at cryogenic temperature, usually at 77 Kelvin. Aringhieri [71] employed an N₂-adsorption experiment to investigate the distribution of 1.5 to 100 nm pores in four clay minerals and soil samples. Ross and Bustin [54] studied illite, montmorillonite, kaolinite and chlorite clay structure using low-pressure N₂ and CO₂ sorption techniques. Kuila [73] employed the N₂ adsorption technique to determine the micropores and mesopores SSA and size distribution in mixed illite-smectite, kaolinite clay and shale rock. Wang [75]

studied the micropores (<1.0 nm) in illite, montmorillonite, kaolinite, and illite-smectite mixed layers using N₂ and CO₂ low-pressure adsorption. On the other hand, gas adsorption and diffusion of sorbed gases in porous media at reservoir condition is performed with a high temperature method which will be reviewed accordingly.

2.1.4 Adsorption and diffusion

Silicate-rich shale has no micro- and meso-pores [54] and so adsorption capacity of quartz will be considered negligible in this study, as quartz intergranular pore mainly contains free gases when pore is over 6 nm [76]. Some experimental and laboratory studies have shown that the clay mineral composition and its micro-pore structure strongly influences adsorption capacity especially for shale rocks rich in clay minerals and with less total organic content [43,77,78]. Ji et al. [43] methane adsorption experiment on different types of crushed clay-rich samples, showed that montmorillonite has the highest affinity to methane, followed by Illite/smectite, kaolinite, chlorite, and Illite has least interaction. Fan et al. [77] experiment showed that adsorption capacity decreases in the following order: montmorillonite > kaolinite > Illite > Illite/smectite > chlorite. Wang et al. [75] experimental investigation revealed that the adsorption capacity of mixed clay minerals matches the linear superposition of pure minerals sorption ability with only 7% error. Furthermore, the authors' results showed that methane adsorption capacity decreases in the order: kaolinite > Illite > montmorillonite > chlorite. **Table 4** outlined the highlights of some adsorption and diffusion studies in clay materials.

Table 4 Highlights of some adsorption and diffusion study in clay minerals

Authors	Highlights
[77–83]	1. Adsorption capacity and selectivity are sensitive to gas volatility 2. The adsorption of hydrocarbon gases on coal and kerogen is stronger than clay 3. There is yet no consensus on the clay mineral with highest or lowest adsorption capacity
[78,81,83,84]	1. Adsorption capacity is dependent on pore sizes 2. adsorption capacity of mixed clay minerals matches the linear superposition of pure minerals sorption ability with only 7% error 3. Adsorption capacity positively correlated to cation exchange capacity and specific pore surface area
[85,86]	1. Interlayer K^+ in slit shaped Illite has a higher affinity for CO_2 than to CH_4 2. Conversely, surface layer of Illite have a better interaction with CH_4 compared to CO_2 because, its partial negative surface will bond H^+ in CH_4
[87]	1. K^+ ion in the inter-layer of hydrated montmorillonite moves away from center towards the clay surface 2. Methane diffusion in Na^+ ion is higher than K^+ ion form of montmorillonite at elevated temperature condition 3. Water saturation increases positive cation mobility, creating vacancy for H^+ in water and swelling
[81,85,86,88]	1. Adsorbed phase density varies with pressure 2. The enhanced methane recovery (EGR) with CO_2 injection could be up to 29%.

[86]	1. Pore wall thickness of simulation cell have no effect on adsorption capacity for an above half-layer clay sheet 2. The impact of cation dynamics on adsorption amount of CO_2 and N_2 is negligible.
[82,89,90]	1. No adsorption of methane above 45% water vapor saturation 2. Gas permeability reduces with increase in water saturation 3. At -18°C, methane hydrate could be formed in clay nanopores

2.2 Kerogen types and chemical structures

Carbon and graphite nanotubes have been widely used for representing kerogen microstructure for molecular dynamics studies [91–98], and are not accurate in terms of their chemical structure characteristics. Depending on the maturity and realistic kerogen type, the pore size distribution and capacity to store and transmit gas from these compartments may vary. X-ray photoelectron spectroscopy (XPS) [99,100], Raman spectra [101,102], ^{13}C nuclear magnetic resonance (^{13}C NMR) [99,100] have confirmed that carbon, hydrogen and oxygen are the three main elemental composition of kerogen macromolecules with some quantities of Sulphur and Nitrogen. However, the different kerogen types are a characteristic of the relative presence of two-dimensional regular structure (C-C sp^2 hybrids), carbon-hydrogen (C-H) and carbon-oxygen (C-O) bonds [7]. Therefore, several authors have proposed different versions of kerogen models on the ground of experimental data obtained from multiple shale samples. The results of previous

pyrolytic experimental and molecular simulation studies revealed that the functional groups and elemental ratios of kerogen structure changes from one source to another.

Figure 8 summarizes the widely utilized kerogen models proposed by Ungerer et al. [103], Liang et al. [99], Wang et al. [104] and Pan et al. [100].

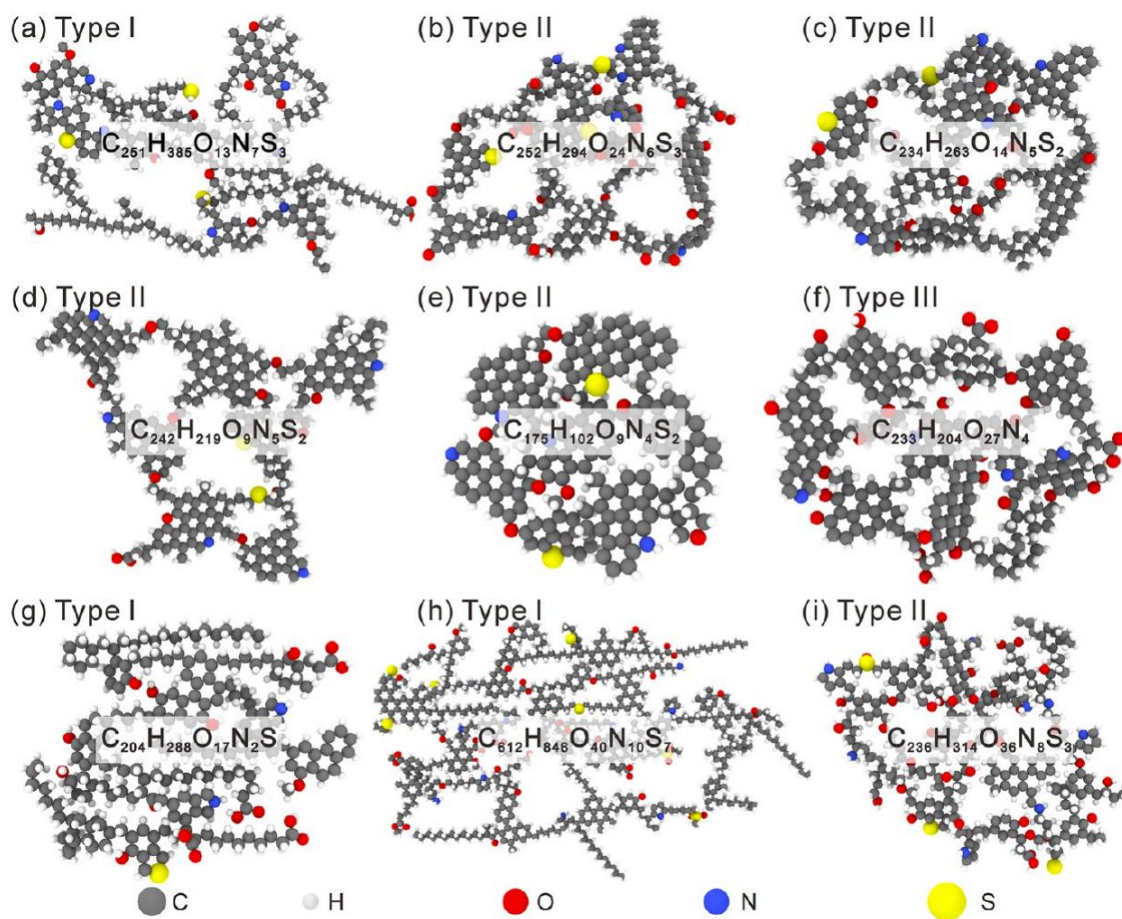


Figure 8 Structure of kerogen macromolecules constructed by pyrolysis based on experimental data from different shale sources such as (a) Green River [103] (b-e) Duvernay series [103] (f) Gippsland [103] (g) Songliao [99], (h) Songliao [104] and (i) Longkou [100]. Gray (carbon), red (oxygen), white (hydrogen), yellow (Sulphur), and blue (nitrogen) [7].

In addition, Yu [7] presented the basic elemental ratios of various types of kerogen model according to different authors. The Ungerer et al. [103] type IID of the six kerogen types

have the capability to contain micropores which could host significant quantities of natural gas in shale. The trapped gas experiences a pressure and concentration which causes it to diffuse into the inorganic pores and fractures through the microcracks in the organic matter and will be considered as organic matter for this study. Further details of the processes of sorption, effective diffusion and critical barriers influencing the transport mechanism and corresponding studies will be expounded.

2.3 Kerogen gas sorption, effective diffusion and tortuosity

2.3.1 Gas sorption and gas diffusion

There are numerous experimental and theoretical studies of pore diffusion and gas sorption in organic-rich shale rock. Etminan et al. [16] employed a batch pressure decay technique to determine the free gas, adsorbed and dissolved gas diffusions in kerogen. Sheng et al. [105] studied the surface diffusion of gas through the adsorbed phase of OM, and revealed that gas desorption resulted in an additional contribution to gas slippage in inorganic matrix pores. Kang et al. [106] studied the competitive sorption of carbon dioxide, water, and methane in kerogen. The research showed that the adsorption preference of OM to carbon dioxide and water could lead to enhanced surface methane diffusion. It is noteworthy that the adsorbed phase gas is in equilibrium with compressed gas through an interconnected pore network [107], and molecular transport from source rock to the wellbore occurs when there is a concentration gradient between the adsorbed and the free gas phases [108]. Besides, the complete diffusion transport from kerogen through inorganic matrix pores to a wellbore involves multiple diffusion phenomena, which is dependent on pore scale and

operating pressure and temperature conditions. The main transport mechanisms in OM are dissolved gas diffusion, desorbed gas diffusion in organic walls, and restricted pore diffusion in meso- and micropores. These transport mechanisms can be summed as effective sorbed gas diffusion if the adsorption and desorption processes are in equilibrium.

Kerogen pore sizes range in scale from mesoporous to microporous [109–111]. Gas transport in the organic materials of shale is at a length scale where continuum modeling breaks apart. Transport mechanisms in shale can be classified into three diffusion regime [105,112]; Fick, transition, and Knudsen diffusion; they are valid within the corresponding domains: $Kn < 0.1$, $0.1 \leq Kn \leq 10$, and $Kn > 10$, respectively [105,106]. This grouping is based on a dimensionless parameter called Knudsen number Kn .

In Fick's diffusion, the interaction between gas molecules is more frequent than between gas and kerogen molecules. On the contrary, gas molecules colliding with the wall is the dominant action in Knudsen diffusion. Relatively, the numbers of atomic-atomic and atomic-wall collisions in transition diffusion are equally important [113]. **Figure 9** conceptually depicts the phenomena of Fick's, Knudsen, and transition diffusion in the kerogen bulk phase.

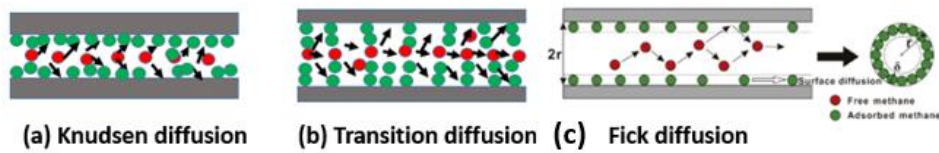


Figure 9 Schematic of gas diffusion regimes in kerogen pores.

The equation for calculating Fick's gas diffusion coefficient (m^2/s), D_{Fick} is as follows:

$$D_{Fick} = \frac{\lambda}{3} \sqrt{\frac{8RT}{\pi M}}. \quad (2.1)$$

Knudsen diffusion (m^2/s) is computed as follows:

$$D_{Knudsen} = \frac{d}{3} \sqrt{\frac{8RT}{\pi M}}, \quad (2.2)$$

where, all units are in standard international units, and their physical meaning consistency is checked. $\lambda = k_B T / (\sqrt{2} \pi d_m^2 p)$ is the mean free path of the gas molecules (m). $R = 8.314 J/(K \cdot mol)$ is the universal gas constant, T is the absolute temperature (K), M is gas molecular mass per mole (kg/mol). $d = 2\bar{r}$ is effective pore size (m) for circular geometry and $d = h_{eff}$ for square geometry, h_{eff} is effective pore height, $\bar{r}$ is the mean pore radius extracted from the pore size distribution (m). $k_B = R/N_A$ is the Boltzmann constant (J/K), $N_A = 6.023 \times 10^{23}$ (number of molecules/mole) is the Avogadro's number of molecules present in one mole of gas, d_m is the diameter of the gas molecule (m), and p is the pressure of gas in the pores (Pa). Some transition diffusion models are summarized in **Table 5**. Such models can be used to calculate the transition diffusion coefficient.

Table 5 Transition Diffusion Models for modeling unrestricted diffusion flux

Author(s)	Equation
Bosanquet [39]	$D_{transition} = \frac{D_{Knudsen} D_{Fick}}{D_{Knudsen} + D_{Fick}}$
Cai et al. [113]	$D_{transition} = \frac{Kn}{Kn + 1} D_{Knudsen} = \frac{1}{Kn + 1} D_{Fick}$

Zheng et al. [114]	$D_{transition} = (1 - \exp(-1/Kn))D_{Fick}$
Geng et al. [115]	$D_{transition} = \frac{Kn^2 + Kn}{Kn^2 + 1} D_{Knudsen}$
He Y et al. [112]	$D_{transition} = \frac{Kn - 0.1}{10 - 0.1} D_{Knudsen}$ $+ \frac{Kn - 10}{0.1 - 10} D_{Fick}$

where mathematically, Knudsen number $Kn = \lambda/d$, the weighting factors in Cai et al. [113] model are consistent with that introduced by Wu et al. [116]. If $Kn \leq 0.1$, then $\lambda \ll d$ when $Kn \geq 10$, $\lambda \gg d$.

Knudsen number was introduced to classify flow regimes in porous media as a function of characteristic pore size and pore fluid pressure [117]. It is defined as the ratio of mean free path to characteristic length of micropores [118]. For the organic micropores, which is the main subject of this study, Knudsen number $Kn = \lambda_g/h_{eff}$ can be illustrated and mapped for some range of pressure and pore sizes as given in **Figure 10**. Darcy law finds application in the continuum flow domain and this region is represented by the lowest limit of Knudsen domain, $Kn < 0.001$. **Figure 10a** shows that Knudsen number increases as typical pore size and pressure reduces. Slip boundary condition is dominant at $0.001 \leq Kn \leq 0.1$. Meanwhile transition diffusion occurs in ultra-right and organic-rich systems with a significant amount of micropores at a much higher interval, $0.1 \leq Kn \leq 10$. Free molecular diffusion regime, $Kn > 10$, controls the transport at $h_{eff} < 0.5 \text{ nm}$ and reservoir pressure less than 1.0 MPa [7,119,120].

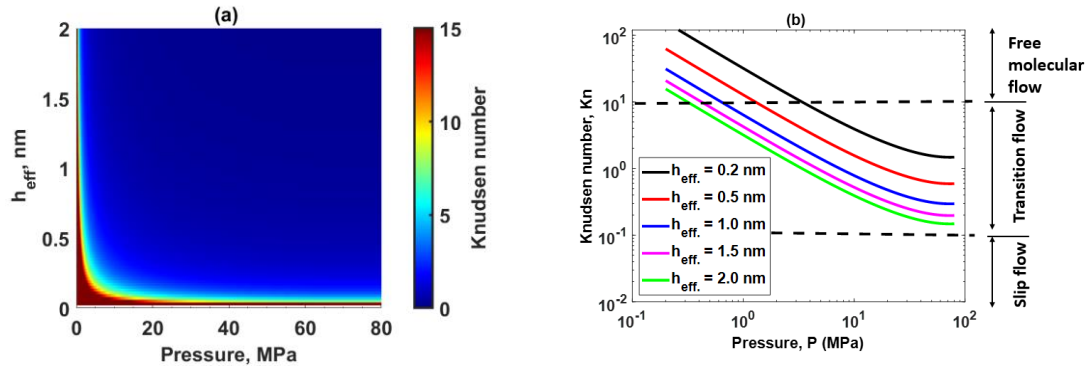


Figure 10 The effect of reservoir pressure and characteristic pore size on Knudsen number in micropores a) shows that Knudsen number increases as pore size and pressure reduces b) shows that transition boundary condition is applicable in the kerogen micropores system for pressure range up to 80 Mpa.

Figure 10b showed that methane transport in kerogen micropores is primarily within the transition domain. Transition diffusion is a state of transport where there is an equally important contribution of both intermolecular and molecular-surface interactions (i.e. Knudsen and Fick's diffusions). Hence, the analysis of methane transport in the organic micropores is limited to self-diffusion in this study.

Modeling the total diffusion transport in source rock to a producing well requires a proper understanding of the kerogen microstructure, in order to correct for the influence of its complex pore network on mass transport.

Diffusion tortuosity is one of the important parameter to express kerogen heterogeneity, and exist as a form of barrier to gas diffusion due to pore structure and geometry constraint and will be discussed in section 2.3.2 alongside a thorough review of the concept of the general concept of tortuosity in porous materials.

2.3.2 Effective diffusion tortuosity

Tortuosity is a general term that represents the average elongation of fluid streamlines (as compared to free flow) [121–123]. There are several models for estimating tortuosity in porous media. The choice of equation depends on the prevailing transport concepts of the porous media. The four most widely applicable models, defined based on their guiding principles, are: geometric (τ_g) [124–126], electrical (τ_e) [127,128], hydraulic (τ_h) [121–123,126], and diffusion tortuosity (τ_d) [129–132].

Irrespective of the underlying theories, most tortuosity models are porosity-dependent [121]. From a dimensional analysis point of view, the qualitative relationship between the tortuosity models should hold as $\tau_g < \tau_d \approx \tau_e < \tau_h$ [121]. Geometric tortuosity varies for pores of different shapes; for instance, the geometry factor for uniform spherical pores differs from that of non-uniform spheres and cylinders. This type of model depends strongly on packing arrangement, media homogeneity, and channel shape, and can be determined using empirical equations like Bruggeman [125]. The hydraulic tortuosity model is based on fluid mechanics and determined from the Kozeny-Carman relation, where advective flux is the primary mechanism [126]. Basically, electrical tortuosity is defined as the ratio of the pore fluid's conductivity to the electrical conductivity of the materials [133]. The Einstein equation provides the relationship between the electrical conductivity of a rigid material and the diffusion coefficient [133]. Usually, electrical tortuosity is determined experimentally, by fitting the porosity data from at least three cores with Archie's resistivity model [134]. Nevertheless, He et al. [135] showed that the relative contribution of electrical tortuosity in kerogen is negligible compared to the diffusion tortuosity. For this reason, the electrical tortuosity will not be discussed in this research.

Conversely, the concept of diffusion tortuosity is pertinent in systems where fluid transport occurs primarily through diffusion, which is the case when there is a concentration gradient of molecules in two different regions.

The transport mechanisms in a shale structure are very sensitive to the pore size distribution, geometry and the operating subsurface pressure [105,113,136,137]. Shen and Chen [132] suggested that a scale factor, otherwise regarded as tortuosity, is required to correct for the impact of a bulk phase complex structure on the estimation of effective diffusion through pores spaces. Generally, the diffusion tortuosity factor in heterogeneous materials like kerogen is defined as the ratio of bulk diffusivity to effective diffusivity [132,138–140]. Bulk diffusivity models for unrestricted gas diffusion in straight nanopores have been reviewed previously in section 2.3.1, and now the available studies regarding effective diffusion studies are surveyed.

It is noteworthy that there are several experimental and theoretical methods available for characterizing effective diffusion and diffusion tortuosity, which are inseparable concepts in the discussion of gas transport in the meso- and macroscale pores system. Experimental measurement studies will first be reviewed; however, the molecular simulation approach is the main technique to determine fluid transport coefficients in micropores because of its extremely confined nature.

Chen et al. [13] reconstructed shale samples using a Markov chain Monte Carlo method based on SEM images. The authors adopted the lattice Boltzmann process to simulate methane diffusion through mesoscale pores and computed effective diffusion and diffusion tortuosity. The results showed that the diffusion tortuosity in shale was higher than the

tortuosity estimated via Bruggeman's empirical correlation. Thomas and Clouse [138] performed experiments on rock samples with different total organic content (TOC) levels to determine the primary diffusion coefficient of bitumen and diffusion tortuosity of kerogen. The results showed that a high degree of OM distribution enhanced the transport rate through kerogen, and diffusion tortuosity was greater in high TOC samples. Thomas and Clouse [141] also studied rocks with different mineral contents and TOC values. Their research revealed that calcite-rich rocks had a higher adsorption capacity than did silicate-rich rocks. With regards to the molecular transport of gas, Tozzi et al. [129] studied the impact of adsorption equilibrium on the effective diffusion of a solute in two cellulosic fiber samples, coupling magnetic resonance (MR) imaging and a solution to Fick diffusion. Elwinger et al. [142] characterized the effective diffusion of a mixture of pure solvent by applying an H^1 and H^2 nuclear MR technique.

Equilibrium molecular dynamics (EMD) simulation was employed by Collet et al. [143] to study the transport of a hydrocarbon mixture of methane to dodecane. The outcome revealed that the Onsager's cross-correlation diffusion coefficient made a negligible contribution to the effective diffusion of the mixture, as compared to the autocorrelation coefficient of pure components. Vasileiadis et al. [6] studied the diffusion of a mixture of methane, ethane, and carbon dioxide. The results showed with a high degree of accuracy that the diffusion coefficient of each component in the mixture was similar to the self-diffusion coefficient of pure components. Therefore, the cross-interaction diffusion coefficient of the mixture was negligible. Vasileiadis et al. [144] constructed 24 possible kerogen-condensed structures with a combination setup of Lennard-Jones (LJ) particle sizes of $3 \times 20 \text{ \AA}$, $1 \times 30 \text{ \AA}$, $2 \times 30 \text{ \AA}$, and $1 \times 40 \text{ \AA}$ for different numbers of kerogen

molecules and various temperature conditions. The results of the molecular dynamics (MD) simulation showed that the established LJ parameter sizes, in addition to the temperature and size of the condensed structure, controlled the pore size distribution. Wu and Firoozabadi [145] studied the diffusion of methane in a flexible and rigid kerogen using a boundary-driven non-EMD simulation. The results showed that though the adsorption capacity of a non-rigid kerogen was high, the diffusion of gas through rigid kerogen was greater than in flexible kerogen.

In addition to kerogen flexibility, some researchers [111,135] have shown that diffusion tortuosity depends on pore size, gas molecular sizes and chemical composition. Gonciaruk et al. [111] showed, using adsorption microcalorimetry, that gas adsorption in kerogen is governed by both pore width and chemical composition of gases. He et al. [135] performed a study of kerogen with four noble gases to investigate the effects of molecular size and pore size on diffusion tortuosity. The results showed that the adsorption negatively affects the diffusion of Helium, Neon, Argon, and Krypton gases in the kerogen pore network by a factor up to 1.688, 3.073, 5.494, and 4.983 respectively.

The review of some effective diffusion-tortuosity relationship and advanced effective diffusion-adsorption-tortuosity models which correct for the restriction to gas diffusion created by both the sorbed layer and pore geometry is provided accordingly.

Diffusion tortuosity models

Tortuosity models for the sorption effect have been reported in different forms, ranging from diffusion-tortuosity to adsorption-diffusion-tortuosity. However, all models share the same basis of relating tortuosity to the ratio of unrestricted diffusion in straight pores to the

effective diffusion, and are commonly expressed as square root of unrestricted to restricted diffusion, because diffusion is a tensor quantity like permeability. The equations for calculating the unrestricted pore diffusion is provided already in section 2.3.1 (Equation 2.1, Equation 2.2 and Table 5). Meanwhile, **Table 6** summarizes some of these models for computing kerogen tortuosity.

Table 6 Diffusion-Tortuosity and Diffusion-Adsorption-Tortuosity Models

Author(s)	Model(s)
Cussler, Thomas and Clouse [108,138,141,146]	$\tau_d^2 = \frac{D_{Fick}}{D_{eff}}$
Mueller et al. [147]	$\tau_d^2 = \frac{D_{Knudsen}}{D_{eff}}, \tau_d^2 = \frac{D_{Fick}}{D_{eff}}, \tau_d^2 = \frac{D_{transition}}{D_{eff}}$
Lavenson and Tozzi [129,148]	$\tau_d'^2 = \frac{D_{Fick}}{(1 + \beta)D_{eff}}$
He et al. [135]	$\tau_d'^2 = \frac{D_{transition}}{(1 + \beta) D_{eff}}$

where D_{eff} is the effective diffusion coefficient (m^2/s) or self-diffusion coefficient for gas with a negligible Onsager's cross-correlation diffusion coefficient [6,143], τ_d is the diffusion tortuosity, and τ_d' is the tortuosity corrected for the adsorption effect through β , which is defined as follows [129,135,148]:

$$1 + \beta = \frac{\text{concentration of adsorbed species}}{\text{concentration of mobile species}} \equiv \frac{\rho_{ads}}{\rho_b}, \quad (2.3)$$

where ρ_b is the bulk gas density (mol/m^3) computed with NIST miniREFPROP experimental database software [149] and ρ_{ads} is the adsorbed density (mol/m^3) of methane. Adsorbed methane can accumulate as a single layer (following the idealistic Langmuir model) or in a multilayer system, which requires more rigorous adsorption models. For multi-layered sorption, the adsorbed methane density gradually changes across the pore, a situation that renders the effectiveness of applying Eq. (2.3) rather uncertain.

To investigate the tortuosity of the OM of shale, a realistic kerogen model will be needed to perform the effective diffusion and adsorption calculations. In chapter 5, the construction of a kerogen nanostructure on a molecular platform will be described, followed by the GCMC and MD calculations required for adsorption and effective diffusion respectively.

The reviews so far have shown that several factors affects the storage and transport mechanisms in kerogen nanopores such as pore width, operating condition, atomic size of gas molecules, kerogen types, maturity, wettability, water saturation, wall roughness, pore geometry amongst others [89,103,150–152]. **Table 7** summarizes the highlights of some adsorption and diffusion studies in kerogen, conducted both experimentally and using molecular simulations.

Table 7 Highlights of some adsorption and transport study in kerogen

Authors	Highlights
[18,106,107,153–158]	1. Adsorption capacity varies with kerogen type and thermal maturity

	2. Kerogen has a higher affinity for CO_2 and H_2O compared to CH_4 3. Adsorbed gas and free gas are in equilibrium through an interconnected pore network
[16,105,135,159]	1. Effective pore diffusion is sensitive to atomic size of gas molecules 2. Surface diffusion is significant in gas production as pressure and pore size decreases 3. There is a reasonable contribution of dissolved gas in total Gas in place (GIP)
[6,143,145]	1. In a hydrocarbon gas mixture, the contribution of cross-interaction diffusion to effective diffusion is negligible compared to self-diffusion. 2. Adsorption in flexible is higher than in fixed kerogen, which restricts the main flow path, despite the occasional opening of the pore throat.
[160]	1. Transport coefficient can be expressed as a function of microstructure porosity 2. Transport coefficient decreases with increase in adsorbed gas
[152,161]	1. The velocity profile of methane and water in nanopores depends on the wettability of the material 2. Methane slippage in kerogen nano-channels (hydrophobic) improves as water saturation

	increases, velocity profile changes from parabolic to piston-like flow. 3. On the other hand, methane slip flow collapses in hydrophilic nanopores like some inorganic materials as water saturation increases.
[151,162]	1. Slippage phenomenon breaks down in confined rough pores and velocity profile remain parabolic 2. Traditional slippage model are proved to overestimate slip flow in rough kerogen nanopores as proved using MD simulation and theoretical analysis

2.4 Shale transport models

Shale has complex pore geometry because of the multiple storage modes. During pore fluid depletion, pressure and concentration gradient are imposed that causes the release of gases through the interconnected organic pores at nanoscale and then to the kerogen microfractures, inorganic minerals' pores/macrofractures until the gas reaches the wellbore. The reviewed analytical and numerically gas transport methods in section 2.4.1 and 2.4.2 respectively do not consider hydraulic fractures imposed gradient. The limitations and relevance of the available models will be highlighted especially as it concerns computational time versus accuracy and adequate representation of organic matter models used for effective diffusion components of shale gas flux models.

2.4.1 Analytical

The mass balance equation for a shale system [105,163] is

$$-\nabla \cdot \vec{J}_T = \frac{\partial}{\partial t} (\phi \rho_b + (1 - \phi) \rho_{ads}), \quad (2.4)$$

where, $\vec{J}_T$, which is the total mass flux is defined as [112]

$$\vec{J}_T = - \left(\rho_b \frac{k_{app}}{\mu} \right) \nabla p, \quad (2.5)$$

Moreover, k_{app} , is the apparent permeability of gas that is pore scale dependent.

Summary of some apparent permeability models that is widely available in literature is presented in **Table 8**.

Table 8 Multiscale shale permeability models

Authors	Transport mechanisms	Models	Limitation
[137]	Viscous flow, gas, and surface diffusion	$k_{app} = \frac{d^2}{32} + \mu D_{eff} c_g + \frac{\mu D_s V_{sL} \rho_{grain} B_g}{TOC} \frac{p_L}{(p + p_L)^2}$	• No correction for pore geometry factor for non-ideal structure • Neglect Darcy-scale correction for non-zero gas slippage velocity near the pore wall. • Does not consider surface diffusion in other semi-solid organics like bitumen aside total organic content (TOC).

[136]	Viscous flow, gas, transition, and surface diffusion	k_{app} $= \frac{d^2}{32} + \frac{Kn^2 + Kn}{Kn^2 + 1} \cdot \frac{d\mu}{3p} \sqrt{\frac{8RT}{\pi M}}$ $+ 4 \frac{D_s p_L M C_L \mu}{(p + p_L)^2 \rho} \cdot \frac{(dd_m \theta - d_m^2 \theta^2)}{d^2}$	• No correction for pore geometry factor for non-ideal structure • Neglect Darcy-scale correction for non-zero gas slippage velocity near the pore wall. • Disregards the correction for adsorbed gas layer influence on effective pore diffusion
[113]	Viscous flow, gas, transition, and surface diffusion	k_{app} $= \frac{d^2}{32} + \frac{Kn}{Kn + 1} \cdot \frac{d\mu}{3p} \sqrt{\frac{8RT}{\pi M}}$ $+ 4 \frac{D_s p_L M C_L \mu}{(p + p_L)^2 \rho} \cdot \frac{(dd_m \theta - d_m^2 \theta^2)}{d^2}$	• No correction for pore geometry factor for non-ideal structure • Neglect Darcy-scale correction for non-zero gas slippage velocity near the pore wall.

			Disregards the correction for adsorbed gas layer influence on effective pore diffusion
[112]	Viscous, slippage, transition diffusion and surface diffusion	$k_{app} = \frac{Fd^2}{32} + D_{eff} \cdot \frac{\mu M}{\rho RT}$ $+ \frac{D_s \xi_{ms} \rho_{ads}}{p} \cdot \frac{\mu}{\rho}$	- No correction for pore geometry factor for non-ideal structure - The surface diffusion correction factor is static; however, it should be pressure dependent especially in confined pore space

[164]	Viscous, pore diffusion, surface diffusion	k_{app} $= \left\{ \frac{\phi}{\tau} \frac{k_{\infty} p V_{std}}{RT} \frac{(1 + \alpha(Kn))}{1 + Kn} \left(1 + \frac{6Kn}{1 + Kn} \right) \right\}$ $+ \left\{ \frac{2\phi}{3\tau} r \left(\frac{d_m}{2r} \right)^{D_f - 2} \left(\frac{8}{\pi R T M} \right)^{0.5} V_{std} \mu \frac{1}{1 + \alpha(Kn)} \right\}$ $+ \left\{ \frac{\phi}{\tau} \left(\left(1 - \frac{d_m}{r} \right)^{-2} - 1 \right) D_s \frac{C_s V_{std} \mu}{p M} \right\}$ where, $C_s = (4\theta M)/(\pi N_A d_m^2)$	• Disregards the correction for adsorbed gas layer influence on effective pore diffusion • Contain some empirical parameter difficult to compute • Maybe a little bit cumbersome to implement
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The basic types of numerical models that are available to describe the velocity profiling of gas particles as it changes from parabolic to piston-like flow shape will be explained accordingly. Analytical or semi-analytical models are simpler to implement, however numerical methods are more accurate but computationally costly. There is a need to improve accuracy of the organic flux component of the shale analytical model based on validation with MD simulation method with realistic kerogen structure.

2.4.2 Numerical methods

Theoretical models discussed in section 2.4.1 may contain some fitting parameters that suggest some level of uncertainties in the performance of the analytical and semi-analytical equations. Besides, the shale velocity distribution in three-dimensional shale is complex and pore scale dependent. Numerical methods which are although less affordable have been useful in resolving the behavior of fluid transport in nanopores and micropores scale. These particle-based techniques are lattice Boltzmann method (LBM) [165–167] for microscale simulations, pore network model (PNM) [168–170], and molecular dynamics (MD) [171–174] for nanoscale investigations. The numerical approaches, summarized in **Figure 11** are the important components for the multiscale modeling framework of shale gas reservoirs. The PNM which was first developed by [175], employs both the connected pore size and pore throat distribution of a 3D geometry of the porous media. In other words, it can be employed to model pore throat connected by organic (inlet) and inorganic pores (outlet) in shale [169]. In addition, the network model is extracted from 3D shale binary models like digital rock images reconstruction, according to the maxima ball fitting method [176]. Nevertheless, the pressure distribution and gas permeability computed with this technique is based on a regular (circular, square, triangle or slit) cross-sectional pore geometry with

cylindrical shape [168,170]. Alternatively, LBM can be used to simulate microscale gas flow since slip boundary condition was proposed [177] for transport near the pore wall. However, for diffusion near the Knudsen layer, a high order lattice Boltzmann equation is required [178] or the relaxation time in the generalized model needs correction based on the Knudsen number [179] for the diffusion regime. MD on the other hand is applied to study gas transport in 3D pore geometry by describing the interactions between atom-atom and atom-wall. In addition, a force field is used to fit the atoms and mimic the chemical interactions. The type of force field depends on the adsorbent and adsorbate chemical composition amongst other parameters. Some common force fields for kerogen molecules are Dreiding, COMPASS, PCFF+, ReaxFF and CVFF [162]. While one of the popular force fields for clay and inorganic matter molecules are ClayFF [88]. The force field parameters for clays in MD simulations was summarized by Yu [7]. Besides, the adsorption forces which are assumed to be negligible in some LBM applications, can be described with these force fields using grand canonical Monte Carlo (GCMC) simulation [119,171–174,180]. In some studies [165,180], the molecular simulation is employed as a basis of comparing the performance of Boltzmann and Bhatnagar-Gross-Krook (BGK) equation based model, especially in the few LBM studies where the surface diffusion through the adsorbed gas layer is calculated. **Table 9** presents the main highlights of different numerical models and underlying assumptions at nanoscale and microscale.

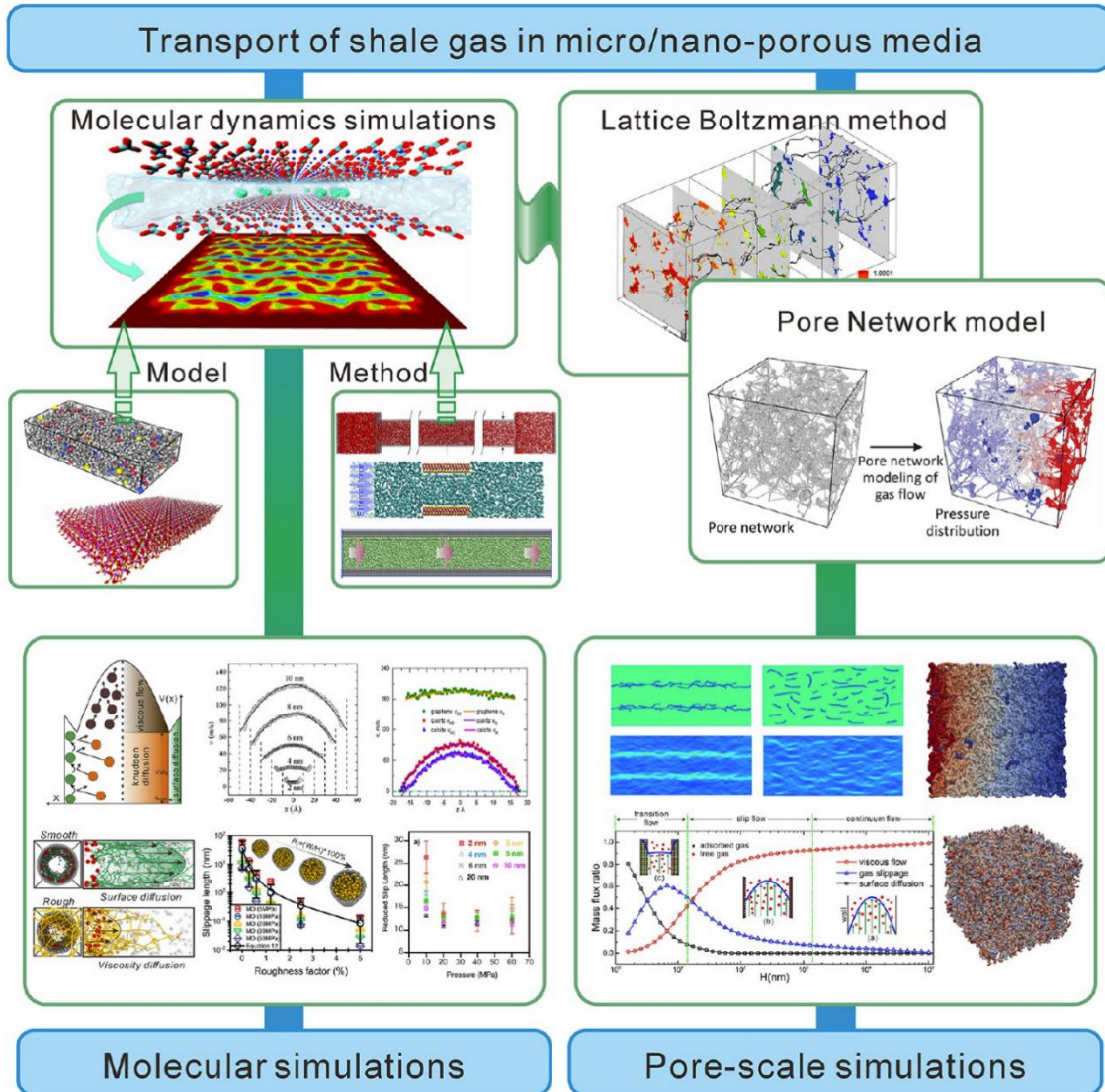


Figure 11 Numerical simulation framework for describing the multiscale gas transport processes in microporous and nanopores systems [7].

Table 9 Summary of the basic equations, transport mechanisms and limitations for various methods employed for gas permeability simulation at the pore scale.

Methods	Basis Equation	Condition(s) satisfied/transport mechanism	Limitation(s)
Klinkenberg [181]	Navier-Stoke plus slip boundary	Arbitrary Kn/viscous flow and slippage	Need calibration for model parameters
Ordinary LBM [167,182–188,190] DSMC [191–193]	Bhatnagar-Gross-Krook (simplified Boltzmann) equation	Low Kn and arbitrary speed/viscous flow, slippage, and transition diffusion	Invalid at high Kn

	Boltzmann equation	Arbitrary Kn but high speed/viscous flow, slippage, transition, and Knudsen diffusion	Time-consuming at low speed, grid refinement at low Kn
DVM [194–196]	Boltzmann equation	Arbitrary Kn and speed/viscous flow, slippage, transition, and Knudsen diffusion	Costly in 3D due to high memory usage, grid refinement at low Kn

DSBGK [197–205]	Bhatnagar-Gross-Krook (simplified Boltzmann) equation	Arbitrary Kn and low speed/viscous flow, slippage, transition, and Knudsen diffusion	Inaccurate at high speed, grid refinement at low Kn
Hybrid DSBGK-LBM [120]	Bhatnagar-Gross-Krook (simplified Boltzmann) equation	Arbitrary Kn and low speed/viscous flow, slippage, and Knudsen diffusion	Inaccurate at high speed
LBM [119,165,166,180]	D2Q9 scheme Bhatnagar- Gross-Krook (simplified and generalized Boltzmann) and diffusion equation	Arbitrary Kn and low speed/viscous flow, slippage, transition, Knudsen and surface diffusion	Inaccurate at high speed
PNM [168–170,176]	Network and momentum (Navier-Stokes) equations	Slip, transition, surface diffusion, ad/desorption	Regular pore geometry like circular, square, slit

			and triangular cross-section
MD [102,165,173,174,180,206,207]	Lennard-Jones, mixing rule, Canonical, Gibbs and Einstein equations	Effective diffusion (Fick, transition, Knudsen, surface diffusion/desorption), and adsorption	High computational cost

2.5 Simulation of hydraulic fractured shale reservoirs

Production forecasting is an essential component of hydrocarbon asset development, as the projected well rates are used to inform decisions regarding the optimal exploitation of hydrocarbon-bearing formations. In a general sense, production forecasting is either based on extrapolating existing data through time-dependent mathematical relationships (with some fitting parameters) in an approach known as decline curve analysis (DCA) [208,209] or through physics-based reservoir simulation schemes. The former approach is simpler, but its application is restricted to the preservation of the status quo of the formation, which can be subject to variation through different upstream operations such as changing the well placement, water injection, and application of tertiary recovery techniques. Reservoir simulation, on the other hand, requires a detailed description of the rock and fluid properties incorporated into specific transport and geological models. Over the years, Darcy's law has remained the primary mathematical framework linking pressure drawdown to production rate. It was originally derived for incompressible single-phase laminar flow but has been supplemented with some additional equations to account for multiphase flow (i.e. relative permeability curves), compressibility effects (i.e. real gas law), capillary pressure effects (i.e. J-functions), and other aspects. Furthermore, fine-scale gridding of the reservoir was introduced through structured and unstructured grids to capture the local heterogeneity [210]. Nevertheless, this approach has faced limitations when applied to shale formations.

Much effort has been made in the literature to explain that the detailed mass transport mechanisms responsible for the well rate when producing from shale formations differ from simulation models used in conventional reservoir engineering [25]. The

sedimentation processes responsible for shale formation in a quiet marine environment reduces the petrophysical quality of the reservoir (i.e. porosity and permeability), while the presence of quartz induces brittleness that renders shales subject to abundant natural fractures upon deep burial [30,31]. The presence of organic matter adds more complexity, as the hydrocarbon accumulation in the formation is self-sourced, with a significant amount of gas trapped in the nano- and micropores associated with the organic matter [10,32–38]. Kerogen is an insoluble organic compound present in shale reservoirs with its elemental composition varying based on its origin and maturation. The skeleton of kerogen has micropores that host hydrocarbons in the sorbed phase. The sorption capacity is determined by the degree of organic matter maturity, and temperature and pressure conditions [109,211]. Hydrocarbons are expelled from the pores to the inorganic matrix system as the pressure declines [137].

Solving complex engineering mathematical relationships for the purpose of reservoir simulation is achieved through discretization of equations over space and time, honoring the geological heterogeneity of the reservoir, and thermodynamic properties of the fluid. To facilitate the reservoir simulation process in conventional hydrocarbon reservoirs, different software packages have been established, including Eclipse (owned by Schlumberger), Intersect (co-jointly owned by different ventures), tNavigator Rock Flow Dynamics, Nexus (developed by ARAMCO and owned by Landmark Graphics), Petrel Schlumberger, CMG, and other licensed and open-source interfaces. However, the different nature of shales as so-called unconventional, ultra-low permeability reservoirs, impacts the accuracy of these software platforms when used to describe mass transport dynamics and kinematics in shale reservoirs during typical production spans. Researchers

have repeatedly approached this knowledge gap by refining the existing tools rather than establishing new schemes. In this context, complex analysis methods attempted to shift the attention to the transport of fluids in the vicinity of natural and hydraulic fractures (HFs) as the primary source of permeability [212]. The results were used to generate type curves that can be used for production forecasting of different scenarios [213]. Some grid-based simulation [214–216] and machine learning [217,218] solutions exist to describe the multiscale transport physics in hydraulic fractured shale gas systems and could require much time and extra technical know-how to implement at field scale.

Alternatively, one could look at shale's characteristics as an opportunity for simplification, even though such simplification runs counter to current trends in modeling shales. Weijermars [219] revolutionized the way shale formations are simulated by introducing the Gaussian Pressure Transient (GPT) method, which was conceptualized based on several assumptions. The primary assumption is production with a constant bottom hole pressure (BHP), with pressure interference between adjacent hydraulic fractures accounted for via superposition, using a closed-form, gridless solution method. These assumptions are reasonable when considering shale resources, as they are of low permeability, have an extended transient period, with mass transport affected by internal boundary effects (such as pressure interference via the hydraulic fractures).

Numerical simulation methods seem to be more common to model transport process hydraulic fractured shale because it is more accurate for macropores scale modeling. However, the numerical approach can be time consuming and may not completely capture the nanopores scale adsorption, diffusion tortuosity and complete transition diffusion phenomenon in microporous kerogen structure. For this reason, it is important to improve

the accuracy of analytical apparent permeability models to be more representative of the multiscale physics in both the organic and inorganic modes of shale. In addition, a unique reservoir simulation framework is required to uniquely upscale multiscale physics analytical transport models to predict production profile in a hydraulic fractured shale gas reservoir.

CHAPTER 3

PROBLEM STATEMENT

Based on the reviews of clay chemistry, pore system and adsorption characterization methods, it is clear that there is still room for further investigation of pore systems in the common clay types. Clay pore structures, geometry and distribution need to be analyzed and discussed in relationship with the chemical and physical properties to add more insight to literature. Therefore, the first study will investigate the pore volume characteristics of four clay types; Illite, chlorite, montmorillonite and chlorite role of clay types and further establish the order of adsorption capacity. This study will also provide insight to the pore systems to expect in clay-rich shale gas reservoirs.

Further review also showed that some of the adsorption, diffusion and shale gas permeability studies in the literature were conducted with carbon [92–95,97] and graphite nanotubes [7,91,96,98], which are not representative of the realistic kerogen structures as presented in Figure 8. At best some research that utilizes recreated shale structure from SEM images does not completely capture the micropores ($< 2\text{nm}$ pores size) mainly contained in the organic phase of shale.

It is noteworthy that the mechanisms that characterized movement of molecules in a porous media are sensitive to the transport domain and transition diffusion is the predominant diffusion regime in the kerogen microporous system. Transition regime occurs when there is an equal contribution of wall-gas molecules and intermolecular collision [105]. Usually,

this late transition regime that occurs mainly in micropores is not captured in most shale transport studies.

The review of transport models also showed that numerical methods like MD simulation, PNM, LBM are more accurate compared to analytical apparent permeability models however have a higher computational cost. Extensive GCMC and MD simulation studies are required to understand the sorption and effective diffusion characteristics of a realistic kerogen geometry. Interestingly, the accuracy of the apparent permeability models can be improved by updating the organic flux term to incorporate well understood and defined kerogen pore structural parameters that can be calibrated with molecular simulation data using realistic kerogen structure.

Finally, the updated and physics based analytical transport models can be integrated and applied to large scale simulation of hydraulic fractured reservoirs to serve as an alternative modeling framework to the common numerical simulation approaches. A forward simulation workflow would make it quite easy to simulate flow in hydraulic fractured reservoirs and readily couple shale apparent permeability transport models with pressure transient solutions that are accurate at macropores, mesopores and micropores scale. Therefore, the research gaps and objectives are formulated as follows in section 3.1 and 3.2 respectively.

3.1 Research gaps

The research gaps are summarized as follows:

1. The order of gas adsorption preference of the four common types of clay; Illite, Montmorillonite, Kaolinite and Chlorite are still debatable
2. Adsorption and diffusion with realistic organic matter structures require more understanding as regards the pore structure and geometry of kerogen.
3. The accuracy of existing shale apparent permeability could be improved by updating the organic flux based on molecular simulation of realistic kerogen structure to capture the full pore scale diffusion regimes, especially for higher Knudsen number flow that occur around early transition, late transition and Knudsen diffusion regimes.
4. A unique way to simulate flow in fractured shale gas reservoirs is required that will capture the transport physics in micropores and mesopores present in shale especially.

3.2 Research objectives

To resolve some of the highlighted research gaps and contribute to the literature of shale gas reservoirs especially as it relates to micropores transport physics, we formulate the objectives as follows:

1. Perform experimental study of the pore volume and adsorption characteristics of Illite, Kaolinite, Montmorillonite and Chlorite rich shale.
2. Employ molecular simulation to study pore structure and adsorption behavior, and gas self-diffusivity of a realistic kerogen micropores present in shale.
3. Develop a self-diffusivity model validated with GCMC adsorption and MD diffusion simulation results respectively for predicting micropores early transition,

late transition and Knudsen diffusion transport phenomena and complex kerogen geometry.

4. Based on the insight from kerogen study, update organic flux term in the shale apparent permeability model that will be accurate for complex shale systems.
5. Propose a new simulation scheme that couples the multiscale physics to forward model production rate in hydraulic fractured shale gas reservoir based on Gaussian Pressure Transient.

CHAPTER 4

PORE VOLUME CHARACTERISTICS OF CLAY-RICH SHALES: CRITICAL INSIGHTS INTO THE ROLE OF CLAY TYPES, ALUMINIUM AND SILICON CONCENTRATION¹

Abstract

Shale resources contain a significant quantity of clay minerals and organic matter. These material components influence the evolution of intra- and inter-granular pore features. This study investigates the role of clay's elemental concentration, purity and types on its pore attributes. Four samples; illite, chlorite, montmorillonite, and kaolinite-rich clay samples were studied. Clay elemental composition, purity, pore shape, and structural parameters were determined. X-ray fluorescence and diffraction techniques were used to compute the elemental and mineralogical compositions of clay samples, respectively. Rock surfaces were mapped using the energy dispersive x-ray spectroscopy and scanning electron

¹ This chapter is copied from the manuscript: **C Afagwu**, M Mahmoud, S Alafnan, A Alqubalee, A ElHusseiny, S Patil (2022). Pore Volume Characteristics of Clay-Rich Shale: Critical Insight into the Role of Clay Types, Aluminum and Silicon Concentration. Arabian Journal for Science and Engineering, 1-17.

microscopy to confirm the distribution of elements and clay homogeneity, respectively in the four phyllosilicate materials. Total organic content analysis confirms the quantity of organic matter. N₂ adsorption/desorption experiment at 77 K and over a relative pressure range up to 0.995 was executed with a surface area and porosity analyzer, to extract information regarding the pore shape, and determine the pore volume and specific surface area. The interrelation of the purity and computed pore structure properties was established. Mineralogy and elemental analyses showed that the studied samples with clay purities of 60–98% have a combined 80–96 wt.% of Aluminum (Al), Silicon (Si), and Iron (Fe). The adsorption–desorption curve at $p/p_0 < 0.04$ and carbon content analysis indicate that clays accommodate negligible micropores. The type III and IV isotherms combined with H1, H2, and H3 hysteresis loop implied that clay had connected complex pores with plate-like, uniform cylindrical, and inkbottle shapes. Capillary condensation and evaporation curves revealed more mesopores and macropores of 2–50 nm and > 50 nm, respectively. The pore distribution plateaued around an average of 100 nm, which confirmed the suitability of the Barrett-Joyner-Halenda technique to characterize clay mesopores. Kaolinite has the highest capacity (74.43 cm³/g) to host N₂ gas at a standard temperature and pressure followed by montmorillonite (65.08 cm³/g), chlorite (21.01 cm³/g) and illite (16.59 cm³/g) in that order. The capacity of the pores to store fluid and their average size follow a similar pattern and increase with aluminum and clay contents. A specific surface area of the non-micropores is directly related to silicon concentration. The study provides an insight regarding the potential of kaolinite (with the highest aluminum concentration of 39.5wt.%) as a good catalytic material required to speed up the esterification reaction. In addition, it can serve as a waste repository and a material for the treatment of phosphorus-containing

contaminants in polluted areas. This research confirms that montmorillonite with the largest specific surface area in non-micropores and silicon content of 63.9 wt.% promotes reactivity and cation exchange interaction. However, this high basal spacing attribute of the material means that swelling will occur in the presence of water.

Keywords: Pore volume characteristics, Clay-rich shale, Mineralogy, Clay minerals, aluminum and silicon

4.1 Introduction

The pore structures, chemical composition and physical properties of clay materials are widely characterized in literature by combining multiple approaches [220–224]. Hassan et al. [220] utilized both Atomic Force Microscopy (AFM) and low-pressure argon adsorption analysis to determine the specific surface area (SSA) of non-swelling kaolinite edge face coupled with edge and basal face of illite. Chen [225] coupled nano-indentation, SEM, and Energy Dispersive X-ray Spectroscopy (EDX) methods to study the effect of crystalline Calcium Silicate Hydrated (C-S-H) composite on the mechanical properties of cement with a low water/cement ratio. Macht [221] computed the edge and basal specific surface area in illite and montmorillonite clay using AFM, N₂ gas adsorption, and Ethylene Glycol Monomethyl Ether (EGME) liquid adsorption methods. Boulingui et al. [226] characterized the mineralogy, physical and chemical properties of raw kaolinite and illite-rich clay using XRD, Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) and SEM techniques. The outcome showed that Gabon-originated clays are rich in silicate and poor in aluminum elements. Zaffar and Lu [227] integrated MIP and N₂ adsorption to study the pore distribution in three clayey soils. Li [228] combined SEM,

focused ion beam (FIB)-SEM, areal porosity method (APM), and MIP to study the organic and inorganic porosities in mudstone and dolomite. Wilson et al. [229] employed Nano-Indentation and Quantitative EDX to study the micro-chemo-visco-mechanical properties in a heterogeneous cement paste. Elgamouz [230] studied the elemental oxides in clay and their relationship with porosity and SSA using XRD, thermal analysis, infrared spectral and SEM techniques. Kariem [222] integrated SEM, EDX, and XRD measurements to compute the volume fractions of these mineral phases in fired clay materials and studied the impact on their mechanical behavior. Qian [231] summarized the application of surface analytical techniques like Low Energy Electron Diffraction (LEED), Electron Backscatter Diffraction (EBSD), Quantitative Evaluation of Minerals by SEM (QEMSCAN), three-Dimensional Secondary Ion Mass Spectroscopy (3D-SIMS) and many others for earth science applications. Nuclei Magnetic Resonance (NMR) have also been utilized alongside other radiation and/or penetrating fluid techniques to investigate clay pores structures [232,233]. In summary, it is clear that there are some established experimental workflows to determine the chemical composition, physical properties and porous structure of different clay types using XRD/XRF, AFM, thermal analysis, SEM, SEM-EDX, NMR, low temperature gas adsorption and other specialized methods. However, more unified studies to investigate the role of clay chemical composition and mineralogy on the development of intra-granular pore volumes attributes in clay-rich shale are required. It is notable that the role of kerogen types and maturity [157,160,234,235] on the pore development of organic-rich shale has been studied in detail compared to clay-containing unconventional reservoirs. Furthermore, the insights gained from establishing the connection between the pore structure properties, clay types and elemental analysis will

advance the development of synthetic clay materials with specific chemical compositions for improved repositories and surface reactivity applications.

In this study, the role of clay purity and elemental composition on the pore structural properties of the phyllosilicate materials was investigated. The four clay types utilized for the research were kaolinite, montmorillonite, chlorite and illite. Clay elemental concentrations and purity were computed with Micro-XRF (μ XRF) and XRD, and further confirmed using image maps from XDS and SEM respectively. A low-temperature N_2 adsorption/desorption experiment was performed at 77 kelvin and over a relative pressure range up to 0.995. Pore shape was inferred from the hysteresis loop and isotherm type.

Consequently, the interrelation between the clay purity, elemental concentration, specific surface area and pore volume at different pore-scale was established. This article was organized as follows: Section 4.2 provides the detail of the materials and methods utilized for this study such as, μ XRF, XRD, organic content analysis, SEM-EDX and low-pressure adsorption using nitrogen probes. Section 4.3 presents the results, and specifically highlights the relationship between the mineral composition and clay purity and the average pore size, pore volume, and specific surface area of studied clays. Section 4.4 discusses the implications of using aluminum and silica-rich clay in waste management and reaction processes. Finally, section 4.5 concludes this research with insight into future research focus.

4.2 Materials and Methods

This study utilized four outcrops' samples of clay-rich rocks with different degrees of purity, and were obtained from a vendor in the United States of America. The four samples

include montmorillonite, kaolinite, chlorite and illite. All samples have been pulverized with a mortar and pestle to improve the surface area responsible for the interactions between fluid and rock. Crushed clay is widely used in the literature in adsorption studies and for XRD analysis [80,156]. The phyllosilicate materials were granulated in such a way as to maintain a relatively large grain, with a mean diameter that is less than 250 μm to prevent inter-particle nanoporosity from forming among the clay grains. The chemical and mineralogical composition of the studied clay samples were determined using μXRF and XRD techniques respectively. The distinction between these samples was mapped using SEM-EDX of QEMSCAN 650F. JEOL JCM-7000 NeoScope Benchtop SEM was used to image the variation in the purity of the studied samples at 200 μm resolution. Organic content analysis was performed on kaolinite, montmorillonite, illite and chlorite-rich rocks. Surface area and porosity analyzer were utilized to conduct N_2 adsorption/desorption experiments at 77.4 K and over a range of relative pressure up to 0.995. The experiments will be described in detail afterward.

4.2.1 μXRF analysis

Brucker M4-Tornado μXRF instrument was utilized to determine the elements and oxides present in the clay materials. The equipment contains a rhodium source with voltage and current of 50 kV and 600 μA respectively. In addition, the device has a polycapillary optic that is around 20 μm spot-size and two silicon drift detectors. Five spots were selected randomly per sample to ensure reproducibility. Then, the samples were scanned with a high-energy X-ray, followed by the emission of a characteristic fluorescent X-ray. The secondary rays emitted afterwards were examined with the Module M-Quant available in the M4 software package. This software provides dependable results of the bulk samples'

composition, because it is based on the fundamental parameters models that use less standard analysis. Results were presented as normalized percentages of the elemental concentration.

4.2.2 XRD analysis

Malvern PANalytical Empyrean was used to identify and quantify the mineralogical phases of the studied samples. After pulverizing the samples, this XRD instrument collected the phase peaks, which have been spotted and measured using the Highscore plus of PANalytical™ attached with ICCD PDF-4+ 2022. Phase concentration was estimated by summing the XRD in automated full pattern summation mode. The alignment or maximum shift was set at 0.3° . A Limit of detection, set at 1.0 wt.% was utilized during the fitting process to evaluate the phase-detection limits. At the same time, the reference patterns that are below the lowest concentration were eliminated.

4.2.3 SEM-EDX and SEM analyses

SEM-EDX of QEMSCAN 650 F was deployed to map the elemental concentration in the clay samples. This instrument operates on the SEM principles and is attached with two Bruker EDX detectors. The capability and applications of QEMSCAN 650F are present in the literature [236]. Before SEM-EDX scanning, the same samples used for μ XRF and XRD analyses were compressed and coated with platinum. The SEM backscatter electron (BSE) images and EDX mapping were generated at 15 kV with a 13 mm working distance.

The compressed studied samples coated with platinum were scanned via JEOL JCM-7000 NeoScope Benchtop SEM. This technique was run on 15 kV and 12 mm working distances to scan all the sampled surfaces.

4.2.4 Total organic content (TOC) analysis

Carbon-containing rocks host significant micropores that could impact clay pore size distribution. A detailed examination of clay micropore distribution will not be required if the $\text{TOC} < 1\text{wt.}\%$ [237]. TOC analysis was performed to determine the extent of the presence or absence of carbon compounds in the studied clay samples. This inspection employs the principle of aerobic combustion of organic compounds by using a catalyst to produce CO_2 . A direct non-dispersive infrared detection was utilized to determine the produced carbon dioxide. Approximately 200mg of homogenized and dried clay samples were weighed and placed into a pre-combusted and clean carbon-free ceramic boat. Afterwards, the samples were treated with a small volume of concentrated hydrochloric acid and at least 2 hrs. were allowed to remove the inorganic carbon from the sample completely. Before the boats containing the inorganic carbon-free samples were placed on Shimadzu SSM 5000A assembly and combusted at 900°C in a stream of O_2 gas, they were dried on a hot plate at 105°C . Finally, a TOC-VCPH carbon analyzer equipped with a non-destructive Infrared (NDIR) detector was used to measure the produced CO_2 for each sample.

4.2.5 Low-pressure N_2 adsorption

Micromeritics ASAP 2020, an automatic surface area and pore size analyzer was used for the measurements. Each clay sample used was crushed to $<250\ \mu\text{m}$ (about 60-mesh number). It is worthy to note that the grain surface area utilized for this analysis is at a scale where there is a negligible effect of sedimentary or macro fabrics on the clays' sorption capacity [73,238]. First, a dried and empty sample tube that contains a filler rod and seal

frit was weighed in an analytical balance. The second step was to weigh and record an appropriate sample ranging from 0.20g to 0.35g.

Furthermore, the sample was added to the empty tube and the new weight was recorded. The same procedure was used for the other three samples. The clay materials were degassed under vacuum for 80 minutes at 220°C. The weight employed for analysis is the difference in sample weight before and after degassing. After that, the sample analysis proceeded, and N₂ adsorption and desorption branch measurements were accomplished at 77.4K, between $p \sim 0.001 p^o$ and $p \sim 0.995 p^o$. Brunauer-Emmet-Teller (BET) equation, Barrett-Joyner-Halenda (BJH) based on Kelvin equation, and Harkins and Jura t-plot method were used to determining the SSA, pore distribution at various pore-scales, and micropores properties, respectively. The theoretical foundation of these constant temperature models will be expounded.

Brunauer-Emmett-Teller (BET) equation

BET is a multilayer adsorption model that describes the distinct energy of different adsorption sites. This isotherm equation, that is employed to compute the total SSA of mesoporous to microporous materials [239] is as follows:

$$V_{ads} = V_m \frac{c_{BET}(p/p^o)}{(1-p/p^o)(1+(c_{BET}-1)p/p^o)} \quad (4.1)$$

where, V_m is monolayer adsorption capacity (cm³/g), p/p^o is the relative pressure of nitrogen gas at a given pressure and temperature. $c_{BET} = \exp((\Delta H_1 - \Delta H_m)/RT)$ is constant, ΔH_1 , is the heat of adsorption (J/mol), ΔH_m , is the heat of gas condensation, $R = 8.314$ J/Kmol is a universal gas constant, T is the temperature (K). Then, $s_{BET} = V_m V_{std} N_A A_m$, is total specific surface area (m²/g), where, ($N_A = 6.022 \times 10^{22}$ number/

mol), $A_m = 0.162 \text{ nm}^2$ is the surface area of nitrogen molecules at 77 K [240], and $V_{std} = 22.4 \times 10^3 \text{ cm}^3/\text{mol}$ of gas at STP. It is important to state that the model is valid for $0.05 < p/p^o < 0.35$. To avoid a complex model fitting procedure, the original BET Eq. (4.1) is re-written in a linear form [241,242] as:

$$\frac{p/p^o}{V_{ads} \cdot (1 - p/p^o)} = \frac{1}{V_m \cdot c_{BET}} + \frac{c_{BET} - 1}{V_m \cdot c_{BET}} \cdot \frac{p}{p^o} \quad (4.2)$$

where, the slope and the intercept of the plot of $\frac{p}{p^o}$ versus $\frac{p/p^o}{V_{ads} \cdot (1 - p/p^o)}$ are utilized to compute V_m and c_{BET} respectively. To guide the selection of p/p^o fitting range, which should not be the same for all materials, the criteria suggested by Rouquerol et al. [243] must hold. First the c_{BET} must be positive. Second, the BET-plot intercept is positive, and the term $V_{ads}(p^o - p)$ should continuously increase with p/p^o . Otherwise, if the conditions fail, the relative pressure range should be narrowed, while the fitting is repeated. It is worthy to note that the monolayer adsorption parameter V_m , over-estimate the micropores volume by accounting for not only the adsorbate filled in the micropores but also the content of the statistical monolayer in the non-micropores [243].

Harkins and Jura t-plot model

‘t-plot’ is one of the models utilized to compute micropores volume and specific surface area in a material. It captures the amount of fluid that could be contained in supermicropores and some ultramicropores within $0.4 \sim 2.0 \text{ nm}$ [242], and is represented as a graph of adsorbed volume (V_{ads}) versus a statistical thickness (t_{ads}) of the adsorbed layer (angstrom). The presence of these pore categories in this material will be confirmed from TOC analysis, so that any need for micropores characterization using more advanced techniques will be justified. More importantly, there are several developed models to

estimate t_{ads} . However, the Harkins and Jura thickness equation (Eq. 4.3), which is the most widely applied for N₂ adsorption [244] was utilized in this study.

$$t_{ads} = \left[\frac{13.99}{0.034 - \log(p/p^o)} \right]^{1/2} \quad (4.3)$$

Interestingly, a t-plot for a material that hosts a negligible amount of micropores will produce a straight line that passes through the point (0, 0) of the graph. Conversely, a micropores-containing material shows a straight line and a concave-down curve at medium and lower t_{ads} values respectively. Meanwhile, a convex up deviation from the linear trend at higher t_{ads} indicates capillary condensation in mesopores. The slope m_{tplot} and intercept b_{tplot} of the straight-line portion at the medium of t_{ads} were employed to compute the external specific surface area, $S_{ext} = 15.47m_{tplot}(\text{m}^2/\text{g})$ and micropores volume of adsorbed gas, $V_{mic} = 0.001547b_{tplot} (\text{cm}^3/\text{g})$ respectively. Finally, the micropores SSA, $S_{mic} = s_{BET} - S_{ext}$, and s_{BET} is the total SSA (s_{BET}) while, S_{ext} is the non-micropores SSA [73,242].

Barrett-Joyner-Halenda (BJH) equation

BJH method mainly characterizes the pore distribution in mesoporous materials, and is based on Kelvin equations in cylindrical pores. Pore size distribution computed with this model is possible by analyzing the capillary condensation phenomenon in the net pore space after discounting t_{ads} from pore radius, r .

$$\ln(p/p^o) = - \frac{\alpha \gamma V_{mol}}{RT(r - t_{ads})} \quad (4.4)$$

where, α is the shape factor of the gas/liquid interface during the adsorption process. Assumption of $\alpha = 1$ is made in the interpretation of the pore distribution with this method, and it signifies that the interface has a cylindrical shape [245], γ is the surface tension of liquid nitrogen (N/m), V_{mol} is molar volume (m^3/mol), r is pore radius (m). The shape factor also denotes the topology and influences the interpretation of the capillary condensation phenomenon. Depending on the assumptions, the adsorption-desorption hysteresis loop could be asymmetrical (ellipsoidal) for the pores with constrictions and symmetrical for regular cylindrical pores [245] because of condensation pressure difference for the two cases. Kelvin-based model (Eq. 4.4) could under-estimate the pore volume in a material with almost 20-30% of micropores because pore shape is usually asymmetric in small pores. However, in mesopores- and macropores-dominated structures, the consequences of this phenomenon will be negligible. The results of the elemental and mineralogy analysis coupled with low-pressure adsorption/desorption studies will be presented in the results section. Integration of the clay purity, the concentration of dominant elements and adsorption information will provide further insights into the storage capacity in clay mineral grains and its associated properties such as pore shapes complexity, pore volume and SSA at multiscale.

4.3 Results and Discussions

4.3.1 Sample characterization

The elemental concentration, clay purity and surface mapping of elements obtained from the μXRF , XRD and SEM-EDX respectively are summarized in this section. First, the elemental composition results from μXRF are presented. Furthermore, the X-ray

diffraction results from which the main minerals in the sample are identified by the peak positions and with reference to an established literature library are reported. The outcome of the TOC analysis and mineralogy summary is also presented in tabular form. Finally, the SEM-EDX surface maps, which show the distribution of elements in the studied clay samples are provided.

Elemental composition of μ XRF

The combined Table 10 and Figure 12a explains the elemental concentration in each clay-rich sample obtained from μ XRF. The non-destructive analytical technique showed a significant quantity of aluminum and silicon in the four clay samples. It is obvious from Figure 12a that there is a great contribution of aluminum and silicon weight percentage (wt.%) compared to Titanium, Potassium, Calcium, Manganese, Iron, Sulfur, Magnesium and Sodium elements in clay. Si, Al and Fe, are the major sandstone components, and account for over 80-96% elemental compositions of the studied clay samples. The high content of silicon provides the first hint that the materials will contain some macropores, commonly associated with the Silica found in quartz-rich rocks. The aluminum content is fairly related to the clay purity in wt.% (Figure 12b). In other words, irrespective of the clay type, increase in clay purity implies a higher aluminum concentration.

Table 10 Micro-XRF elemental composition in the four studied samples

<u>Clay types/ elements</u>	<u>Al</u>	<u>Si</u>	<u>S</u>	<u>K</u>	<u>Ca</u>	<u>Ti</u>	<u>Mn</u>	<u>Fe</u>	<u>Mg</u>	<u>Na</u>	<u>Others</u>
Illite	14.73	55.50	0.02	13.65	2.67	1.50	0.09	9.94	1.64	0.00	0.25
Chlorite	22.99	42.05	2.16	6.16	0.39	1.78	0.12	22.26	1.68	0.00	0.40
Kaolinite	39.49	55.67	0.01	0.00	0.10	3.44	0.01	0.80	0.00	0.00	0.47
Montmorillonite	17.89	63.90	0.51	0.94	2.29	0.26	0.10	10.74	1.91	1.31	0.14

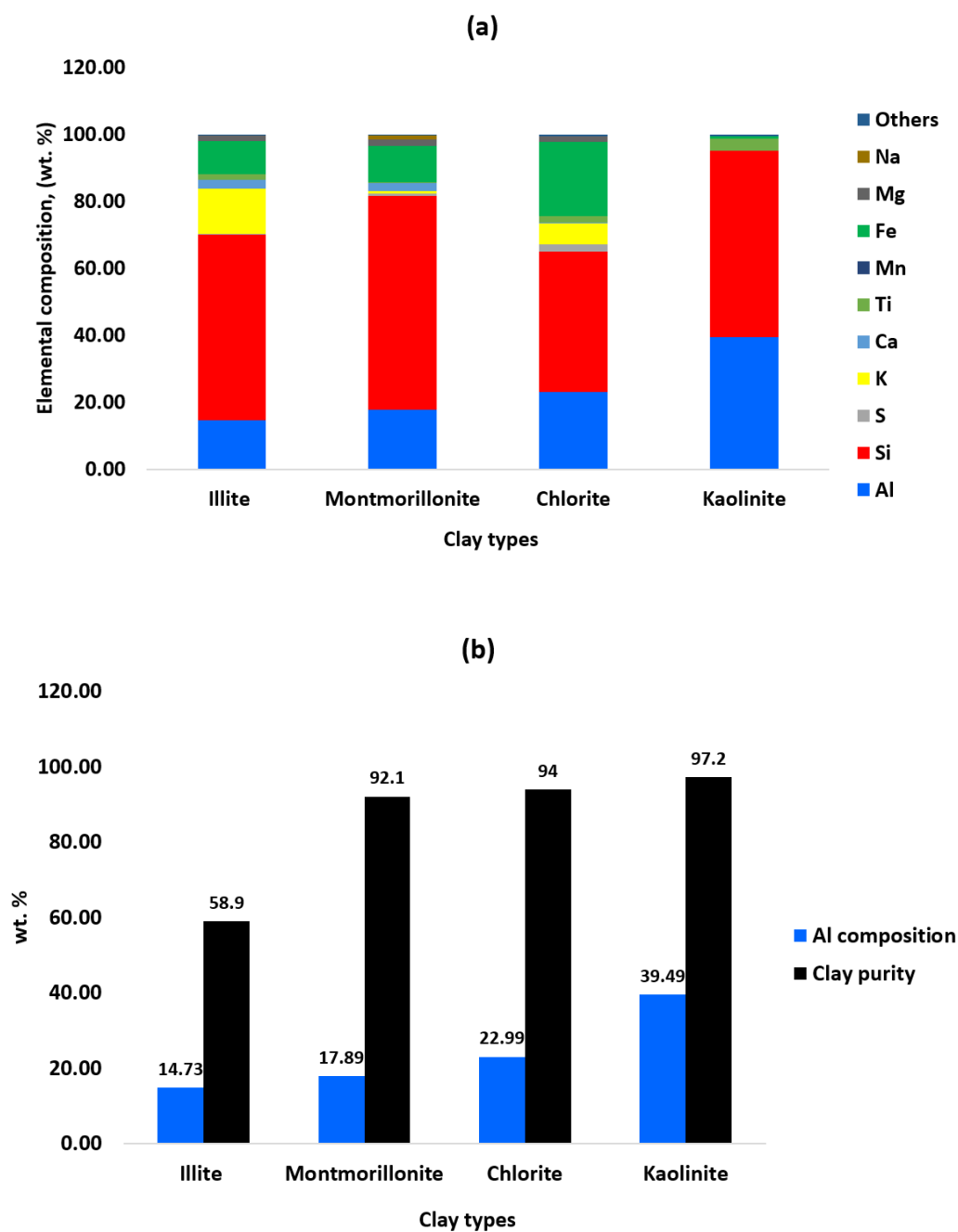


Figure 12 (a) Elemental composition by clay types (b) relationship between clay wt. % from XRD and aluminum wt. % from μ XRF for chlorite, illite, kaolinite and montmorillonite-containing clay samples

XRD mineralogy and TOC analyses

XRD mineralogical analysis in **Figure 13** hints that clay minerals are present in the samples of kaolinite, montmorillonite, chlorite and illite. From the XRD data, the montmorillonite sample has an average purity of 92.1% with traces of quartz (av. 7.9%) and vermiculite clay minerals (av. 2.3%). The kaolinite sample has an average of 97.2% purity, and a very small amount of calcite (av. 2.2%) and strontianite minerals (av. 0.6%). On the other hand, chlorite does not only contain chlorite clay minerals (avg. 94%) but also minor fractions of anorthoclase (av. 5.4%), pyrite (av. 0.5%) and quartz minerals (av. 0.1%). Furthermore, illite average purity is 58.9%, quartz (15.7%) and chlorite clay (6%). In the four samples, clay crystalline materials account for about 58.9-97.2% weight. The TOCs of the four samples, ranging from less than 0.005% to 0.76%, are generally low, implying that there are negligible amounts of micropores, which are usually associated with the organic matter constituents. For this reason, no further analysis will be required to uncover the amount of intra-granular micropores in this study.

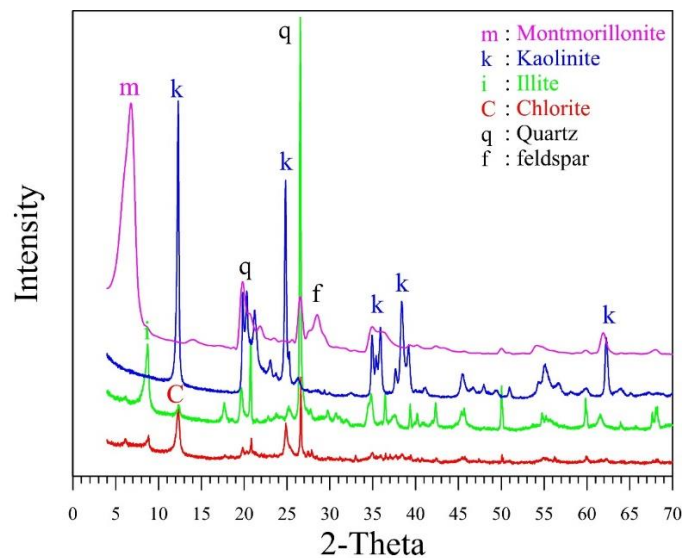


Figure 13 XRD patterns from montmorillonite, kaolinite, illite and chlorite-rich samples.

Table 11 presents the TOC analysis results and clay purity wt.% of the four samples obtained from XRD.

Table 11 TOC and clay purity from organic content and XRD analysis

Sample ID	TOC, wt. %	Clay purity, wt. %	Others, wt. %
Illite	0.005	58.9	41.1
Montmorillonite	0.010	92.1	7.9
Chlorite	0.750	94	6
Kaolinite	0.760	97.2	2.8

SEM-EDX surface elemental mapping

The presence of major elements in the studied clay samples such as silicon, aluminum, iron, and other minor elements can be visualized in **Figure 14**. The dispersive x-ray spectroscopy map is a better representation of the elemental compositions in kaolinite, chlorite, montmorillonite and Illite samples. The blue color signifies aluminum and confirms the results from μ XRF analysis (Table 10), that the aluminum concentration is the highest in kaolinite, followed by chlorite, montmorillonite, and the least in the illite clay sample. Similarly, the silicon content representing the deepest red is the highest in montmorillonite, followed by kaolinite and illite, and the least in chlorite (Table 10).

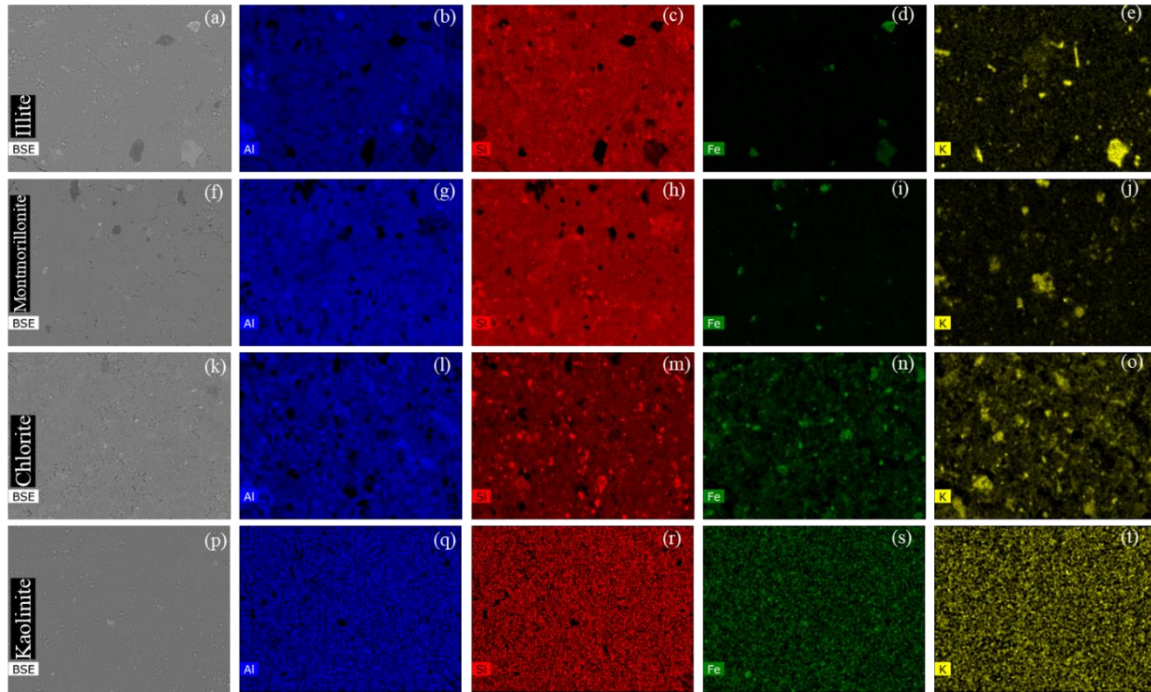


Figure 14 Images from SEM-EDX showing aluminum (Al), silicon (Si), iron (Fe) and potassium (K) in clay minerals: a-e) illite and f-j) montmorillonite k-o) chlorite and p-t) kaolinite samples.

4.3.2 Morphological characteristics using SEM

SEM backscattered images present the morphology of the clay samples in **Figure 15**. The purpose of clay surface mapping is to show the material form, shape and structure. It is clear that kaolinite is more homogeneous and this observation confirms the results of the individual mineral purity. Kaolinite clay has the highest purity of 97.2% according to Table 11. However, the pore shapes may be challenging to infer from a 200 μm resolution of surface imaging. Thus, a more detailed mapping of higher resolution will be required. Again, the current study is limited by the absence of solid samples for all the clay samples under consideration. A compressed pulverized material is used as an alternative for this analysis (detailed in section 4.2). The dark features in Figure 15 may represent artifacts like pores, carbon content or any other feature, which will require further analysis to

confirm. More importantly, detailed information regarding the physical properties of clay structures like pore shapes will be determined from the adsorption-desorption data.

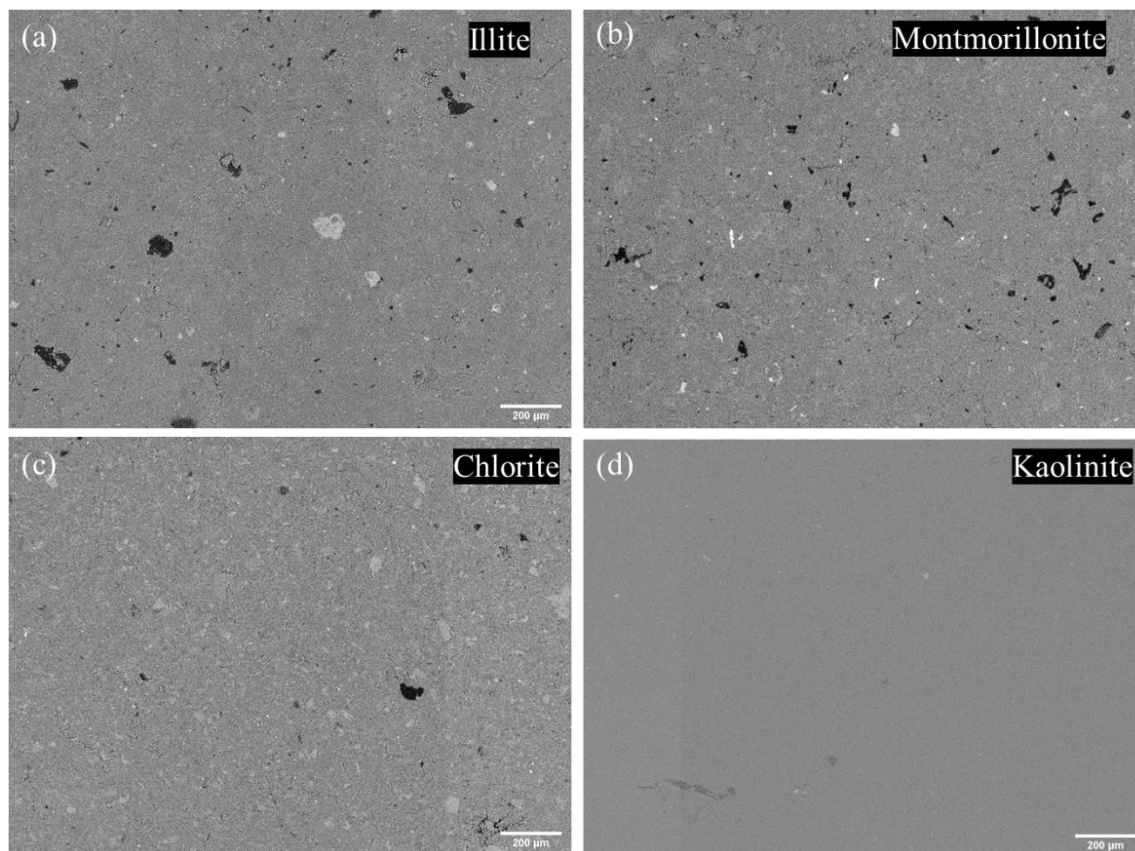


Figure 15 SEM images of L to R a) illite and b) montmorillonite c) chlorite and d) kaolinite samples showing vividly the degree of homogeneity of the clay materials.

4.3.3 Low-pressure N₂ isothermal measurements

The behavior of adsorption capacity versus relative pressure profiles depends on the pore morphology and degree of interactions between the adsorbent and adsorbate system. In other words, the adsorbate-adsorbent system, pore-size scale and storage mechanisms are inter-related. Micropores filling for instance is the controlling process in micropores (<2.0 nm), while capillary condensation and multilayer adsorption are prevalent mechanisms in

mesopores (2.0 – 50 nm) and macropores (> 50 nm) respectively [73]. In the adsorption-desorption curve, a reversible path occurs in <2.0 nm pores filling process at a very low relative pressure. However, at a higher relative pressure p/p^0 , capillary condensation and desorption occurs mainly in the 2-50 nm pores. At this stage, if a limiting adsorption or plateau is observed, this indicates a complete mesopores filling. Contrary to the behavior in the mesopores, the macropores in the materials will exhibit a complete reversible isotherm. More description of the pore shape complexity, pore size, specific surface area, and volume can be obtained from the constant temperature measurement [72–74].

The physisorption mechanisms for this study were characterized according to IUPAC classification, based on six possible types of observed adsorption isotherms and four types of hysteresis loops as; I to VI [73,74] and H1 to H4 [246] respectively. Nitrogen adsorption and desorption curves at STP for the different clay-rich samples in this study are presented in **Figure 16**. The measured adsorption isotherms (Figure 16) depict a combination of type III and IV type, consistent with the observations within the relative low-pressure and intermediate-to-high pressure range respectively [246]. The isotherm type III suggests that the quantity of micropores is negligible, while type IV indicates that the clay samples have a significant amount of mesopores. In other words, the property of type IV is the hysteresis loop, which confirms the presence of mesopores in the clay samples studied. While type III is characterized by a very small amount of microporous materials with negligible adsorption amount at relatively low-pressure region $p/p^0 < 0.04$. Besides, the phyllosilicate material has a TOC below 1% according to the organic content analysis, and insinuates that the amount of micropores, commonly hosted in the organic phase of the clays is negligible. The adsorption capacity steadily increases after the very slight

micropores filling process, which reflects the stage of completing the monolayer adsorption process. Multilayer adsorption process starts afterward. Capillary condensation of N_2 is the final mechanism in the mesopores, and represents the filling of the mesopores above 0.9 relative pressure (Figure 16a to d). Nevertheless, no plateau was observed even at the experimental relative pressure of 0.995, and this suggests an incomplete multilayer adsorption in the large pores (macropores).

Conversely, the desorption process starts from the macropores as pore pressure declines. Interestingly, a gap was observed between the adsorption and desorption path in the 2-50 nm pores region. The space between the evaporation and condensation phase in the mesopores is called the hysteresis loop. Again, the loop existing at high relative pressure supports the type IV adsorption isotherm class, and the size of the envelope could infer how much mesopores are present in the clay. Interestingly, this observation is consistent with the adsorption-desorption study on clay minerals in the literature [75,109]. Several reasons that explain the occurrence of hysteresis include pore-blocking effects, deformation of adsorbent, metastability of adsorbate and adsorbate molecular chain length and so on. The pore-blocking process by the mesopores could provide a good reason for the absence of capillary evaporation in some large pores. Precisely, the condensation pressure in larger pores is higher than in small pores, which creates a prevention of capillary evaporation from large pores by the liquid nitrogen in the connected small pores. The small pores are required to be emptied before desorption can take place in those macropores compartments. The adsorption curve provides information regarding the pore size distribution and rock properties.

Meanwhile the desorption and hysteresis loops tell the pore blocking phenomenon [247]. From Figure 16a, the illite shows a smaller and asymmetric hysteresis loop of type H2 with a relatively less steep desorption branch, and hints at ink bottle-shaped pores' dominance. In addition, the absence of an obvious limiting adsorption at high relative pressure suggests the presence of some type of H3 slit-shaped pores and/or macropores. A similar pattern was observed in the chlorite (Figure 16b). It contains the same degree of hysteresis loop as illite, which means that the two samples may contain relatively equal amounts of mesopores.

Contrariwise, the montmorillonite depicts a wide and asymmetric loop in Figure 16c, of type H2 with a steep desorption branch, and could hint that the rock contains mainly ink bottle-shaped pores and more mesopores. Besides, there is no horizontal peak at high relative pressure. The absence of adsorption plateau similarly insinuates the presence of some type H3 plate-like pores and/or macropores in the material. Again, these observations are consistent with previous studies in clay [72,75]. Finally, the sample with abundant kaolinite clay showed a hysteresis loop but with a very small-sized envelope (Figure 16d). The narrow gap implies nearly complete desorption and may infer the pore-scale homogeneity [247]. In other words, the kaolinite-rich material has larger pores and as substantiated from the size distribution. The interesting characteristic is the vertically narrow shape that resembles type H1 loop, nevertheless does not exhibit a plateau at high p/p^o . This feature matches type H3 loop or slit-shaped/macropores.

Forced closure of the desorption branch is seen in Figure 16a, 16b and 16d at $p/p^o \sim 0.44$, and it is called the 'Tensile Strength Effect' due to the instability of the hemispherical meniscus during desorption in pores with critical diameters of approximately 4 nm

(mesopores) [248]. It is noteworthy that the volume of adsorbed nitrogen displayed in Figure 16 was measured at standard temperature (0°C) and pressure (14.7 psi), above the two-phase critical temperature of N₂ (-147°C). Since, gas expands and its volume increases with temperature, the volume at STP is expected to be higher than the volume at -196°C, the condition at which the pore attributes were assessed.

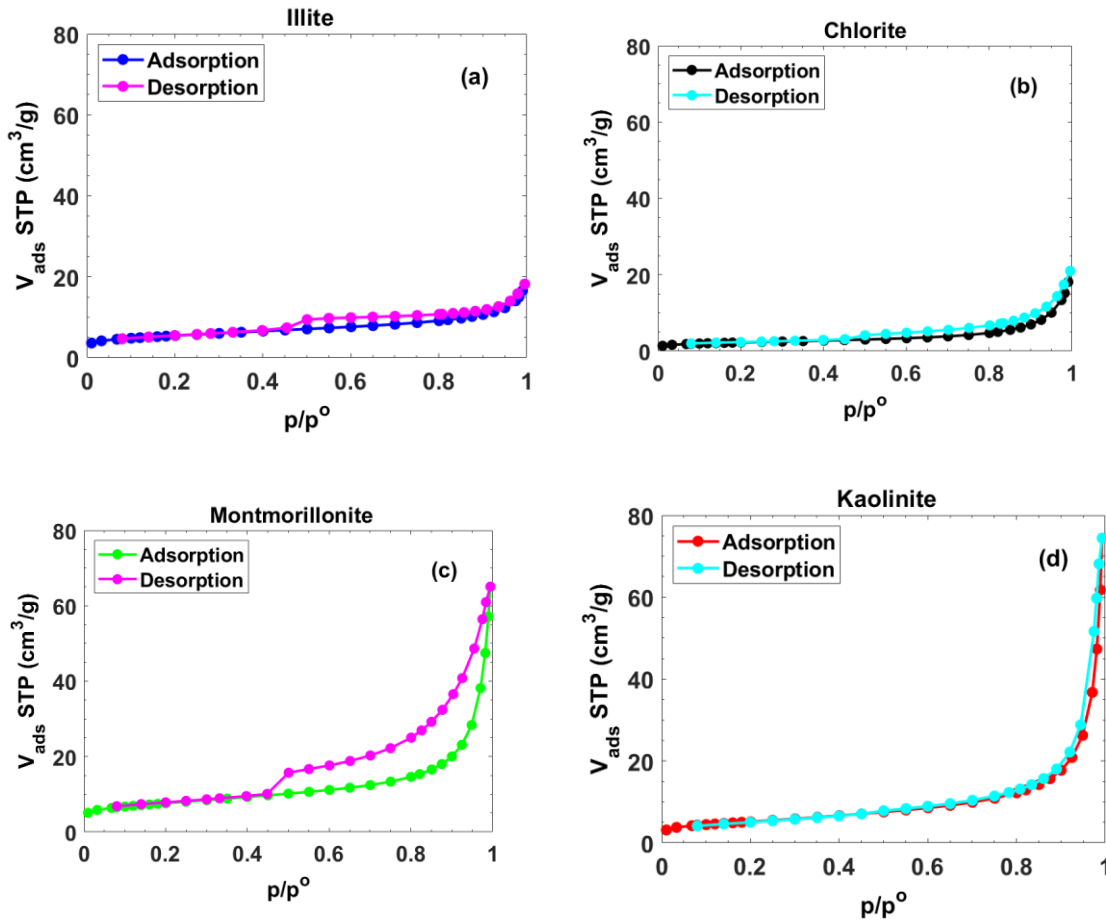


Figure 16 Shows the N₂ adsorption and desorption plots at standard temperature and pressure (STP) a) chlorite b) illite c) kaolinite and d) montmorillonite rich samples

The data used to compare maximum adsorption capacity and clay purity for the four clays in **Figure 17** was extracted at the highest relative pressure of $p/p^0 \sim 0.994$, and revealed

that kaolinite hosts the highest nitrogen adsorption capacity at STP ($74.43 \text{ cm}^3/\text{g}$) followed by montmorillonite ($65.08 \text{ cm}^3/\text{g}$), chlorite ($21.01 \text{ cm}^3/\text{g}$) and least in illite ($16.59 \text{ cm}^3/\text{g}$). Notably, there is a near linear relationship between the total adsorption capacity and the clay purity wt.% (Figure 17). The actual pore structure characterization at a temperature of 77.4 K will be discussed in section 4.3.4.

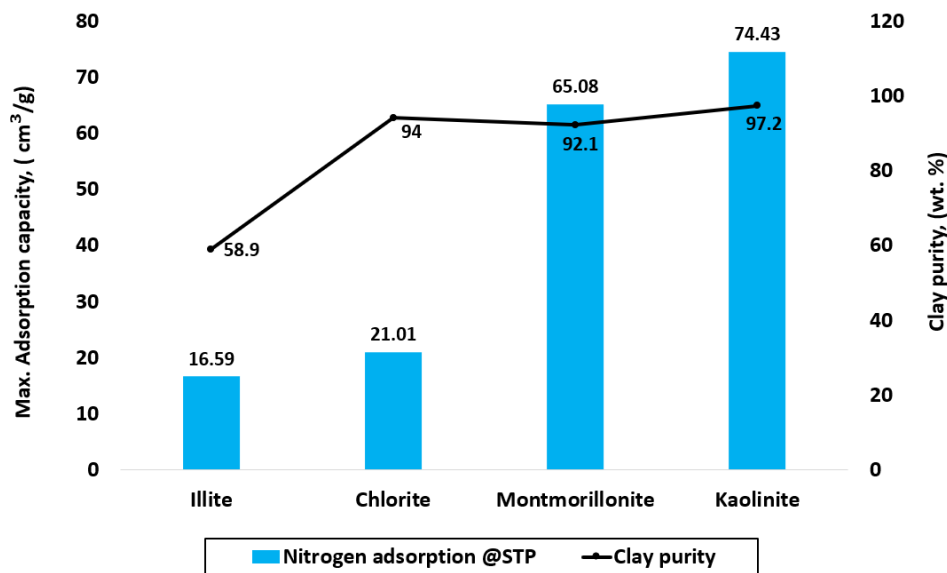


Figure 17 Shows the relationship between maximum adsorption capacity at STP ($p/p_0 = 0.995$) and clay purity

4.3.4 BJH pore size distributions (PSDs)

The Kevin-based N_2 -BJH technique is reliable in the description of the capillary condensation phenomenon in cylindrical pores [249], in order to accurately obtain the mesopores' average sizes and pore distribution. However, the Gurwitsch rule assumptions of cylindrical and homogeneous pore geometry could limit the model's reliability. This premise is partially correct in this study, as the hysteresis curves confirm the presence of cylindrical-shaped pores to some degree depending on the clay types. Furthermore, the

BJH pore distribution (PSD) data was verified with observations from the SEM. The challenge is accurately computing the pore volume evaluated at 77K across the pore-scales ranges.

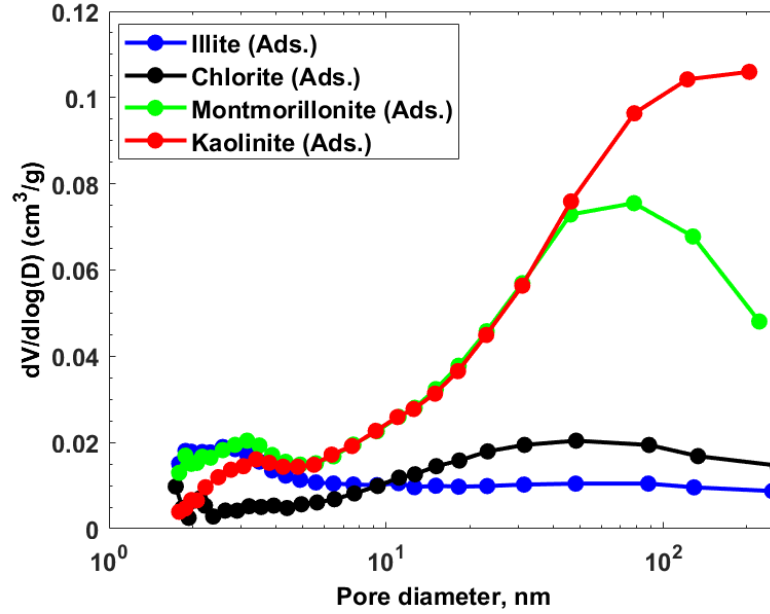


Figure 18 Shows the BJH pore distribution obtained by inversion of N₂ gas adsorption data at 77K. (a) chlorite (b) illite (c) kaolinite (d) montmorillonite

The area under the N₂-BJH differential volume distribution (**Figure 18**) showed that mesopores and macropores contribute significantly to the total volume available in studied samples. Nevertheless, kaolinite has the highest distribution of large pores, followed by montmorillonite and chlorite. Aside from kaolinite-enriched rock, the differential volume of other clay samples reaches the peak and starts to decline. This limiting distribution means that the 2-50 nm volume capacity available in the materials is well characterized. There is a notable contribution of mesopores to the total volume capacity, and the amount of pore volume above 50 nm will be large in kaolinite compared to the three samples.

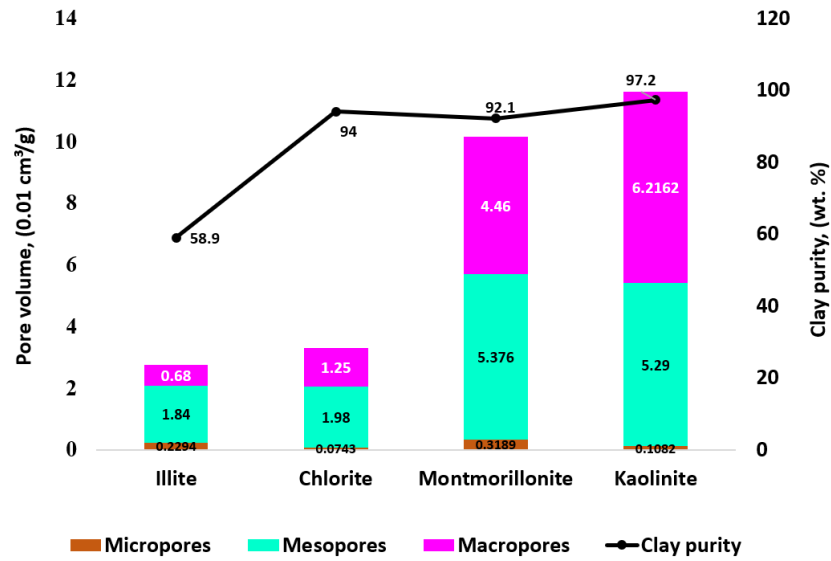


Figure 19 Shows the relationship between the clay minerals and pore volumes contribution from macropores, mesopores, and micropores in clay-rich samples with a pore size range of $50 < d \leq 300$, $2 \leq d \leq 50$, and $0.4 < d \leq 2$ nm respectively, evaluated at 77K.

Figure 19 shows a direct relationship between the cumulative pore volume and clay purity. Kaolinite has the highest capacity to host fluid due to the significant mesopores and macropores followed by montmorillonite, chlorite and least in illite clay. The volume of 2-50 nm pores is highest in montmorillonite/kaolinite and least in illite. Kaolinite has the largest macropores volume and illite is the least. This observation is also confirmed by the Wang 2020 study [75]. Meanwhile, the mesopores volume fraction is the least in kaolinite abundant rock.

Figure 20 showed that the rock containing the highest clay purity has the largest average pore size, while the least amount of the element has the least average compartment sizes. However, the average pore size computed with the adsorption data will underestimate the volume of >50 nm pores present in the layered phyllosilicate structure, since the N_2 -BJH model did not capture wider macropores (only count for 50-300 nm pores sizes). The role

of the clay chemical composition on the pore attributes evolution, gas storage, and production will be interesting to consider at typical reservoir pressure and temperature conditions.

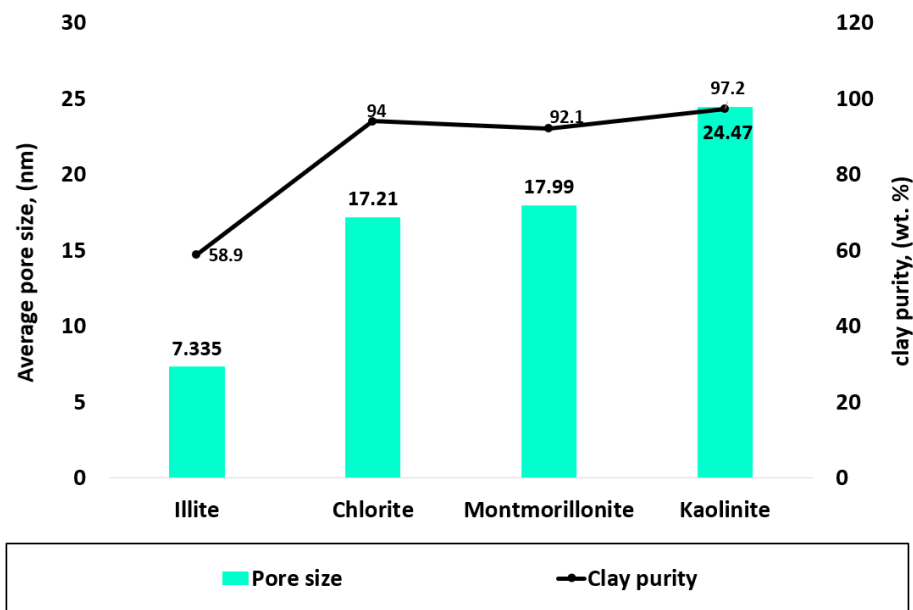


Figure 20 The average pore size connection with clay purity in wt. %. The measurement in this study pore using the BJH method considered the distribution of 1.7-300 nm, while the average pore falls within the mesopore-scale at 77K.

Ultimately, the type of clay present in shale and their relative elemental concentration significantly affect the storage capacity and gas production. Several adsorption experiments compute the sorbed and free gas capacity in pure clay or clay-rich shale rocks at high pressure [78,80]. However, the capacity of the clay materials to host fluid at high pressure has not been connected with their elemental concentration and clay purity. A similar pattern is expected with the adsorption of nitrogen at low-pressure STP. The limitation of the BJH N₂ adsorption model remains that it can only resolve the minimum pore size of approximately 1.7 nm, and the nitrogen probe is diffusion restricted in narrow micropores (<0.7 nm). CO₂ adsorption at 273.15K [75,250] and Harkins and Jura t-plot

[251] are commonly employed in the literature for characterizing materials with significant micropores.

4.3.5 Micropores and non-micropores specific surface area

The relationship between the silicon concentration and specific surface area is provided in **Figure 21**. The specific surface area in non-micropores is referred to as the external SSA of the clay. Montmorillonite has the highest value, and chlorite contains the least. This trend is similar to the total specific surface area reported in the literature. The high SSA in non-micropores of the montmorillonite is coming from the edge and basal-specific surface area contributions. However, care must be taken to understand that the total SSA using the N₂ probe does not access the <2.0 nm interlayer spaces, even in swelling clay minerals like montmorillonite and chlorite. Regardless, the SSA of illite and kaolinite are reliable as they are non-swelling and their microstructure will be unchanged if the sample is wet [252,253]. Also, the relatively large volume and specific surface area of micropores in montmorillonite as shown in Figure 20 and Figure 21 respectively, are consistent with the outcome of Wang's studies [75]. Finally, in the same vein, the micropores and non-micropores specific surface areas are in descending order: montmorillonite>kaolinite>illite>chlorite clay-rich samples. Finally, the clays purity, aluminum and silicon concentration, specific surface area, average pore size, TOC and pore volume at all pore-scales are presented in **Table 12**.

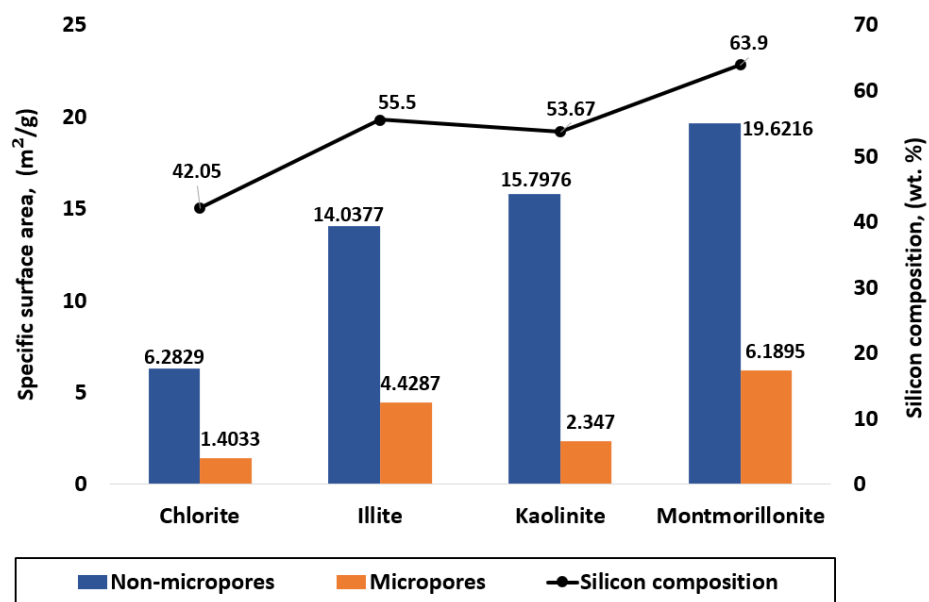


Figure 21 Shows the relationship between the micropores and non-micropores specific surface area in clay and the amount of silicon present evaluated at 77K.

Table 12 Summary of BJH adsorption, BET, and t-plot method for characterizing clay pore volume, average pore size, total surface and external specific surface area versus elemental concentration and clay purity.

Sample ID	Clay, wt. %	Al., wt. %	Si., wt. %	BET	BJH adsorption (Micropores 1.7-2nm, Mesopores 2-50 nm, Macropores 50-300 nm, and Total pores 1.7-300 nm)					Harkins and Jura t-plot (Micropores 0.4-2nm)		
				S_{tot} , m ² /g	d_{avg} , nm	V_{tot} , 0.01cm ³ /g	V_{mic} , 0.01cm ³ /g	V_{mes} , 0.01cm ³ /g	V_{mac} , 0.01cm ³ /g	S_{mic} m ² /g	S_{ext} m ² /g	V_{mic} , 0.01cm ³ /g
Montmori llonite	92.1	17.90	63.90	25.80	18.00	9.90	0.98	5.38	4.46	6.19	19.62	0.32
Kaolinite	97.20	39.50	55.70	18.10	24.50	11.50	0.03	5.29	6.22	2.35	15.80	0.11
Illite	58.90	14.70	55.50	18.50	7.30	2.60	0.11	1.84	0.68	4.43	14.04	0.23
Chlorite	94.00	23.00	42.10	7.70	17.20	3.30	0.04	1.98	1.25	1.40	6.28	0.07

4.4 Implications of using aluminum and silica-rich clay

Table 12 showed a direct association between the aluminum content and clay purity. Kaolinite clay has the highest aluminum concentration of 39.5 wt.% compared to chlorite, montmorillonite and illite with 23.0, 17.9 and 14.7 wt.% respectively. Figures 17, 19, and 20 revealed the connection between the clay wt.% and its pore structural attributes such as the total pore volume, non-micropore volume and average pore sizes respectively. A combined analysis of all the stated figures suggests that the capacity of clay to host fluids is enhanced by the concentration of aluminum present in the clay. This information is suitable for a meaningful understanding of the storage capacity of clay-rich shale plays depending on the clay types.

Additionally, the presence of aluminum in a material could cause an acceleration of surface reactivity [254] and serve as a reactant in the treatment of contaminants in polluted areas [255,256]. Fatimah and Wijaya [254] study substantiated that the increase in the quantity of aluminum in montmorillonite clay speeds up the surface acidity reaction. Furthermore, Yang et al. [255] and Wang et al. [256] confirmed that an aluminum modified clay is applicable for phosphate and contaminant removal in polluted areas in the absence of air.

At this point, it is clear from this research that kaolinite-rich clay (with the highest aluminum concentration of 39.5 wt.%) has the potential to act as a good catalytic material required to speed up esterification reaction. In addition, it can serve as a waste repository and a material for the treatment of phosphorus-containing contaminants in polluted areas.

The relationship between silicon content and clay structural properties was also studied. Montmorillonite (63.9 wt.%) has the highest amount of silicon followed by illite (55.5

wt.%), kaolinite (53.7 wt.%), and chlorite (42.05 wt.%) in this order. The increase in this crystal-like mineral favors the development of the specific surface area in the non-micropores. Studies have shown the significance of silicon in clay research [257,258]. Depending on the clay type, the presence of silica in clay can reduce the repulsive double-layer forces and, at the same time improve the attractive force between the replaced interlayer cation and clay surface. This phenomenon increases stabilization and reduces pore throat plugging in clay-rich shale [257]. Sadek [258] has also supported the observation that silica nanoparticles prepared at 200°C contain macropores structure. However, these studies considered the use of silicon in pure form. Silicon in clay exists as an impure form. The existence of silica in sandstone increases the volume of macropores attributed to the high porosity in silicate-rich rocks [54]. In addition to the role of surface charge density on the clay-specific surface area [259], the concentration by wt.% of silica in clay was one of the surface area controlling factors. This research confirms that montmorillonite with the largest specific surface area in non-micropores and silicon content of 63.9 wt.% promotes reactivity and cation exchange interaction. However, this property of high basal spacing will prompt clay swelling in the presence of water [260].

4.5 Conclusions

In this research, four clay-rich rocks samples were characterized using an integrated approach to understand the relationship between aluminum, silicon concentration, clay purity and the intra-granular pore structural parameters. The combination of techniques such as μ XRF, XRD, SEM-EDX, and low-temperature adsorption analyses showed some

interesting relationship between their mineral's composition, specific surface area, pore distribution and volume. Furthermore, the following conclusions are drawn:

1. The results from mineralogy and elemental analyses showed that the studied samples with clay purities of 60-98% have a combined 80-96 wt.% composition of aluminum, silicon, and Iron. SEM backscattered electron image confirms the degree of sample clay homogeneity. Similarly, the SEM-EDS images validate the elemental analysis by μ XRF.
2. Both the total organic content analysis and adsorption-desorption curve at $p/p^o < 0.04$, indicate that clays accommodate negligible micropores.
3. The inferred adsorption isotherm types hint that the materials contain a negligible amount of micropores and may be undergoing some pore-blocking phenomenon. Meanwhile, the hysteresis loop implies that clay has a plate-like/larger pore system. This observation is consistent in all the analyzed samples. Nevertheless, the pore shape complexity depends on the clay type.
4. Capillary condensation and evaporation curves revealed more mesopores and macropores of 2-50 nm and >50 nm, respectively. The pore distribution plateaued around an average of 100 nm. The limiting distribution confirmed the suitability of the Barrett-Joyner-Halenda technique to compute most of the fluid volume contained in clay mesopores.
5. Kaolinite ($74.43 \text{ cm}^3/\text{g}$) hosts the highest amount of N_2 adsorbed at STP followed by montmorillonite ($65.08 \text{ cm}^3/\text{g}$), chlorite ($21.01 \text{ cm}^3/\text{g}$) and illite ($16.59 \text{ cm}^3/\text{g}$) has the least capacity. In the same vein, the pore capacity to store

fluid and average pore size assessed at 77.4 K follow a similar pattern and increase with aluminum and clay contents.

6. On the other hand, the specific surface area of the non-micropores is directly related to silicon composition. Montmorillonite with the largest specific surface area in non-micropores has a silicon content of 63.9 wt.%.
7. The novelty of linking elemental composition and intra-granular pore attributes in this study can be utilized to develop synthetic clay materials with improved surface and pore volume properties for waste treatment and catalyst for accelerating chemical reactions. The study also confirmed that clay-rich shale can be said to host multiple mesopores and macropores for gas storage from the inorganic clay mineral phase.

CHAPTER 5

THE IMPACT OF PORE STRUCTURE AND ADSORPTION BEHAVIOR ON KEROGEN TORTUOSITY²

Abstract

Diffusion tortuosity is an important microstructural parameter for computing effective gas transport coefficients in porous media. In this study, a realistic kerogen structure was built to quantitatively establish a clear understanding of the adsorption impact on diffusion tortuosity in the organic materials of shale. A molecular simulation study was employed to reconstruct a Type II-D kerogen model on a computational platform. A structure of five kerogen macromolecules was obtained through a series of NVT – NPT ensembles. There was a thorough characterization of the porosity and pore size distribution of the final structure. A grand canonical Monte Carlo method was used to compute the adsorption of methane for a pressure range up to 40 MPa. Freundlich and Langmuir models were employed to further parameterize the adsorption capacity. A molecular dynamics diffusion

² This chapter is copied from the manuscript: **C Afagwu**, S Al-Afnan, S Patil, J Aljaberi, MA Mahmoud, J Li (2021). The impact of pore structure and adsorption behavior on kerogen tortuosity. Fuel 303, 121261.

study was performed on the kerogen-adsorbed molecule configurations to obtain the effective diffusion, which was then used to estimate the tortuosity. Methane molecules follow tortuous pathways of diffusion, imposed by the heterogeneity and confinement of kerogen. The tortuosity is further impacted by the adsorption effect. Kerogen-methane interactions increase this tortuosity by a factor as high as 3.6 compared to an adsorption-corrected tortuosity.

Keywords: Kerogen micropores, Effective methane diffusion, Molecular simulation, Diffusion tortuosity, Adsorption

5.1 Introduction

The importance of tortuosity as a critical microstructure parameter to predict effective mass transport properties in porous media cannot be overemphasized. In organic-rich shale for instance, kerogen surface and pore diffusion will be significant, mainly in micropores and at low pressure. So far, some researchers have computed the diffusion tortuosity in porous media [147,261–263]. To the best of our knowledge, the study of realistic kerogen structure tortuosity and the impact of adsorption on methane diffusion is lacking. More importantly, the traditional approach of calculating diffusion tortuosity will require some modification to account for the adsorption behavior due to the chemical composition of the organic matter and the confined gas. Thus, giving rise to the molecular study of the impact of pore structure and adsorption phenomena on the real kerogen tortuosity, by combining MD simulation and grand canonical Monte Carlo (GCMC) methods. The kerogen type II-D structure was constructed by following similar approach as recommended by Philippe Ungerer [103], and using an extended version of the polymer consistent force field (PCFF+). The remainder of this research is organized as follows: the commonly employed

Knudsen number dependent pore diffusion model for unrestricted gas transport, coupled with some diffusion tortuosity model has been reviewed in chapter 2. In section 5.2, the details of the method adopted for this work, coupled with the MD protocols, molecular simulation and adsorption calculations, and necessary input parameters are outlined. Consequently, adsorption, self-diffusivity and diffusion tortuosity results are presented in section 5.3. Finally, a kerogen – crack system transport is used to delineate the microscopic diffusion/adsorption influence at a larger macroscopic permeability framework and conclusion to the study is provided in section 5.4.

5.2 Methodology

A systematic approach was adopted to investigate the impact of adsorbed gas film accumulating at a wall surface on the tortuosity of a kerogen structures' gas diffusion. The computational workflow is summarized in **Figure 22**. The framework shows a progression of steps followed from the atomic scale (i.e. consistent with the approach adopted by Wang et al. [264]).

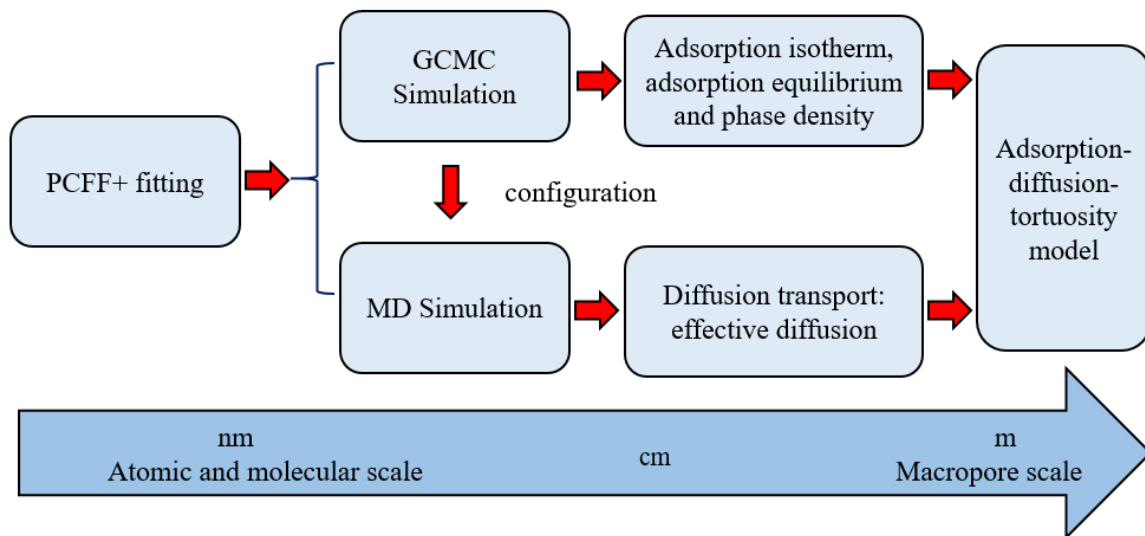


Figure 22 Computational models at different scales that were followed to study diffusion tortuosity.

5.2.1 Construction of the kerogen structure

A representative kerogen nano-porous structure for the diffusion-adsorption calculations was created through the molecular protocol depicted in **Figure 23**. The MD simulations are performed with the large-scale atomic/molecular massively parallel simulator (LAMMPS) and the Medea environment, [265] and the GCMC calculations are calculated with GIBBS code [71] as integrated in the *Medea* environment, [72]. First, a kerogen Type II-D macromolecule unit was reconstructed, as derived by Ungerer et al. [103] (**Figure 24**). The molecular weight of a Type II-D kerogen molecule is 2.466 kg/mol , with a chemical formula of $\text{C}_{175}\text{H}_{102}\text{O}_9\text{N}_4\text{S}_2$. The PCFF+ force field [73,74] is utilized in the simulation, whereby the Lennard-Jones (LJ) 9-6 model with the Waldman and Hagler mixing rules [150] describes the atomic-atomic van der Waals interaction forces among the 292 atoms of carbon, hydrogen, oxygen, nitrogen, and sulfur present in the kerogen molecule. A cutoff of $9.5 \text{ \AA}$ is used in evaluating explicit LJ and Coulombic interactions between assigned atomic charges, which was already successfully applied in various MD simulations with kerogen models [51,59]. Long distance corrections are used to estimate LJ energy beyond the cutoff, [75,76] and the particle-particle-particle mesh (PPPM) method [70] and the Ewald summation [76] are used in the MD simulations with LAMMPS and the MC simulations with GIBBS.

Thereafter, a configuration of the initial structure was built as an ensemble of five kerogen macromolecules in a cubic simulation box. At initialization, the density of the OM was 0.2 g/cc . To create the final structure, a MD simulation within the canonical (NVT) ensemble is performed (temperature, number of atoms, and volume are kept constant) at T

= 900 K and for $t = 250$ picoseconds (ps), followed by a series of MD simulations within the isobaric-isothermal (NPT) ensemble (temperature, number of atoms, and pressure are kept constant). The pressure in all the NPT MD simulations is set to 20 MPa, whereby the temperature is reduced in the sequence 900 K, 700 K, 500 K, to 350 K. A Nosé–Hoover barostat and thermostat [266] is utilized in the MD simulation runs to control the pressure and temperature, respectively. The real time that is captured in the NPT-MD simulations are 200 ps , 200 ps , 400 ps , and 400 ps . In all MD simulations, the time step to evolve the equations of motions is 1.0 femtosecond (fs). At the final pressure and temperature conditions, the density was calculated to be around 1.3 g/cm^3 , and it closely agreed with the experimental values of $1.3\text{-}1.4 \text{ g/cm}^3$ reported for type-IID kerogen obtained from Kimmeridge clay formation [103,235]. Most times, another critical question is the degree of representation of few condensed kerogen macromolecules for molecular studies. There is a trade-off for researchers between degree of representation and computational cost involved. More light will be shed on how both key criteria were managed in section 5.2.2.

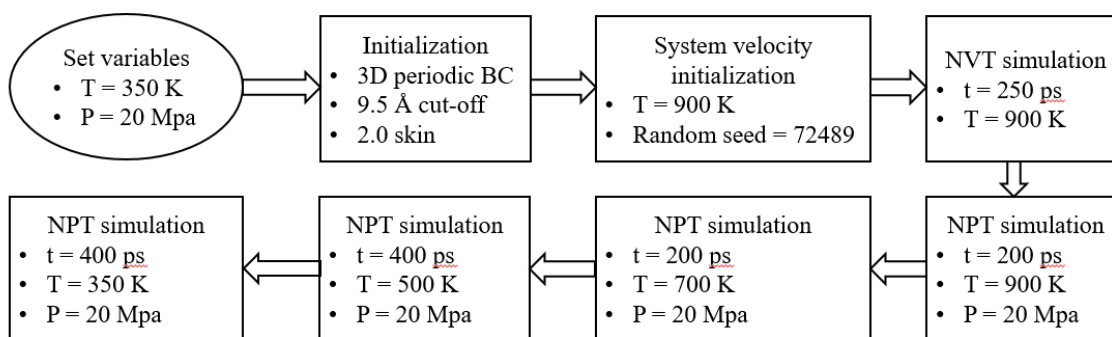


Figure 23 LAMMPS protocol workflow for constructing the final kerogen structure.

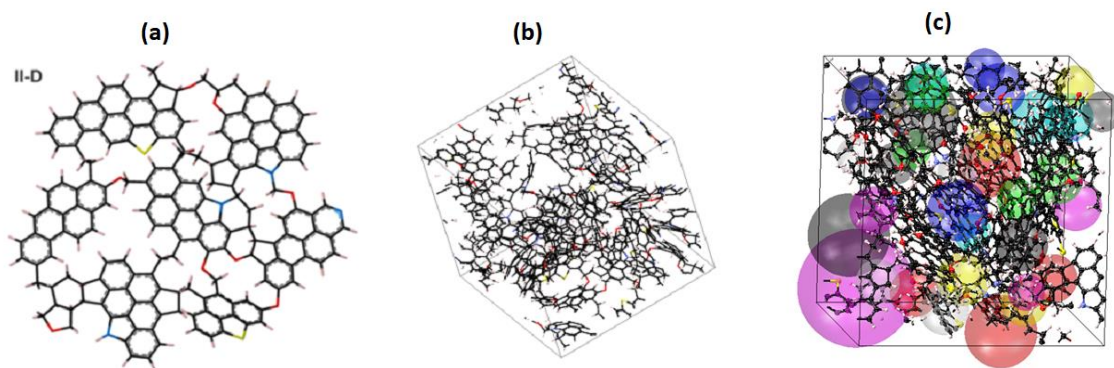


Figure 24 Kerogen Type II-D structure: (a) single cell with chemical formula $C_{175}H_{102}O_9N_4S_2$ [53], (b) five condensed and configured units, and (c) distribution of the rigid skeleton with non-overlapping spheres of random sizes represented in different colors.

5.2.2 Representative elementary volume

The number of kerogen macromolecule units selected determines the volume of the final kerogen structure. A sensitivity analysis was carried out to check if the assumed five units formed a meaningful representative elementary volume (REV). The molecular construction protocol described in **Figure 23** was used with an increasing number of macromolecules, beginning with two units. In each case, the density and volume of the final structure were obtained. **Figure 25** shows a convergence of density to a value of 1.3 g/cm^3 , with a kerogen size of 16 nm^3 (corresponding to the four-kerogen macromolecule units) and above.

Although five kerogen units was deemed sufficient for this study based on this analysis, this does not suggest that it is completely representative of kerogen bulk for practical purposes. In addition, it is noteworthy that a representative volume obtained from simulation is sensitive to kerogen maturity and kerogen molecules of different sizes [144]. Generally, more kerogen macromolecules in the simulation box will improve the reliability of the MD results. However, there is a trade-off between computational cost and degree of

representation. Ungerer et al. [103] procedure was applied to create a condensed kerogen and the density obtained matched the experimental values reported for type IID kerogen from Kimmeridge clay formation [235]. To create a structure with a void ratio sufficient to host methane, the same procedure was repeated with 25 ‘director’ molecules (i.e., heptane) inserted during the initialization phase and then removed upon convergence to the final assigned pressure and temperature. The details for making porosity-controlled structure required for the adsorption and diffusion studies will be explained in the coming sub-section.

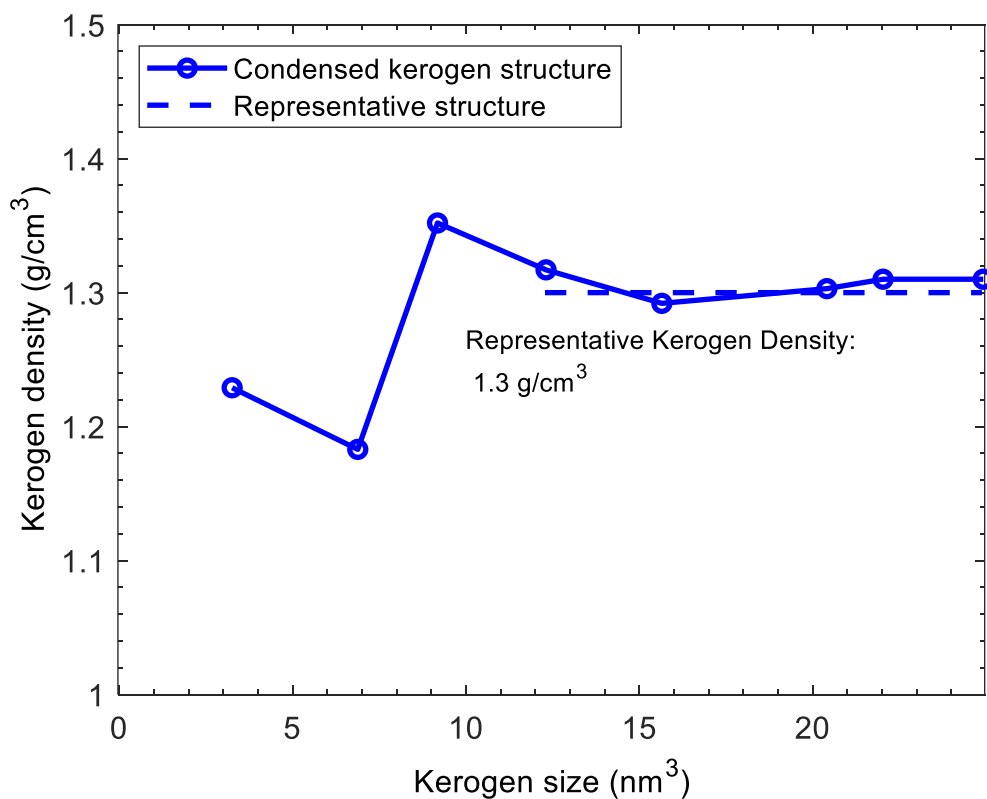


Figure 25 REV analysis for Type II-D kerogen at 20 MPa and 350 K, showing a density convergence to 1.3 g/cm³ for the final structure’s volume of 16 nm³; a volume corresponding to four kerogen macromolecule units.

5.2.3 Characterization of the porous media structure

The analysis of the petrophysical characteristics of the created kerogen structure (e.g., porosity, pore size distribution) was performed with combined helium gas adsorption and non-overlapping sphere insertion methods. Inert gases are non-adsorbing, however, not only does adsorption occur due to the chemical composition of the gas but because of pore space confinement [111,135]. The porosity of the final kerogen structure, upon removal of 25 ‘director’ units, was computed to be 29%, using a helium adsorption calculation approach (computational pycnometry) [88,267]:

$$\phi = \frac{V_{pore}}{V_{bulk}} = \frac{\frac{N_{total,He} - n_{excess,He}}{\rho_{He,b}}}{L_x \cdot L_y \cdot L_z} \quad (5.1)$$

where V_{pore} and V_{bulk} are the volumes of the pore and total kerogen box model, respectively (m^3); L_x , L_y , and L_z are the lattice dimensions in the x, y, and z directions, respectively (m); $n_{excess,He}$ and $N_{total,He}$ are the number of excess and total adsorbed molecules of helium, respectively (mole); and $\rho_{He,b}$ is the bulk density of the helium (mol/m^3). Under the assumption of zero excess molecules at low pressure and at such a degree of confinement, the above equation could be used to estimate the porosity.

Pore size distribution (PSD) governs the transport of fluid in porous media. Therefore, an understanding of the pore arrangement in kerogen is required for an accurate characterization of gas diffusion through a kerogen body. Same approach proposed by Bhattacharya and Gubbins [150,268], was utilized to extract the PSD. The algorithm involves placing non-overlapping spheres at the vertices of a polyhedral, followed by a random distribution of points within the structure [269]. A point is randomly picked as the

sphere center and the radius of the biggest sphere r_s that does not overlap with the solid is calculated; it must satisfy the relation, as follows [150]:

$$r_{ij} \geq \frac{\sigma_i}{2} + r_s, \quad (5.2)$$

here, r_{ij} is the distance between the sphere center and nearest solid (m), σ_i is the LJ diameter of the nearest particle, and r_s is an admissible sphere radius, from which the radius of the biggest sphere can be obtained as a sample at the random point selected. Upon repeating the procedure for pre-defined cycles, the PSD is normalized as follows:

$$\int_0^{+\infty} P(r_s) dr_s = 1 \quad (5.3)$$

The total pore volume available to host methane in the confined structure, determined from the helium gas adsorption was validated by the sphere insertion method [150,268]. The pore volume, pore size distribution, and average pore size ($\bar{r}$) were determined. Consequently, the porosity matched closely the helium measurement at around 30%. The procedure creating the final kerogen structure was repeated five times starting from independent initial configurations to assure the reliability and reproducibility of the approach. For each arrangement, the density, largest, average, and smallest pores of each structure are summarized in **Table 13**.

Table 13 Pore size distribution statistics of five independent configurations

Configuration	Pore radius,	Pore radius, max (10 ⁻⁹ m)	Pore radius, avg (10 ⁻⁹ m)	Structure Density, (kg/m ³)

	min (10 ⁻⁹ m)			
1	0.219	0.530	0.305	979
2	0.208	0.650	0.275	1014
3	0.200	0.648	0.288	1000
4	0.202	0.766	0.279	984
5	0.203	0.618	0.286	978
Statistics				
Standard dev.	0.0068	0.0756	0.0103	0.0139
Coef. of variation (%)	3.27%	11.77%	3.59%	1.40%

The re-computed density of the structure averaged within 1000 kg/m³ with a lattice dimension of around (27 Å x 27 Å x 27 Å) for all of them. Similarly, the average pore sizes of the five configurations are consistently within 0.3 nm radius. Post-construction of kerogen structure, the calculations of fugacity and LJ interactions energy, required for GCMC simulations, are discussed in the next section.

5.2.4 GCMC adsorption calculations

GCMC was utilized to estimate the adsorbed molecules in the system. The fixed parameters (i.e., as input) in the GCMC ensemble were the volume and temperature and chemical

potential of the adsorbed molecules [270]. The chemical potential for methane was estimated as follows [86]:

$$\mu_i = \mu_{io} + RT \ln \left(\frac{\hat{f}_i^v}{\hat{f}_{io}} \right), \quad (5.4)$$

where i represents methane; μ_i and $\hat{f}_i^v$ are the chemical potential ($J/mole$) and fugacity (Pa) for methane in vapor phase, respectively; and $\hat{f}_i^v = y_i p \hat{\phi}_i$ is the fugacity of methane in the vapor phase (Pa), $\hat{\phi}_i$ is fugacity coefficient of real methane gas, $\hat{f}_{io} = p \hat{\phi}_{io}$, is fugacity of ideal gas, and $\hat{\phi}_{io} = 1$, is the fugacity coefficient of an ideal gas. The Peng-Robinson equation of state model was employed to calculate the fugacity coefficient [76]. Fugacity of a real gas is the effective partial pressure, which corrects for the non-ideality of the gas molecules as operating condition changes. Besides, the fugacity of methane utilized as an input parameter to the GCMC model is presented in **Table 14**.

Table 14 Fugacity of methane gas at 350 K

Pressure (MPa)	2.067	3.445	6.890	10.335	20.670	31.010	41.340
Fugacity (MPa)	2.028	3.340	6.494	9.503	18.056	26.958	35.842

The PCFF+ force field (FF) was not only utilized to parameterize the kerogen atoms, but also the methane gas and ‘director’ heptane molecules. In other words, the LJ 9-6 potential is employed in GCMC simulations to describe the interactions between the different atoms types in the modified kerogen structure and methane gas, and the model is as follows [271,272]:

$$E^{LJ} = \varepsilon \left[2 \left(\frac{\sigma}{r_{ij}} \right)^9 - 3 \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}, \quad (5.5)$$

here, E^{LJ} is potential energy due to Leonard Jones interaction forces between like and unlike atoms (*Joules*). r_{ij} is the distance between atoms i and j (m), σ is distance at which the interaction potential between the two force centers is zero (m), ε is the depth or maximum amplitude of the potential well (*Joules*), q_i and q_j are charges of atoms i and j respectively, ϵ_0 is dielectric constant, subscript i and j are different atoms types in modified kerogen structure and methane gas respectively. It is noteworthy that the Lennard-Jones parameters, σ and ε are given for a force center of the same type in the PCFF+ force field in **Tables 15** and **16** for methane and modified kerogen structure respectively. Nonetheless, the Waldman and Hagler combining rules is utilized to compute LJ parameters between unlike atoms of type i and j , and is as follows [273]:

$$\sigma = \left(\frac{(\sigma_i)^6 + (\sigma_j)^6}{2} \right)^{1/6}; \quad \varepsilon = 2\sqrt{\varepsilon_i \varepsilon_j} \left(\frac{(\sigma_i)^3 (\sigma_j)^3}{(\sigma_i)^6 + (\sigma_j)^6} \right) \quad (5.6)$$

The methane gas force field types of atoms of carbon and hydrogen present, in addition to their partial charges, is available in **Table 15**.

Table 15 Methane atom types, description, LJ parameters and charges

Elements	Atom type (s)	Description	σ , (Å)	ϵ , (kcal/mol)	q, (e)
Carbon, C	c	Generic SP3 carbon	4.014	0.0667	-0.212
Hydrogen , H	hc	Hydrogen bonded to carbon	2.878	0.023	0.053
where, 1e = 1.602×10^{-19} coulomb and 1 kcal/mol = 4184 J/mol					

Similarly, the types and description of atoms of kerogen and ‘director’ heptane molecules that constitute the modified kerogen structure is summarized in **Table 16**.

Table 16 Parameterized atom types of carbon, hydrogen, nitrogen, oxygen and nitrogen and LJ parameters in the modified kerogen structure using PCFF+ fitting method

<u>Kerogen IID</u>				
Elements	Atom type (s)	Description	σ , (Å)	ε , (kcal/mol)
Carbon, C	c1	Sp3 carbon with 1 H 3 heavies	3.75	0.035
	c1oe	Alpha carbon in ether containing secondary alkyl group	3.77	0.027
	c2	Sp3 carbon with 2 H's, 2 Heavy's	3.76	0.063
	c2oe	Alpha carbon in ether containing primary alkyl group, -C-OCH2-R	3.63	0.067
	c5	Sp2 aromatic carbon in five membered rings	3.75	0.041
	cp	Sp2 aromatic carbon	3.92	0.067
	nb	Sp2 nitrogen in aromatic amines	3.89	0.092
	cpc	Alpha/ipso carbon in aromatic ethers -C-O-C	3.91	0.057
Hydrogen, H	hc	Hydrogen bonded to carbon	2.88	0.023
	hn	Hydrogen bonded to nitrogen	1.09	0.008
Oxygen	oc	Sp3 oxygen in ether or acetals	3.30	0.120
Nitrogen	np	Sp2 nitrogen in 5- or 6- membered ring	3.58	0.046
	nb	Sp2 nitrogen in aromatic amines	3.89	0.092

	cp	Sp2 aromatic carbon	3.92	0.067
Sulphur	sp	Sulfur in an aromatic ring (e.g. thiophene)	4.07	0.302
<u>'Director' molecule, Heptane</u>				
Carbon, C	c2	Sp3 carbon with 2 H's, 2 Heavy's	3.76	0.063
	c3	Sp3 carbon with 3 hHs 1 heavy	3.88	0.071
Hydrogen, H	hc	Hydrogen bonded to carbon	2.88	0.023

Some important calculations are necessary to express the direct output from the GCMC simulator to some meaningful macroscopic adsorption parameters are presented in the next section.

The output from the GCMC simulations is the Gibbs' number of loaded gas molecules N_{am} in the structure at some certain pressure and temperature [86,88]. The dimensionless output is expressed in moles as $N_{total} = N_{am}/N_A$ [274]. The excess adsorption is obtained by subtracting the total free gas present in the pore from the total loading capacity of kerogen as follows [6,76,88]:

$$n_{excess} = N_{total} - \rho_{bulk}V_{pore}, \quad (5.7)$$

where n_{excess} is excess adsorbed amount of methane (mol). To validate the computed excess amount of adsorbed, Eq. (5.7) is re-written in terms of the amount of excess gas adsorbed per unit mass of a condensed kerogen, $\hat{n}_{excess}$ (mol/kg) as follows [17,19,275]:

$$\hat{n}_{excess} = (N_{total} - \rho_{bulk}V_{pore})/m_{ker}, \quad (5.8)$$

where m_{ker} is the mass of kerogen (kg). Similarly, the total amount of loaded methane at each simulation pressure was expressed in terms of the adsorbed methane density as follows [276]:

$$\rho_{ads} = \frac{N_{total}M}{V_{pore}}, \quad (5.9)$$

To determine the adsorption mechanism in kerogen, a comparison between the predictability of Langmuir [277] and Freundlich [278] isotherms are established; both isotherms were based mainly on chemical and physical adsorption principles respectively. The procedure detailed by Tian et al. [88] was adopted to compute the adsorbed gas volume and density by parameterizing the Monte Carlo simulation results with the three-parameter Langmuir and Freundlich isotherms. The Langmuir model, extensively applied to parameterize the adsorption for pressures up to 30 MPa (4,351 psi), was employed to determine adsorbed phase properties in this study as follows [88]:

$$n_{excess} = n_L \frac{p}{p_L + p} - \rho_{bulk}(p, T)V_{ads}. \quad (5.10)$$

where, V_{ads} (m^3), n_L (mol), and p_L (Pa) are adsorbed phase volume, maximum adsorbed capacity for the adsorbent, and corresponding Langmuir pressure respectively. Similarly, the Freundlich three-parameter empirical model was employed as follows [88]:

$$n_{excess} = k_f p^{\alpha_f} - \rho_{bulk}(p, T)V_{ads}, \quad (5.11)$$

where $k_f(mol)$ and α_f are Freundlich empirical constants. Consequently, the absolute adsorption capacity, $n(mol)$ was determined, once V_{ads} is determined from Eqs. (5.10) and (5.11) [76,88,279]:

$$n = n_{excess} + \rho_{bulk}(p, T)V_{ads}, \quad (5.12)$$

Finally, the adsorbed gas density is evaluated by utilizing the adsorbed gas volume and absolute adsorption capacity [88] obtained from both isotherms. They were compared against the simulation results.

5.2.5 MD self-diffusion calculations

Methane self-diffusion in the kerogen structure was investigated in the present research using molecular dynamics simulations. The self-diffusivity coefficient was extracted as the entrapped methane molecules in the kerogen reached Brownian motion [264]. In the simulation process, gas atoms changed positions and momenta when energized according to Newtonian equations of motion [264]. Effective diffusion in the kerogen matrix was primarily self-diffusion with a negligible cross-interaction coefficient, due to the small cell sizes [4, 11, 42]. The self-diffusion coefficient $D_{d,eff}$ along direction $d = x, y, z$ was computed with the Einstein relationship between $D_{d,eff}$ and the mean square displacement (MSD) of the molecules, as follows [6,17,135,150,280]:

$$D_{d,eff} = \lim_{t \rightarrow \infty} \frac{\langle |r^d(t) - r^d(0)|^2 \rangle}{2t}, \quad (5.13)$$

where, $\langle |r^d(t) - r^d(0)|^2 \rangle$ is mean-squared displacement (MSD) at time t in d -direction relative to initial coordinate (m^2), $r^d(t)$ and $r^d(0)$ are positions at time t in a given

direction and initial position respectively. The arithmetic average of diffusion coefficient in three dimension gives the methane diffusion coefficient D_{eff} , as follows:

$$D_{eff} = \frac{D_{x,eff} + D_{y,eff} + D_{z,eff}}{3}, \quad (5.14)$$

$D_{x,eff}$, $D_{y,eff}$, and $D_{z,eff}$ are the effective diffusivity coefficients in the x, y, and z directions, respectively. Technically, self-diffusivity is the slope of the mean MSD linearity over a time interval [264]. Prior to the computation of D_{eff} , the presence of Brownian diffusion is confirmed by checking for linearity and a unit gradient through a plot of $\log_{10}(MSD)$ versus $\log_{10}(t)$. In the present research, the effective diffusion coefficient was computed for the kerogen structures loaded with methane molecules based on the sorption calculations (ranging from 2.07 MPa up to 41.37 MPa) to investigate the impact of sorption on diffusion. For each sorption case, the tortuosity was calculated as the square root of the ratio of the equivalent diffusivity coefficient to the calculated self-diffusivity, using Eq. (5.15). The range of Knudsen numbers of the system was evaluated, and based on the classification by Sheng et al. [105], the transition diffusion coefficient was employed to compute the equivalent diffusion coefficient. The list of some recognized equations to describe gas diffusion within the transition diffusion regime was shown in **Table 5 (chapter 2)**. The widely known Bosanquet approximation was re-written (Eq. 5.16) as a harmonic average of Fick and Knudsen diffusion coefficients. Furthermore, the tortuosity factor model in Eq. (5.17) reflects the impact of two barriers: the tortuous pathways of the pore structure and the adsorption effect.

$$\tau_d^2 = \frac{D_{transition}}{D_{eff}} \quad (5.15)$$

$$D_{\text{transition}} = \frac{1}{\frac{1}{D_{\text{Knudsen}}} + \frac{1}{D_{\text{Fick}}}} \quad (5.16)$$

In other words, the tortuosity imposed by the kerogen structure was isolated by correcting for the adsorption effect by introducing $(\beta + 1)$ [34, 40, 54].

$$\tau_d'^2 = \frac{D_{\text{transition}}}{(\beta + 1)D_{\text{eff}}} \quad (5.17)$$

5.2.6 Physical properties of kerogen

The properties of the kerogen structure determined from the molecular simulation, as input parameters for adsorption and diffusion studies are summarized in **Table 17**.

Table 17 Molecular studies input parameters

Properties	Value
Volume of cubic simulation box, V_{total} (10^{-27} m^3)	19.32
Molecular weight of kerogen type, M_{ker} , (kg/mol)	2.47
Number of kerogen macromolecule units	5
Avogadro's number, N_A , ($10^{23}/\text{mol}$)	6.023
Mass of kerogen matrix, m_{ker} , (10^{-23} kg)	2.05
Density of condensed kerogen, ρ_{ker} , (kg/m^3)	1,000
Molecular diameter of methane, d_{mol} , (10^{-9} m)	0.38

Average pore radius, $\bar{r}$, (10^{-9}m)	0.3
Pore Volume, V_{pore} (10^{-27}m^3)	5.60
Porosity of condensed structure, ϕ (dimensionless)	29%
Molar mass of methane gas (10^{-3}kg)	16
Universal gas constant, R , ((J/K. mol)	8.314
Equilibrium temperature, T (K)	350

5.3 Results and discussion

5.3.1 Adsorption

A parameterization of the excess GCMC sorption data was needed to explore the kerogen adsorption behavior. The outcome was compared with what was obtained by the Langmuir and Freundlich isotherms. Prior to this analysis, NIST-miniREFPROP experimental database software [149] was employed to evaluate the density of methane in bulk phase, and its performance was compared against other routinely applied models. **Figure 26** shows a great deal of agreement among various databases of methane density as a function of pressure, and the dataset is available as **Table S1** in the supplementary materials.

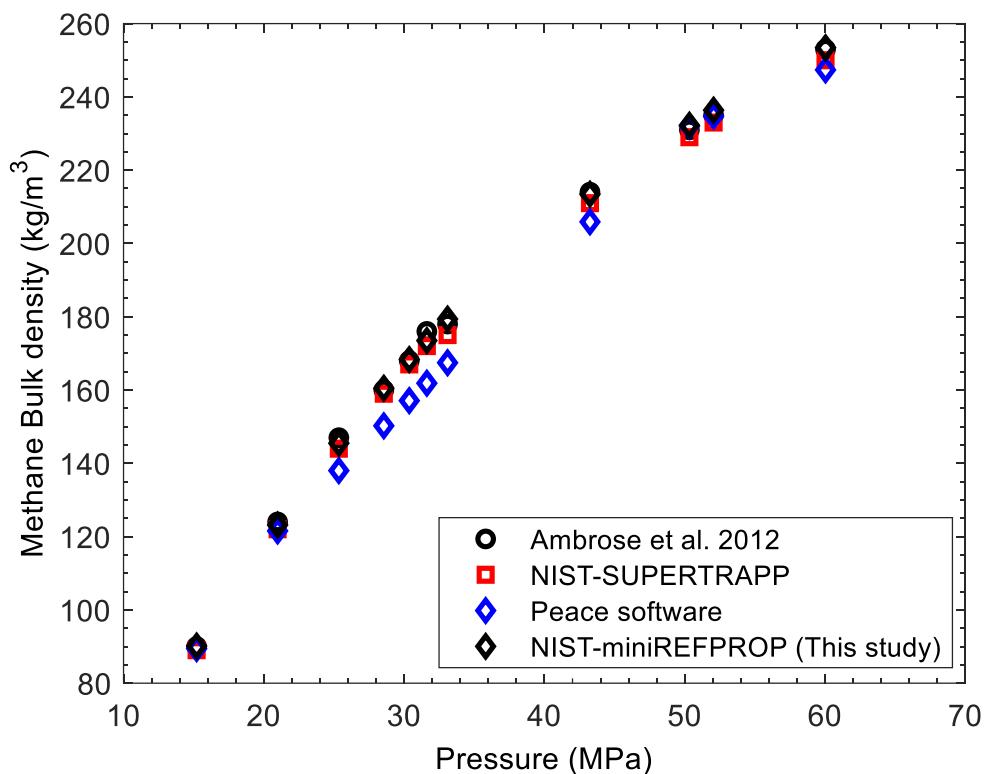


Figure 26 Bulk density validation of methane at a temperature of 350 K.

The chemical energy potential that was computed using LJ 9-6 is given in **Figure 27**. The potential energy is positively correlated to the pressure loading of gas molecules in the confined pore, which validates the observed adsorption behavior with pressure. The total amount of loaded gas molecules from GCMC simulation, recorded at each equilibrium pressure, coupled with the input parameters in **Table 17** is useful to assess the adsorption capacity of kerogen structure. Thus, the confidence in the results was improved by comparing with existing knowledge. Several researchers have parameterized the excess adsorption by utilizing the total methane loading from Monte Carlo simulation. **Figure 28** shows that the excess gas adsorbed in kerogen does not only vary with temperature and pressure, but also with kerogen maturity and origin [17,19,29,76,275] .

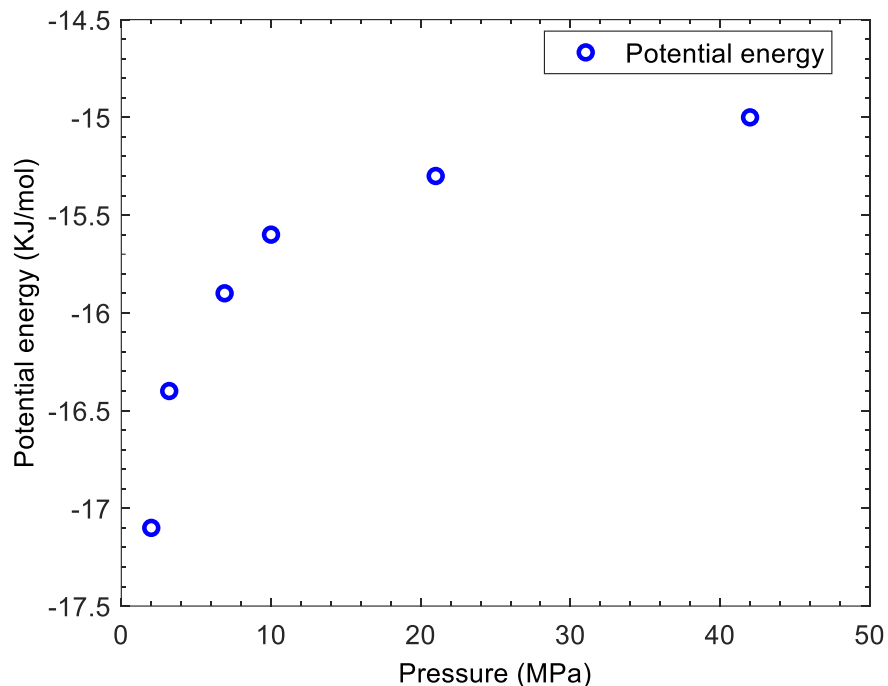


Figure 27 Potential energy of kerogen structure at different sorption states showing an increase in the attraction forces as the number of methane molecules decreases at low pressure.

Furthermore, the excess adsorbed amount from the Monte Carlo simulations that was parameterized with the Langmuir and Freundlich three-parameter isotherm is shown in **Figure 29**. Fitting the adsorption data using the Langmuir isotherm revealed an adequate level of decency up to 40 MPa in pressure; interestingly, other researchers [88,275,276] obtained similar trends. Conversely, the Freundlich isotherm's predictability was accurate up to a saturation pressure of 10 MPa, but it deviated with additional fitting errors above this pressure. **Table 18** summarizes the fitted model results for both isotherms, including the root mean square error (RMSE) and R-squared values.

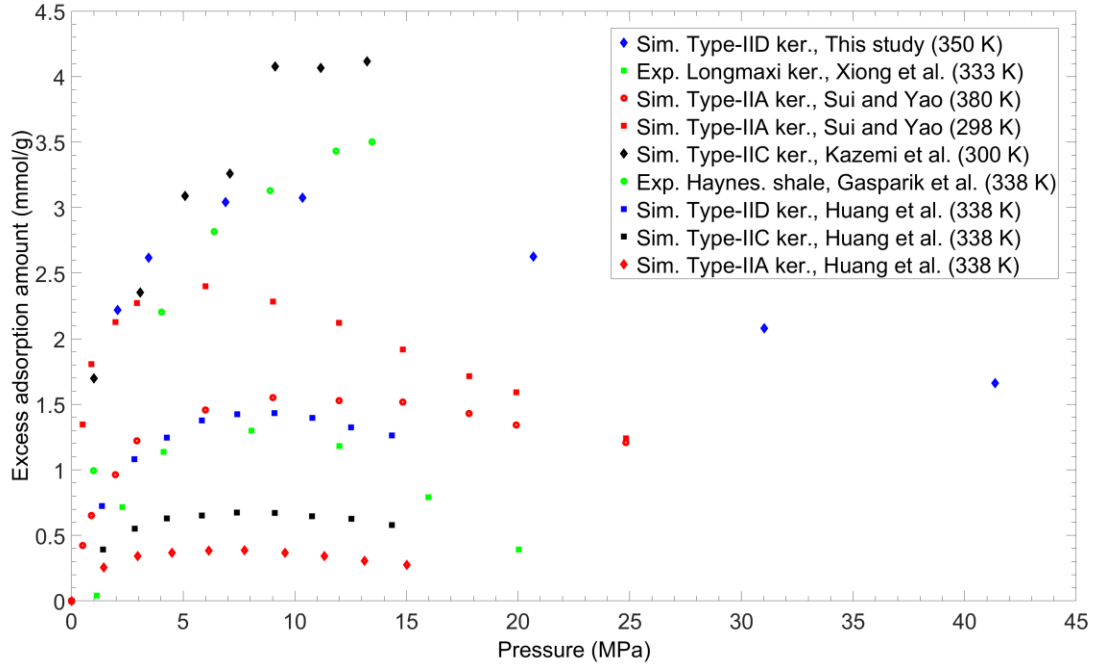


Figure 28 Validation of the GCMC-computed excess adsorption amount with experimental and simulation data obtained from the literature.

Table 18 Langmuir and Freundlich adsorption parameters of kerogen type II-D - methane at 350 K

Langmuir		Freundlich	
$n_L(10^{-23}\text{mol})$	9.4705	$k_f(10^{-26}\text{mol})$	8.9624
p_L (MPa)	2.02	α	0.4428
$V_{ads} (10^{-27}\text{m}^3)$	4.2743	$V_{ads} (10^{-27}\text{m}^3)$	13.385
R-squared	0.9978	R-squared	0.9890
RMSE	0.0225	RMSE	0.0503

Although the Freundlich model accounted for the physisorbed gas molecules in addition to the chemisorbed molecules (unlike the monolayer Langmuir model), the volume of adsorbed gas was overestimated and unrealistically more than the pore volume. In addition to the adsorbed gas, there was free gas present in the adsorbed gas phase [86,88]; thus, the

absolute adsorption capacity, which is the sum of the free and excess gas available in the adsorbed gas phase, was estimated using Eq. (5.12).

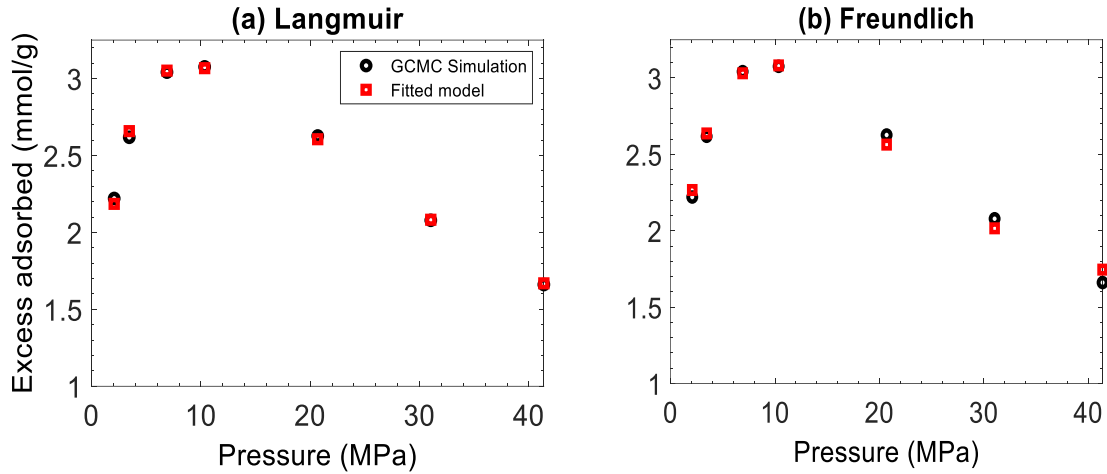


Figure 29 GCMC simulation and fitted isotherms for Type II-D kerogen at 350 K: a) Langmuir and b) Freundlich models.

The excess gas stored in the adsorbed phase increased steadily until it reached a saturation condition. Then, it began to decrease slowly above that pressure state. In general, as predicted by the Langmuir model, absolute gas stored in the sorbed phase increases steadily up to a maximum pressure, after which it reaches a plateau. The Freundlich isotherm's fitting results did not match the molecular simulation data.

The adsorption correction factor ($\beta + 1$) for the diffusion tortuosity was evaluated using Eq. (2.3) (chapter 2). Langmuir and Freundlich isotherms were used to approximate the sorbed phase density required to obtain β . The results were compared to what was obtained using the actual adsorption data from the GCMC simulation (**Figure 30**). Figure 30 shows that a single model may not be sufficient to provide information regarding the adsorption properties of kerogen. A combination of isotherms is needed to manage the uncertainty

better considering the lower and upper bounds. In this case, since the Langmuir trend predicts the adsorption factor with a relatively better precision than Freundlich, this may suggest that methane adsorption in kerogen porous structure is mainly of chemical rather than physical adsorption type, which agrees with previous research [18,19] observations. However, the behavior may be different for other cases depending on the pore scale, pressure and temperature conditions.

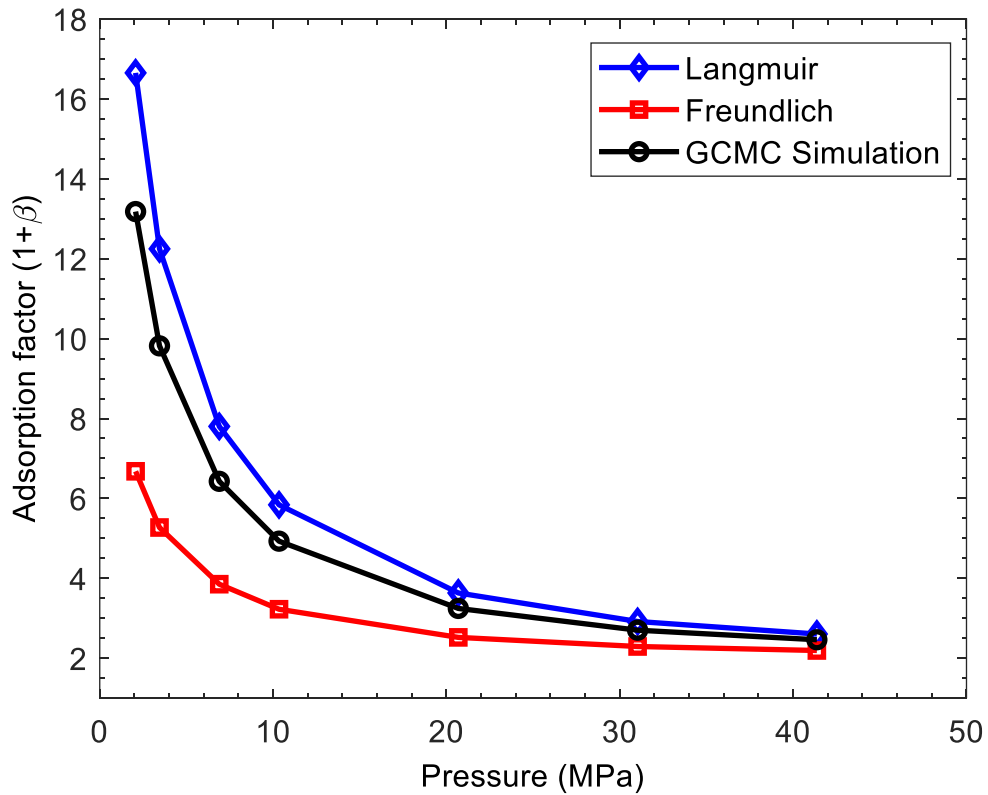


Figure 30 Tortuosity correction factor for the adsorption effect, as obtained by the GCMC simulations, Langmuir and Freundlich isotherms.

5.3.2 Effective diffusion and diffusion tortuosity

The kerogen structure, loaded with methane at the pressure range under consideration, was subjected to a diffusion analysis using Eqs. (5.13) - (5.17). From the axial position of the mass center, the MSD of the methane molecules in every 1 fs was recorded for 3,000 time-steps. An example of one of the measurements performed is presented in **Figure 31**. The slope of the MSD linearity was sufficient to calculate the self-diffusion coefficients of the methane [281]. It is noteworthy that the MSDs of the methane exhibited large fluctuations during the simulations, indicating that the kerogen model contained an abundance of small pore throats. The gas frequently jumped from small to large pores, due to non-Einstein diffusion [135]. Parallel and radial diffusion approaches can be used in the characterization of anisotropic diffusivity. Thus, effective diffusion is configuration-dependent. The calculations were repeated on three independent kerogen-methane configurations at each pressure stage to ensure a proper statistical representation. Given Figure 31, the presence of Brownian diffusion was confirmed through a plot of $\log_{10}(MSD)$ versus $\log_{10}(t)$, as the plot is approximately linear and has a unit gradient. The computed methane self-diffusion coefficient in the kerogen structure is between 1.44×10^{-9} and $2.90 \times 10^{-9} \text{ m}^2/\text{s}$ over the pressure range of 2.07 to 41.34 MPa. The order of magnitude of the methane self-diffusion coefficient in our simulation is in agreement with Collell et al. [150] ($3.2 \pm 1.8 \times 10^{-9} \text{ m}^2/\text{s}$ obtained for 20 structures of modified organic matter at 300 K and 20 MPa) and Sui and Yao [17] (1.45 to $3.05 \times 10^{-9} \text{ m}^2/\text{s}$ for type IIA kerogen within 1 to 30 MPa at 350 K). The average effective diffusion was used to obtain the diffusion tortuosity τ_d and the corrected value for the adsorption effect τ'_d (**Figure 32**).

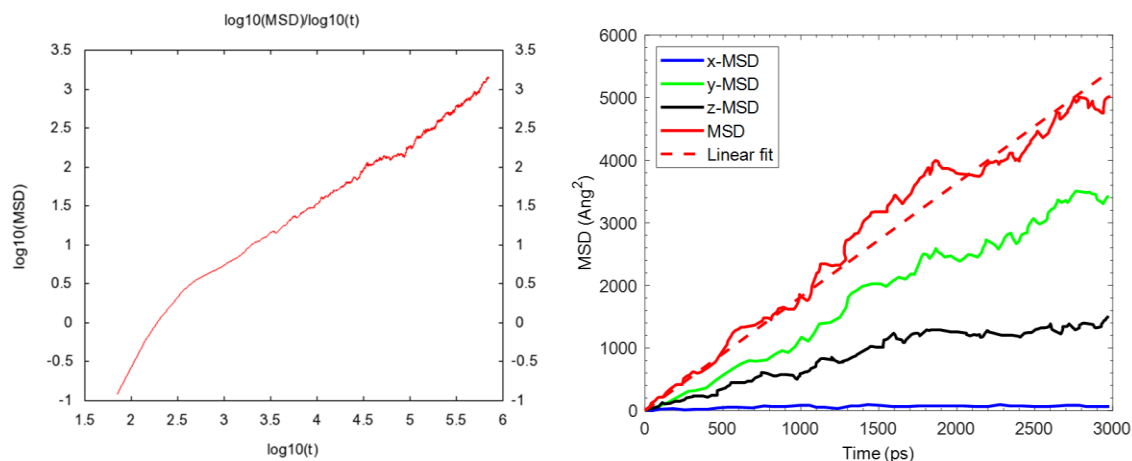


Figure 31 On the left a sample log-log plot of MSD versus time indicating a Brownian's motion state, and, on the right, the corresponding plot used to calculate the diffusivity coefficient.

The relative impact of the gas in the adsorbed phase on methane effective diffusion is low at elevated pressure state, and reaches a high value at low pressure. At a lower pressure of 2.0 MPa for instance, where the adsorption barrier factor was around 12 and the tortuosity was at its peak. Conversely, at a high pressure, the factor reduced to 2.2 and the tortuosity was at its lowest. The trend revealed that the sorption occurred simultaneously as the methane molecules moved from one point to another, limiting the effective amount of gas that diffused within the kerogen. The resistance imposed by adsorption reduced gradually as the structure was loaded with more methane molecules, indicating that the attraction energy exerted by the kerogen per molecule of methane decreased. Thus, the methane was able to diffuse more freely.

The diffusion tortuosity imposed by the pore structure of the kerogen was filtered from the adsorption effect using Eq. (5.17), as shown in **Figure 32**. The results revealed a tortuosity factor fluctuating around 2.55 at different pressure stages, with a 10% coefficient of variation (deemed acceptable for molecular calculations). It can be inferred that the molecular interactions between the kerogen and methane imposed an additional barrier. In

this study, the tortuosity increased from 2.52 to 9.02 at a low pressure, and from 2.74 to 4.26 at a high pressure; these findings have implications for the rate of recovery from such resources. The results are based on the specific kerogen structure considered in this study. The workflow adopted in this study can be applied to investigate the adsorption behavior for different kerogen configurations matching the characteristics of the formation of interest on a case-by-case basis.

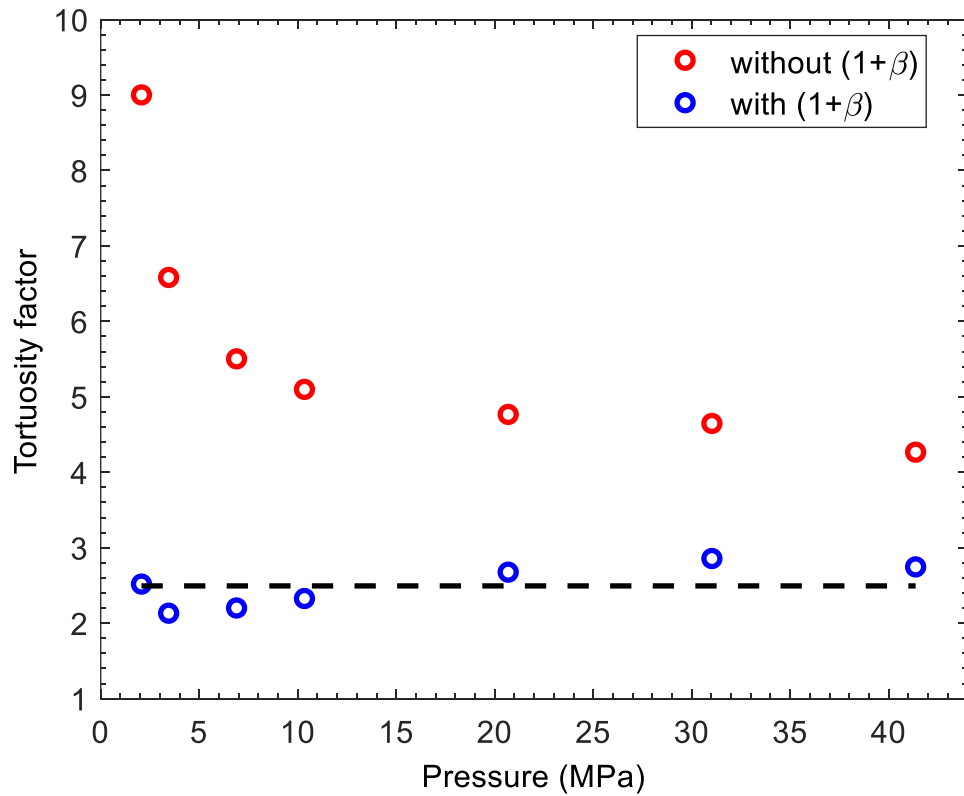


Figure 32 Diffusion tortuosity with and without the sorption effect. GCMC adsorption data were used to calculate the adsorption factor.

Kerogen diffusion data can be fed to a multiscale permeability model to investigate the impact of microscopic intricacies at some meaningful macroscopic level. The permeability model as proposed by Wasaki and Akkutlu [137] and Gangi [282] can serve as a proxy for that purpose. The model has been selected because it describes the multiscale transport in

a stress-sensitive matrix system, thus can be applied to model combined cracks of mesoporous scales, and diffusion in a coupled matrix-crack kerogen system for a pressure range typical to what is encountered during reservoir depletion.

5.3.3 Macroscopic shale permeability implications

The difficulty in describing the shale permeability arises from the different transport mechanisms that contribute to the total permeability (i.e. apparent permeability). Accurate assessment of the shale gas permeability is a vital task as it can greatly influence the anticipated production rate and the factors controlling it. Wasaki and Akkutlu permeability model [137] accounts for viscous flow in the cracks, surface diffusion flux, and self-diffusion flux hence reflecting the multiscale and multiphysics nature of shales. The conceptual kerogen model, modeled after Wasaki and Akkutlu [137] is shown in **Figure 33**.

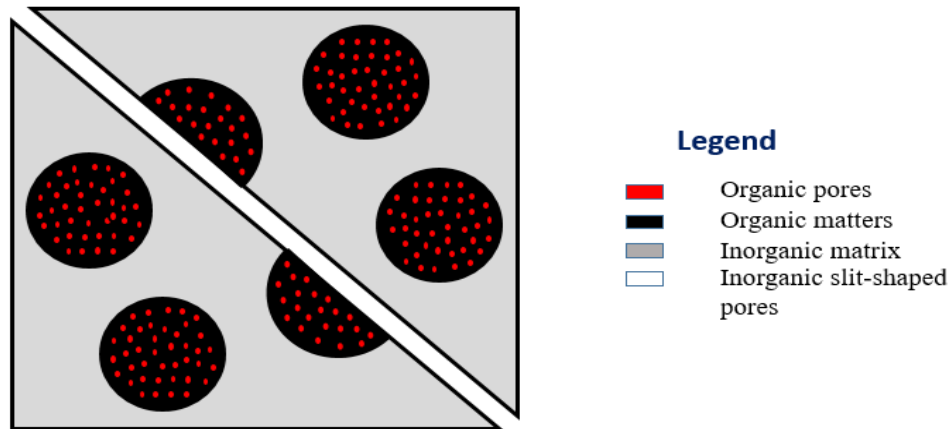


Figure 33 Conceptual kerogen - crack multiscale system

Wasaki and Akkutlu apparent permeability (k_{app}) can be calculated as follows:

$$k_{app} = k_m + \mu D_{eff} c_g + \frac{\mu D_s V_{sL} \rho_{grain} B_g}{\epsilon_{ks}} \frac{p_L}{(p + p_L)^2} \quad (5.18)$$

where $k_m, \mu, c_g, D_s, V_{sL}, \rho_{grain}, B_g$, and ϵ_{ks} represent permeability of slit shape cracks (m^2) as function of the effective stress, viscosity (pa.s), gas compressibility (1/pa), surface diffusion (m^2/s), Langmuir volume (m^3/kg), grain density (m^3/kg), gas formation factor, and total organic-grain volume per total grain volume respectively.

The first term in the previous equation is the permeability attributed to the viscous flow in the stress dependent cracks (k_m), second term accounts for the self-diffusion in the nanopores (k_{DT}), and the last term represents the surface diffusion (k_{Ds}). The first term can be estimated using Gangi model which was developed on the basis of permeability dependency on the stress [282], it has the following form:

$$k_m = k_o \left[1 - \left(\frac{(p_c - \alpha p)}{p_1} \right)^m \right]^3 \quad (5.19)$$

where, k_o, p_c, p_1, α , and m are zero-stress effective permeability (m^2), confining pressure (pa), stress required to close a slit shaped pore (pa), aspect ratio, and conductive pore geometry factor, respectively.

The focus of this study was mainly on self-diffusion, which is represented by the second term in Eq. (5.18). To investigate the impact of methane self-diffusion in kerogen, a case study was performed. The parameters used in this case study are based on published data for the Eagle Ford field which is shown in **Table 19** [137,159]. The gas properties such as

viscosity, gas formation volume factor and gas compressibility were computed with NIST miniREFPROP experimental database software.

According to Stoke's theorem, a laminar flow in a slit pore, can be estimated as follows [283]:

$$q = \frac{h^2}{12} \frac{h \cdot w}{\mu} \frac{\Delta p}{L} \quad (5.20)$$

where $h, L, \text{ and } w$ represent the height (m), length (m) and width (m) dimensions respectively of the slit shaped pore. Comparing that equation with Darcy equation, the crack width can be used to estimate permeability at zero effective stress [283]:

$$k_o = \frac{h^2}{12} \quad (5.21)$$

Five different cases were considered for the crack width including 2, 5, 10, 25, 50 nm. The contribution of self-diffusion permeability with respect to apparent permeability at different crack widths is shown in **Figure 34**. The self-diffusion importance gradually becomes negligible as the crack width approaches the upper limit of mesopores scale. For instance, at around 41 MPa, the contribution of pore diffusion dropped from 4% to 0.007% for 2.0 nm, and 50 nm pore size respectively. Generally, effective pore diffusion plays a significant role as the pore pressure drops for smaller cracks (i.e. inorganic slit pores).

Table 19 Parameters used for the case study.

Reservoir properties		
Porosity, ϕ	0.06	---
Sorption properties		
Grain density, ρ_{grain}	2659.06	kg/m ³

Total organic grain volume per total grain volume, ϵ_{ks}	0.01	---
Langmuir volume, V_{sL}	3.12×10^{-3}	m^3/kg
Langmuir pressure, p_L	1.379×10^7	pa
Surface-diffusion coefficient, D_s	10^{-9}	m^2/s
Gangi model parameters		
Permeability at zero effective stress, k_o	$h^2/12$	mD
h	2, 10	m $\times 10^{-9}$
m	0.5	---
p_1	1.793×10^8	pa
Confining pressure, p_c	1.034×10^8	pa
Effective-stress coefficient, α	0.5	---
Gas properties		
Gas composition	C_1 - 100%	

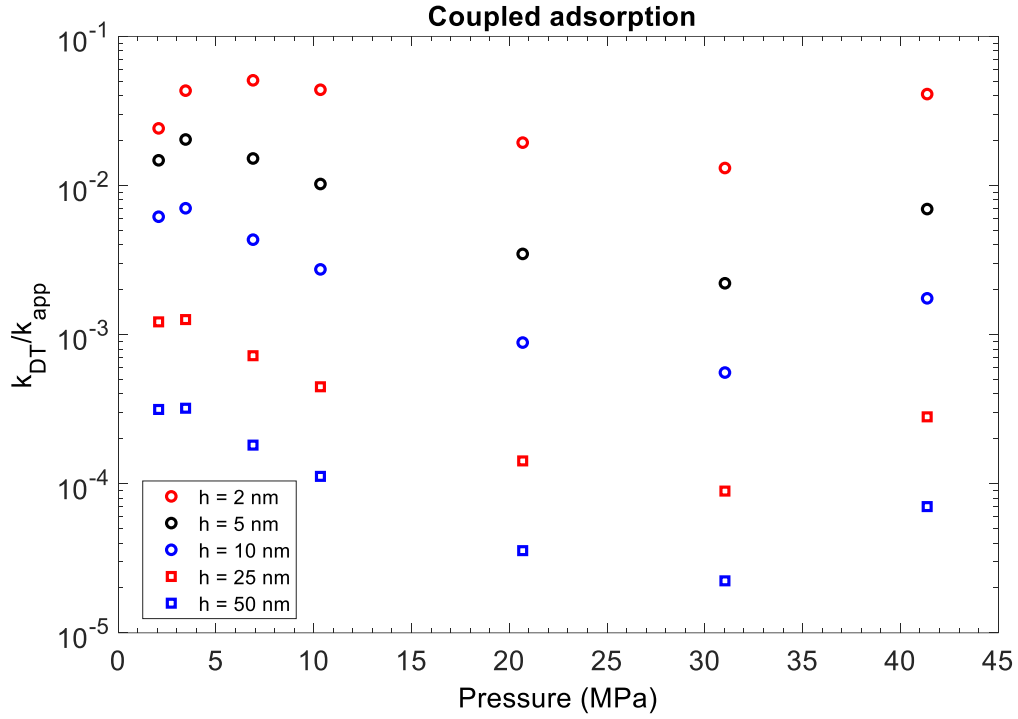


Figure 34 Fraction of the diffusion permeability to the apparent permeability as a function of crack width

Figure 34 shows that the contribution of the pore diffusion is below 10% for all considered crack sizes. Decoupling the adsorption effect from the diffusion can be erroneous especially at lower pressure. The contribution of diffusion to the total permeability, for instance, appeared to be around 10% and 0.05% for a crack size of 10 nm when adsorption effect was decoupled and coupled, respectively at 2.067 MPa (**Figure 35**). The severity of overestimating the diffusion can be seen higher for the smaller crack sizes. Therefore, ignoring the adsorption effect could lead to a misleading result, such as overestimating the permeability by a factor of 3.5 to 4 times at high pressure and by 13.9 to 16.5 at low pressure.

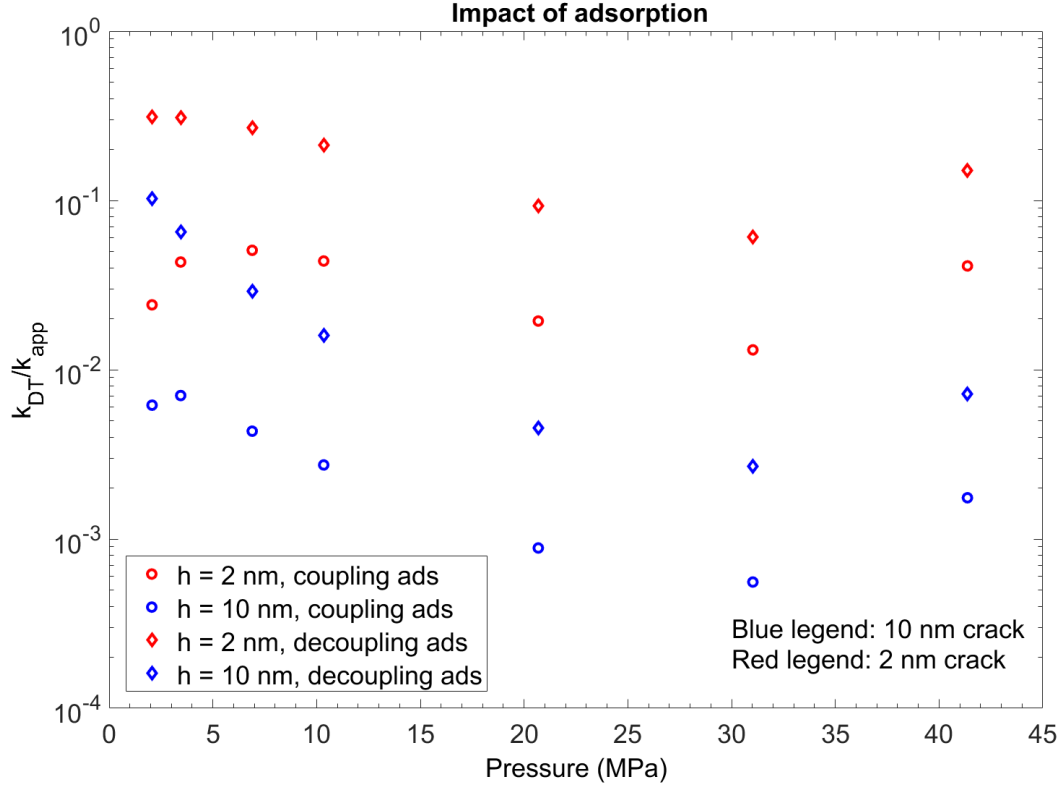


Figure 35 Relative contribution of diffusion for cases when the adsorption effect on diffusion is coupled and decoupled at crack width of 2.0 and 10 nm.

5.4 Conclusions

This work explored the impact of adsorption on methane diffusion tortuosity in a representative kerogen structure. The following major conclusions were drawn:

- Kerogen is a highly tortuous confined mesoporous medium. A realistic kerogen structure can be formed from single kerogen macromolecules through molecular dynamics simulation.
- Methane recovery from kerogen is believed to be controlled by self-diffusivity. The degree of tortuosity reduces the methane diffusion coefficient from the theoretically calculated value.

- Kerogen exerts some attraction forces on methane, causing physi- and chemisorption. Adsorption effects impose an additional barrier on methane self-diffusivity.
- The adsorption effect can be parameterized by adsorption isotherms such as Langmuir and Freundlich.
- In this study, tortuosity was augmented by the adsorption effect. It was increased by a factor of 2.0 to 3.6 compared to an adsorption-corrected tortuosity and depending on the pressure state.
- The role of diffusion is very sensitive to the size of the cracks present in the rock. Diffusion is anticipated to have a significant role for smaller cracks.
- Decoupling the adsorption effect when calculating the self-diffusivity could significantly overestimate the total permeability.
- It is recommended that the findings of this work be validated experimentally and extended to the investigation of other kerogen types and inorganic constituents that exhibit high adsorption behavior.

CHAPTER 6

MODELING OF NATURAL GAS SELF-DIFFUSION IN THE MICRO-PORES OF ORGANIC-RICH SHALES COUPLING SORPTION AND GEOMECHANICAL EFFECTS³

Abstract

A significant amount of the natural gas in shale formations is contained in the micro- and mesopores as dissolved (absorbed) phase and on the surfaces of associated microcracks as (adsorbed) phase. The transport of natural gas in such confined spaces is primarily governed by self-diffusion as could be deduced from Knudsen number. Self-diffusion is governed by the pressure and the space confinement. In this study, realistic kerogen structures possessing both tortuous micropores and larger microcracks were formed and used to assess self-diffusion behavior during the depletion of shale reservoirs through some comprehensive molecular simulation workflow. Analysis of the transport modes revealed

³ This chapter is copied from the manuscript: **C Afagwu**, S Alafnan, M Mahmoud, W. Akkutlu (2022). Modeling of natural gas self-diffusion in the micro-pores of organic-rich shales coupling sorption and geomechanical effects. Journal of Natural Gas Science and Engineering, 104757

transition self-diffusion as the primary transport mechanism in these micropores. The sorption behavior and the mechanical properties were analyzed and incorporated to derive a transition diffusion model that is sensitive to changes in the pore pressure and the stress field. The proposed model was compared and validated against similar work in the literature. The results showed that during a typical production span, a pressure drop influences the sorption profile, the net overburden stress on the pores, and the mean free path, altering the magnitude of self-diffusivity. The calibrated pore scale model produced decent predictive ability with a relative error of 2.5–16%. The implications of structure tortuosity, sorption profile, and pore pressure on the effective diffusion coefficient and gas desorption are discussed in depth. This work provides a novel methodology for studying the effect of coupled multiphysics processes on methane transport in a realistic kerogen geometry, which could be used to calibrate a suitable pore scale model for upscaled reservoir simulation applications and accurate assessment of reservoir dynamics and ultimate recovery.

Keywords: Kerogen micropores, Effective methane diffusion, Geomechanics, Sorption, Molecular dynamics

6.1 Introduction

Kinetic theory of gases offers some framework to describe molecular diffusion taking into consideration the mean free path that is primarily controlled by the pressure and the pore size. However, such an idealistic approach fails to account for organic micropores intricacies such as fluid-wall induced interactions, tortuosity of pores, and changes in the pore size as the net overburden pressure varies during the production scheme [284].

Over the years, many studies have discussed the role of diffusion in transport processes [6,13,144,150,206]. Beside the porous structure, the chemical and physical interactions between the heterogeneous organic materials and gas result in additional restriction to the movement of molecules. Both experimental [111,129,142,148] and simulation studies [135,145,285,286] have been carried out to understand the impact of adsorption alongside the pore distribution on methane diffusion in kerogen. The affinity between kerogen and methane adds more restriction to the diffusion [286].

Upon reservoir depletion, shales experience an increased net confining stress acting to restrict fluid flow in the larger pores [170,206,287–290]. In some studies, porosity-transport, stress-porosity and stress-permeability relationships were developed, and results have shown that these correlations could be modeled using exponential, power law functions, and Hooks' law models. Some of the outcomes from similar studies [118,170,288,289,291] have consistently hinted that shale containing slit-shaped pores and micro-fractures are more affected by changes in the stress field. It was observed that the effect of confining pressure is more pronounced on permeability than porosity [289]. Induced stress will result in actual low recovery rate, such that a large proportion of the gas would not be recovered [170,292]. The changes in the field stress could affect the integrity of the organic micropores as well. The response of organic materials to changes in the stress is, however, ambiguous with little insights available in the literature owed to the occurrence of organic materials as nano-scale constituents which limits direct assessment of their mechanical behavior [293].

Quite a number of shale transport models to a large extent mainly captured the effects of different physics by utilizing a realistic kerogen system [113,143,207] or carbon nanotubes

[91]. However, high resolution scanning electron microscopy (SEM) images employed in several studies to examine shale samples in major plays have shown cracks of different sizes in some organic-rich shale (**Figure 36**). These microcracks are most likely developed during oil and gas generation in the organic microstructure [32,33,294]. Hence, organic materials constitute smaller tortuous micropores (i.e. pore size less than 0.5 nm) which offers active spots to absorb gas and larger microcracks that host methane as free compressed gas and adsorbed on their surfaces. The net amount of gas in such systems is referred to as sorption (i.e. sorption is the summation of adsorption and absorption) [10,106]. Accurate modeling of the gas transport necessitates updating diffusion models with the active sorption.

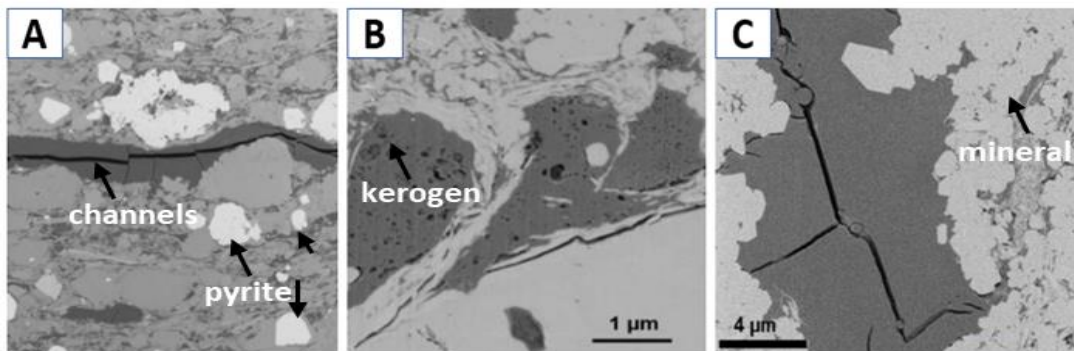


Figure 36 SEM images [283,294] showing organic matter (OM) in darker color a) Bakken shale with slit-shaped cracks dominated transport network within the OM [294] b) Woodford shale with cylindrical pores distributed within the OM [294] c) Avalon shale with multiple slit-shape cracks cutting through OM.

In assessing the molecular diffusion of methane in the organic materials of shales, organic samples similar to those shown in Figure 36 are needed. This could be achieved through either experimental extraction followed by diffusivity measurements or replication of such systems on a computational platform. While the former offers a direct approach, the preservation of the structure and its associated micropores structures is uncertain during pyrolysis [295] and faces some technical limitations [296–298]. The recreation of organic

materials on a computational platform, on the other hand, offers more flexibility in delineating multiple factors. Starting from realistic kerogen structures, thorough assessment of the sorption profile, self-diffusion, and mechanical properties are conducted and incorporated to derive a diffusion model for methane in the organic materials of shales. The remainder of this research is organized as follows. Flow regime in kerogen highlighting the significance of self-diffusion has already been presented in chapter 2. The sensitivity analysis in Figure 10 (section 2.2) showed that the methane transport mechanism of kerogen micropores is primarily controlled by the transition regime. For this reason, the well validated self-diffusivity model developed in this study will be valid within the transition domain. The methods adopted for this work such as the MD simulation protocols, mechanical assessment approach, pore size characterization, sorption modeling, diffusion tortuosity calculations, and effective diffusion model development are outlined in section 6.2. Results and model validation are executed in section 6.3. A detailed explanation of the multiphysics and microstructural implications on methane transport are detailed in discussions section 6.4. Finally, limitations and opportunities to close some research gaps are provided in section 6.5, while conclusions are available in section 6.6.

6.2 Methodology

Figure 37 shows the schematic of the kerogen system consisting of kerogen that has tortuous micropores of cylindrical shape and microcracks mimicking observations made from SEM shale plays [294]. In the organic materials, cylindrical micropores are tortuous of sizes less than 0.5 nm while microcracks are slit-shaped pores of sizes ranging from 0.5 to 2.0 nm. Dissolved molecules in the cylindrical pores and adsorbed molecules in the microcracks diffuse through the kerogen microstructure to the inorganic matrix.

Typically, reservoir rocks are under coupled net overburden stress and sorption dynamics loading processes that causes a reduction in representative pore size for gas transport. Methane self-diffusivity in this study was computed for both realistic kerogen geometries under sorption loading using combined Grand Canonical Monte Carlo (GCMC) ensemble and MD simulation approach.

The methods employed in this study are as follows. Realistic kerogen structures formed from the individual macromolecules of type II-D were formed following the procedure outlined in previous research [206,286]. The kerogen macromolecule's atomic centers interact within the same unit and with centers in other units through 9-6 Lennard Jones potential. The extension of the polymer consistent force fields (PCFF+) force field was utilized in the present simulations to parameterized the atomic centers. PCFF+ is an extension of the PCFF class II force field developed in the 1990s for modeling a variety of polymers and organic materials as a continuation of the earlier efforts of force fields such as COMPASS and CFF93 [272]. The Waldman and Hagler mixing rules [273] were used to describe the self and cross atom-atom parameters. The explicit LJ and Coulombic interactions between assigned atomic charges was evaluated at a cutoff distance of 9.5 Å. This threshold was employed successfully in various MD simulations with kerogen models. Additionally, tail corrections in LJ energy were applied beyond the cutoff radius [88,267]. While the particle-particle-particle mesh (PPPM) coupled with the Ewald summation approaches [88] were used to calculate long-range coulomb interaction energies in the MD simulations with Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) and the Monte Carlo (MC) simulations with GIBBS.

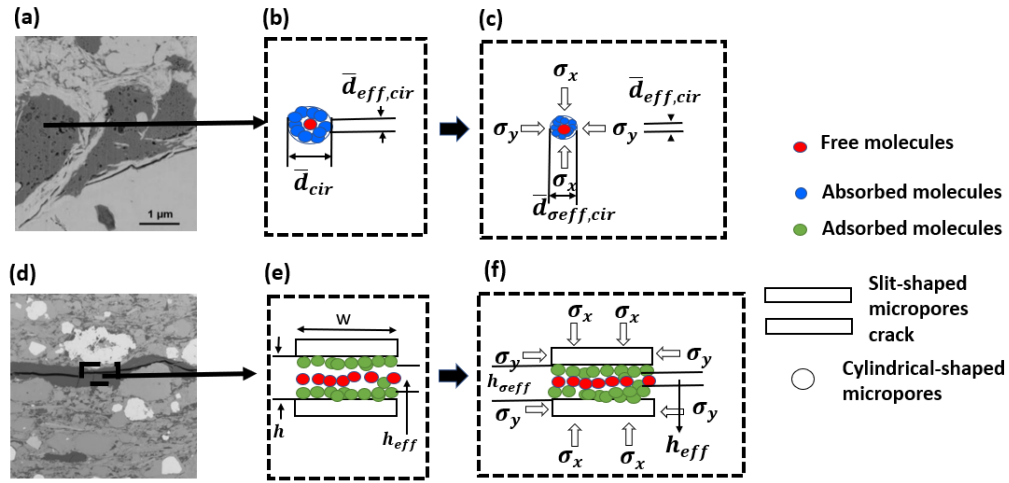


Figure 37 A 2D Schematic of pore diffusion in kerogen nanopores and cracks under coupled stress regime and sorption effect. a) SEM image showing organic matter in darker color with mainly cylindrical tortuous pores distributed within the organic matter [294] b) A conceptual view of the micropores with initial diameter of $\bar{d}_{cir}$ and an effective circular pore diameter in no-loading condition is $\bar{d}_{eff,cir}$ c) Under stress regime, the circular pore diameter is $\bar{d}_{seff,cir}$ and its effective circular diameter corrected for sorbed gas layer thickness is $\bar{d}_{eff,cir}$ d) SEM image showing organic matter in dark color and cracks in black cutting through it [294] e) A conceptual view of a crack with width, w and height, h with no loading but corrected for adsorption to give effective pore height, h_{eff} f) Under loading effect, the pore height is h_{seff} and correction for adsorbed gas layer gives an effective pore height, h_{eff} .

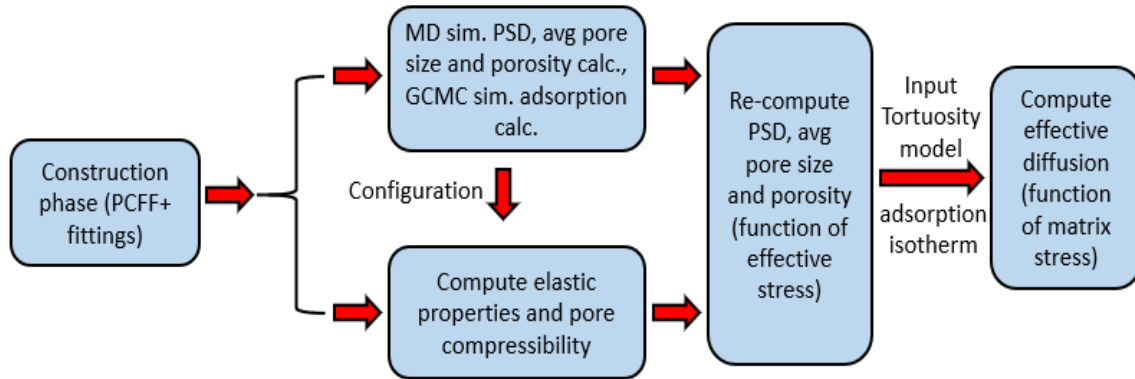


Figure 38 Adopted abridged workflow for the case study of self-diffusion in cylindrical pore considering the impact of pore compressibility

The Class II PCFF + force field energy expression utilized to describe the non-bonded interactions between different atoms in the modified kerogen structure and methane gas

can be written as follows [272,273]:

$$E^{NB} = \varepsilon \left[2 \left(\frac{r^*}{r_{ij}} \right)^9 - 3 \left(\frac{r^*}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}, \quad (6.1)$$

where, E^{NB} is potential energy resulting from the non-bonded interaction forces between atoms (*Joules*). r_{ij} is the distance between atoms i and j (m), r^* is distance at which the interaction potential between pairs of force centers exhibits a minimum (m), ε is the depth of the potential well (*Joules*), q_i and q_j are charges of atoms i and j respectively, and ε_0 is dielectric constant. Subscripts i and j refer to atoms of the same and different types in the kerogen structure and methane gas. The Waldman and Hagler combining rules utilized to compute LJ parameters between unlike atoms of type i and j , and is given as follows [273]:

$$r^* = \left(\frac{(r^*_{,i})^6 + (r^*_{,j})^6}{2} \right)^{1/6}; \quad \varepsilon = 2\sqrt{\varepsilon_i \varepsilon_j} \left(\frac{(r^*_{,i})^3 (r^*_{,j})^3}{(r^*_{,i})^6 + (r^*_{,j})^6} \right). \quad (6.2)$$

Three kerogen structures at some ranges of density were obtained by performing the following procedures. The first structure was constructed by placing twelve type II-D macromolecule units in a low-density cell with full periodic boundary condition, followed by a sequence of velocity initialization, energy minimization, isochoric-isothermal (NVT) ensemble for 200 ps at high temperature and 1.0 fs time step. Isobaric-isothermal (NPT) ensemble stages were performed for 250 – 400 ps at a decreasing temperature until a final temperature of 350 K was attained at the same time step. The initial high temperature was used to accelerate the relaxation process of molecules. The two additional structures with modified microporosity were constructed as follows. During the initialization process,

some molecular directors (i.e., heptane) were inserted and removed upon forming the final structure to control porosity. Aljaberi et al. [206] and Afagwu et al. [286] in their works described the entire procedures utilized to build the porosity-controlled kerogen structures similar to the ones employed in this study. The final structures resemble kerogen with cylindrical tortuous micropores of sizes less than 0.5 nm. Such pore spaces intake methane in the absorbed state. The workflow illustrated in **Figure 38** was employed for full assessment of kerogen mechanical properties, pore size distribution, sorption and self-diffusivity of methane in the associated pore spaces.

Furthermore, a novel methodology was utilized to construct some realistic slit-shaped kerogen pores. The initial kerogen structure was compressed using the compression module of Mede LAMMPS where a target density was set and the thickness in the z-direction was modified accordingly. This was followed by an energy minimization and NVT ensemble for 100 ps. This outlined process forms a kerogen slab. Stacking two slabs at some predefined distance yields a slit-shaped pore of a desired size [299]. Several slit-shaped structures of different pore volumes with same square geometry of 40 by 40 Å were created by mirroring the kerogen slabs at different separation of 5, 10, and 15 Å. A freezing feature in MedeA was used to fix the kerogen molecules in place during subsequent MD calculations. Such systems of slit-shaped pores of the aforementioned sizes offer active sites for methane adsorption on the surfaces rather than absorbed or dissolved within the kerogen tortuous smaller pores. The important molecular simulation parameters for parametrizing kerogen and methane atoms are available in **Table S1** and **Table S2** respectively of the supplementary materials.

6.2.1 Mechanical properties assessment

Understanding the mechanical properties of kerogen is a vital task to predict the structural changes during typical production span. Molecular simulation can be invoked to delineate the changes in the pore size as a function of net overburden stress.

Cubic systems are the simplest where the elastic constants can easily be modeled because their stiffness matrix contains only three independent constants, such as the two Lamé's constant, λ and μ , in addition to p-wave modulus of elasticity, M . Other systems with above four elastic constants are triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal systems. The unit cell of a cubic structure, which is a Bravais lattice vector, $\vec{L}(L_x \ L_y \ L_z)$ changes to $\vec{L}'(L'_x \ L'_y \ L'_z)$ in a changed stress field condition (m), and their relationship gives the elements of the strain tensor as follows:

$$\frac{\vec{L}'(L'_x \ L'_y \ L'_z)}{\vec{L}(L_x \ L_y \ L_z)} = \begin{pmatrix} 1 + e_{xx} & \frac{1}{2}e_{xy} & \frac{1}{2}e_{xz} \\ \frac{1}{2}e_{yx} & 1 + e_{yy} & \frac{1}{2}e_{yz} \\ \frac{1}{2}e_{zx} & \frac{1}{2}e_{zy} & 1 + e_{zz} \end{pmatrix}. \quad (6.3)$$

The deformation leads to change in total energy, represented as follows:

$$U = \frac{E_{total} - E_0}{V_0}, \quad (6.4)$$

where, E_{total} is total energy of the system after deformation (Joules), E_0 is energy of unrestricted cell, and V_0 is the volume of the unrestricted cell (m^3). The changes in total energy is related to the elements of the stiffness matrix, C_{ij} as follows [300]:

$$U = \frac{1}{2} \sum_{i=1}^e \sum_{j=1}^e C_{ij} e_i e_j, \quad (6.5)$$

where, i and j runs from 1...6 in the sequence $\{xx, yy, zz, yz, xz, xy\}$, that is, $e_i =$

$|e_{xx}, e_{yy}, e_{zz}, e_{yz}, e_{xz}, e_{xy}|, e_j = |e_{xx}, e_{yy}, e_{zz}, e_{yz}, e_{xz}, e_{xy}|^T$, 'T' signifies transpose, thus, Eq. (6.3), gives rise to a stiffness matrix, C_{ij} with 36 elements. Meanwhile, only 21 elements are maximally independent. The least square method can be used to calculate the elastic coefficients for the crystal structure, and has been implemented in this study, where, $C_{11} = M, C_{12} = \lambda, C_{44} = \mu = G$ is shear modulus and Bulk modulus, $K = (C_{11} + 2C_{12})/3$ [301]. Le Page [300] showed that the result from this approach matches experimental results for a number of elements and compounds spanning a range of crystal symmetries. Notably, the inverse of the stiffness matrix gives the compliance matrix, $S_{ij} = C_{ij}^{-1}$. In the same vein, the other elastic constants, and moduli like young's modulus, can be obtained from the compliance matrix, as, $E = 1/S_{11}, S_{12} = \nu/E$, and $S_{44} = 1/G$, where ν is Poisson ratio. Birch [302] summarized the relationships between the elastic parameters and moduli. Unlike the mean crystal system, the effect of temperature is significant in harmonic lattice, so it is important to integrate the coefficient of thermal expansion when describing the material deformation [301,303]. Thus, the procedure outlined by Mayer [301], that integrates the coefficient of thermal expansion in the modified stress-strain model could be employed. Even if the parent material is homogeneous and ordered, the unit cells may vary in arrangements. For this reason, the application of the method described with Eqs. 6.3, 6.4 and 6.5 in a system with an imperfect arrangement of lattice structure will give erroneous results.

In this study, the Hill-Walpole equation was employed in the MedeA environment to compute the elastic properties at nanoscale. The strain can be applied in any direction of interest. In our case, the kerogen structures were strained in different directions to assess the mechanical elastic moduli by applying an axial load. Then, a pressure was applied in

an orthogonal direction to the kerogen structure to mimic the confining stress that is experienced in the reservoir. **Figure 39** presents the summarized steps employed to compute the pore compressibility. The bulk kerogen was considered in the elastic moduli calculations. The stress-strain relationship was obtained through energy quantification using molecular dynamics before and after deformation. Consequently, the pore size distributions were evaluated pre- and post-deformation and energy quantification to study the impact of pore compressibility on Bhattacharya and Gubbins number of pores size distribution.

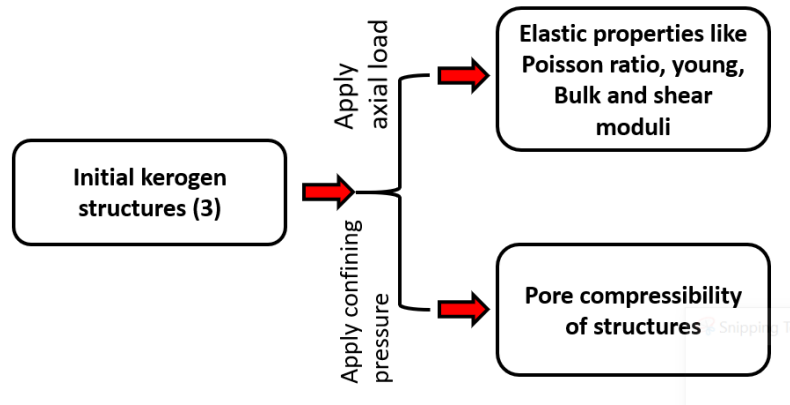


Figure 39 Summarized steps employed to compute elastic properties and pore compressibility in this study

6.2.2 Pore structure characterization

A non-overlapping sphere insertion method introduced by Bhattacharya [268] was employed to characterize the pore sizes of the structures. Spheres of different sizes are placed at the vertices of a polyhedral and some points are distributed randomly in the structure. A point is selected randomly as the sphere center, and the distance between that biggest possible radius of that sphere and a non-overlapping nearest solid must satisfy Eq. 6.6. The procedure is repeated for pre-defined spheres, to obtain a normalized PSD (Eq.

6.7). Consequently, the number of each pore size and pore volume is calculated at each point. Gaussian distribution function (Eq. 6.8) was another approach utilized to describe the local heterogeneity of the micropores circular geometry in order to probe the most suitable of both methods for obtaining a representative pore size in this study.

$$r_{ij} \geq \frac{\sigma_i}{2} + r, \quad (6.6)$$

$$\int_0^{+\infty} P(r)dr = 1, \quad (6.7)$$

$$P(r) = \frac{\alpha_r}{\sqrt{\pi/2}r_{SD}} \exp\left(-2\left(\frac{r - r_{mean}}{r_{SD}}\right)^2\right), \quad (6.8)$$

where, r_{ij} is distance between the nearest solid and sphere center (m), σ_i is LJ diameter of the nearest particle (m), r is admissible sphere radius which could be the biggest sphere radius (m), $\alpha_r = 1$ represents the relative proportion of the distribution, r_{mean} is mean pore radius (m), and r_{SD} is the standard deviation of pore radius (m). The most suitable pore distribution function for computing the typical pore radius ($\bar{r}_{cir}$) for each kerogen pore is still uncertain at this stage as it depends on pore heterogeneity. In this study, a robust fitting process of the computationally measured diffusion and validated proposed model will be utilized to determine the typical pore radius. The fitted pore size will be compared to the average of the minimum (r_{min}) and maximum pore size (r_{max}) obtained from Bhattacharya PSD profile and the modal size from Gaussian method. Porosity is the ratio of total pore volume (V_{pore}) and the bulk volume of the condensed structure (V_{total}), assuming a fully connected pore network model. This assumption is valid in micropores [304]. After deformation of the structures on the z-direction and energy quantification changes, the distribution of micropores was re-calculated, and the impact of pore compressibility on PSD was presented in the results section.

6.2.3 GCMC sorption calculations

The absorbed and adsorbed gas molecules were computed in the different configurations of kerogens through running Gibbs calculations. Chemical potential, volume and temperature of the adsorbed molecules were the fixed parameters (i.e., as input) in the GCMC ensemble [270]. Methane chemical potential was estimated as follows [86]:

$$\mu_i = \mu_{io} + RT \ln \left(\frac{\hat{f}_i^v}{\hat{f}_{io}} \right), \quad (6.9)$$

where, $R = 8.314 J/(K.mol)$ is the universal gas constant, T is the absolute temperature (K), i represents methane; μ_i and $\hat{f}_i^v = y_i p \hat{\phi}_i$ are the chemical potential ($J/mole$) and fugacity (Pa) for methane in the vapor phase, respectively. $\hat{\phi}_i$ is the fugacity coefficient of real methane gas, $\hat{f}_{io} = p \hat{\phi}_{io}$ is the fugacity of ideal gas, and $\hat{\phi}_{io} = 1$, is the fugacity coefficient of an ideal gas. The fugacity coefficient was calculated with the Peng-Robinson equation of state [76]. Fugacity of a real gas is the effective partial pressure, which corrects for the non-ideality of the gas molecules as operating condition changes. The real gas effect is very critical at high gas pressure states (**Table 20**).

Table 20 Fugacity of methane gas at 350 K

Pressure (MPa)	2.067	3.445	6.890	10.335	20.670	31.010	41.340	82.68
Fugacity (MPa)	2.028	3.340	6.494	9.503	18.056	26.958	35.842	86.43

Methane molecules were loaded in the pores during the GCMC simulation and Gibbs' number of loaded gas molecules N_{am} at a wide pressure range and equilibrium temperature of 350 K were calculated. Furthermore, the total number of loaded methane molecules at each simulation pressure were parameterized with, $N_{total} = N_{am}/N_A$ [274]. The dimensionless output was expressed in moles. Dissolved and gas density respectively was obtained as follows:

$$\rho_{abs} = \frac{N_{total}M}{V_{pore,kerogen}}; \rho_{ads} = \frac{N_{total}M}{V_{pore,slit}}, \quad (6.10)$$

where, $N_A = 6.023 \times 10^{23}$ (number of molecules/mole) is the Avogadro's number of molecules present in one mole of gas, $V_{pore,kerogen}$ is total bulk volume of the tortuous pores in the kerogen (m^3), $V_{pore,slit}$ is pore volume of slit-shaped pore system (m^3), and M is gas molecular mass per mole (kg/mol). Similarly, the sorption equilibrium factor, β , that quantitatively describe the relative density of sorbed layer to the bulk phase as pressure changes was defined as follows [129,135,148]:

$$\beta_{abs} = \frac{\rho_{abs}}{\rho_{bulk}}; \beta_{ads} = \frac{\rho_{ads}}{\rho_{bulk}}, \quad (6.11)$$

where ρ_{bulk} is the bulk gas density (kg/m^3) computed with NIST miniREFPROP experimental database software [149]. Alternatively, the density ratio was computed with Langmuir sorption isotherms, which has been successfully utilized to provide the best fit in kerogen [286]. First, excess amount of sorbed gas hosted per unit mass of condensed geometry system (m_{ker}) was evaluated from the GCMC simulation output by discounting the free gas present in the pore volume as follows:

$$\hat{n}_{excess} = (N_{total} - \rho_{bulk}V_{pore}/M)/m_{ker}. \quad (6.12)$$

The calculated specific excess sorption for each geometry using Eq. 6.12 was fitted to a Langmuir isotherm (Eq. 6.13) to determine the specific Langmuir amount ($\hat{n}_L$) and corresponding pressure (p_L), where M is methane molecular weight.

$$\hat{n}_{excess} = \hat{n}_L \frac{p}{p_L + p} - \frac{\rho_{bulk}(p, T)V_{pore}}{m_{ker}M}, \quad (6.13)$$

$$\hat{n} = \hat{n}_L \frac{p}{p_L + p}. \quad (6.14)$$

Consequently, the specific absolute adsorption capacities ($\hat{n}$) (Eq. 6.14) were used to determine the sorbed phase densities of methane molecules present in the condensed structure as follows:

$$\rho_{abs} = \frac{\hat{n}}{V_{total,cir}}; \rho_{ads} = \frac{\hat{n}}{V_{pore,squ}}. \quad (6.15)$$

The suitability of the Langmuir model to predict the sorbed gas densities and density ratios using Eq. 6.15 will be validated by comparing with simulation computed values obtained with Eq. 6.10. Consequently, the role of augmented barrier to methane transport in an adsorbed and absorbed gas systems will be compared and discussed in results and discussion sections.

6.2.4 Diffusion tortuosity

The diffusion tortuosity according to the workflow successfully employed in previous studies [135,286] was computed as follows:

$$\tau_d'^2 = \frac{D_{transition}}{(1 + \beta_{abs})D_{eff}} \quad (6.16)$$

where, $D_{transition}$ is transition diffusion calculated with Bosanquet equation [39], τ'_d is the diffusion tortuosity, D_{eff} is self-diffusivity computed from MD in circular and square geometry respectively. The literature reported methane diffusion tortuosity in kerogen micropores [286] is within an uncertainty of 2.0 to 3.6. The realistic diffusion tortuosity that is representative of the geometry is obtained by selecting the diffusion tortuosity value at equivalent high pressure computed with Eq. 6.16. Adsorption forces are negligible as adsorption factor, $(1 + \beta_{abs})$ or $(1 + \beta_{ads})$ approaches unity at very high pressure. The tortuosity range of 2.0 - 3.6 will serve as a constraint in the calibration of the proposed model with MD data for the cylindrical pore system. On the other hand, the slit-shape square geometry is a straight micropore with expected diffusion tortuosity of 1.0, which was confirmed with the theoretical Eq. 6.16. Details of model development can be found in the next sub-section.

6.2.5 Effective diffusion model development

As discussed in the diffusion regime classification in section 2.3 (chapter 2), transition diffusion governs the overall transport in pores of sizes less than 2.0 nm at some range of gas pressure. Several proposed transition diffusion models are available in literature [39,113,114,135,136]. In summary, these models were conceptualized on averaging the self-diffusivity based on Knudsen and Fick's diffusions.

In a non-circular pore geometry system, the equivalent pore radius should be corrected for the geometry through a shape factor. The equivalent pore radius for a slit pore in kerogen with a dimension of $w \times w \times h$ was given as $\bar{r}_{squ} = (A_p)/(P_d)$ [170], where w and h are crack width and height respectively, $A_p = wh$ and $P_d = 2(w + h)$ are crack cross sectional

area and perimeter respectively. The other tortuous pores within kerogen were assumed circular and denoted as $\bar{r}_{cir}$.

The degree of representation of this equivalent pore radius model will be assessed using calibrated pore radius determined from MD diffusion calculations. Consequently, applying the augmented influence of nanoscale geometry tortuosity, corrected for adsorption, a modified effective diffusion equation in transition flow domain is obtained as follows:

$$D_{eff,geo} = \frac{1}{\tau_{d,geo}^2} \left(\frac{D_{eff,K,geo} D_F}{D_{eff,K,geo} + D_F} \right) \quad (6.17)$$

The effective transition diffusion is a harmonic average of effective Knudsen (Eq. 18) and Fick diffusion (Eq. 6.19), where, $D_{eff,K,geo}$ is effective Knudsen diffusion (m^2/s) for circular and square geometry and computed as follows:

$$D_{eff,K,geo} = \frac{2\bar{r}_{eff,geo}}{3} \sqrt{\frac{8RT}{\pi M}}. \quad (6.18)$$

Similarly, D_F is Fick's gas diffusion coefficient (m^2/s), and is calculated as follows:

$$D_F = \frac{\lambda_g}{3} \sqrt{\frac{8RT}{\pi M}}, \quad (6.19)$$

where, all units are in standard international (SI) units and their physical consistency is checked. $\bar{r}_{eff,geo}$ is the effective pore expressed as difference between the equivalent pore radius after deformation and adsorbed gas layer thickness [170,290]:

$$\bar{r}_{eff,cir} = \bar{r}_{\sigma eff,cir} - r_{ads}, \quad (6.20)$$

and,

$$\bar{r}_{eff,squ} = \bar{r}_{eff,squ} - r_{ads}, \quad (6.21)$$

for circular and square geometry respectively, $\bar{r}_{eff,cir}$ and $\bar{r}_{eff,squ}$ are effective pore radii re-computed from molecular simulation after accounting for pore compressibility in the cylindrical pores and slit-shaped cracks respectively, as illustrated in the workflow (Figure 39). $\bar{r}_{eff,cir} = \bar{d}_{eff,cir}/2$ and $\bar{r}_{eff,squ} = (wh_{eff})/2(w + h_{eff})$ for circular geometry and square geometry, respectively [170], where, h_{eff} is crack height in square geometry under loading consideration. It is important to note that $\bar{r}_{eff,cir} = \bar{r}_{cir}$ and $h_{eff} = h$, if the impact of pore compressibility is ignored, r_{ads} is the thickness of the sorbed gas layer. According to Ambrose et al. [10], adsorbed phase in organic matter using a carbon nanotube (CNT) follows Langmuir theory for most of the pores and takes up one molecule thick portion of a pore, such that $r_{ads} = d_m\theta$. However, due to surface roughness of a realistic kerogen and stronger interaction, a thickness correction factor, ε_s was introduced in this work, such that, $r_{ads} = \varepsilon_s d_m\theta$, d_m is the diameter of the gas molecule (m), θ is dimensionless surface real gas coverage:

$$\theta = \frac{p/Z}{p_L + p/Z}, \quad (6.22)$$

where, Z is gas compressibility factor, and, the mean free path of the real gas, λ_g :

$$\lambda_g = \frac{\mu_g}{p} \sqrt{\frac{\pi ZRT}{2M}} \quad (6.23)$$

μ_g is apparent gas viscosity (Pa. s), and p is the pressure of gas in the pores (Pa). Substituting Eqs. (6.18 – 6.23) into Eq. 6.17, the proposed effective diffusion model for kerogen microporous structure for both cylindrical pores and slit-shaped microcracks is:

$$D_{eff,geo} = \frac{4}{3\tau_{d,geo}'^2} \left(\frac{\frac{\mu_g}{p} \frac{RT(\bar{r}_{\sigma eff,geo} - \varepsilon_s d_m p / (p + Z p_L))}{M} \sqrt{\frac{2ZRT}{\pi M}}}{(\bar{r}_{\sigma eff,geo} - \varepsilon_s d_m p / (p + Z p_L)) \sqrt{\frac{8RT}{\pi M}} + \frac{\mu_g}{p} \frac{RT}{M} \sqrt{Z}} \right) \quad (6.24)$$

In this study, $\bar{r}_{\sigma eff,cir}$ versus σ_{eff} was obtained from simulation and fitted to Eq. 6.25a to derive some matrix stress constant such as effective stress required to close the pores, p_1 (Pa.) and roughness factor, m [288,290]. Similarly, $h_{\sigma eff}$ is obtained by coupling the equivalent pore size equation for a very wide crack (where, $w \gg h$) of square geometry (Song et al. [290]) and Wua et al. [288] equation that relates pore size and stress as follows (Eq. 6.25b):

$$\bar{r}_{\sigma eff,cir} = \bar{r}_{cir} \left(\frac{1 - \left(\frac{\sigma_{eff}}{p_1} \right)^m}{1 - \left(\frac{\sigma_{eff,0}}{p_1} \right)^m} \right)^{3/5} ; \quad h_{\sigma eff} = h \left(\frac{1 - \left(\frac{\sigma_{eff}}{p_1} \right)^m}{1 - \left(\frac{\sigma_{eff,0}}{p_1} \right)^m} \right)^{3/5} \quad (6.25)$$

where, $\sigma_{eff} = \sigma_{conf} - \alpha_{Biot} p$, is effective stress or net overburden pressure (Pa), σ_{conf} is confining pressure, α_{Biot} is a coefficient described as follows [305,306]:

$$\alpha_{Biot} = 1 - \left(\frac{K}{K_s} \right) = \frac{\Delta \sigma_{conf} - K \Delta \varepsilon_v}{\Delta p}, \quad (6.26)$$

where, $K = \Delta \sigma_{eff} / \Delta \varepsilon_v$ and K_s are bulk and solid modulus measured using drained and undrained experiments, respectively, Δp is changes in reservoir pressure. The drained bulk modulus is obtained as the ratio of changes in both effective stress to volumetric strain.

6.3 Results

6.3.1 Petrophysical and mechanical properties

Table 21 summarized the required input parameters required for the analysis of results in this study and they include pore structural, physical properties of kerogen, gas properties and elastic moduli. It is known knowledge that young modulus measures the stiffness of the materials. Primarily, this elastic parameter computed from simulation for type IID kerogen, obtained prior to structural adjustments, matched MD simulation results obtained by Wu and Firoozabadi [307]. The authors reported that the stiffness parameter is in the range of 1.5-3.6 GPa, after calculating the mechanical properties of type I, type II and type III kerogen matrix. Similarly, the range of Poisson's ratio obtained by Wu and Firoozabadi [307] is from 0.24 to 0.42, and within the bracket of values obtained in Table 21. Similarly, the experimental stiffness modulus reported for Avalon, Bakken and Eagle ford shales is 18.83 – 36.0 GPa [308], which shows shale is stiffer by almost a factor of 10 compared to organic matter. The difference in mechanical properties of kerogen and shale formation is due to the presence of other minerals like clay, calcite and quartz with variable concentration. Porosity of the material is another deciding factor, it was observed that the elastic parameters vary as the porosity in the structure is increased for the second and third structures. Evidently, the more porous materials are less stiff.

Table 21 Original Structure elastic and input parameters for molecular study

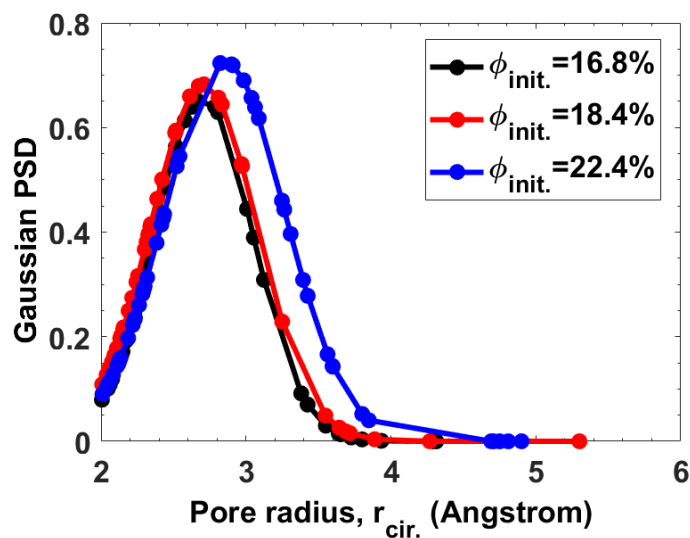
Structural initial properties and constants	Ker IID-1	Ker IID-2	Ker IID-3
Volume of cubic simulation box, V_{total} (10^{-27}m^3)	27.93	30.63	33.658
Molecular weight of kerogen type, M_{ker} , (kg/mol)	2.47	2.47	2.47

Number of kerogen macromolecule units	12	12	12
Avogadro's number, N_A , (10^{23} /mol)	6.023	6.023	6.023
Mass of condensed kerogen structure, m_{ker} , (10^{-23} kg)	2.7930	3.0625	3.3659
Density of condensed kerogen, ρ_{ker} , (kg/m ³)	1,000	1,000	1,000
Molecular diameter of methane, d_m , (10^{-9} m)	0.38	0.38	0.38
Minimum pore radius, r_{min} , (10^{-9} m)	0.20	0.20	0.20
Maximum pore radius, r_{max} , (10^{-9} m)	0.48	0.66	0.67
Porosity of condensed structure, ϕ (dimensionless)	16.8%	18.4%	22.4%
Total Pore Volume, V_{pore} (10^{-27} m ³)	4.69	5.63	7.54
Minimum kerogen tortuosity, $\tau'_{d,cir}$	2.0	2.0	2.0
Maximum kerogen tortuosity, $\tau'_{d,cir}$	3.6	3.6	3.6
Molar mass of methane gas (10^{-3} kg)	16	16	16
Universal gas constant, R, (J/K.mol)	8.314	8.314	8.314
Equilibrium temperature, T (K)	350	350	350
Elastic properties			
Young modulus, E (GPa)	1.14	1.06	0.7
Poisson's ratio, ν	0.38	0.34	0.28
Bulk modulus, K (GPa)	1.54	1.13	0.54
Shear modulus, G (GPa)	0.41	0.39	0.27

6.3.2 Pore size distribution

Original structures

The detailed algorithm that was described in the methodology section was applied to the original structures (i.e. structures containing circular micropores excluding the introduced slit shape pore which is of known geometry and size). The PSDs (**Figures 40a** and **40b**) showed that micropores in kerogen have a unimodal distribution with a lognormal profile. The Gaussian PSD revealed that the most frequently occurring pore radii in Figure 40a are 2.7, 2.7 and 2.9 Å in structures 1, 2 and 3 respectively. Bhattacharya NPD in Figure 40b showed a modal pore radius of within 3.0 - 3.5 Å. Calibrating the self-diffusion measurements based on Newton's method with the proposed model will give the most representative pore distribution function for the kerogen structures.



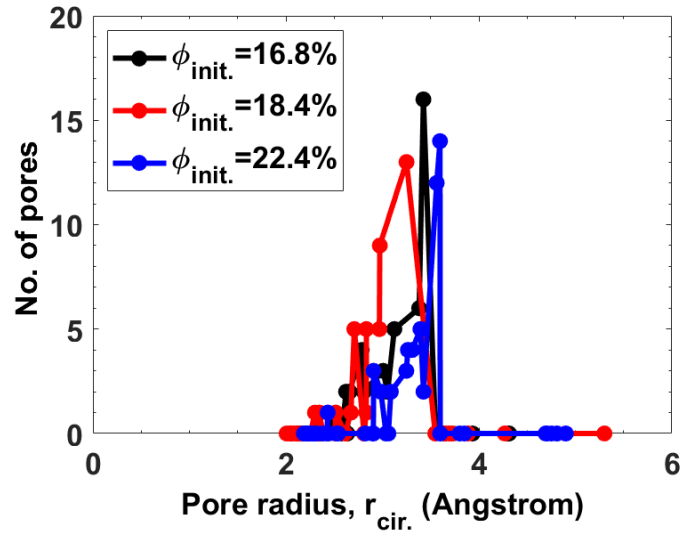
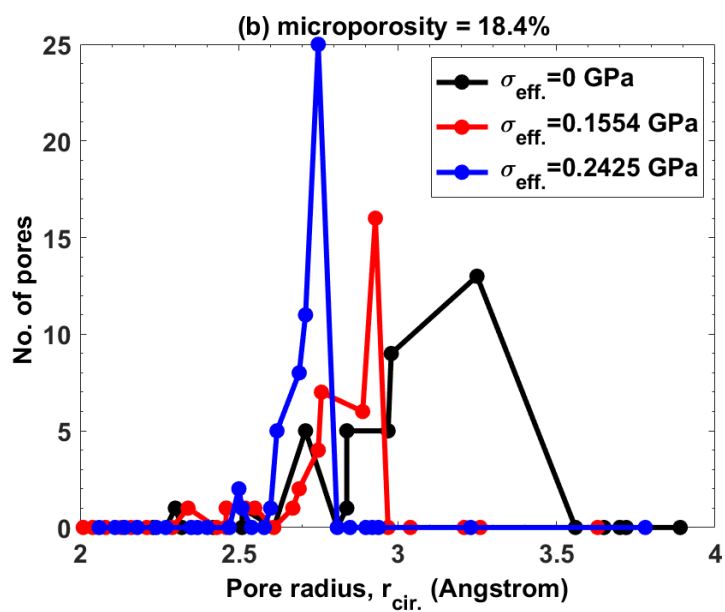
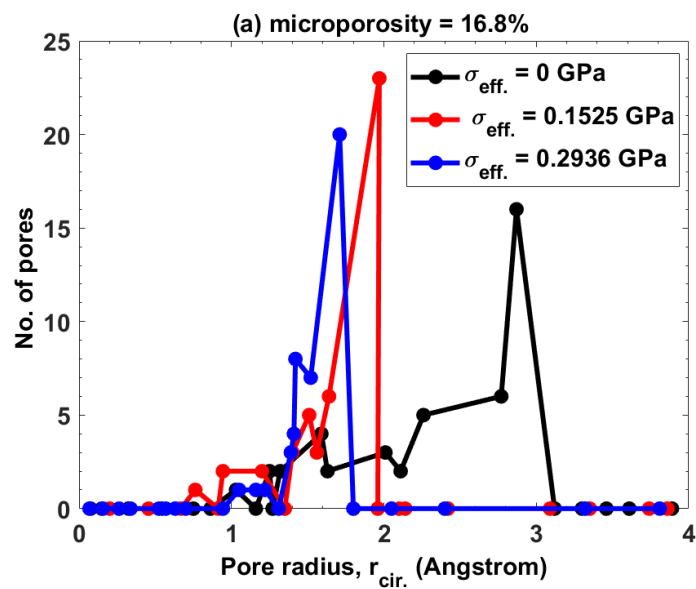


Figure 40 a) Gaussian probability distribution function b) Bhattacharya NPD function for three kerogen configurations under zero confined stress

Effect of pore compressibility

The role of pore compressibility on some basic pore structure parameters of the original three kerogen configurations such as NPD, mean pore radius and porosity is discussed in this subsection. As the matrix shrinks under increasing stress, the pore size distribution and all the associated parameters would change. **Figure 41** illustrates the dependence of pore compressibility on the NPD of the structures. The impact of effective stress on pore radius less than 1.3 - 2.6 Å could be negligible relative to larger pores. This behavior is consistent in the three structural configurations of kerogen.



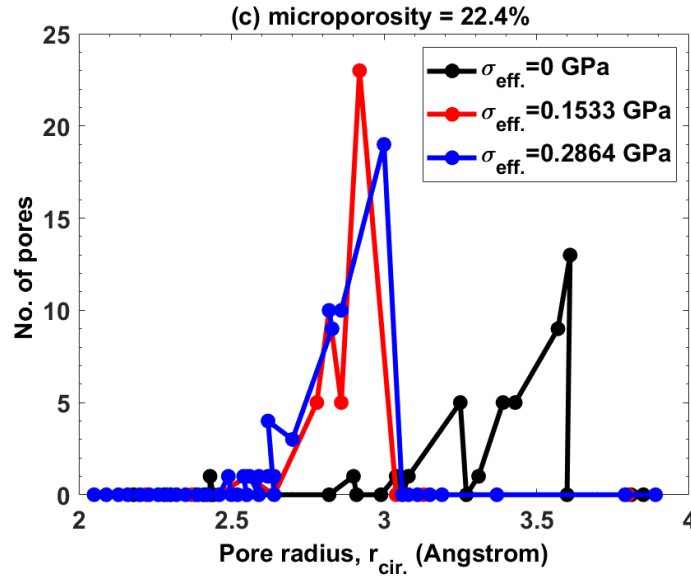


Figure 41 Dependency of pore size distribution on matrix stress for the three kerogen configurations (a) phi=16.8% (b) phi=18.4% (c) phi=22.4%.

Consequently, **Figure 42** shows the impact of pore compressibility on average pore size and porosity for the same structures, irrespective of their initial porosities. From the average pore radius and stress profile, a nonlinear fitting algorithm in MATLAB is utilized to calibrate Eq. 6.25a with a stress profile derived from post-deformation energy quantification to determine the pore roughness factor (m) and the effective stress required to close the pores (p_1).

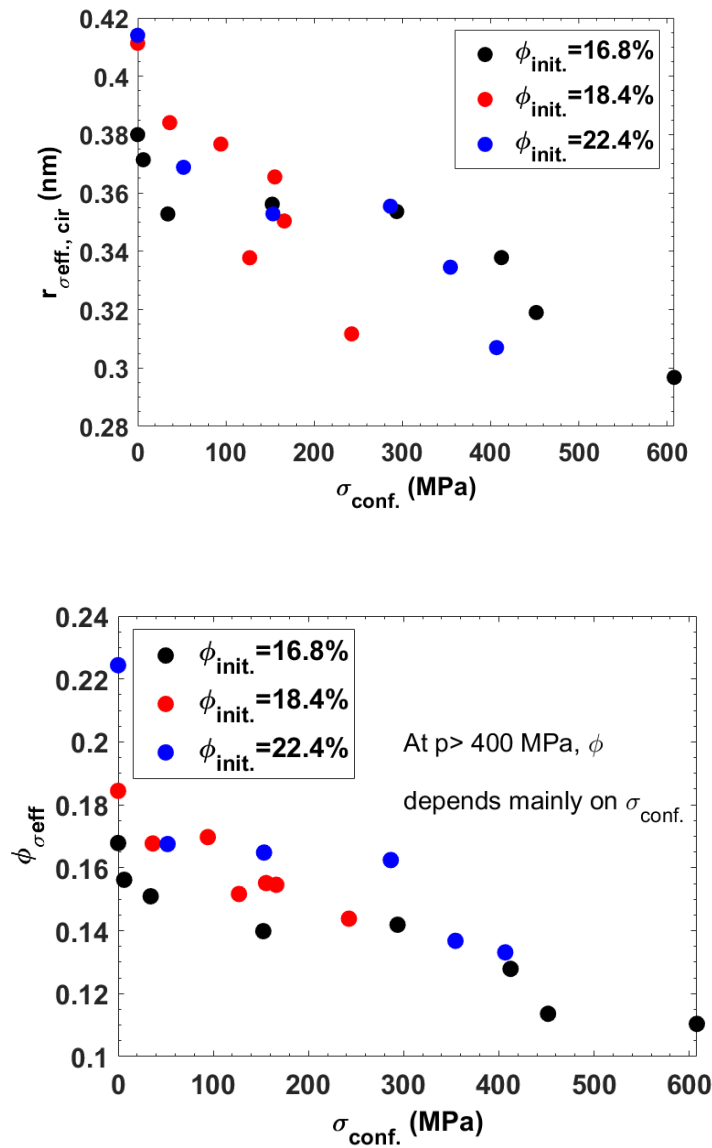


Figure 42 Impact of stress on (a) pore size and (b) porosity.

Table 22 summarizes the stress fitting constants for the structures, alongside the R-squared values and root mean square error (RMSE) during the fittings process. The analysis revealed that the structure with the highest microporosity has more roughness factor than the least porosity. This suggests the presence of more space in the grooves or rough surface for methane molecules to be hosted compared to lower porosity materials. Kerogen has a

rougher surface compared to shale studied by Wasaki and Akkutlu [137], while the authors obtained a 0.5 factor, a range of 1.5 - 3.7 was obtained for the kerogen structured in this research. Conversely, the least porous structure has the highest closing stress. Wasaki and Akkutlu [137] obtained a closing stress of 179.26 Mpa in 5.0 nm nanotubes, while 554 - 1331 Mpa was determined from this study in a micropore size range of 0.76 – 0.828 nm.

Table 22 Stress constant parameters obtained by fitting effective pore size and stress from simulation

Structures	$\phi_{init.} = 16.8\%$	$\phi_{init.} = 18.4\%$	$\phi_{init.} = 22.4\%$
p_1 (MPa)	1331	554	586
m	1.495	1.462	3.7
RMSE (10^{-10})	0.0822	0.115	0.0659
R-squared	0.879	0.78	0.905

6.3.3 Sorption phenomena

Absorption and adsorption assessments are reported in the kerogen micropores and microcracks respectively in this section. Again, the methane bulk density employed for the analysis was evaluated using the NIST- miniREFPROP experimental database software (see **Table S3**). This method has been successfully employed in the literature [149,286]. **Figure 43** shows that the excess gas sorbed in kerogen structures does not only vary with temperature and pressure, but also with kerogen maturity and origin [17,19,76]. It was consistently observed in both geometries that more molecules are sorbed in the kerogen system with higher microporosity and slit-pore height.

The excess methane sorption is more dependent on reservoir pressure compared to the

micropore storage capacity. In the cylindrical pores for instance (**Figure 43a**), the concentration of methane at the non-mobile phase changed by a factor of 3.0 from 2.067 Mpa to 82 Mpa, and by less than 50% increase for a porosity change from 16.8 to 22.4%. For this reason, there may be a good argument that for the same material, the influence of porosity on the maximum absorption capacity is negligible. However, the small changes in pore sizes should be accounted for to ensure a reliable description of methane interactions with kerogen surface atoms.

Accordingly, the absorption and adsorption factors computed with Eq. 6.11 are graphed in **Figure 44**. However, a comparison of Figure 44a and 44b revealed that, the barrier to the movement of methane molecules through the slit-pores undergoing adsorption is higher than in the cylindrical pores, which hints that the thickness of the sorbed gas layer is dependent on the inherent mechanism.

In relation to the effect of sorption mechanisms, the density ratios computed by Ju [276], and Sun [285] in the square geometry are almost two to three times higher than in the cylindrical pore system (Figure 44a). It is important to note that, Ju [276] and Sun [285] characterized adsorption capacity in type-I kerogen and carbon nanotube respectively, contrary to the absorption phenomenon in a realistic kerogen with circular geometry described in this study.

In terms of the influence of micropore storage capacity and pore fluid pressure, the absorption for instance is slightly higher in the most porous structures with 22.4% porosity compared to the 16.8% porosity. Investigating the role of pressure shows that, at the lowest pressure of 2.067 Mpa, the absorbed layer density is between 2.5 to 3.5 denser than mobile gas phase depending on the microporosity. This view is consistent with the computed

adsorbed gas density in kerogen available in the literature [10,135].

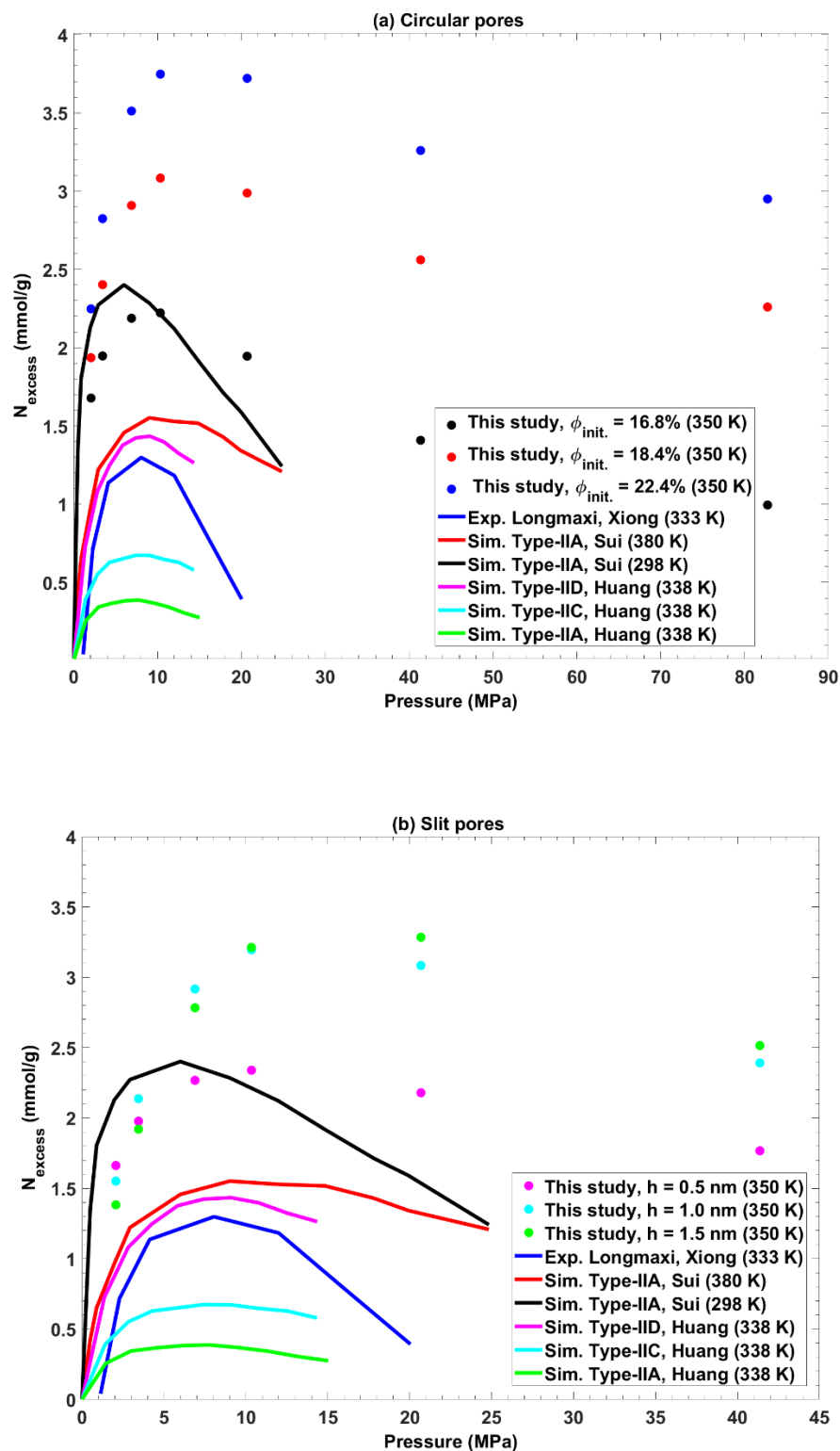
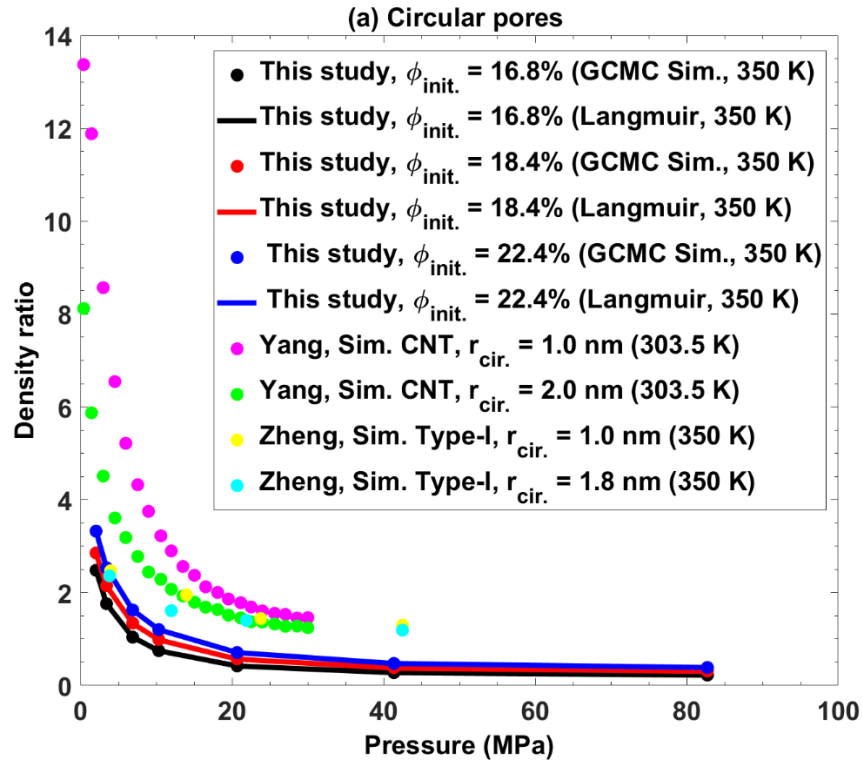


Figure 43 GCMC computed excess sorption amount for three kerogen structures and compared against experimental and molecular simulation data available in the literature; a) dissolved gas capacity b) adsorbed gas amount.

Conversely, the effect of the characteristic pore size on the adsorption process is different from the absorption phenomenon. Rather, the density ratio in the slit-shaped microcracks drops rapidly from 17 to 6 as pore height increases from 0.5 to 1.5 nm microcrack. This behavior suggests that the impact of adsorption will decrease as pore height increases due to weaker interaction of the gas molecules with the crack surface. It is noteworthy to point out that the Langmuir isotherm showed a great capability in predicting the density ratio in microporous systems experiencing sorption processes. In addition, the Langmuir parameters and error analysis for both geometries are summarized in **Table 23**.



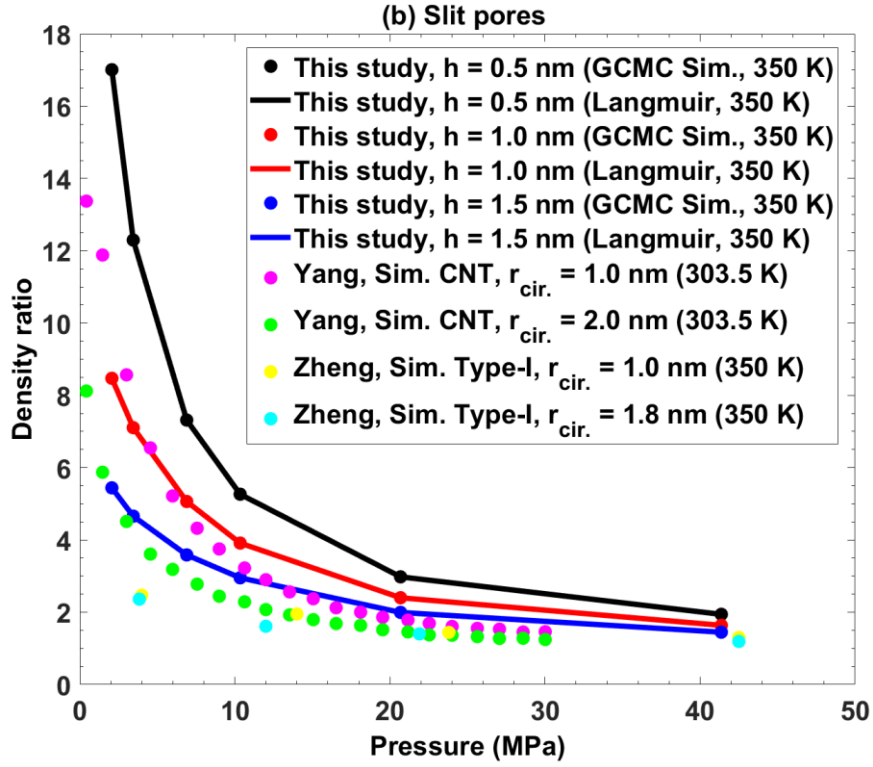


Figure 44 Impact of kerogen structure and pressure on adsorption equilibrium factor a) circular pore experiencing absorption process and b) slit-shaped pore with adsorption mechanism

Table 23 Langmuir parameters in circular and square geometry encountering absorption and adsorption processes respectively

Geometry	Circular			Square		
Structures	$\phi_{init.}$ = 16.8%	$\phi_{init.}$ = 18.4%	$\phi_{init.}$ = 22.4%	$h = 0.5 \text{ nm}$	$h = 1.0 \text{ nm}$	$h = 1.5 \text{ nm}$
n_L (mmol/g)	3.907	5.571	7.044	3.736	7.023	10.328
p_L (MPa)	2.995	4.196	4.788	2.582	6.402	11.403
RMSE	0.168	0.194	0.235	0.0895	0.0500	0.0654
R-squared	0.839	0.761	0.787	0.875	0.993	0.991

6.3.4 Proposed model validation

The predictability of the proposed model was tested with MD diffusion data measured by

Kazemi [29] and Sui [17] for type II-C and type II-A kerogen respectively. The data published by the authors was employed as input parameters in Eq. (24). It is noteworthy that the data presented by both Sui [17] and Kazemi [29] were performed without considering the effect of pore compressibility in the cylindrical kerogen pores system, such that $\bar{r}_{\sigma eff, cir} = \bar{r}_{cir}$. The representative pore radius for the type IIA and type IIC kerogen structures will be obtained by calibrating the proposed model with the self-diffusion data. **Table 24** summarizes the data adopted from the authors' work. The bulk methane properties required for the validation like the viscosity and the gas compressibility factor at specified pressure and temperature were calculated using miniREFPROP experimental database software [149] and presented in **Table S4** of the supplementary materials. Again, the two main uncertain parameters in these kerogen structures are the characteristics pore radius and diffusion tortuosity of the geometry, otherwise regarded as a tortuosity factor. The pore volume (V_{pore}) and specific surface area (S_{pore}) of the type II-A kerogen utilized by Sui 2016 are $0.181 \times 10^{-6} \text{ m}^3/\text{g}$ and $1548 \text{ m}^2/\text{g}$ respectively.

The characteristic radius using Brunauer-Emmett-Teller (BET) method, is computed as $\bar{r}_{cir} = 4V_{pore}/S_{pore}$, and similarly, if assumed that the pore has a perfectly spherical shape, then $\bar{r}_{cir} = 3V_{pore}/S_{pore}$. However, the typical pore radius obtained during fitting process matches $\bar{r}_{cir} = 2.4V_{pore}/S_{pore}$, which hints that the pores are not perfectly spherical. Furthermore, an adsorption-free tortuosity of 2.8 was obtained, which is within a close proximity to the range of 2.0-3.6 reported literature.

Similarly, the proposed model closely resembles the Kazemi [29] MD methane diffusion data measured for kerogen type II-C structure with a representative pore radius and diffusion tortuosity of 0.55 nm and 2.0 respectively. The effective transport of methane in

type II-C determined by Kazemi [29] is higher than in kerogen type II-A by Sui [17]. The discrepancy in measured self-diffusivity is attributed to the structural configuration, as reflected in the higher accommodation size and less tortuous geometry in type II-C employed by Kazemi [29].

Table 24 MD simulation diffusion data from kerogen type II-A [17] and II-C [29] for validating proposed model

Parameters	Symbol	Unit	Sui [17] values	Kazemi [29] values
Pressure	p	Pa	Table S3	Table S3
Temperature	T	K	298	300
Viscosity	μ_g	Pa. s	Table S3	Table S3
Representative pore size	$\bar{r}_{cir}$	m	0.405×10^{-9}	0.55×10^{-9}
Gas deviation factor	Z	dimensionless	Table S3	Table S3
Langmuir pressure	p_L	Pa	0.93×10^6	1.1×10^6
Universal gas constant	R	J/Kmol	8.314	8.314
Gas molecular size	d_m	m	0.38×10^{-9}	0.38×10^{-9}
Gas molecular mass	M	Kg/mol	0.0016	0.0016
Diffusion	$\tau'_{d,cir}$	dimensionless	2.8	2.0

tortuosity				
Adsorbed layer correction	ε_s	dimensionless	1.0	1.0

The graphs illustrating the predictability of the proposed effective diffusion equation against two independent MD simulation effective diffusion data in microporous kerogen structures are given in **Figure 45**.

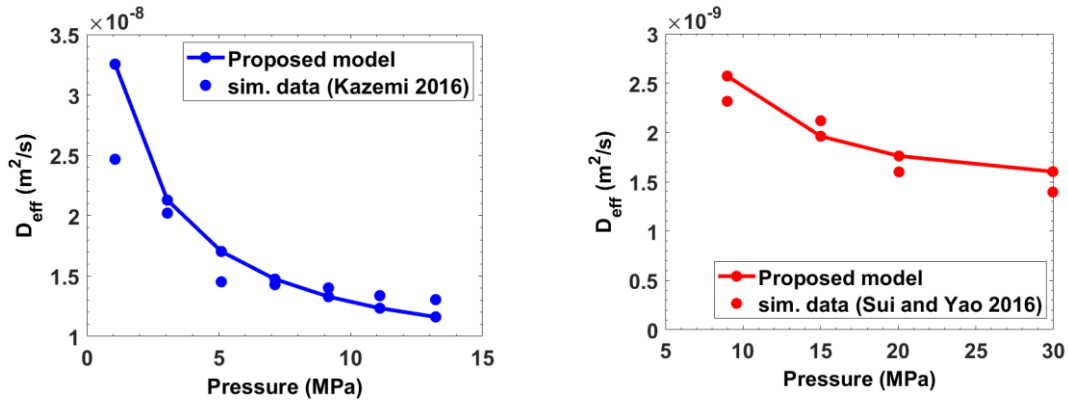


Figure 45 Validation of proposed effective diffusion model in kerogen using MD diffusion data utilized by a) Kazemi [29] b) Sui [17]

Figure 46 shows, in a combined validation data plot, that the proposed model is reliable across a wide pressure range from 1.0 Mpa to 30 Mpa. Moreover, the accuracy is higher at higher pressure compared to lower pressure states where Knudsen diffusion becomes extremely significant. Afterwards, the MD diffusion data obtained for the kerogen type II-D in this study was employed to calibrate the proposed model, and extract relevant pore structural features for this type of kerogen structure.

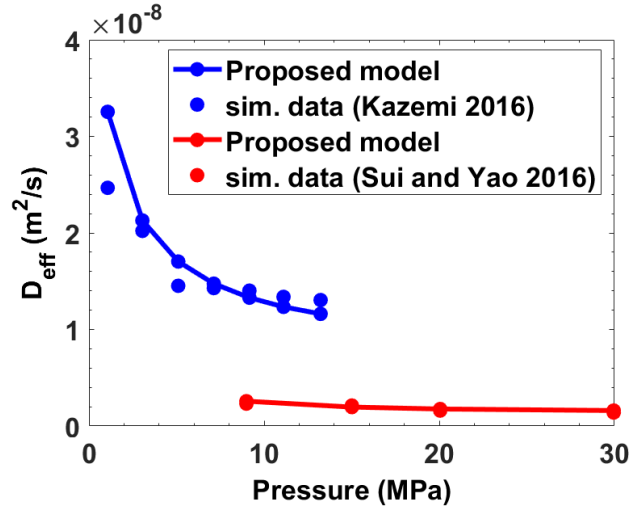


Figure 46 Combined MD diffusion data across pressure range of 1-30 Mpa employed for model validation

6.3.5 Effective diffusion

Original structure

Figure 47 shows the comparison of effective diffusion from MD simulation and proposed model for a wide range of pressure from 2.068 Mpa to 82.68 Mpa in a type IID structure. The simulation is compared to the model performance in both circular and square geometries. There is a reasonable agreement between the model and simulation data, and this assurance proves the viability of the model as a calibration tool for further predictive and sensitivity studies in organic component transport of shale reservoirs. Sorption mechanisms had a relatively more pronounced effect on self-diffusion at low pressure because of high Knudsen diffusion relative to compressed gas diffusion. The observed density ratio reduces until a saturation pressure is reached where it flattens out due to gradual reduction of Knudsen flow process. In other words, as pressure increases, sorption forces of methane molecules gradually drop relative to the pressure loading of the molecules. This is envisioned as the decrease in density ratio in both adsorbed and absorbed gas phases. Above 10-20 Mpa, absorption interaction potential is small due to the

molecular loading interactions. This gradual growth in the role of molecular mean free path takes place at much higher pressure above 40 MPa in the slit-shape adsorption process when Knudsen effect drops drastically.

For both sorption processes, there is a reduction in the mass transfer of methane molecules when the gas molecules are further compressed under pressure loading, resulting in an additional barrier to gas transport. Several authors have computed diffusion tortuosity that is reflective of the kerogen geometry at this condition when Knudsen effect is negligible [135,286]. It is intuitive that the effective diffusion will be directly correlated to microstructure porosity and slit pore height [206] as shown in **Figure 47**. In addition, sorption forces severely affect the effective diffusion at a pressure state that is below the critical pressure where Knudsen diffusion is very strong. Ignoring the sorption forces at low pressure would significantly overestimate the effective diffusion. **Table 25** shows the updated representative pore radius, sorbed layer thickness correction and diffusion tortuosity obtained from the calibration of the proposed model using self-diffusion data from molecular dynamics simulation. The root mean square error (RMSE) between the model and MD data was also reported in Table 25.

Table 25 Updated pore structural and stress constant parameters utilized for calibrating proposed model to self-diffusion data for type IID kerogen system of circular and square geometry. The data of the first case was not reported as Brownian's motion couldn't be reached for the first structure with high certainty.

Geometry	Kerogen tortuous “circular” pores		Slit shape “square” pore		
Structures	$\phi_{init.}$ = 18.4%	$\phi_{init.}$ = 22.4%	h = 0.5 nm	h = 1.0 nm	h = 1.5 nm

$\bar{r}$ (10^{-9} nm)	0.26	0.24	0.19	0.39	0.58
ε_s	0.46	0.00	0.44	0.91	1.36
τ'_d	3.19	3.11	1.0	1.0	1.0
RMSE (10^{-5})	0.76	0.71	3.38	7.70	9.15

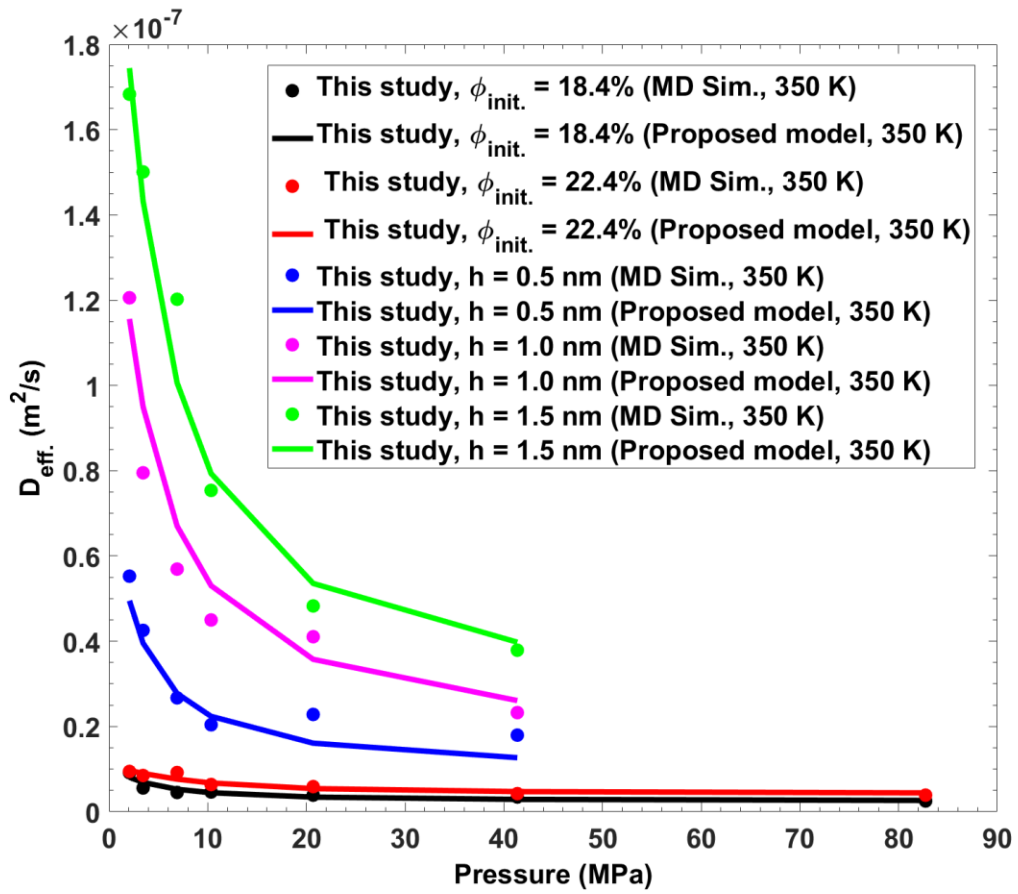


Figure 47 Impact of pressure, adsorption, and pore structure effect on effective diffusion

In general, the representative pore size and diffusion tortuosity obtained from the calibration exercise is within the expected theoretically ranges computed in Table 21. Interestingly, Table 21 showed the typical pore radius of the tortuous structures is within

2.4-2.6 Å, which better matched the prediction of Gaussian rather than Bhattacharya PSD in Figure 40. The equivalent pore radius for the square geometry almost follows perfectly with the equation, $\bar{r}_{squ} = (A_p)/(P_d)$ by [170]. The Song [170] model is representative for the slit-shaped pores utilized for their studies and gives equivalent pore radius of 0.22, 0.40 and 0.5 nm for pore heights of 0.5, 1.0 and 1.5 nm respectively. Meanwhile, MD diffusion calibration gives an equivalent pore radius of 0.19, 0.39 and 0.58 respectively. On the other hand, the adsorbed gas thickness multiplier, ε_s , is observed to be directly proportional to the increases in pore heights.

Influence of pore compressibility

The proposed model has the robustness to couple the sorption and geomechanics. To avoid erroneous results in assuming that p_L , is unchanged with stress, the sensitivity study will only consider the effect of pore compressibility. The impact of wide range pore compressibility on effective diffusion is given in **Figure 48** for the three structures with different initial porosities. It is notable from **Figure 48** that the effective diffusion is more sensitive to gas pressure and pore compressibility changes compared to variable microporosity of the bulk kerogen undergoing absorption process. Nevertheless, the predicted effective diffusion in **Figure 48** will be higher than actual results if the changes in adsorbed gas layer with Langmuir pressure p_L is integrated in the calculations.

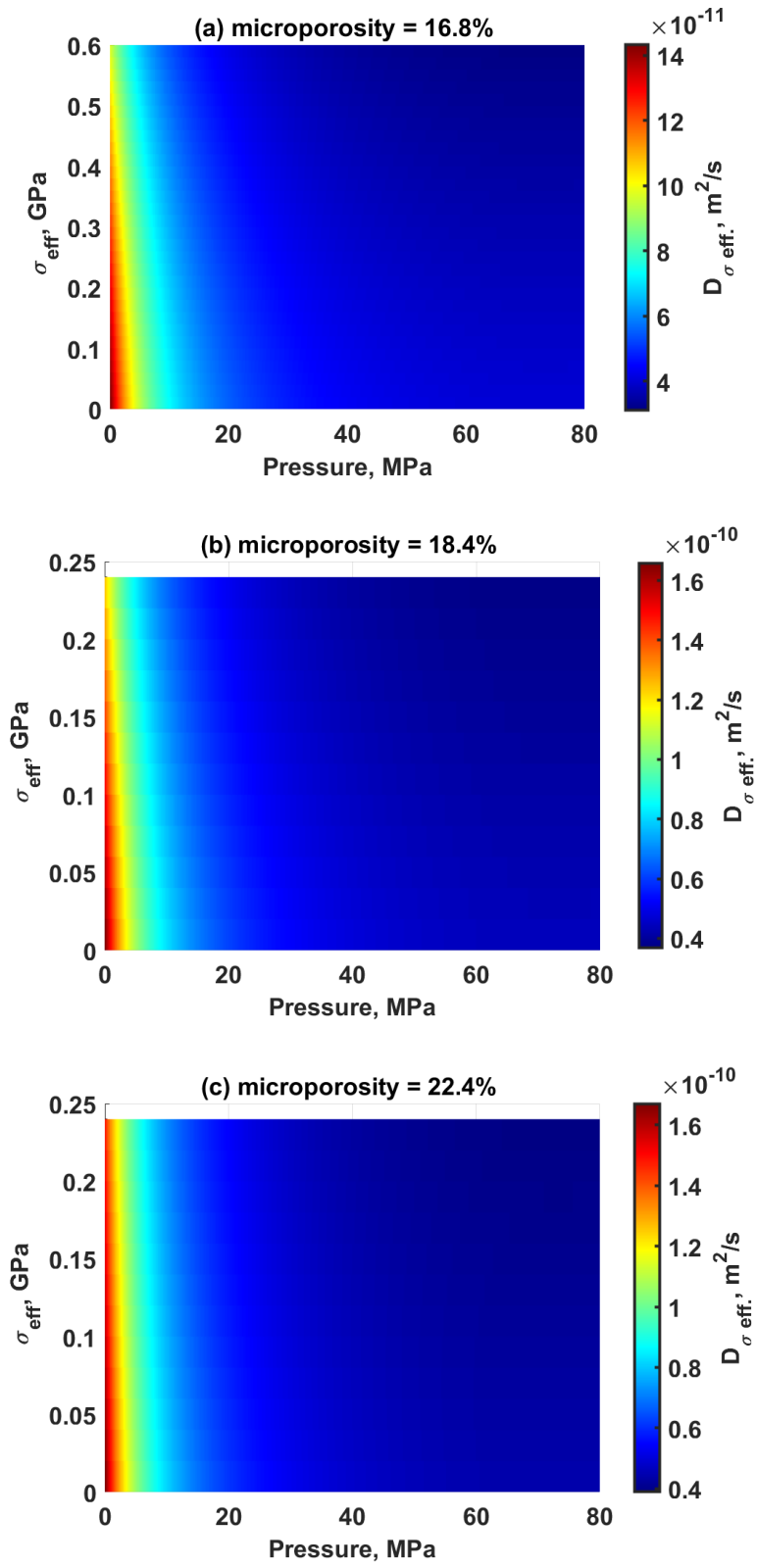


Figure 48 Impact of pressure and stress on effective diffusion (a) $\phi=16.8\%$ (b) $\phi=18.4\%$ (c) $\phi=22.4\%$

6.4 Conclusions

This study computationally measured the mechanical properties, sorption and methane diffusivity in both kerogen geometries. Furthermore, a coupled diffusivity-mechanical-sorption model, which was validated by MD and GCMC simulation data for both cylindrical and slit-shaped pore systems, was proposed. The following major conclusions can be drawn:

- Computationally generated data could serve as a useful calibration tool for the proposed multiphysics-based effective diffusion model. The equation is accurate in predicting effective diffusion in different kerogen type II-A, II-C and II-D configurations and over a wide range of pressure.
- Gaussian distribution function showed that kerogen structure is log-normally distributed, exhibits a unimodal pore profile and best describes a characteristic pore size in circular pores geometry. There is no unique fitted model based on spherical or circular pore shape assumptions to describe the local pore heterogeneity and characterize the representative pore size in kerogen.
- Methane is present as an absorbed phase within kerogen and adsorbed on the surfaces. The transport barrier created by adsorbed gas is higher compared to absorbed gas systems of equivalent pore sizes. The role of adsorption as an augmented barrier to methane transport becomes smaller as microcrack sizes increase.
- The number of larger pores reduces while the smaller pores volume remains relatively constant in a microporous kerogen structure ($<2\text{nm}$ pore sizes) under the influence of pore compressibility.

CHAPTER 7

PERMEABILITY MODEL FOR SHALE AND ULTRA-TIGHT GAS FORMATIONS: CRITICAL INSIGHTS INTO THE IMPACT OF DYNAMIC ADSORPTION⁴

Abstract

Gas transport in ultra-tight rock is non-Darcian. In addition to continuum flow, there are multiple other flow mechanisms such as slip flow and pore and surface diffusion. Various multi-physics models have been put forth in the literature to forecast the apparent permeability of gas in shales and ultratight formations. However, a means of accurately describing the relative contributions of physics in multiscale pore systems remains a challenge. Moreover, it is important to explain pore size, pressure dependency, and the relationships among adsorption, diffusion, and permeability in porous media. For these reasons, a semi-analytical model is proposed to predict gas permeability according to the viscous flux, pore diffusion and surface diffusion and establish control of the adsorbed gas layer. The reliability of the equations developed was checked by validation using

⁴ This chapter is copied from the manuscript: **C Afagwu**, S Alafnan, MA Mahmoud, S Patil (2021). Permeability model for shale and ultra-tight gas formations: Critical insights into the impact of dynamic adsorption. Energy Reports 7, 3302-3316.

experimental and molecular simulation data obtained from macropore- and micropore-sized nanotubes systems respectively. Furthermore, the equations' performance for micropores was compared to existing theoretical shale permeability models. The subsequent sensitivity analysis showed that permeability is sensitive to the nanoscale geometry factor and adsorption mechanisms. Moreover, the relevance of the surface diffusion was found to increase as the pore size decreased. For instance, surface diffusion constituted over 50% of the apparent permeability below the 10 MPa and 5.0 MPa conditions in micro- and mesopore systems, respectively, while the Darcy scale phenomenon controlled the transport of gas in macropores. Across all diffusion regimes, the microstructure geometry and sorption dynamics significantly influenced the total diffusion of methane, particularly at low pressures and decreased pore sizes. The decline in reservoir pressure during production shifted the relative importance of the adsorption and diffusion mechanisms, consequently altering the apparent gas permeability. Therefore, reservoir management teams should consider the dynamics of gas permeability at different pressures and representative pore sizes throughout the life cycle of the asset.

Keywords: Apparent gas permeability, Shale gas, Tight formation, Diffusion tortuosity, Adsorption behavior

7.1 Introduction

Several researchers developed models coupling slippage and pore diffusion on multiple pore scales in order to predict gas permeability. Javadpour [309] forecasted gas permeability in the nanopores of mud rocks; predictions were based on rock and gas type and operating conditions and accounted for slip flux and Knudsen diffusion. Ziarani and

Aguilera [310] proposed a model for estimating permeability in tight sand as a function of Knudsen diffusion. Darabi et al. [311] applied the apparent permeability function to predict the intrinsic permeability of ultra-tight shale rock. The authors showed that Knudsen diffusion constitutes 10-fold the Darcy and slippage flux values in very low permeability rocks. Singh and Javadpour [312] presented a non-empirical model that integrates the effects of the pore geometry factor and rock and gas properties to predict permeability in ultra-tight formations. The authors suggested that slip flux is indistinguishable from Knudsen diffusion in transition regimes, and thus classified transport in the transition domain as viscous Knudsen diffusion. Guo et al. [313] opined that gas slippage and Knudsen diffusion would be difficult to isolate; therefore, the authors introduced an advection-diffusion model to correct for the total slippage in nanopores of shale gas rock. The models discussed couple viscosity and pore diffusion transport in tight and ultra-tight formations. These models assume that the energy associated with the interaction of gas and rock is negligible. It is noteworthy that chemical potential exists in a material when chemical attraction interactions exist between molecules of the adsorbent and gas. This phenomenon gives rise to an adsorbed layer that possesses a phase density that depends on pore size characteristics, gas properties, and operating condition [88].

Some researchers have derived transport models to account for the surface diffusion of gas molecules in the adsorbed phase [22, 27] in systems undergoing adsorption/desorption. Gonciaruk et al. [111] used adsorption microcalorimetry to show that gas storage and recovery mechanisms in shale are governed by both the nanoscale pore geometry and chemical composition of the gases. Cui et al. [314] developed a model that uses a pressure-decay test to correct for adsorbed layer gas diffusion during experimental measurements of

permeability in tight rocks. Wu et al. [116], Yanfeng et al. [112], Cai et al. [113], and Geng et al. [136] independently developed semi-analytical permeability equations to estimate the relative contributions to gas permeability of various transport mechanisms existing in shale nanopores, including viscosity (or slippage), Knudsen diffusion, transition, and surface diffusion. The results of their work showed that relative to viscous flux, surface diffusion is a more dominant transport flux at pressure states below 10 MPa; Darcy flow equations control the total transport flux in pore sizes larger than 100 nm. Similarly, Wasaki and Akkutlu [137] derived a model to capture surface diffusion, pore diffusion, and slit-shaped macropore-sized flux in shale. In addition, the authors corrected for the effective stress factor in viscous flux permeability.

There are various formulations of empirical, semi-analytical, and analytical equations for calculating the apparent permeability of multi-scale pore systems. Nevertheless, the inter-relationship between the pore geometry factor and adsorption behavior across the entire range of pore scales and pressure variations is rarely considered. Notably, commonly available models employ a constant factor that is independent of combined pore size and pressure to represent the adsorbed gas layer in surface diffusion. In the present research, a semi-analytical permeability model was developed for shale and tight reservoirs that depends on dynamic adsorption behavior. In addition, pore diffusion is modeled as a step function of Fick, Knudsen, or transition diffusion, depending on the transport regime. It is of note that sorption mechanisms and pore diffusion occur simultaneously, and the degree of their occurrence depends on the Knudsen number regime, a dimensionless parameter that quantitatively represents the flow domain as a function of pressure, pore size, and fluid properties. In the proposed model, diffusion coefficients are connected to the dynamic

adsorption phenomenon through the pore scale geometry factor. The remainder of this study is organized as follows. Section 7.2 explained the equations commonly used to quantitatively describe pore scale geometry and its relationship to the adsorption and recovery processes. In Section 7.3, a rigorous model is proposed that integrates the microstructure parameters and adsorption behavior in the prediction of apparent gas permeability. In Section 7.4, the model is validated with experimental and molecular simulation data. In addition, compared to widely available theoretical models on various pore scales. A sensitivity analysis is performed in Section 7.5 to study the effects of pressure, pore diameter, the geometry factor, and adsorption dynamics. In addition, a discussion of how to compute a representative pore size that accurately describes the apparent permeability is provided in Section 7.6. Key findings and implications are summarized in Section 7.7.

7.2 Modeling Pore-Scale Geometry in Porous Media

Tortuosity, a general term that represents the average fluid stream elongation compared to free flow, is one concise parameter widely employed to describe the quantitative effect of pore scale geometry on recovery. There are a number of empirical and theoretical equations that relate to tortuosity as a function of effective porosity [315–319]. **Table 26** provides a summary of a number of simplified theoretical and empirical tortuosity models commonly cited in the literature. The empirical equations were derived from laboratory experiments performed under ideal grain arrangements. In other words, in these experiments, the pore sizes were uniform and mainly represented homogeneous rock. Furthermore, the grains were presented in an ordered packing arrangement and not compacted, and a single capillary tube of porous media with one conductive pathway was assumed [320]. For

instance, the models by Iversen and Jorgensen [321] and Sweerts et al. [322] are only accurate at $\phi \geq 0.275$ and $\phi \geq 0.4$, respectively, a range of porosity not typical for organic-rich shale. Hence, typical tortuosity models are limited to the larger pores in shale. Moreover, these models do not completely reflect the consolidated nature of matrix grains in actual organic-rich shale with more than one conductive pathway and primarily low-diffusivity flow systems.

Table 26 Empirical and Theoretical Tortuosity Models Defined in Terms of Some Rock Properties

<u>Empirical Model</u>	<u>Condition(s) Satisfied</u> <u>(Geometry/Rock Type)</u>	<u>Reference(s)</u>
$\tau^2 = (A\phi^{(1-m)})^n$	Sands and muds (model accurate at the best least square fitting parameter of $A, n = 1, m = 2.14 \pm 0.02$ and $R^2 = 0.54$) [132]	Lerman [315]; Ullman and Aller [316]; Boudreau [317]; van Cappellen and Gaillard [323]
$\tau^2 = \phi + B(1 - \phi)$	Soils, catalyst (model accurate at the best least square fitting parameter of $B = 3.79 \pm 0.1$ and $R^2 = 0.63$) [132]	Iversen and Jorgensen [321]; Dowdy and Low [324]

$\tau^2 = 1 - C \ln \phi$	Fine-grained unlithified sediments (model accurate at the best least square fitting parameter of $C = 2.02 \pm 0.09$ and $R^2 = 0.64$) [132]	Boudreau [317]; Weissberg [139]
$\tau = 1 + a \frac{(1 - \phi_{tot})}{(\phi_{tot} - \phi_c)^m}$	Large 3D fiber web to rep. random porous media; a, ϕ_c, and m are fitting parameters, where ϕ_c is the fraction of unconnected pores	Koponen et al. [325]
<u>Theoretical Model</u>	<u>Condition(s) Satisfied (Geometry/Rock Type)</u>	<u>Reference(s)</u>
$\tau^2 = (3 - \phi)/2$	Random homogeneous and isotropic sphere packing [132]	Neale and Nader [326]
$\tau^2 = 2 - \phi$	Hyperbola of revolution [132]	Petersen [327]; Rayleigh [318]

$\tau^2 = \phi^{-1/2}$	Not for mono-sized spheres [132]	Bruggeman [328]
$\tau^2 = \phi^{-1/3}$	Partly saturated, homogeneous, and isotropic [132]	Millington [319]; van Brakel and Heertjes [329]
$\tau^2 = 1 - 0.5 \ln(\phi)$	Overlapping spheres [132]	Akanni et al. [330]; Ho and Striender [331]; van Brakel and Heertjes [329]; Weissberg [139]
$\tau^2 = 1 - \ln \phi$	Random array of freely overlapping cylinders [132]	Tomadakis and Sotirchos [332]
$\tau^2 = \phi / \{1 - (1 - \phi)^{1/3}\}$	Heterogeneous catalyst [132]	Beeckman [140]
$\tau^2 = \{(2 - \phi)/\phi\}^2$	Cation-exchange resin membrane	Jackie and Meares [333]

Depending on the mineralogy, environment of deposition, and depositional processes, typical shale rocks in carbonates have porosity values of 1% to 35% [334]. Interestingly, equations have recently been developed to compute tortuosity to gas diffusion in very low permeability materials. Such models have gone through several modifications for sorption-

related studies, from diffusion-tortuosity to adsorption-diffusion-tortuosity equations.

Table 6 (chapter 2) summarizes some of these models.

7.3 Pore-Scale Modeling of Gas Flux

7.3.1 Continuity Equation

The mass balance equation for a three-dimensional shale system with multiple mechanisms such as viscous flux, bulk phase pore diffusion, and adsorbed phase surface diffusion can be written as [28, 68]:

$$-\nabla \cdot \vec{J} = \frac{\partial}{\partial t} (\phi \rho + (1 - \phi) \rho_{ads}), \quad (7.1)$$

where ϕ is the porosity, ρ is the gas density in the bulk phase (kg/m^3), ρ_{ads} is the adsorbed phase gas density (kg/m^3), $\nabla = [\partial/\partial x; \partial/\partial y; \partial/\partial z]$ is the divergence ($1/m$), t is the time (s), and $\vec{J}$ is the total mass flux induced by various gas flow regimes (kg/m^2s). The bulk density is obtained by an equation of states or the NIST experimental database software. The adsorbed gas density is determined by fitting the excess adsorption data into an isotherm model or from density functional theory. Some scholars [33, 69–71] have used the Langmuir three-parameter model (Eq. (7.2)) to fit the excess data for pressure up to 30 MPa (4,351 psi), determining the adsorbed phase volume, maximum adsorbed capacity for the adsorbent, and corresponding Langmuir pressure required, which are represented as V_{ads} , n_L , and p_L , respectively.

$$n_{excess} = n_L \frac{p}{p_L + p} - \rho(p, T) V_{ads}. \quad (7.2)$$

However, the modified monolayer model does not account for adsorbate-adsorbate interaction (physisorbed gas molecules). In addition, some discrepancies can be anticipated in moderate to high-pressure gas sorption cases. Thus, a multi-layer isotherm like Freundlich [278] can be used to account for both adsorbate-adsorbate and adsorbate-adsorbent interactions. The Freundlich three-parameter empirical model is as follows:

$$n_{excess} = k_f p^\alpha - \rho(p, T) V_{ads}, \quad (7.3)$$

where k_f and α are the Freundlich empirical constants; consequently, the absolute adsorption capacity n is determined as follows [33, 73]:

$$n = n_{excess} + \rho(p, T) V_{ads}, \quad (7.4)$$

where p is the pressure (Pa), n_L is the maximum adsorption capacity, and p_L is the Langmuir pressure. Then, the adsorbed gas density can be computed as $\rho_{ads} = n/V_{ads}$, (mol/m^3), where V_{ads} is the adsorbed phase volume (m^3/kg). Finally, the adsorption equilibrium factor β is the ratio of the adsorbed phase concentration to mobile phase concentration [63, 64]. The overall flux in a porous media is the sum of the individual fluxes, including the viscous flux $\vec{J}_V$, pore diffusion flux $\vec{J}_P$, and surface diffusion $\vec{J}_S$ [112]:

$$\vec{J} = \vec{J}_V + \vec{J}_P + \vec{J}_S \quad . \quad (7.5)$$

It is noteworthy that the choice of model for describing gas transport in a system depends on the flow regime. The Knudsen number is a parameter widely employed to classify these flow domains. The dimensionless parameter is defined as follows [17, 74]:

$$Kn = \frac{\lambda}{2r} , \quad (7.6)$$

where $\lambda = \frac{\mu}{p} \sqrt{\frac{\pi ZRT}{2M}}$ is the mean free path of molecules with a real gas effect (m) [287], $r = d/2$ is the pore radius (m), d is the pore diameter, $R = 8.314(J/K.mol)$ is the universal gas constant, T is the temperature (K), Z is the gas compressibility factor, M is the molar mass (kg/mol), and μ is the gas viscosity ($Pa.s$). Based on the Knudsen number classification, there are three regimes of shale gas diffusion in nanopores – Fick's, transition, and Knudsen diffusion – with $Kn \leq 0.1$, $0.1 < Kn < 10$, and $Kn \geq 10$, respectively [105]. Technically, from **Figure 9 (chapter 2)**, the Fick's domain suggests that the intermolecular interaction of the molecules exceeds the collision of gas molecules with the wall. Conversely, at a lower pressure or smaller pore diameter, a reverse phenomenon sets in to give rise to the Knudsen domain [309]. Transition diffusion is difficult to describe, and there are several models available. The Bosanquet et al. [337] approximation is most commonly used in the literature.

Viscous flux exists when there is a negligible or no collision of gas molecules with pore walls. Thus, in the presence of viscous flux, gas movement near the wall, and/or diffusion flux, Karniadakis and Beskok [117] presented a generic classification of flow regimes: continuum $Kn \leq 0.001$, slip $0.001 < Kn < 0.1$, transition $0.1 < Kn < 10$, and Knudsen $Kn \geq 10$. Viscous flux describes both the continuum and slippage transport mechanisms [14, 23]. A schematic of the different diffusion regimes as presented in **Figure 9 (chapter 2)**. Similarly, using the dimensionless Knudsen number, variations in the methane diffusion regime with pore scales and pressure states for microporous materials are shown in **Figure 49**. There is an obvious switch to a transition and Knudsen diffusion regime at higher

Knudsen numbers or low pressure and pore sizes. The image was focused within a pore size and pressure of 0 to 5 nm and 2 to 14 Mpa to allow for clear visualization of the Knudsen diffusion regime.

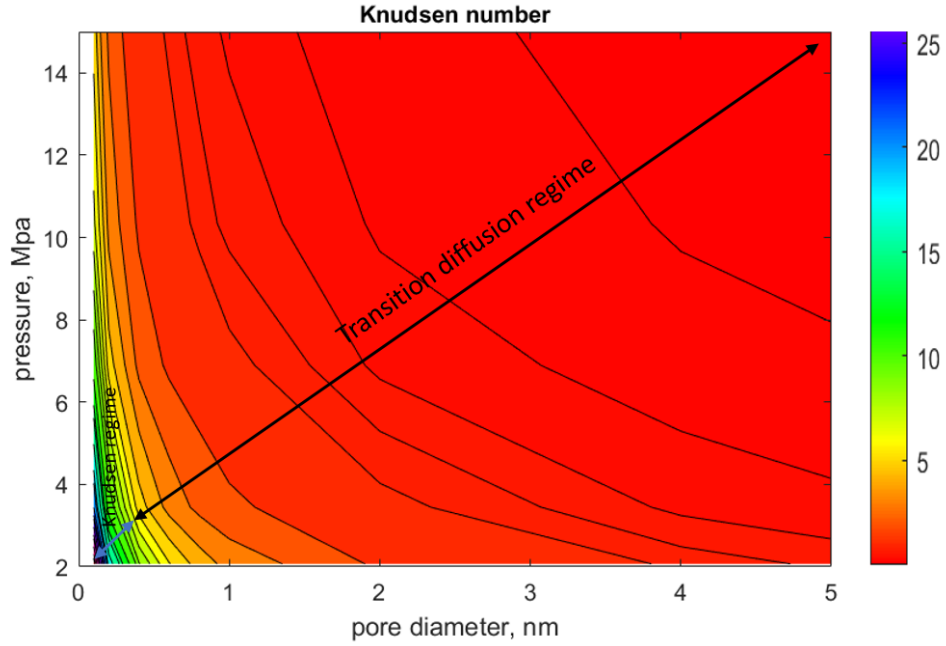


Figure 49 Methane gas Knudsen number based on pore scale and pressure state at 350 K.

7.3.2 Viscous Flow

The equation of laminar flow for an ideal gas in a circular tube, derived from Hagen-Poiseuille's equation [338] and corrected for the gas slippage effect, can be applied to describe viscous flux:

$$\vec{J}_V = -\frac{F\rho r^2}{8\mu} \nabla p, \quad (7.7)$$

where F is the conceptual dimensionless coefficient that corrects for additional flux, due to the non-zero velocity of gas close to the wall [14, 17, 78]:

$$F = 1 + \left(\frac{8\pi RT}{M} \right)^{0.5} \frac{\mu}{p_{avg} r} \left(\frac{2}{\alpha} - 1 \right) , \quad (7.8)$$

where p_{avg} is the average pressure (Pa) and α is tangential momentum accommodation coefficient (TAMAC), which indicates the fraction of diffused gas molecules reflected from the tube wall relative to the specular reflection. It is a function of surface roughness, pressure, and temperature, and can be determined experimentally for specific mud rock systems. Noticeably, Brown et al. [339] accounted for gas slippage with an experiment performed in a vacuum. In other words, the correction model is mainly accurate at low-pressure conditions and in large-volume vacuums, depicting ideality. For this reason, in a confined pore state, the flow regimes change and other fluxes (like pore diffusion) set in. Shale transport is multiscale and multi-physical, so in addition to viscous flux, pore diffusion takes place when as pore size decreases, gas collides with the wall [42].

7.3.3 Pore Diffusion

Pore diffusion is classified based on the Knudsen number as either Fick, transition, or Knudsen diffusion (Figure 49) [105]. In the presence of viscous flux, the gas mass pore diffusion flux modified after Yanfeng et al. [112], corrected for the microstructure geometry and adsorbed gas film effect on pore diffusion, can be written as:

$$\vec{J}_p = -D_{eff} \nabla \rho , \quad (7.9)$$

where D_{eff} is the effective pore diffusion of the gas (m^2/s), corrected for adsorption and tortuosity. In addition, the bulk density of a real gas is as follows:

$$\rho = \frac{pM}{ZRT} . \quad (7.10)$$

Thus, Eq. (7.9) can be rewritten as:

$$\vec{J}_p = -\frac{MD_{eff}}{ZRT}\nabla p . \quad (7.11)$$

$$D_{eff} = \frac{D_p}{\tau_d^2(1+\beta)}, \quad (7.12)$$

where $\beta = \rho_{ads}/\rho$ is the adsorption equilibrium factor and τ_d is the diffusion tortuosity for pure geometry. The adsorption-diffusion tortuosity model (Eq. 7.12) describes the relationship between effective diffusion and unrestricted pore diffusion in the bulk phase [63, 64, 80]. More importantly, the adsorbed gas density is not constant, but rather varies with pressure [88]. Therefore, an isotherm model based on a constant volume (as opposed to a constant density) is more suitable for parametrizing the excess adsorption data in order to determine the dynamic adsorbed gas density as it varies with pressure. It is important to understand that the adsorbed phase affects the molecular movement, and hence the pore diffusion, as it changes with the pressure of the gas molecules. Again, this effect is quantified with the adsorption factor β , which is the ratio of adsorbed phase concentration to mobile phase concentration [129]. A non-empirical and dynamic molecular diffusion factor in the pore (ω_{mp}) and surface diffusion flux (ω_{ms}) that is dependent on the adsorption equilibrium factor is introduced below, such that $\omega_{mp} = 1/(1 + \beta)$ and $\omega_{ms} = 1 - \omega_{mp}$. At a very large β value, $\omega_{mp} \approx 0$ and $\omega_{ms} \approx 1$, suggesting that the contribution from the molecular diffusion is negligible compared to the surface diffusion of the adsorbed gas. At reference pressure and temperature conditions, D_{eff} and β are determined through molecular simulation; consequently, the diffusion tortuosity can be computed [81]. Eq.

(7.12) can then be substituted into Eq. (7.11) to determine the second pore diffusion mass flux:

$$\vec{J}_P = -\frac{\omega_{mp}M}{ZRT} \frac{D_p}{\tau_d^2} \nabla p, \quad (7.13)$$

where D_p is the pore diffusion with the real gas effect described by a step function, as follows:

$$D_p = \begin{cases} D_{Fick} = \frac{\lambda}{3} \sqrt{\frac{8RT}{\pi M}}, & Kn \leq 0.1 \\ D_{transition} = \frac{D_F D_K}{D_F + D_K}, & 0.1 < Kn < 10 \\ D_{Knudsen} = \frac{2r}{3} \sqrt{\frac{8RT}{\pi M}}, & Kn \geq 10 \end{cases} \quad (7.14)$$

If D_{eff} is measured experimentally or from an MD simulation [63, 64], then Eq. (7.11) should be used; otherwise, Eq. (7.14) is suitable to compute pore diffusion, provided that the pore geometry and adsorption equilibrium factor are known.

7.3.4 Surface Diffusion

Wu et al. [21, 82] derived surface diffusion mass flux based on the Maxwell-Stefan method, modified as follows:

$$\vec{J}_S = -L_m \xi_{ms} \rho_{ads} \nabla \mu \quad (7.15)$$

and

$$\mu = \mu_o + RT \ln(p) \quad (7.16)$$

where L_m , $\xi_{ms} = \left(1 - \frac{d_m}{r}\right)^{-2} - 1$, μ_o , and μ are the gas mobility ($mol.s/kg$), shale surface diffusion correction coefficient, reference chemical potential (J/mol), and chemical potential, respectively. Here, the ξ_{ms} factor is replaced with ω_{ms} , a dynamic surface diffusion factor that depends on the adsorption equilibrium.

$$\vec{J}_s = - \frac{L_m \omega_{ms} \rho_{ads} RT \nabla p}{p} \quad (7.17)$$

Recall that the surface diffusivity D_s is modeled after Chen et al. [83] and Wu et al. [116]:

$$D_s = D_s^o \frac{(1 - \theta) + \frac{\kappa}{2} \theta (2 - \theta) + [H(1 - \kappa)](1 - \kappa) \frac{\kappa}{2} \theta^2}{\left(1 - \theta + \frac{\kappa}{2} \theta\right)^2}, \quad (7.18)$$

where D_s^o and θ are the surface diffusion coefficient at zero loading and the loading factor, respectively:

$$D_s^o = L_m RT, \quad (7.19)$$

$$\theta = \frac{p}{p + p_L}, \quad (7.20)$$

and

$$H(1 - \kappa) = \begin{cases} 0, & \kappa \geq 1 \\ 1, & 0 \leq \kappa \leq 1 \end{cases} \quad (7.21)$$

where $\kappa = \frac{\kappa_b}{\kappa_m}$ is the surface gas molecule block coefficient, κ_b is the blocking velocity coefficient, κ_m is the migration velocity coefficient of the gas molecules, and $H(1 - \kappa)$ is

a Heaviside function. If $\kappa_m \gg \kappa_b$, surface diffusion will occur and κ will approach zero.

Consequently, Eq. (7.18) can be reduced as follows:

$$D_s^o = D_s(1 - \theta) . \quad (7.22)$$

Further, combining Eqs. (7.19) and (7.22) and solving for L_m :

$$L_m = \frac{D_s(1 - \theta)}{RT} . \quad (7.23)$$

Finally, substituting Eq. (7.23) into Eq. (7.17) to obtain the final form of surface diffusion yields:

$$\vec{J}_S = - \frac{D_s(1 - \theta)\omega_{ms}\rho_{ads}\nabla p}{p} . \quad (7.24)$$

7.3.5 Total Gas Mass Flux and Apparent Permeability

The total mass flux $\vec{J}_T$, which is the sum of the continuum/slip flux, pore diffusion, and surface diffusion fluxes $\vec{J}_T$, is determined by substituting Eqs. (7.7), (7.13), and (7.24) into Eq. (7.5), giving:

$$\vec{J}_T = - \left(\frac{F\rho r^2}{8\mu} + \frac{\omega_{mp}M}{ZRT} \frac{D_p}{\tau_d^2} + \frac{D_s(1-\theta)\omega_{ms}\rho_{ads}}{p} \right) \nabla p . \quad (7.25)$$

Alternatively, the pore diffusion term can be written in terms of the effective diffusion:

$$\vec{J}_T = - \left(\frac{F\rho r^2}{8\mu} + \frac{MD_{eff}}{ZRT} + \frac{D_s(1-\theta)\omega_{ms}\rho_{ads}}{p} \right) \nabla p . \quad (7.26)$$

Recall that the total mass flux is given as [112]:

$$\vec{J}_T = - \left(\rho \frac{k_{app}}{\mu} \right) \nabla p . \quad (7.27)$$

Equating Eqs. (7.25), (7.26), and (7.27), and then solving for k_{app} gives:

$$\kappa_{app} = \frac{\mu}{\rho} \left(\frac{F\rho r^2}{8\mu} + \frac{\omega_{mp}M}{ZRT} \frac{D_p}{\tau_d^2} + \frac{D_s(1-\theta)\omega_{ms}\rho_{ads}}{p} \right) \quad (7.28)$$

or

$$\kappa_{app} = \frac{\mu}{\rho} \left(\frac{F\rho r^2}{8\mu} + \frac{MD_{eff}}{ZRT} + \frac{D_s(1-\theta)\omega_{ms}\rho_{ads}}{p} \right). \quad (7.29)$$

Furthermore, the viscous flux permeability κ_{visc} , pore diffusivity permeability κ_{pore} , and surface diffusivity permeability κ_{surf} , contribute to the permeability model as:

$$\kappa_{visc} = \frac{Fr^2}{8}, \quad (7.30)$$

$$\kappa_{pore} = \frac{\omega_{mp}\mu}{p} \frac{D_p}{\tau_d^2}, \quad (7.31)$$

$$\kappa_{pore} = \frac{\mu D_{eff}}{p}, \quad (7.32)$$

and

$$\kappa_{surf} = \frac{\mu D_s(1-\theta)\omega_{ms}\rho_{ads}}{\rho p}, \quad (7.33)$$

respectively.

7.4 Model Validation and Comparison

The reliability of the developed model across a wide range of pore scales was validated using experimental data from Guo et al. [313] and via comparisons with widely available slippage and diffusion models. Oxygen gas flowing in a nanotube of 235 nm was employed

at 300 K. The laboratory inlet and outlet pressures, tube length, molecular weight of the gas, and recorded pressure drop and molar flux are all summarized in **Table 27**. The viscosity, bulk phase density, and gas compressibility factor were computed using NIST database experimental software called miniREFPROP [149]. These dynamic bulk property data points are available in the supplementary material found in **Table S1**. TAMAC was the only fit parameter used during the validation process.

Table 27. Calculation Parameters for Validation with Experimental Data

Parameter	Symbol	Unit	Value(s)
Nanotube length	L or Δx	m	60×10^{-6}
Nanotube diameter	d	m	235×10^{-9}
Outlet pressure	P_{out}	Pa	4.8×10^3
Pressure drop	$\Delta p = P_{out} - P_{in}$	Pa	Table S1
Average pressure	$P_{avg} = (P_{out} + P_{in})/2$	Pa	Table S1
Average bulk density	ρ	Kg/m^3	Table S1
Oxygen gas mol. Wt.	M	Kg/mol	0.032
Gas comp. factor	Z	dimensionless	Table S1
Gas viscosity	μ	Pa.s	Table S1
Temperature	T	K	300
TAMAC	α	dimensionless	0.79

As seen in **Figure 50**, the performance of the proposed model was better than the Knudsen diffusion and forced viscous Hagen-Poiseuille flow (K/HP) analytical models and Javadpour model when validated with the experimental data from Guo et al. Although that mode is performed best with the experimental data obtained, the laboratory experiment was

performed with a nanotube and oxygen gas diffused in ideal geometry, conditions that could not accurately represent the possibly complex geometry of shale on a nanoscale. Moreover, such models are only applicable when describing viscous flux and pore diffusion in nanopores and do not consider the surface diffusion in adsorbed layers. Finally, the nanopore size was 235 nm within the macropores; thus, these models' stability could come into question with higher Knudsen number diffusive flows.

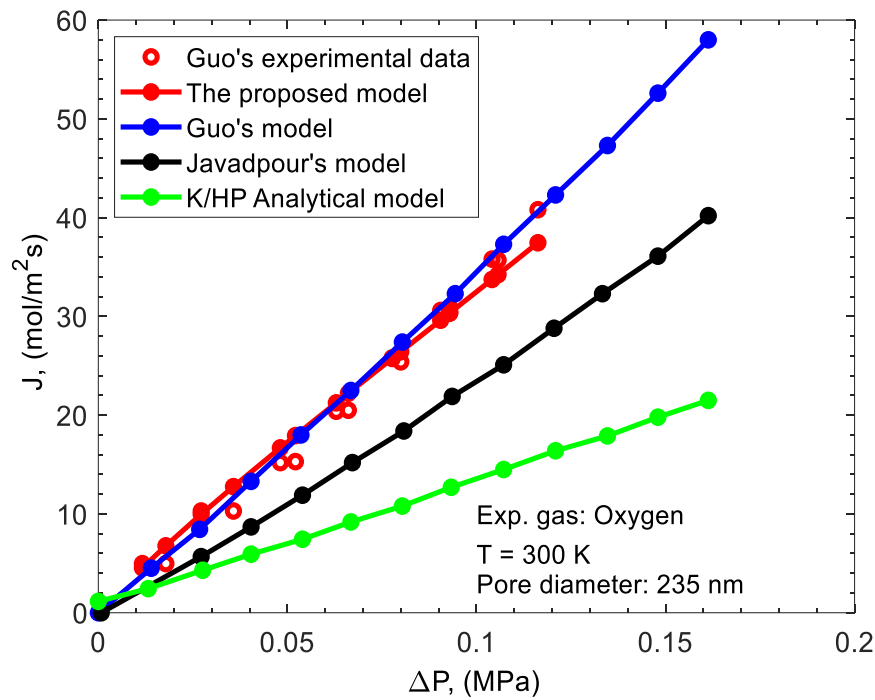


Figure 50 Flux and pressure drop relationship for the proposed model and models by Guo et al., Javadpour, and the K/HP analytical model, as well as the experimental data acquired from Guo et al. for ideal nanotube geometry.

It is noteworthy that the validation data using the nanotube is within the macropores size classification, and may require further validation within a 2 - 50 nm pore system. The challenge however is to obtain experimental data at such higher confined space due to difficulty of injecting the ultra-tight core samples. For these reasons, a molecular dynamics (MD) simulation data coupled with a published model by Kou et al. [91] was employed to

test the proposed model at a constant temperature and pressure state. The author obtained the correction factor for permeability in 2.0, 3, 5 and 6 nm kerogen pores hosting a supercritical methane, the MD information of the gas above critical pressure and temperature condition is available in **Table 28**.

Table 28 Calculation Parameters for Validation with Kerogen Molecular simulation Data of Kou et al. 2017

Parameter	Symbol	Unit	Value(s)
Kerogen pore diameters	d	m	$2, 3, 5, 6 \times 10^{-9}$
Pressure	p	MPa	17.237
Average bulk density	ρ	Kg/m ³	101.7
Methane gas mol. Wt.	M	Kg/mol	0.016
Gas comp. factor	Z	dimensionless	0.9223
Gas viscosity	μ	Pa.s	8.79×10^{-6}
Temperature	T	K	353
Gas slippage factor	F	dimensionless	1.0
Tortuosity	τ_d	dimensionless	1.0
Adsorption factor	$1 + \beta$	dimensionless	9.0

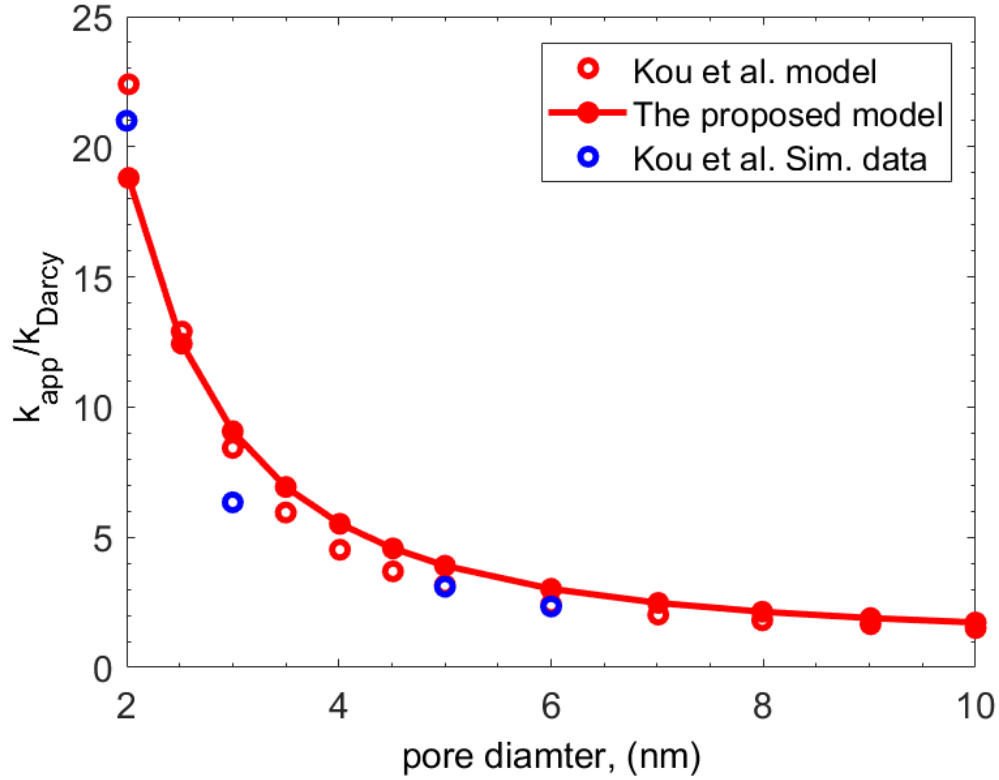


Figure 51 Validation of proposed model using kerogen permeability data and proposed model from the work of Kou et al. 2017

The authors of the utilized data introduced an empirical model to predict the adsorption factor as a function of pressure only and some fitting constant but lacks theoretical basis, thus the assessment of the influence of adsorption remains uncertain. Besides, the graph in **Figure 51** depicts the validity of the model within the mesoporous kerogen system. Again, the only fitting parameter that is uncertain is the adsorption equilibrium factor. Interestingly, the fit in Figure 51 was obtained at an adsorption factor of 9.0 for a given MD data of a smooth nanocapillary kerogen network with negligible slippage flux compared to the surface diffusion in adsorbed layer. Several transport equations (**Table 29**) exist for modeling viscous, pore, and surface diffusion in shale to overcome the limitations of laboratory measurements of permeability [22, 23, 27, 84]. Some mechanisms, such as a high Knudsen number diffusive regime that is beyond mesoscale-

based core measurements, in addition to the inherent significant volume of sorbed gas, add to the complexity of these data. The equations presented in **Table 29** were employed to compare their descriptions of the transport to that of the proposed model, which corrects for the influence of the combined nanoscale geometry and dynamic adsorption equilibrium factors on gas mass flux.

Table 29 Summary of Selected Permeability Models for Shale

Authors	Transport Mechanisms	Models
Wasaki and Akkutlu [137]	Viscous flow, gas, and surface diffusion	$\kappa_{app} = \frac{d^2}{32} + \mu D_{eff} c_g + \frac{\mu D_s V_{sL} \rho_{grain} B_g}{TOC} \frac{p_L}{(p + p_L)^2}$
Geng et al. [342]	Viscous flow, gas, transition, and surface diffusion	$\kappa_{app} = \frac{d^2}{32} + \frac{Kn^2 + Kn}{Kn^2 + 1} \cdot \frac{d\mu}{3p} \sqrt{\frac{8RT}{\pi M}} + 4 \frac{D_s p_L M C_L \mu}{(p + p_L)^2 \rho} \cdot \frac{(d d_m \theta - d_m^2 \theta^2)}{d^2}$
Cai et al. [113]	Viscous flow, gas, transition, and surface diffusion	$\kappa_{app} = \frac{d^2}{32} + \frac{Kn}{Kn + 1} \cdot \frac{d\mu}{3p} \sqrt{\frac{8RT}{\pi M}} + 4 \frac{D_s p_L M C_L \mu}{(p + p_L)^2 \rho} \cdot \frac{(d d_m \theta - d_m^2 \theta^2)}{d^2}$
Yanfeng et al. [112]	Viscous flow, slippage, transition diffusion, and surface diffusion	$\kappa_{app} = \frac{F d^2}{32} + D_{eff} \cdot \frac{\mu M}{\rho R T} + \frac{D_s \xi_{ms} \rho_{ads}}{p} \cdot \frac{\mu}{\rho}$

Wu et al. [164]	Viscous flow, pore diffusion, and surface diffusion	κ_{app} $= \left\{ \frac{\phi}{\tau} \frac{k_{\infty} p V_{std}}{RT} \frac{(1 + \alpha(Kn))}{1 + Kn} \left(1 + \frac{6Kn}{1 + Kn} \right) \right\}$ $+ \left\{ \frac{2\phi}{3\tau} r \left(\frac{d_m}{2r} \right)^{D_f-2} \left(\frac{8}{\pi RTM} \right)^{0.5} V_{std} \mu \frac{1}{1 + 1/Kn} \right\}$ $+ \left\{ \frac{\phi}{\tau} \left(\left(1 - \frac{d_m}{r} \right)^{-2} - 1 \right) D_s \frac{C_s V_{std} \mu}{pM} \right\}$ where $C_s = (4\theta M)/(\pi N_A d_m^2)$
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where k_{∞} is the liquid permeability, $\alpha(Kn)$ is the rarefaction coefficient [17, 75], C_L is the maximum adsorbed gas concentration (mol/m^3), c_g is the gas compressibility (1/pa), ρ_{grain} is the grain density (kg/m^3), $V_{sL} = n_L V_{std}$ is the maximum adsorbed gas volume (m^3/kg), $V_{std} = 0.0224$ is the molar volume of gas at standard temperature and pressure (m^3/mol), TOC is the total organic content of the rock, and B_g is the gas formation volume factor. D_f is a quantitative measure of the surface roughness varying between 2 (for smooth surfaces) and 3 (for space-filled surfaces). The dynamic and static parameters used in the present study to compare transport modeling by the developed model against those listed in **Table 29** are summarized in **Table 30**. It is noteworthy that the data sources and theoretical background are explained in detail by Aljaberi et al. [206]. The author studied the impact of kerogen tortuosity in shale permeability.

The surface diffusivity, pore diffusion, apparent permeability, and correction factor $\kappa_{app}/\kappa_{visc}$ were predicted for all models. The slippage flux correction F was neglected; that is, there was no slippage flow. Interestingly, from **Figure 52**, the proposed model

predicted the surface diffusivity permeability at the same level of accuracy as the models by Cai et al. [113] and Geng et al. [84]. Conversely, the predictions by Yanfeng et al. [112] and Wasaki et al. [137] represented cases of high and low permeability in the adsorbed gas phase.

Table 30 Dynamic and Static Parameters, Symbols, and Units for Model Comparison

Parameter	Values	Symbol/(unit)
Pressure	2.1, 3.4, 6.9, 10.3, 20.7, 31, and 41.3	P/(MPa)
Temperature	350	T/K
Bulk gas density	11.64, 19.58, 40.16, 61.38, 123.22, 173.20, and 210.05	$\rho/(kg/m^3)$
Gas compressibility (10^{-3})	3.392, 2.056, 1.045, 0.696, 0.309, 0.165, and 0.100	$c_g/(1/psia)$
Gas viscosity (10^{-5})	1.3, 1.32, 1.39, 1.47, 1.82, 2.22, and 2.6	$\mu/(pa.s)$
Gas compressibility factor	0.9818, 0.9706, 0.9464, 0.9289, 0.9254, 0.9875, and 1.0857	Z-factor
Formation volume factor	0.0565, 0.0335, 0.0163, 0.0107, 0.0053, 0.0038, and 0.0031	B_g
Adsorbed gas density	466.7, 565.3, 701.5, 762.7, 833.1, 853.6, and 866	$\rho_{ads}/(kg/m^3)$
Max. adsorbed gas conc.	0.05688	$C_L/(mol/m^3)$

Max. adsorbed amount	4.6262	$n_L/(mol/kg)$
Langmuir pressure	2.026	$p_L/(MPa)$
TOC	100	%
Grain/kerogen density	1300	$\rho_{grain}/(kg/m^3)$
Gas molar mass	0.016	$M/(kg/mol)$
Diameter of methane mol.	0.38×10^{-9}	$d_m/(m)$
Self-diffusion (10^{-9})	1.1179, 1.5412, 2.2433, 2.938, 4.4457, 5.1722, and 5.3857	$D_{self}/(m^2/s)$
Surface diffusion (10^{-9})	0.1105, 0.10314, 9.909, 9.466, 8.484, 7.8743, and 7.9467	$D_s/(m^2/s)$
Tortuosity	1.72	τ_d
Mean pore radius	0.6×10^{-9}	$r/(m)$
Gas slippage factor	1.0	F

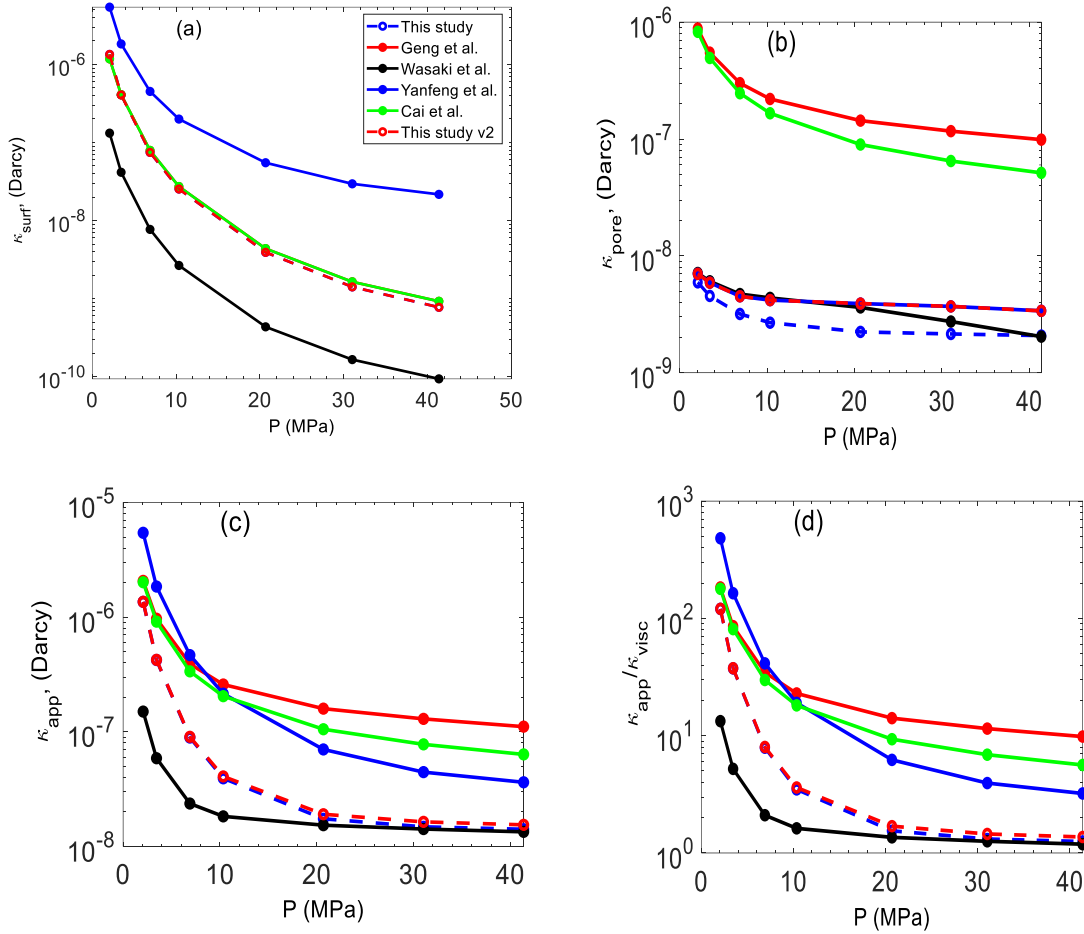


Figure 52 Comparison of the proposed model and existing theoretical models for: (a) surface diffusion transport, (b) pore diffusion, (c) apparent permeability, and (d) correction factor for non-Darcy fluxes.

The proposed model's predictions of the different transport mechanisms were in reasonable agreement with those of the existing models (Figure 52). However, there was a substantial deviation in the pore diffusion flux predicted by the Cai et al. [113] and Geng et al. [136] equations, which was obviously due to the absence of a microstructure parameter (i.e., the effective diffusivity coefficient or tortuosity factor); this parameter was not considered by the authors in their model development. The Waskai model prediction for pore diffusion permeability was similar to that of the proposed model. However, there were discrepancies

in the overall gas permeability values resulting from the physics of the surface diffusion in the adsorbed phase. The authors' model provides a conservative estimate of diffusion in the phase nearest the pore wall. Conversely, the proposed model aligns best with the pore diffusion equations of the Cai and Geng models, while the Yanfeng model provided a high estimate. Therefore, the proposed apparent permeability model appears to behave within a mean set of cases between the conservative estimates of the Wasaki model and optimistic computations provided by the Yanfeng model. Interestingly, the reason for this behavior is that these models consider a static factor to mimic the adsorbed layer effect in the surface flux, rather than a dynamic factor that impacts the entire diffusion flux.

7.5 Characteristics size of 3D Pore Geometry

In nature, shale and tight gas reservoirs have complex 3D geometries with random pore networks of different sizes. Modeling the permeability of a system of organic and inorganic compartments with multiple pore sizes and levels of connectivity requires a detailed approach for estimating the sizes of characteristics of the capillary system. Percolation theory is widely employed to determine the representative pore width, which may defer from the average measurements, depending on the degree of heterogeneity and connectivity of the empty spaces. It is important not to over or underestimate the pore throat size, which mainly controls the apparent gas permeability. Organic and inorganic matrices in shale, for instance, have different effective pore channels that connect the effective pores and throat to the hydraulic fractures or wellbore. Organic matter such as kerogen has interconnected networks of meso- and micropores and throats. Similarly, the meso- and macropores in the inorganic phase of a shale matrix possess a unique gas flow path to the wellbore. To obtain the characteristic capillary size, the pore bodies and throats are

randomly sampled using lognormal normal and/or multimodal distributions. The average size is taken as representative if the normal distribution is used, but that may not be the case if a multimodal distribution is employed for the sampling. Percolation theory is based on multimodal distribution analysis, as proposed by O'Carroll and Sorbie [343] and established on the Poiseuille law generalization for the total flow of a single-phase fluid.

The principle assumes that flow only occurs in a system with distribution through pores of different radii above a threshold or percolation radius R_p . Initially, the conductive tubes are closed; then, they are randomly opened until a certain fraction of clusters p_c with pore sizes above the percolation radius connects to a fraction of the pores, allowing for flow to occur. The conductivity of the distribution of pores is given by $f(r)$. The radius of this inserted tube R_p that connects a fraction of these clusters across the network (allowing for flow to begin) is referred to as a representative pore throat. The relationships among the distribution of pores, fraction of connected clusters, percolation, and maximum pore size is given by Eq. (7.34):

$$p_c = \int_{R_p}^{R_{max}} r f(r) dr, \quad (7.34)$$

where R_{max} is the maximum pore capillary radius. Interestingly, the percolation threshold p_c depends on the geometric structure of the network, and for a simple cubic lattice with a network containing 6,100 bonds, $p_c = 0.25$ with a high degree of accuracy. It is important to note that percolation theory does not always provide a complete description of network flow, due to uncertainty surrounding the determination of appropriate p_c and $f(r)$ values, which differ with the geometric structure and distribution, respectively. For the sensitivity

studies performed, it was assumed that the pore throat size used to compute permeability was representative.

7.6 Sensitivity Analysis, Results, and Discussion

The developed model was utilized to explore shale gas permeability, with an emphasis on the impacts of changes in pore radius, pore geometry, and pressure. The details are presented in Sections 7.6.1, 7.6.2, 7.6.3, and 7.6.4.

7.6.1 Transport Fluxes

The individual contribution of each transport mechanism was calculated and reported in Darcy units. The apparent permeability was also calculated as the sum of the three mechanisms. Intuitively, the viscous permeability was solely dictated by the pore size, regardless of the pressure (**Figure 53-c**). Conversely, surface diffusion was only sensitive to pressure, regardless of pore size (**Figure 53-a**). In other words, the Darcy flow contribution to the total transport in porous media was unaffected by a decline in reservoir pressure (assuming no changes in the stress field as the pore fluid pressure changed). The amount of sorption was determined to be very sensitive to pressure changes during production, making surface diffusion highly dependent on pressure. Furthermore, pore diffusion was significantly influenced by both pore size and pressure, as can be seen in **Figure 53-d** (i.e., the pore diffusion at a low pressure was 10 times greater than its value at a higher pressure and the same pore size). The apparent permeability could predominantly be controlled by viscous flux for pore sizes larger than 10 nm, as shown in **Figure 53-b**. For smaller pore sizes, both surface and pore diffusion mechanisms were found to control the overall transport, especially at low to intermediate pressure values. These observations are consistent with several reported in the literature [14, 22, 24].

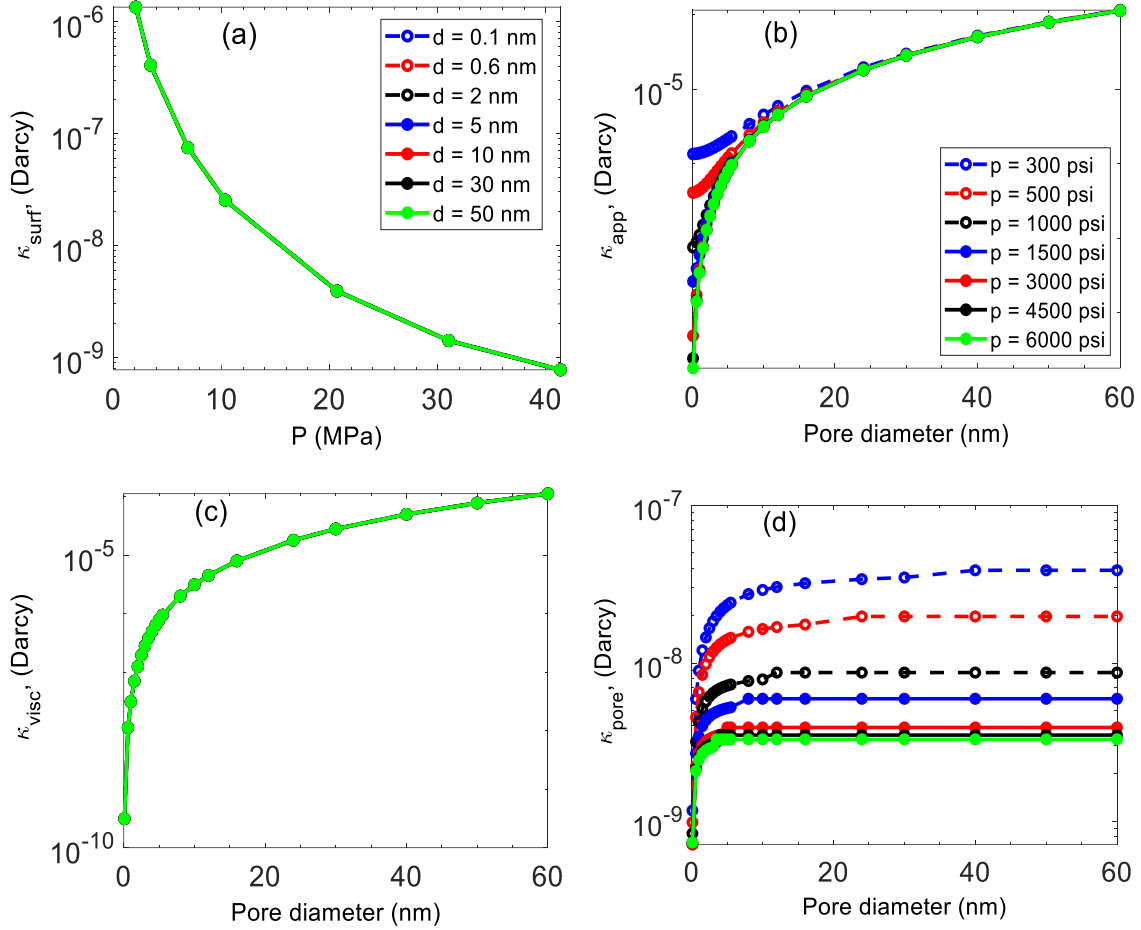


Figure 53 Influence of pressure and pore radius on the: (a) surface diffusivity, (b) apparent diffusivity, (c) viscosity, and (d) pore diffusivity permeability models.

7.6.2 Relativity of Transport Fluxes

Per the observations made in the previous section, **Figure 54** provides deeper insights into the dependency of apparent permeability on the multiscale fluxes present in shale, as a function of pressure. Again, the definitions of the terms macropores, mesopores, and micropores were assumed to be consistent with the IUPAC definitions, where pore diameters > 50 nm are referred to as macropores, 2 to 50 nm are mesopores, and less than 2 nm are micropores [5, 88]. The impact of pore scale and pressure on the intermolecular interactions within nanopores, and hence the overall transport and governing mechanisms,

were investigated in the present research. A study of the influence of pressure loading of gas in mesopores and micropores was performed, and the outcomes found to be consistent with earlier observations that above 10 nm and at pressures beyond 10 MPa, molecular diffusivity flux is negligible. Yet, the relative contribution of viscous flux in smaller pores was more than the surface diffusion at pressures higher than 30 MPa. The surface diffusion consistently constituted more than 50% of the apparent permeability below 10 MPa and 5 MPa at 0.6 and 2 nm pore sizes, respectively. However, a crossover was found at levels above these pressure states, where molecule size-induced barriers restricted pore and surface diffusion. However, it was noted that pore diffusion permeability was negligible in mesopores and macropores along the entirety of the pressure range. Viscous flux dominated at 50 nm macropores and could constitute up to 100% of transport flux above 5.0 MPa. This was in agreement with what was reported by Cai et al. [113].

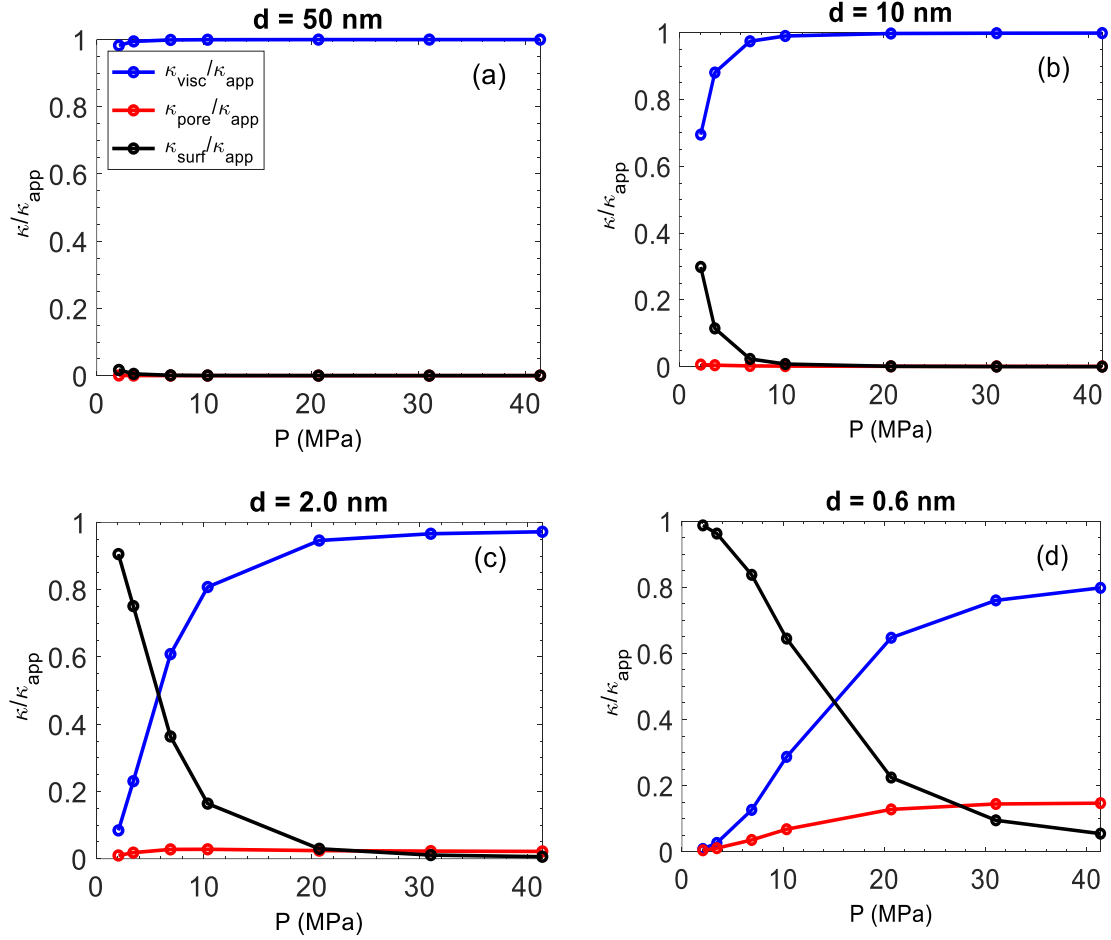


Figure 54 Relative contributions of viscosity, pore diffusion, and surface diffusion flux at different pressures and pore scales of: (a) 50 nm, (b) 10 nm, (c) 2 nm, and (d) 0.6 nm

7.6.3 Apparent Permeability of Gas

Accurate estimation of the ratio k_{app}/k_{Darcy} is needed to account for the impact of gas and surface diffusions and accomplish retrieval of the intrinsic permeability. The deviation of apparent gas from intrinsic permeability is given in **Figure 55**.

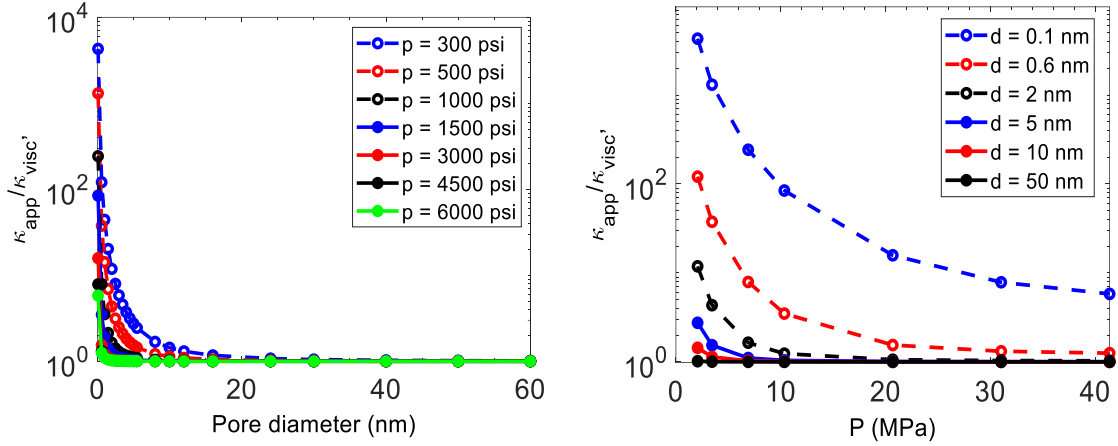


Figure 55 Gas correction factors at different pore scales and pressure conditions.

As compared to macropores, at lower pressures, corrections of a higher order of magnitude are required for micropores; this is consistent with the trend observed by Javadpour et al. [309]. Above a 20 nm pore size, the correction factor is 1.0, irrespective of the pressure conditions.

7.6.4 Impact of the Pore Scale Geometry Factor

In porous media, diffusion tortuosity is required to compute the pore diffusion permeability and account for the average elongation of the fluid stream relative to the free flow. In this example, it should be noted that the influence of the geometry factor on viscous flux permeability was assumed to be negligible. **Figure 56** illustrates the impact of tortuosity on pore diffusion. The outcomes showed that although pore diffusion permeability was reduced with the diffusion tortuosity, in an average pore size of 0.6 nm, the gas apparent permeability and non-Darcy correction factor were unaffected by the micropore structure parameter, except at pressures above 10 MPa. Therefore, in micropores, the impact of tortuosity was determined to be negligible at lower pressures, due to the dominance of the surface diffusion transport.

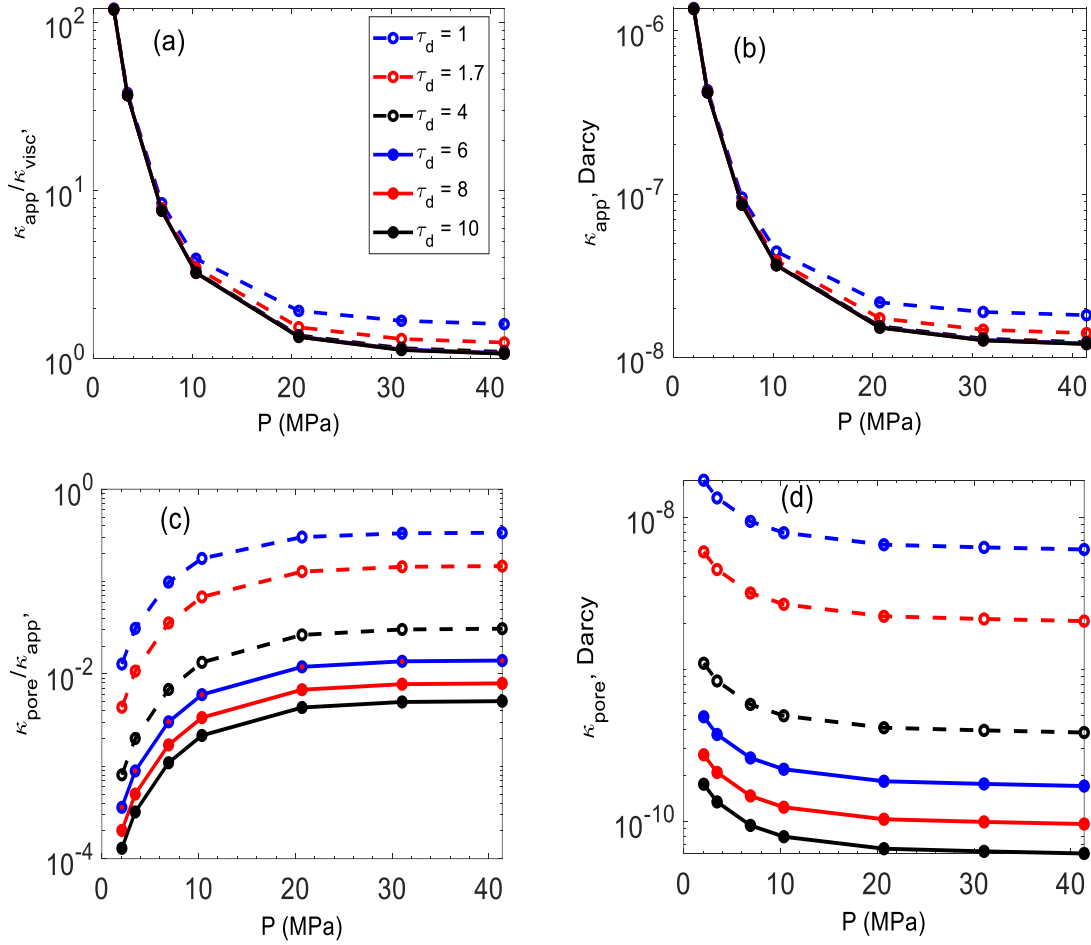
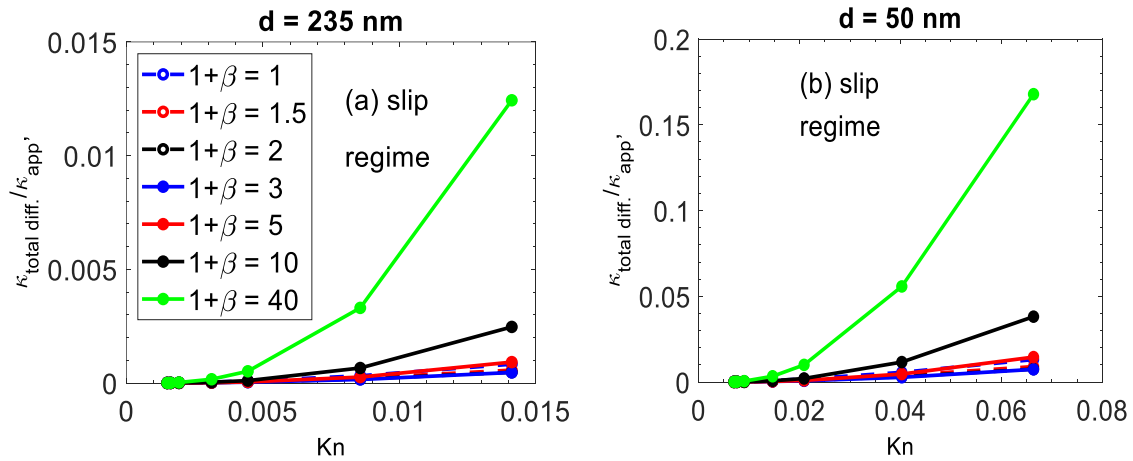


Figure 56 Impact of tortuosity on the: (a) Darcy permeability correction factor, (b) apparent permeability, (c) contribution of pore diffusion to apparent permeability, and (d) pore diffusion permeability in micropores of an average size of 0.6 nm.

7.6.5 Impact of the Dynamic Adsorption Factor

The dimensionless Knudsen parameter was considered the dependent variable because it is a function of the gas properties and pore size characteristics of the system. Moreover, it provides an overview of how changes in adsorption behavior may impact the relative contributions of the diffusion flux and gas correction factor in porous media. Some of the data in **Table 30** were employed in the present research, along with a TAMAC of 1.0. The adsorbed phase density and corresponding dynamic parameters were varied to determine

how they affected the relative contribution of total methane diffusion flux, which was composed of the surface and pore diffusion in the different diffusion regimes. **Figure 57** shows that the role of the adsorption factor in modeling diffusion permeability was more significant in the Knudsen diffusion domain and the least significant in the Fick domain. Again, the importance of the diffusive flux was determined to be greater in higher Knudsen number flow systems and confined pores. Generally, a noticeable adsorption layer at, for instance, $1 + \beta = 40$ could suggest a higher total diffusive flux across all transport regimes. Moreover, it is important to note that $1 + \beta = 1$ represented a no-adsorbed-layer scenario. The adsorption equilibrium factor depended on the chemical heterogeneity of the materials, gas properties, and amount of chemical interaction energy that existed between the gas and atoms in the rock. Thus, in cases where the adsorption forces are very high, the impact of the diffusion flux could be immense across all flow regimes.



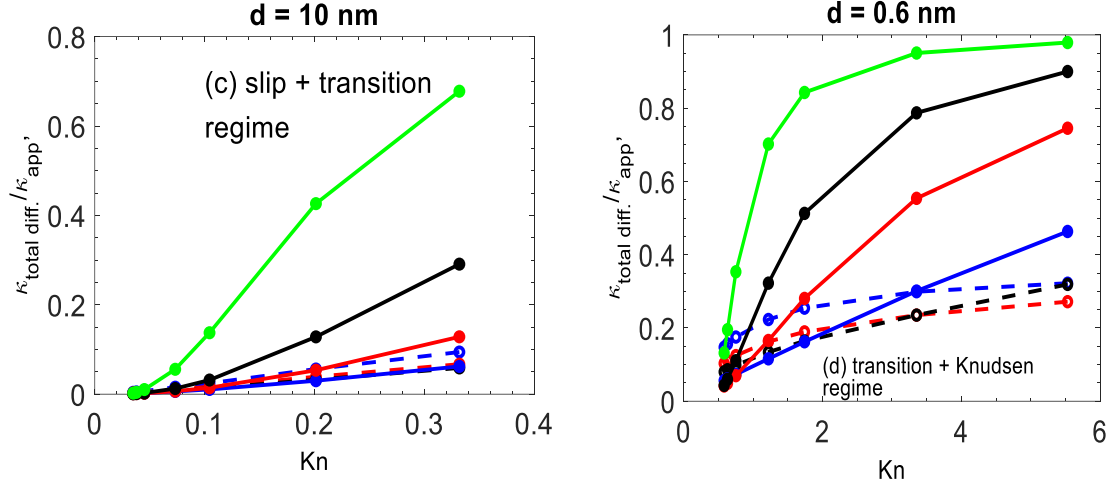


Figure 57 Impact of the adsorption equilibrium factor on the relative contributions of pore and surface diffusion permeability across all transport regimes. Flow regimes were classified according to the dimensionless Knudsen number, according to the Beskok [117] and Sheng [105] classifications, and varied with the pore size scale: (a) lower limit of the slip regime, (b) upper limit of the slip regime, (c) slip and transition regime, and (d) transition and Knudsen regime.

7.7 Conclusion

In this work, an apparent permeability model was developed that couples the pore structure tortuosity and adsorption phenomena to predict the transport of gas in porous media. The model accounts for viscous flux, pore diffusion, and surface diffusion in the adsorbed phase, and more importantly, integrates variations in the physics of pore diffusion across a wide range of pore sizes and pressures, from the Fick regime through the transition to the Knudsen diffusion region. The data acquired by the experiment conducted in Guo et al. [344] to compute the viscous and pore diffusion fluxes of oxygen gas through a 235 nm nanotube was employed to validate the proposed model. Furthermore, permeability data obtained from molecular simulation to describe the transport of supercritical methane gas in a nanocapillary smooth kerogen network of pore sizes 2, 3, 5 and 6 nm was utilized to test the model. The validated model was then compared with the Javadpour and K/HP analytical models. Furthermore, the predictability of the multi-physics equation in

micropores was compared to the performances of four existing theoretical models. A sensitivity analysis was carried out to understand the transport behavior at different pore scales and pressure conditions. Some of the preliminary conclusions drawn were as follows:

- In the validation process, the proposed model agreed reasonably well with the experimental data and had better predictability of oxygen's molar flux through macropore-sized tubes, as compared to the Knudsen diffusion and forced viscous Hagen-Poiseuille flow (K/HP) analytical and Javadpour models. Interestingly, it tests relatively well with mesoporous kerogen permeability data.
- A comparison of the performances of the new multi-physics and existing models showed that the apparent and surface permeability predictions were within the prevailing uncertainty bands. In other words, the descriptions of the relative contributions of the fluxes and total fluxes were within a possible range.
- The sensitivity studies revealed that the role of surface diffusion in the apparent gas permeability expanded substantially as the pore size decreased. Specifically, diffusion in adsorbed gas layers of gas was found to constitute more than 50% of the apparent permeability in that range of pore sizes for pressures below 10 MPa and 5.0 MPa in micropores and mesopores, respectively. At higher pressures, there was a crossover of dominance from surface diffusion to viscous flux. The influence of the Darcy scale flow was notable as the pore size increased.
- Viscous flux based on the Darcy law was determined to be valid for describing the total flux in a material that contains mainly macropores (> 50 nm pore sizes). At the same time, increased intermolecular interactions were found, as compared to

molecule-wall collisions. Thus, the assumption of a continuum flow regime should only be considered valid at extremely high pressures, above 10 MPa in the mesopores considered in the present study. Molecular diffusions such as surface and pore diffusion were negligible at elevated pressure conditions.

- Although pore diffusion permeability is reduced with increased diffusion tortuosity, the apparent permeability and non-Darcy correction factor for gas in 0.6 nm pores (on average) were unaffected by the micropore structure parameter, except at pressures above 10 MPa.
- In 50 nm and 235 nm pores, the total diffusion permeability was negligible relative to the Darcy flow in the slip regime. However, there was a notable influence of the adsorption equilibrium factor, particularly in the slip, transition, and Knudsen diffusion regimes, and interestingly, the overall contributions of the surface layer and pore diffusion increased as the pore size decreased, and that increase was in the same order from the slip to Knudsen regime.
- The deviation of gas permeability from the Darcy flow in shale and ultra-tight rocks was found to be higher across all transport regimes when the influence of the adsorption forces on pore and surface diffusion flux was considered. Thus, reservoir management strategies must consider these dynamics throughout the life cycle of a gas field asset.

CHAPTER 8

MULTISCALE AND MULTIPHYSICS PRODUCTION

FORECASTS OF SHALE GAS RESERVOIRS: NEW

SIMULATION SCHEME BASED ON GAUSSIAN

PRESSURE TRANSIENTS⁵

Abstract

Common numerical solutions for production rate forecasting of shale reservoirs have a limited capability to describe the dynamics of fluid mass transfer during a pressure depletion cycle due to production with hydraulically fractured well systems. The pressure drawdown imposed by the well system triggers continuous expansion of free gas in the larger pores, while molecular diffusion predominates in the smaller pores. The declining reservoir pressure leads to the closure of larger pores, which gives further significance to molecular diffusion as a component of the mass transport process. To capture these multiphysics mechanisms, pressure-diffusion and molecular-diffusion forms of the

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diffusivity equation, discretized in space and time, were simultaneously solved to simulate mass transfer dynamics and kinematics in shale formations. This new approach uses a Gaussian probability function to describe the advance rate of both types of diffusion processes, creating a unique scheme for simulating shale gas reservoirs based on physical parameters that could be either measured or characterized. The adopted algorithms successfully provide solutions that can match the typical shale production profiles. Results are sensitive to the essential reservoir parameters of pressure depletion, matrix permeability, organic content, and local heterogeneity. The simultaneous solution of molecular and pressure diffusivity equations reveals their interdependencies. The production peaks early and then rapidly decline with a growing effect of pore compaction. The flux of the sorbed phase contributes to the production rate by some factor that is determined by the sorption capacity of the organic matter. The methodology provided in this study can be utilized to simulate mass transport in shale reservoirs and predict hydrocarbon production rates, which may greatly aid asset management decisions and maximization of the ultimate recovery.

Keywords: Shale gas, Gaussian pressure transient, Hydraulic fractures, Molecular diffusion flux, Production forecast

8.1 Introduction

Production forecasting is an essential component of hydrocarbon asset development, as the projected well rates are used to inform decisions regarding the optimal exploitation of hydrocarbon-bearing formations. In a general sense, production forecasting is either based

on extrapolating existing data through time-dependent mathematical relationships (with some fitting parameters) in an approach known as decline curve analysis (DCA) [208,209] or through physics-based reservoir simulation schemes. The former approach is simpler, but its application is restricted to the preservation of the status quo of the formation, which can be subject to variation through different upstream operations such as changing the well placement, water injection, and application of tertiary recovery techniques. Reservoir simulation, on the other hand, requires a detailed description of the rock and fluid properties incorporated into specific transport and geological models. Over the years, Darcy's law has remained the primary mathematical framework linking pressure drawdown to production rate. It was originally derived for incompressible single-phase laminar flow but has been supplemented with some additional equations to account for multiphase flow (i.e. relative permeability curves), compressibility effects (i.e. real gas law), capillary pressure effects (i.e. J-functions), and other aspects. Furthermore, fine-scale gridding of the reservoir was introduced through structured and unstructured grids to capture the local heterogeneity [210]. Nevertheless, this approach has faced limitations when applied to shale formations.

Much effort has been made in the literature to explain that the detailed mass transport mechanisms responsible for the well rate when producing from shale formations differ from simulation models used in conventional reservoir engineering [25]. The sedimentation processes responsible for shale formation in a quiet marine environment reduces the petrophysical quality of the reservoir (i.e. porosity and permeability), while the presence of quartz induces brittleness that renders shales subject to abundant natural fractures upon deep burial [30,31]. The presence of organic matter adds more complexity,

as the hydrocarbon accumulation in the formation is self-sourced, with a significant amount of gas trapped in the nano- and micropores associated with the organic matter [10,32–38]. Kerogen is an insoluble organic compound present in shale reservoirs with its elemental composition varying based on its origin and maturation. The skeleton of kerogen has micropores that host hydrocarbons in the sorbed phase. The sorption capacity is determined by the degree of organic matter maturity, and temperature and pressure conditions [109,211]. Hydrocarbons are expelled from the pores to the inorganic matrix system as the pressure declines [137].

Solving complex engineering mathematical relationships for the purpose of reservoir simulation is achieved through discretization of equations over space and time, honoring the geological heterogeneity of the reservoir, and thermodynamic properties of the fluid. To facilitate the reservoir simulation process in conventional hydrocarbon reservoirs, different software packages have been established, including Eclipse (owned by Schlumberger), Intersect (co-jointly owned by different ventures), tNavigator Rock Flow Dynamics, Nexus (developed by ARAMCO and owned by Landmark Graphics), Petrel Schlumberger, CMG, and other licensed and open-source interfaces. However, the different nature of shales as so-called unconventional, ultra-low permeability reservoirs, impacts the accuracy of these software platforms when used to describe mass transport dynamics and kinematics in shale reservoirs during typical production spans. Researchers have repeatedly approached this knowledge gap by refining the existing tools rather than establishing new schemes. In this context, complex analysis methods attempted to shift the attention to the transport of fluids in the vicinity of natural and hydraulic fractures (HFs) as the primary source of permeability [212]. The results were used to generate type curves

that can be used for production forecasting of different scenarios [213]. Some grid-based simulation [214–216] and machine learning [217,218] solutions exist to describe the multiscale transport physics in hydraulic fractured shale gas systems and could require much time and extra technical know-how to implement at field scale.

Alternatively, one could look at shale's characteristics as an opportunity for simplification, even though such simplification runs counter to current trends in modeling shales. Weijermars [219] revolutionized the way shale formations are simulated by introducing the Gaussian Pressure Transient (GPT) method, which was conceptualized based on several assumptions. The primary assumption is production with a constant bottom hole pressure (BHP), with pressure interference between adjacent hydraulic fractures accounted for via superposition, using a closed-form, gridless solution method. These assumptions are reasonable when considering shale resources, as they are of low permeability, have an extended transient period, with mass transport affected by internal boundary effects (such as pressure interference via the hydraulic fractures).

In practice, the production regime of shale wells remains transient throughout the typical pressure depletion over the well's economic life-cycle. The BHP is one of the few engineering parameters that is controlled during the production. Hydraulic fractures are introduced during drilling and completion phases with a decent capability to determine their coordinates and extent. The mathematical framework proposed by Weijermars [219] accounts for the reservoir heterogeneity (i.e., the presence of hydraulic fractures) and the petrophysical and fluid properties are captured in the hydraulic diffusivity of the bulk rock volume. When pervasive micro-fractures occur in the matrix of the stimulated rock volume, these will be accounted for in the effective hydraulic diffusivity via the bulk permeability

that contributes to the diffusivity. The system dynamics (balance of forces) is governed by the continuum equation and kinematics (velocity field) is governed by the equation of motion. For the specific system studied, the continuum equation can be represented as a diffusivity equation and the equation of motion (Navier-Stokes equation) can be simplified into Darcy's Law (neglecting inertia and gravity terms).

In the development of the basic GPT model, the permeability was taken as a constant value (i.e. original Darcian one) [219]. This assumption would only be justified in the absence of pore compaction. However, in real-life reservoirs the pore gas pressure declines near a producing well system, due to production-induced pressure depletion in the drained rock volume. Eventually, permeability reduction of the matrix rock occurs between the hydraulic fractures [137,345]. Such reduction in the convective transport is met with waxing of the sorbed phase flux as the pressure decreases. The sorbed phase constitutes a significant amount of the initial gas in place (i.e., up to 30-40%), which therefore needs to be accounted for when modeling the Darcian sorption flux [10,38,346]. Molecular diffusion is the governing mechanism by which the sorbed phase is transported from the organic matter to the pores of the inorganic rock matrix, and eventually to the hydraulic fractures via a hierarchy of pathways [91,113,115,143,159,299,309,347,348].

The primary objective of the present study is to modify the GPT solution of shale gas transport [219], considering the aforementioned intricacies, and develop an advanced simulation framework that accounts for the multiscale and multi-physics nature of mass transport in shale formations. In particular, the changes in the pressure that influence the effective confining pressure, and molecular diffusion are accounted for in the proposed approach.

8.2 Methodology

The GPT method provides solutions for the spatial and temporal advance of the pressure transient that depends on the effective diffusivity. The term “effective diffusivity” refers to a combination of the gas pressure dependent permeability, viscosity, gas deviation factor and total compressibility in some ratio as to be detailed in the coming subsections. The parameters defining the effective diffusivity change with the pressure as highlighted in the introduction. Hence, an iterative approach is followed in which each iteration is terminated upon pressure convergence at a given time step. The workflow presented in **Figure 58** is utilized for this research. The GPT solution is obtained for shale gas reservoirs through a numerical approach incorporating the geological and the fluid characteristics of shale formations. Subsections 8.2.1 – 8.2.6 outline the details of the adopted scheme including the confining pressure sensitive permeability model [137,282,349], the transport of the sorbed phase in the organic matter [91,159,348,350], and the GPT solution approach [219,351].

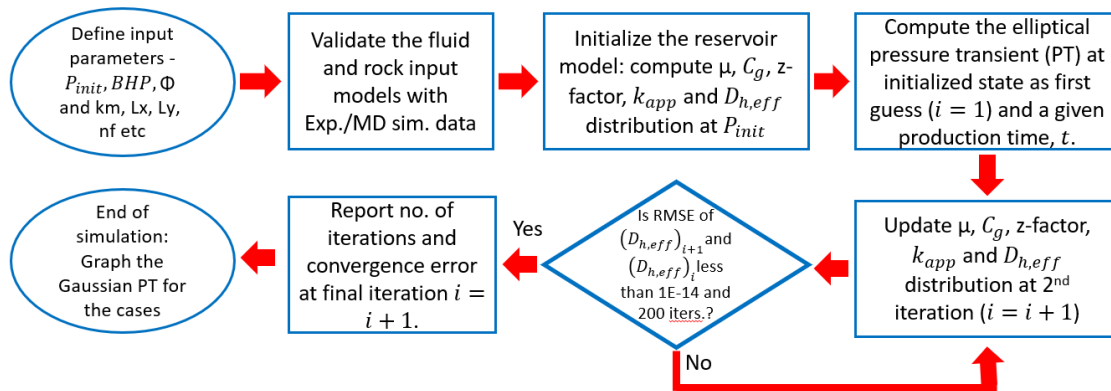


Figure 58 Iterative workflow adopted to simulate pore pressure dependent flux, by coupling molecular and advective mass transport mechanisms based on effective diffusivity in shale gas formations.

8.2.1 Fluid properties

Natural gas production in shales is subject to expansion driven by pressure depletion. The confidence in a production forecast hinges on accounting for the changes in the gas properties such as the viscosity and the isothermal gas compressibility coefficient. Natural gas, represented by methane in this study, has the virtue of having all of its fundamental properties linked to its compressibility factor (i.e., Z-factor) [352], which measures the degree of real gas deviation from ideal behavior at a certain temperature and pressure. The Z-factor could be empirically modeled as [352]:

$$Z = (0.702e^{-2.5T_{pr}})P_{pr}^2 - 5.524e^{-2.5T_{pr}}P_{pr} + 0.044T_{pr}^2 - 0.164T_{pr} + 1.15, \quad (8.1)$$

where $P_{pr} = P/P_c$ is pseudoreduced pressure, P is pore pressure, P_c is critical pressure, $T_{pr} = T/T_c$ is pseudoreduced temperature, T is temperature, and T_c is critical temperature.

The isothermal compressibility coefficient of gas, c_g , is computed as:

$$c_g = \frac{1}{P} - \frac{1}{Z} \left(\frac{\partial Z}{\partial P} \right)_T. \quad (8.2)$$

The convective transport is primarily governed by its viscosity, which represents the internal frictional resistance within the fluid particles at a given state of pressure and temperature. Lee *et al.*'s [353] empirical model was used to describe the gas viscosity (in centipoise), which represents the resistance to flow, as

$$\mu_g = 1.0 \times 10^{-4} Ke \left[x \left(\frac{\rho_g}{62.4} \right)^y \right], \quad (8.3)$$

where all units in Eq. (8.3) are in field, ρ_g is gas density at reservoir condition (units of

lbm/ft^3), and

$$K = \frac{(9.379 + 0.01607M_g)T^{1.5}}{209.2 + 19.26M_g + T}. \quad (8.4)$$

T is in Rankine, M_g (g/mol) is gas molecular weight,

$$X = 3.448 + \frac{986.4}{T} + 0.01009M_g, \quad (8.5)$$

and $Y = 2.447 - 0.224X$.

The predictability of the above set of equations were checked against some experimental data as to be shown in the first part of the results section.

8.2.2 Apparent permeability model derivation

The conservation of mass equation for a shale reservoir containing both free and sorbed gas phases can be written as:

$$-\nabla \cdot (\rho_g \vec{u}) + \nabla \cdot (\bar{\bar{D}}_{eff} \cdot \nabla \rho_{ads}) = \frac{\partial}{\partial t} (\phi \rho_g) + \frac{\partial}{\partial t} [\varepsilon_{gr}(1 - \phi) \rho_{ads}]. \quad (8.6)$$

Here, ρ_g is gas density (kg/m^3), $\vec{u}$ is Darcian flow velocity (m/s), $\bar{\bar{D}}_{eff}$ is the effective molecular diffusion tensor in organic phase (m^2/s), ρ_{ads} is adsorbed phase density (kg/m^3), ϕ is matrix porosity, and ε_{gr} is the ratio of organic matter grain volume to the total rock volume. This ratio is comparable to the total organic content (TOC) in wt.% if the total inorganic carbon is negligible [137]. The left-hand side (LHS) of Eq. (6) represents the sum of the fluxes in the inorganic matrix and organic matter, while the right-hand side (RHS) is the accumulation over time. The shale conceptual model is shown in **Figure 59**, with further details of the flux terms given below.

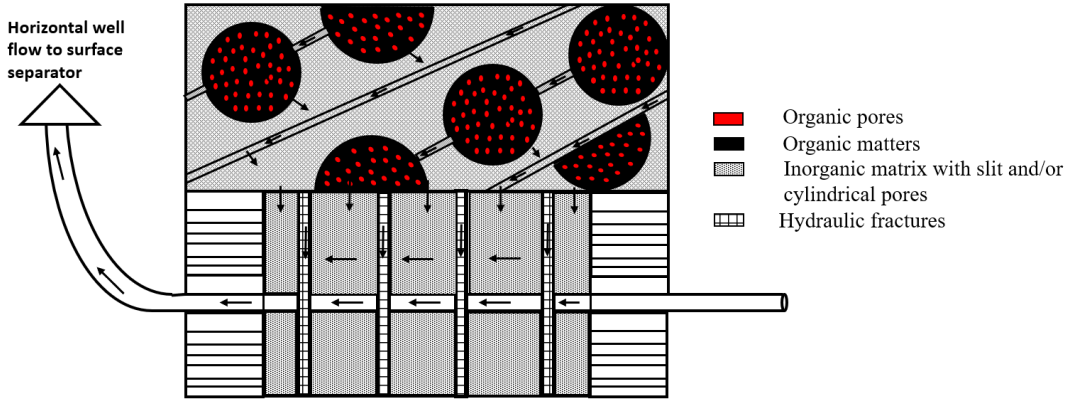


Figure 59 Shale conceptual model showing a 2D vertical cross-section of a hydraulically fractured shale reservoir, with contributing flux from both organic matter and inorganic matrix. The permeability changes in the slit-pore microstructure of shale will in this study be assumed to be governed by Gangi's [282] model.

Inorganic matrix flux

The mass flux rate in the inorganic matrix, $\vec{J}_{in}$ (kg/m²s), is the first term in the LHS of Eq. (8.6). This flux is described by Darcy's velocity as:

$$\vec{J}_{in} = \rho_g \vec{u} = -\rho_g \frac{k_m}{\mu_g} \nabla P, \quad (8.7)$$

where ∇P is the 3D pressure gradient (Pa/m) and k_m is the matrix permeability (m²). The inorganic matrix is assumed to mainly contain mesopores (2-50 nm) and macropores (>50 nm). The pore shape varies among slit, cylindrical, and/or triangular shapes with different aspect ratios. Experimental investigations have shown that the absolute permeability of rock is sensitive to the confining pressure, increasing with decreasing the aspect ratio of pore cross-section. Assuming a slit-shape-dominated matrix with micro- or macrofractures (Figure 59), where the aspect ratio is between 0.1 and 0.01, Gangi [282] introduced the bed of nails compaction model to correct the matrix permeability for the effective confining pressure. Gangi's model, which has been widely adopted in different studies [44,137], is

written in the following form:

$$k_m = k_o \left[1 - \left(\frac{P_{eff.}}{P_1} \right)^m \right]^3, \quad (8.8)$$

where, $P_{eff.} = (P_c - P)$ is the effective confining pressure on the matrix, P_c is the confining pressure, m is the surface roughness factor of the slit-shaped pores (m is close to 1.0 if the characteristic distribution of the asperities length is uniform), k_o is the original permeability in slit-shaped mesopores and macropores at zero effective confining pressure. k_o can be determined with some uncertainty during the transient pulse measurement in the laboratory by ensuring that the difference between the confining pressure and the average pore pressure is very low. P_1 is the effective confining pressure at which the slit-shaped pores are completely closed (i.e., when $k_m = 0$). The laboratory measurement of k_m is usually performed at very high average pressure to eliminate slippage and molecular flux effects on measured gas permeability [137]. Kwon [44] and Wasaki and Akkutlu [137] utilized iterative forward modeling to determine P_1 alongside k_o and m by matching the transient-state measurements of k_m versus P . However, laboratory measurements of P_1 may not be representative of the actual effective compressive strength of the rock at real reservoir conditions.

In the present study, the original definition of $P_1 = K_{sh}(A_p/A_T)$ according to Gangi's [282] definition was followed, where K_{sh} is the bulk modulus of shale material grain, A_p/A_T is the aspect ratio or fraction of the matrix fracture surface area covered by rod-like pores, A_p is the surface area all the asperities covering the fracture surface, and A_T is the total surface area of the fracture face. It can be inferred from the above mathematical

formulation that the resistance to complete closure of the slit-shaped pores varies with the aspect ratio, which is a characteristic of the formation under investigation. Eq. (8.8) is substituted into Eq. (8.7) to give the final expression of the inorganic matrix flux as:

$$\vec{J}_{in} = -\rho_g \frac{k_o}{\mu_g} \left[1 - \left(\frac{P_c - P}{P_1} \right)^m \right]^3 \nabla P. \quad (8.9)$$

If the inorganic matrix contains more cylindrical pores and a negligible number of slit-shaped pores, the inorganic matrix flux $\vec{J}_{in}$ would be best described by Hagen-Poiseuille's equation for a circular tube [287,354]. The impact of pore compaction is negligible in this case, given that its aspect ratio is close to 1.0. The inorganic matrix flux is corrected for the slippage effect, an additional flux due to non-zero gas velocity close to the circular pore walls, as [309,355]:

$$\vec{J}_{in} = -\rho_g \frac{F \bar{r}_{in}^2}{8\mu_g} \nabla P, \quad (8.10)$$

where $\bar{r}_{in}$ is the average pore size of the circular inorganic matrix pore and F is a dimensionless coefficient that corrects for slippage. According to Javadpour [309], F is defined as:

$$F = 1 + \left(\frac{8\pi RT}{M_g} \right)^{0.5} \frac{\mu_g}{P_{avg}} \left(\frac{2}{\alpha_{tam}} - 1 \right), \quad (8.11)$$

where P_{avg} is the average pressure (mean of upstream and downstream pressure) and α_{tam} is a dimensionless tangential momentum accommodation coefficient (TAMAC) that defines the proportion of diffused gas molecules that are reflected from the tube wall

relative to the specular reflection. Eqs. (8.10) and (8.11) are coupled to produce the Darcy's flux term for an inorganic matrix containing cylindrical-shaped pores as:

$$\vec{J}_{in} = -\rho_g \frac{\bar{r}_{in}^2}{8\mu_g} \left[1 + \left(\frac{8\pi RT}{M_g} \right)^{0.5} \frac{\mu_g}{P_{avg}} \left(\frac{2}{\alpha_{tam}} - 1 \right) \right] \nabla P. \quad (8.12)$$

Organic matter flux

Organic pores can be approximated as cylindrical micropores. In the nanoscale degree of pore confinement, the transport mechanism is anticipated to be within the transition diffusion domain, $0.1 \leq Kn \leq 10$, where, $Kn = \lambda_g/2r_{eff,or}$ is the Knudsen number, defined as a the ratio of the mean free path of the gas molecules to the effective pore size (after correcting for the sorbed layer thickness, $r_{eff,or}$). The flux in the organic matter described here is thus mainly valid in micropores (<2.0 nm) and lower limit mesopores (2–10 nm) and over a wide range of pressure. The second term in the LHS of Eq. (8.6), $\vec{J}_{or}$, is defined as:

$$\vec{J}_{or} = D_{eff} \nabla \rho_{ads}. \quad (8.13)$$

The adsorbed phase density is modeled according to the Langmuir isotherm, where, $\rho_{ads,max}$ is the maximum adsorbed phase density and P_L is the Langmuir pressure [277]:

$$\rho_{ads} = \rho_{ads,max} \frac{P}{P + P_L}. \quad (8.14)$$

Eq. (8.14) is substituted into Eq. (8.13) and differentiated with respect to the pore pressure to obtain:

$$\vec{J}_{or} = D_{eff} \rho_{ads,max} \frac{P_L}{(P + P_L)^2} \nabla P. \quad (8.15)$$

Recall that the expression introduced by Wasaki and Akkutlu [137] for the maximum adsorbed gas density is given as:

$$\rho_{ads,max} = \frac{V_{sL} \rho_{g,sc} \rho_{gr}}{\varepsilon_{gr}}, \quad (8.16)$$

where $V_{sL} = n_L V_{std}$ is the maximum adsorbed gas volume in a given mass of organic matter (m^3/kg), n_L is the Langmuir amount (mol/kg), $V_{std} = 22.4 \times 10^{-3}$ is the molar volume of gas at standard temperature and pressure (m^3/mol), $\rho_{g,sc}$ is the gas density at surface temperature and pressure (kg/m^3), and ρ_{gr} is the organic matter matrix density (kg/m^3). Eq. (8.16) is substituted for $\rho_{ads,max}$ into Eq. (8.15) to give:

$$\vec{J}_{or} = D_{eff} \frac{V_{sL} \rho_{g,sc} \rho_{gr}}{\varepsilon_{gr}} \frac{P_L}{(P + P_L)^2} \nabla P. \quad (8.17)$$

The effective diffusion coefficient of sorbed gas, D_{eff} , was developed and validated by Afagwu *et al.* [350]:

$$D_{eff} = \frac{4}{3\tau_d^2} \left(\frac{\frac{\mu_g RT r_{eff,or}}{P} \frac{1}{M_g} \sqrt{\frac{2ZRT}{\pi M_g}}}{r_{eff,or} \sqrt{\frac{8RT}{\pi M_g}} + \frac{\mu_g RT}{P} \frac{1}{M_g} \sqrt{Z}} \right), \quad (8.18)$$

where, $r_{eff,or} = \bar{r}_{or} - r_{ads}$, $\bar{r}_{or}$ is the average pore size of the organic matter (m), $r_{ads} = \varepsilon_s d_m \theta_s$ is the adsorbed layer thickness (m), d_m is the kinetic molecular size (m), ε_s is a dimensionless and non-physical adsorption correction factor, $\theta_s = P/(P + ZP_L)$ is the

surface coverage, and τ_d is the diffusion tortuosity in heterogeneous kerogen, which typically is in the range of 2.2–3.19 [286] for the type II-D kerogen micropores studied using molecular simulation approach. Diffusion tortuosity represents the pathway resistance to the effective gas diffusion. It is mathematically expressed as the square root of unrestricted diffusion flux to the effective diffusion in porous structure [129,135,148,286,356]. Eq. (8.18) is substituted into Eq. (8.17) to give the flux term in the organic matter as:

$$\vec{J}_{or} = \frac{4}{3\tau_d^2} \frac{V_{sL}\rho_{g,sc}\rho_{gr}}{\varepsilon_{gr}} \frac{P_L}{(P + P_L)^2} \left(\frac{\frac{\mu_g}{P} \frac{RT r_{eff,or}}{M_g} \sqrt{\frac{2ZRT}{\pi M_g}}}{r_{eff,or} \sqrt{\frac{8RT}{\pi M_g}} + \frac{\mu_g}{P} \frac{RT}{M_g} \sqrt{Z}} \right) \nabla P. \quad (8.19)$$

Total flux

The total flux term, $\vec{J}_T$, is given in shale as the summation of the molecular diffusion in the organic matter ($\vec{J}_{or}$) and Darcy's flux in the inorganic matrix ($\vec{J}_{in}$):

$$\nabla \cdot \vec{J}_T = -\nabla \cdot \vec{J}_{in} + \nabla \cdot \vec{J}_{or}. \quad (8.20)$$

Eq. (8.20) can be rewritten for shale with a predominantly slit-shaped inorganic matrix and round organic pores by substituting Eqs. (8.9) and (8.19) into Eq. (8.20):

$$\begin{aligned} \nabla \cdot \vec{J}_T = & \nabla \cdot \left[\rho_g \frac{k_o}{\mu_g} \left[1 - \left(\frac{P_c - P}{P_1} \right)^m \right]^3 \nabla P \right] + \\ & \nabla \cdot \left[\frac{4}{3\tau_d^2} \frac{V_{sL}\rho_{g,sc}\rho_{gr}}{\varepsilon_{gr}} \frac{P_L}{(P + P_L)^2} \left(\frac{\frac{\mu_g}{P} \frac{RT r_{eff,or}}{M_g} \sqrt{\frac{2ZRT}{\pi M_g}}}{r_{eff,or} \sqrt{\frac{8RT}{\pi M_g}} + \frac{\mu_g}{P} \frac{RT}{M_g} \sqrt{Z}} \right) \nabla P \right]. \end{aligned} \quad (8.21)$$

The relationship between the total mass flux term and the apparent permeability is [112,355]:

$$\nabla \cdot \vec{J}_T = \nabla \cdot \left(\rho_g \frac{k_{app}}{\mu_g} \nabla P \right), \quad (8.22)$$

where k_{app} is the apparent permeability. k_{app} in Eq. (8.22) could be defined by either assuming (A) predominance of slit-shaped inorganic matrix pores, or (B) inorganic cylindrical pores. In either case, the inorganic flux is coupled with the molecular diffusion of the sorbed phase in the organic matter.

(A) k_{app} for slit-shaped inorganic matrix pores. Eq. (8.21) is equated with Eq. (8.22) to obtain the expression of apparent permeability in shale containing slit-shaped inorganic matrix pores, where $B_g = V_g/V_{g,sc} \approx \rho_{g,sc}/\rho_g$ is a gas formation volume factor:

$$k_{app} = k_o \left[1 - \left(\frac{P_c - P}{P_1} \right)^m \right]^3 + \frac{4\mu_g V_{sL} B_g \rho_{gr}}{3\tau_d^2 \varepsilon_{gr}} \frac{P_L}{(P + P_L)^2} \left(\frac{\frac{\mu_g RT r_{eff,or}}{P M_g} \sqrt{\frac{2ZRT}{\pi M_g}}}{r_{eff,or} \sqrt{\frac{8RT}{\pi M_g}} + \frac{\mu_g RT}{P M_g} \sqrt{Z}} \right). \quad (8.23)$$

(B) k_{app} for cylindrical inorganic pores. Similarly, the apparent permeability for shale containing cylindrical pores in both inorganic and organic phase can be obtained by substituting Eqs. (8.12) and (8.19) into Eq. (8.20) and rearranging accordingly, with $k_o = \frac{\bar{r}_{in}^2}{8}$ for circular inorganic matrix pores, to give:

$$k_{app} = k_o \left[1 + \left(\frac{8\pi RT}{M_g} \right)^{0.5} \frac{\mu_g}{P_{avg}} \left(\frac{2}{\alpha_{tam}} - 1 \right) \right] + \frac{4\mu_g}{3\tau_d^2} \frac{V_{sL} B_g \rho_{gr}}{\varepsilon_{gr}} \frac{P_L}{(P + P_L)^2} \left(\frac{\frac{\mu_g}{P} \frac{RT r_{eff,or}}{M_g} \sqrt{\frac{2ZRT}{\pi M_g}}}{r_{eff,or} \sqrt{\frac{8RT}{\pi M_g}} + \frac{\mu_g}{P} \frac{RT}{M_g} \sqrt{Z}} \right). \quad (8.24)$$

8.2.3 Gaussian pressure transient (GPT) solution

The GPT solution, which serves as the mathematical framework to model the gas transport in shale reservoirs, for a finite-length fracture derived in exact form in Appendix B of Weijermars [219]:

$$P(x, y, t) = P_0 + (BHP - P_0) e^{-\left(\frac{x^2}{4D_{eff}t}\right)} \left[\frac{\operatorname{erf}\left(\frac{y+y_f}{2\sqrt{D_{eff}t}}\right) - \operatorname{erf}\left(\frac{y-y_f}{2\sqrt{D_{eff}t}}\right)}{2\operatorname{erf}\left(\frac{y_f}{2\sqrt{D_{eff}t}}\right)} \right], \quad (8.25)$$

where t is production time, y_f is fracture half-length, P_0 is initial reservoir pressure, BHP is bottom hole pressure, and x and y are positions in the 2D reservoir space. The solution of Eq. (8.25) eliminates the challenge of imposing an uncertain constant well rate, which is required for implementing the traditional pressure transient solutions in the literature [357–359]; only a constant BHP is assumed [219]. The exact GPT solution accounting for pressure interference between multiple fractures has been solved by superposition in Appendix C of Weijermars [219], but the current study was limited to single fracture as the primary objective was to couple different transport mechanisms. The same approach could be easily extended to multi-fractures systems.

In Eq. (8.25), D_{eff} is the effective diffusivity, which is defined as [360]:

$$D_{eff} = \frac{h \cdot T_{eff}}{S} = \frac{k_{app}}{\mu_g [(1 - \phi)c_m + \phi c_g]}, \quad (8.26)$$

where h is the formation thickness (m), $T_{eff} = C_{h,eff}/h$ is the effective gas transmissibility (1/s), $S = \rho_g g [(1 - \phi)c_m + \phi c_g]$ is the gas storativity (1/m), $g = 9.8 \text{ m/s}^2$ is the acceleration due to gravity, c_m is the isothermal shale matrix compressibility, and $C_{h,eff} = k_{app} \rho_g g / \mu_g$ is the effective conductivity, which was originally reported as a function of permeability due to the pressure gradient-driven Darcy's flux [146,361]. The present study overcomes this limitation by replacing Darcian permeability with the new model given in Eq. (8.23) that accounts for the multiphysics and multiscale nature of shales.

8.2.4 Gaussian Péclet number

The Gaussian Péclet number (Pe) is a dimensionless factor that accounts for the time- and space-dependent relevance of Darcian flow (in the inorganic matrix) to the molecular diffusion in the organic matter. This number was first defined mathematically in our previous research as the ratio of advective to molecular diffusion flux in 2D form [360]:

$$\text{Pe} \approx \left[\frac{(x^2 + y^2)}{4t} \left(\frac{1}{D_{eff,or}} - \frac{1}{D_{h,in}} \right) \right], \quad (8.27)$$

where $D_{eff,or}$ is the molecular diffusivity in the organic matter and $D_{h,in}$ is the Darcian diffusivity of the free phase in the inorganic matrix accounting for pore compaction and based on the hydraulic diffusivity originally introduced by Weijermars [219,360]. Both diffusivity values are evaluated iteratively with the workflow in Fig. 1 after convergence by substituting the first and the second terms of the apparent permeability as given by Eq.

(8.23) separately in Eq. (8.26). For $Pe \gg 1$, the advective transport advances faster than molecular diffusion; for $Pe \ll 1$, molecular diffusion outpaces the advective mass transport process. In this study, the Pe was evaluated at a unit distance location from the source along the fracture axis $(x, y) = (0, 1)$ to show the relative controlling mechanisms over the depletion life of the reservoir.

8.2.5 Gaussian production rate and cumulative production

The 2D gradient of the GPT solution (Eq. (8.25)), $\nabla P(x, y, t)$, was computed in a similar manner as the Pythagoras equation, analytically or numerically, and the resulting gradient was integrated along the interval length of the fracture $-y_f < y < y_f$ to give the exact solution for the flux into the fracture plane [219]:

$$q_g(t) = -4n_f h_f \frac{k_{app}}{\mu_g B_g} \int_{-y_f}^{y_f} \nabla P(x, y, t), \quad (8.28)$$

where n_f is the number of fractures (i.e., one in this study) and h_f is the fracture height. The flow rate is evaluated at a location between a unit distance and origin, that is, $(0, 0) < (x, y) \leq (1, 1)$. Weijermars [219] advised that a unit distance in a field unit should be used to assess the rate at a constrained BHP. The cumulative gas produced is numerically expressed as a cumulative summation of the production rate $q_g(t)$ multiplied by the n_t number of discrete equal time interval Δt of the production (Eq. 8.29).

$$G_p(t) = \int q_g(t) dt \approx \sum_i^{n_t} q_g(t) \Delta t \quad (8.29a)$$

Meanwhile, an analytical solution for the planar fractures was derived following the same

procedure in our previous work [360] and was alternatively used for the evaluation of $G_p(t)$ as follows:

$$G_p(t) = -4n_f y_f h_f \frac{k_{app}(BHP - P_0)}{2\mu_g B_g} \frac{x_1}{D_{eff}} E_i \left(-\frac{x_1^2}{4D_{eff}t} \right), \quad (8.29b)$$

where, E_i is an exponential integral function. Similarly, the Gaussian physics-based DCA equation for estimating the effective diffusivity as a constant fitting parameter by history-matching of real well production-rate changes versus time (which requires 6 - 12 months production data are available), is [219,360]:

$$q_g(t) = q_i \frac{1}{t'} e^{\left(\frac{1}{4D'_{eff}} \left(1 - \frac{1}{t'} \right) \right)}, \quad (8.30a)$$

The change in the well rate is controlled by the non-dimensional diffusivity $D'_{h,eff}$ and q_i is the dimensional initial flow rate. Since well performance is normally assessed and reported on a daily basis, the units of q_i and $q_g(t)$ are assumed in Mscf/day for gas wells (bbls/day for oil wells).

The DCA Eq. (8.30a) involves only one matching parameter, the non-dimensional diffusivity D'_{eff} , which can be quickly equated to dimensional diffusivity following standard dimensional scaling principles. An important aspect in the scaling adopted by Weijermars [219], to simplify the use of Eq. (8.30a), is that the units used in the dimensional scaling pegs the unit of D_{eff} . This becomes immediately obvious when retracing the non-dimensionalities steps leading to Eq. (8.30a), starting with the dimensional well rate equation:

$$q_g(t) = q_i \frac{t_1}{t} e^{\left(\frac{x_1^2}{4D_{eff}t} \left(\frac{1}{t_1} - \frac{1}{t}\right)\right)} \quad (8.30b)$$

Defining the non-dimensional time $t'=t/t_1$ used in Eq. (8.30a) and adopting for the typical time t_1 the scaling unit $t_1 = 1$ day, then the non-dimensional time counter t' in Eq. (8.30a) becomes numerically equal to dimensional time counter t in Eq. (8.30b), the latter being expressed in days. Likewise, adopting for the typical length scale $[L]$, which appears in the dimensional diffusivity D_{eff} having dimensions $[L^2 T^{-1}]$, a cleverly chosen non-dimensionalities $D'_{eff} = (D_{eff} t_1)/x_1^2$, and setting x_1 equal to 1 typical length unit (e.g., 1 ft for US shale operators), then we the non-dimensional D'_{eff} in Eq. (8.30a) becomes numerically equal to the dimensional diffusivity D_{eff} in Eq. (8.30b), the latter being expressed in ft^2/day . Also, the time taken to cover -- by diffusion from the planar source (hydraulic fracture) where the BHP was initiated -- the unit distance $x_1 = 1$ ft, corresponds to the period of initial well rate growth (as the pressure gradient becomes established in the reservoir pace) and after the pressure transient passes distance $x_1 = 1$ ft, then the pressure decline sets in. Consequently, the pressure transient time-of-flight to cover the travel distance x_1 corresponds to the peak well rate at $x_1 = 1$.

In accordance with the scaling of real well-rate performance with history-matched hydraulic diffusivities [360], it is worth highlighting that the effective diffusivity, D_{eff} , as defined in this study, is a dynamic parameter that is sensitive to changes in the pressure. However, using Eq. (8.30) would yield a single value of D_{eff} , that best fits the data. This value should be taken with caution and considered as an average value, incorporating different mechanisms over the spanned data.

8.2.6 Case study and Input data for the study

The case study uses the original Gangi's bed-of-nail model of Eqs. (8.8) and (8.9) in our Section 8.2.2, and a dataset provided by Wasaki and Akkutlu [137]. Consequently, Darcy's flow was coupled with molecular diffusion flux of the sorbed phase using the apparent permeability model developed in Section 8.2.2. The input dataset given in **Table 31** contains methane gas properties, rock and fracture specifications, Gangi's model parameters, and diffusion tortuosity range for the sensitivity analysis.

Table 31 Input data for the sensitivity analysis in this research.

<u>Variables</u>	<u>Symbols</u>	<u>Value</u>	<u>Unit</u>
Pressure and methane gas parameters			
Initial reservoir pressure	P_0	4073	psi
Bottom hole pressure	BHP	500	psi
Langmuir amount	n_L	0.1245	mol/kg
Gas molecular mass	M_g	16	g/mol
Size of gas molecule	d_m	0.38	nm
Gas critical pressure	P_c	45.922	bar
Gas critical temperature	T_c	190.56	Kelvin
Langmuir pressure	P_L	2,000	psi
Temperature	T	413	Kelvin
Rock and fracture parameters			
Average porosity	ϕ	6.0	%
Total organic content	ε_{gr}	2.0	wt. %

Representative kerogen pore size	$\bar{r}_{eff,or}$	0.26	nm
Kerogen tortuosity	τ_d	2.0 -3.9	No dim.
Adsorbed layer correction factor	ε_s	0.46	No dim.
Fracture height	h_f	125	ft
No. of fracture(s)	n_f	1	No dim.
Kerogen matrix density	ρ_{gr}	1,300	kg/m ³
Fracture half length	y_f	32.8	ft
Fracture drainage area	A_f	26,910	ft ²
Gangi's bed-of-nails model parameters			
Permeability at zero effective pressure	k_o	100×10^{-6}	mD
Surface roughness factor for slit pore, m	m	0.5	No dim.
Bulk modulus of shale	K_{sh}	20	GPa
Fraction of slit pore surface covered with asperities	A_p/A_T	0.1	No dim.
Confining pressure	P_c	50	Mpa

8.3 Results and discussion

8.3.1 Rock and fluid model validation

Fluid models

The Z-factor, fluid viscosity, and isothermal compressibility coefficient (Eqs 8.1 – 8.3) are inputs to the simulation scheme adopted in this study. The fluid properties were validated against experimental data obtained from the National Institute of Standards and Technology (NIST) database, as shown in **Figure 60a-c**. The NIST comprehensive data

archive allows analytical chemists and scientists to obtain physical and chemical properties of materials. The results show that the selected models are representative of methane gas behavior at some typical reservoir pressure depletion profile (i.e. Z-factor, viscosity, and isothermal compressibility).

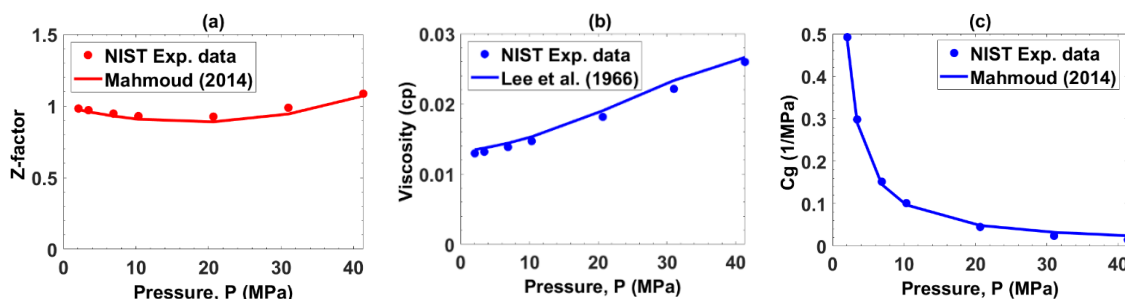


Figure 60 Fluid models employed for the simulation in this study. (a) Gas compressibility/Z-factor; (b) Gas viscosity; (c) Isothermal compressibility coefficient. Models were validated using the NIST database for methane gas at 350 K.

Apparent permeability model performance

In comparison with existing gas permeability models, the one derived in this paper has the advantage of describing coupled Darcian and sorbed gas molecular diffusions. The Darcian component of the model for the slit-shaped inorganic matrix was previously validated experimentally by Wasaki and Akkutlu [137]. However, the self-diffusivity component of the permeability model derived by Wasaki and Akkutlu assumes constant molecular diffusivity coefficient. This assumption, as highlighted by the authors, limits the range in which the model can describe molecular diffusion accurately to high pressure, where diffusion is primarily controlled by the Fickian mode (i.e., Fickian diffusion is linked to the mean free path where there is no boundary effect). This assumption is reasonable in macropores (> 50 nm) at high pore pressure. The pressure, however, is anticipated to be lowest near the hydraulic fractures, and the non-Fickian mode (i.e., considering the boundary effect on self-diffusion imposed by the confined space at lower pressure causes

the molecules to equally collide with the pore walls and themselves). As a significant portion of the sorbed gas resides within the micropores, discounting the non-Fickian effect highly impacts the accuracy of describing sorbed phase flux by around one order of magnitude, as shown in **Figure 61**.

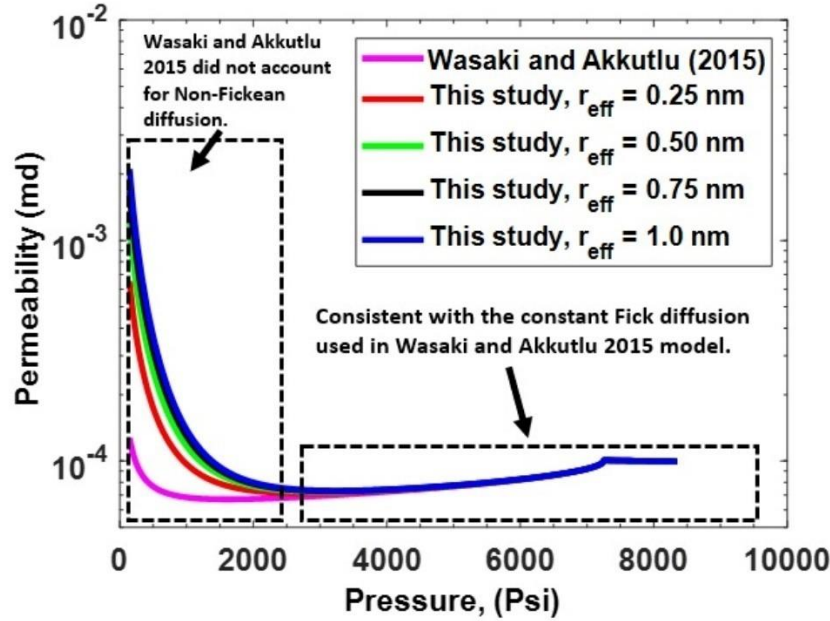


Figure 61 The apparent permeability model adopted in this study in comparison to Wasaki and Akkutlu [137] model, showing a broader range of applicability at high and low pressure.

Knudsen number, Kn is used to characterize the mode of molecular diffusion. Kn depends mainly on pore pressure, properties of the gas and effective size of pores [350,360]. In our previous study [350], we showed that the molecular diffusion in micropores has Kn values within a range that falls into the transition and Knudsen diffusion modes. Fixing the self-diffusivity coefficient at a given value may cause errors in tracking the pressure wave propagation. Moreover, the error is subject to accumulation as the simulation proceeds. The adopted permeability model in this work has the capability to overcome that limitation.

8.3.2 Hydraulic diffusivity

To establish some fundamental understanding of the factors controlling shale productivity, the simulation scheme is applied first without the molecular diffusion term of the apparent permeability. The objective is to quantify the influence of confining pressure. In this context, the effective diffusivity is referred to as the hydraulic diffusivity.

The original matrix permeability at zero effective pressure was assumed as 100 nD (100×10^{-6} mD). This is a typical value of shale matrix permeability reported in the literature [44,137,219]. The permeability is subject to reduction by pore compaction using the Eq. 8.8 model described in section 8.2.2. The impact of confining pressure was studied considering two cases. The first one is ‘without P_{eff} ’, which utilizes k_o (i.e. constant value) to compute the hydraulic diffusivity, and consequently the production rate, cumulative production over a time span of 416 days. The second case is referred to as ‘with P_{eff} ’, where the pore pressure at each time step is used to update the permeability for the new effective confining pressure.

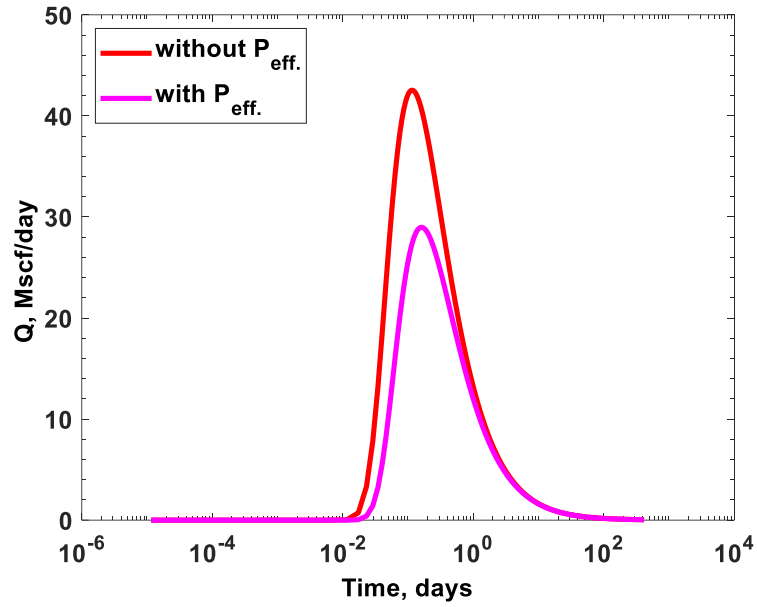


Figure 62 The impact of pore compaction on production rate in shale reservoirs penetrated by a single fracture, with properties defined in Table 31. The log-scale was used to show the variation in the production rate at an early time. The effect observed on peak rate is due to the compaction effect that was coupled to the original Gaussian solution.

A quick assessment of the new matrix permeability under confining pressure shows that the initial permeability is reduced by around 29%, to 71.77×10^{-6} mD. **Figure 62** shows the production profile in 416 days span for the two cases. There is around 32.2% peak rate gap at early time due to pore compaction. The two production curves merged afterwards as the production rate diminished. The cumulative production is calculated using Eq. (8.30) and as shown in **Figure 63**. The results showed around 8.34% cumulative production difference during the same period. All cases presented in the subsequent sections account for the permeability reduction modeled by incorporating the effective confining pressure.

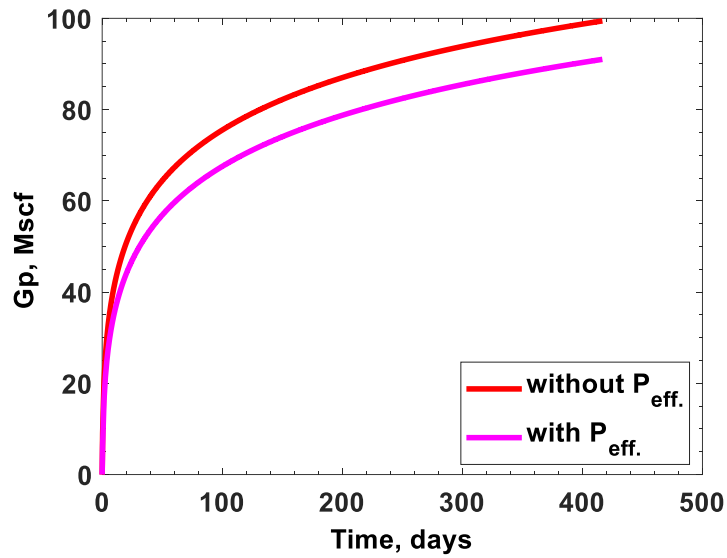


Figure 63 The impact of pore compaction on the cumulative production.

8.3.3 Coupling organic matter flux: effective diffusivity

In this subsection, the same numerical approach is followed but with the full definition of apparent permeability which has both the hydraulic convection corrected for the confining pressure, and the molecular diffusion terms. The flux from the organic matter, as presented in the methodology section, is controlled by the effective organic pore size, the tortuosity, and the sorption capacity. Hence, a parametric study combining all of these factors are needed. The effective pore size and the tortuosity were selected in accordance with a prior study [286] while the range of sorption capacity reported by Wasaki and Akkutlu [137] was used. A summary of the considered cases is given in **Table 32**.

Table 32 Parametric study input cases utilized to show the effect of organic matter transport properties on the production rate and cumulative production for a single fracture miniature model.

Cases	τ_d	V_{sL}	$r_{eff,or}$

		(scf/ton)	(nm)
1	1.5	50	0.26
2	3.19	50	0.26
3	1.5	50	1.0
4	1.5	150	0.26
5	3.19	50	1.0
6	3.19	150	1.0
7	1.5	150	1.0
8	3.19	150	0.26

Gaussian pressure transient profiles

The molecular diffusion term that is part of the permeability model. It could alter the depletion rate and hence, the pressure profile. The degree by which molecular diffusion impacts the reservoir dynamics is linked to a combination of organic matter petrophysical characteristics. Higher values of tortuosity reflect more restriction to the molecular diffusion rate while larger pores positively impact the diffusion. The sorption capacity, on the other hand, controls the amount available for molecular diffusion. **Figure 64** shows the pressure profile of a case that has the lowest tortuosity, largest pore size, and highest

amount of sorbed gas in comparison with a base case that has no contribution of molecular diffusion at all. The two pressure profiles show the minimum and maximum impact of molecular diffusion considering the selected range of parameters in this study. The results suggest that the molecular diffusion could influence the propagation of pressure waves. The pressure profile for the other cases listed in Table 32 were in between the two extreme scenarios depicted in Figure 64. The variation between the cases suggests that the contribution of molecular diffusion to the overall transport is highly sensitive to the amount and the local heterogeneity of the organic matter.

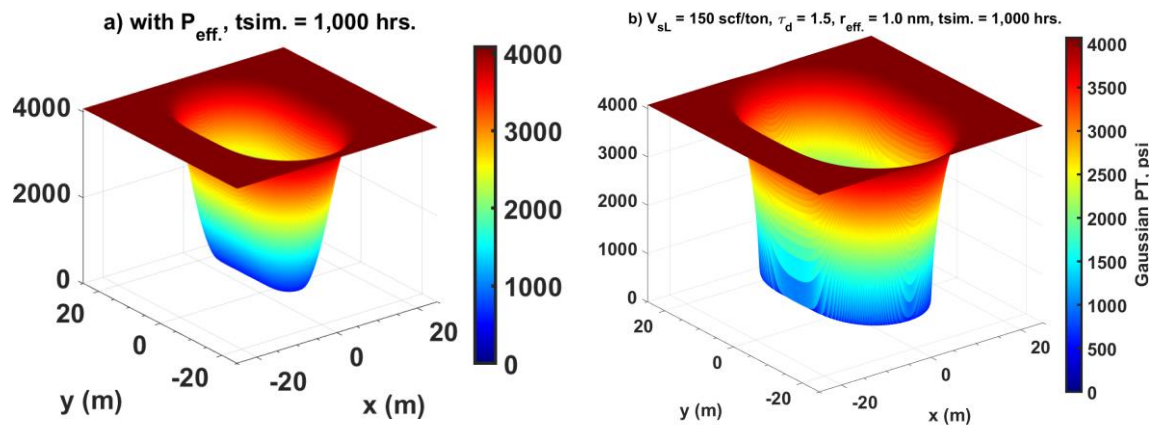


Figure 64 Gaussian pressure transient solution for a) base case decoupling molecular diffusion and b) incorporating the full definition of the apparent permeability as given by Eq. (8.23) with the molecular diffusion parameters given by the seventh case in Table 32.

Gaussian production rate and cumulative production

The rate of production from the matrix through the hydraulic fracture to the wellbore was calculated using Eq. (8.28) for the eight cases in Table 32. The expected trend is largely dependent on the reservoir pressure transient, BHP, production period, and effective diffusivity. It is assumed that the origin (0,0) represents the wellbore location with a constrained BHP (as the sum of the wellhead pressure and the pressure drop in the tubing)

that is controlled by the hydraulic fracture and well completion. As a result, it is accurate to select a well position between 0 and 1, $(0, 0) < (x, y) \leq (0, 1)$, in the evaluation of the production rate using Eq. (8.28).

Combining the pore compaction controlled Darcian flow with self-diffusion from organic matter reveals a dependency of the flow rate on the organic matter heterogeneity and sorption characteristics (**Figure 65**). Figs. 8a and 8b are for organic matter with lower ($V_{sL} = 50 \text{ scf/ton}$) and higher sorption capacities ($V_{sL} = 150 \text{ scf/ton}$) respectively. Given that the pressure in the organic matter and inorganic matrix is at equilibrium, the organic matter with higher capacity is capable of releasing larger amount of sorbed gas than the low sorption capacity cases, by few margins to one-third higher depending on the heterogeneity and effective size of the pores. The magnitude of the peak rate at the onset of the production is higher for the less tortuous ($\tau_d = 1.5$) and larger effective pore size ($r_{eff,or} = 1.0 \text{ nm}$) compared to the more tortuous ($\tau_d = 3.19$) with smaller effective size ($r_{eff,or} = 0.26 \text{ nm}$) case.

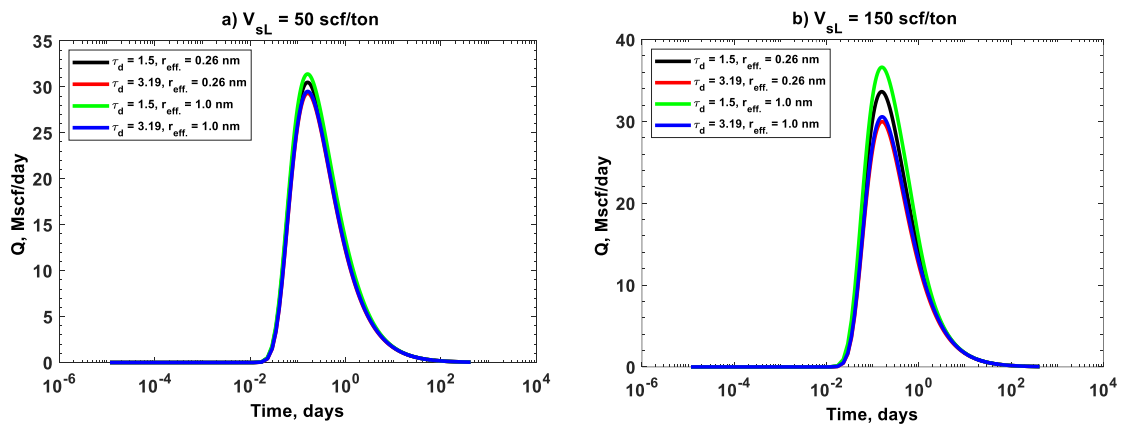


Figure 65 Gaussian production rate profiles for organic matter with maximum sorption capacity of (a) 50 scf/ton (b) 150 scf/ton with a different combination of tortuosity and effective pore size.

Similarly, the cumulative production (in Mscf) over the same production span is presented in **Figure 66**. A corresponding increase in cumulative production ranging between 6.7 – 35.1% compared to the base case of no organic matter flux could be observed.

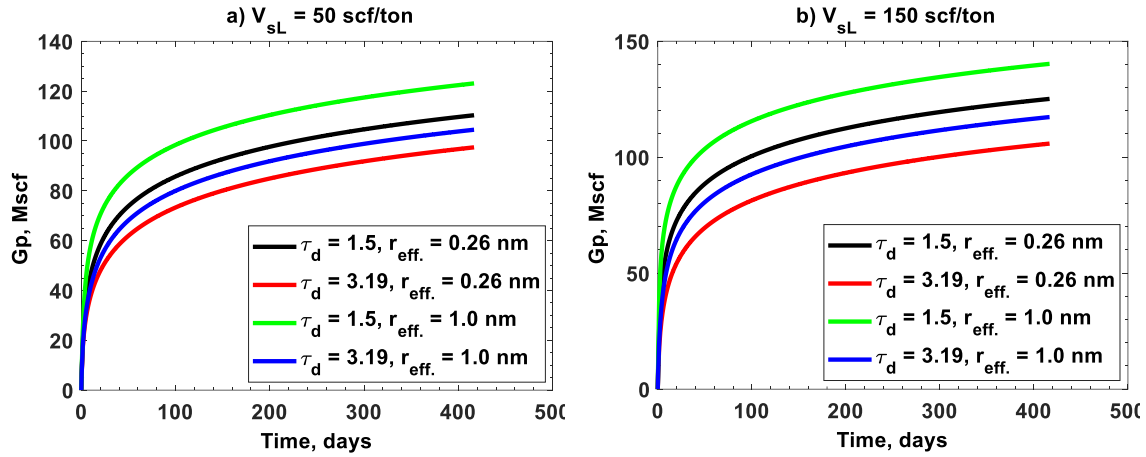


Figure 66 Gaussian cumulative production profiles for organic matter with maximum sorption capacity of (a) 50 scf/ton (b) 150 scf/ton with a different combination of tortuosity and effective pore size.

Relative importance of molecular diffusion to Darcian flow

The Gaussian Péclet number [360] serves as an indicator of the relative importance of the advective and diffusive mechanisms. For $Pe \gg 1$, the advective mass transport advances faster than molecular diffusion. On the other hand, $Pe \ll 1$ suggests that molecular diffusion outpaces the advective one. Here, Péclet number was evaluated at a dimensional unit distance position close to the fracture plane $(x, y) = (0, 1)$. Such an approach makes it possible to estimate the effect of time and local heterogeneity of the organic matter on the overall transport. **Figure 67** shows that, regardless of the organic matter characteristics, Péclet number is high during the early stages of depletion, suggesting that the transport is mainly controlled by the pressure-driven mass flux through the permeable inorganic rock matrix. Over time, the transport shifts more toward molecular diffusion. The molecular

diffusion starts earlier in organic material with higher self-diffusivity characteristics. The contribution of molecular diffusion is latest for the lowest self-diffusion characteristics case (i.e. 3.19 tortuosity and 0.26 nm effective pore size).

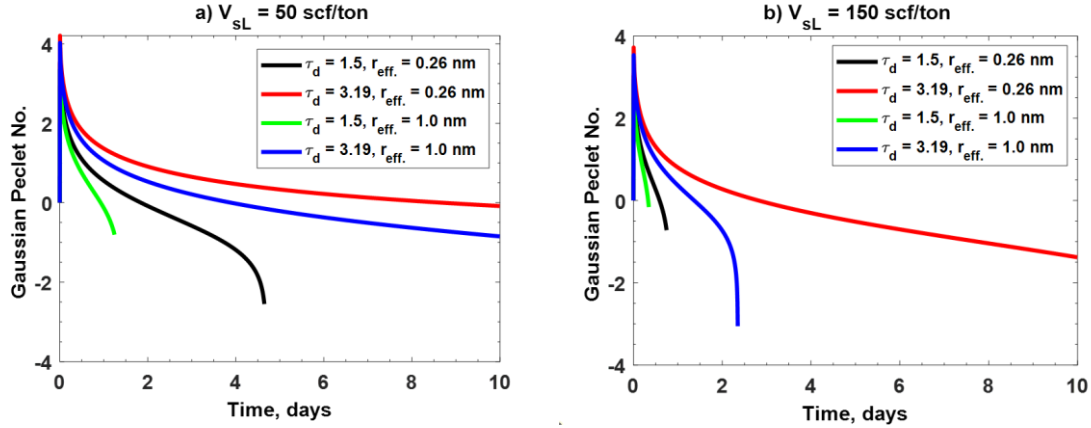


Figure 67 Relative contribution of Darcian flow and molecular diffusion flux to overall mass transport, based on the Gaussian Péclet number equation evaluated at 1 ft from the origin of the pressure change source with maximum sorption capacity of (a) 50 scf/ton (b) 150 scf/ton with a different combination of tortuosity and effective pore size.

8.4 Strengths and limitations of the new approach

8.4.1 Novelties and advantages

Pre-Darcy gas flow processes that predominantly occur in smaller pores have been extensively studied with molecular dynamic, pore network and lattice Boltzmann simulation studies. The needs for sensitivity studies of the effect of multiple physical parameters on the gas transport and integration for reservoir and field scale applications require that researchers develop realistic physical models. There are several theoretical models for accounting for the nanoscale transport mechanisms in shale reservoirs besides the Darcy flux which can be obtained by laboratory scale evidence. The merits and demerits of the existing models have been thoroughly considered by Javadpour et al. [362] and Cai et al. [218]. Accurately mimicking the complexities of the pore shapes as evident from high

resolution scanning of shale samples and material deformation characteristic at nanoscale require more studies. The relationship between the sorption characteristics of the organic matter, diffusion tortuosity, organic matter mechanical properties and self-diffusivity has not gained much attention. Interestingly, molecular simulation frameworks from our research group particularly using realistic kerogen structures [286,293,299,307,350,363], have provided the background to understand the role of diffusion tortuosity, geomechanics in organic matter micropores of different pore shapes undergoing sorption on the self-diffusivity of gases.

In terms of multiscale description of gas flow in hydraulic fractured shale reservoirs, there are some grid-based simulations [214,215] and machine learning coupled solutions [217,218] proposed in the literature. To the best of our knowledge, a physics-based, gridless and fast-forward modeling framework for calculating the production rate in shale gas flow from the hydraulic fractures, to the matrix and organic matters pore scales, based on production data is still challenging. In addition to the existing solutions that may require specialized know-how to implement and time-consuming, the recent breakthrough Gaussian pressure transient solution developed by Weijermars [219] has provided the opportunity for a fast and forward modeling of shale gas production using field data.

Nevertheless, the pressure diffusivity equation was solved in prior studies [219,351,360,364] using the Gaussian pressure transient. The prior applications were conceptualized on constant values of the hydraulic diffusivity. The new addition in the present study is the use of pressure-dependent effective diffusivity that accounts for the changes in permeability due to pore collapse and molecular diffusion flux from the organic matter. The present scheme has the advantage of being a closed-form solution, which gives

infinite resolution and allows for precise computations without the use of any grids. Moreover, it provides a bridge between the hydraulic diffusivity models based on Gaussian pressure transient and nanoscale self-diffusivity equations for complete forward description of the multiscale physics in shale.

8.4.2 Limitations

The coupling of GPT and the traditional pore-scale equation of Gangi [282] brings to the forefront the crucial need to review the validity of Gangi's approach and its underlying assumptions. The Gangi's formula showed that the permeability reduction by pore compaction could be translated to almost 8.34% reduction in cumulative production. One obvious concern is that the effective confining pressure was treated as a scalar quantity, whereas in physical reality the effective stress is a tensor. Updating Gangi's simplistic scalar approach with tensor-based solutions is currently in progress by our research group [365,366].

In addition, the simulation algorithm presented here assumed infinite conductivity. In other words, the integral input factors that controls the dimensionless fracture conductivity (F_{CD}) such as fracture permeability and width are not defined. Rather, the hydraulic fractures' total surface area was considered which is highly uncertain and determined by the hydraulic fracture half length, number of fractures, and fracture height.

Again, the mathematical description of the gaussian solution in this study assumed that the pressure interference from nearby fractures which is controlled by fracture spacing is negligible. However, not accounting for the seemingly apparent boundary effect on the reduction of initial production could introduce some erroneous prediction of flux in a

hydraulic fractured reservoir. For simplicity, this research assumed a constant fracture height and half-length and calculated from the total fracture surface area (TFSA) as $A_f = 2n_f y_f h_f$.

8.5 Conclusions

This study introduced a framework for production forecast modeling in shale gas reservoirs by coupling the traditional Darcian pressure diffusion with molecular diffusion through an apparent permeability model. The Gaussian pressure transient and the derived Gaussian Péclet number provide a mathematical framework for computing the relative contributions of molecular and pressure diffusion to the advance of the pressure depletion in the reservoir through the introduced permeability model. Some preliminary conclusions are drawn:

- The production rate is sensitive to the compaction effect on apparent permeability. Discounting the pore compaction leads to variation in the production rate by up to 32% in the cases considered in this study.
- The contribution of the mass flux from the organic matter is sensitive to the local heterogeneity of the organic matter and the sorption capacity. Up to one-third additional cumulative production rate was observed for the high self-diffusivity case.
- The findings reported in this study highlight the range of organic matter characteristics where non-Darcian molecular flux becomes relevant. Low sorption capacity, and highly heterogeneous tight organic matter may have negligible contribution to the overall production during typical production span.
- It is recommended that future research considers the effects of phase behavior

changes and multi-phase fluid transport in shale reservoirs, following a similar approach. Also, the impact of fracture interference due to spacing and imposed apparent boundary effect on production rate should be investigated

CHAPTER 9

CONCLUSIONS AND RECOMMENDATION

9.1 Conclusions

In this study with realistic kerogen microporous structure, a unique method of computing the diffusion tortuosity which is representative of the organic matter geometry and free of sorption interaction influence. The insights from decoupling and understanding of the kerogen pore structure, and the mechanisms of adsorption and self-diffusivity was utilized to develop novel analytical self-diffusivity and gas permeability models that could be validated with both experimental and molecular simulation data. Consequently, a new simulation workflow was introduced for forward modeling of production rate in hydraulic fractured shale gas reservoirs based upon Gaussian pressure transient solutions. The main outcome from this work is summarized as follows:

- Clay and organic matters host significant quantity nanopores containing stored fluid in shale. Kerogen is heterogeneous and representative of common organic matter found in shale by composition of carbon, hydrogen, oxygen, nitrogen and Sulphur.
- Capillary condensation and evaporation curves revealed clays contain more mesopores and macropores of 2-50 nm and >50 nm, respectively. The pore distribution plateaued around an average of 100 nm. The limiting distribution confirmed the suitability of the Barrett-Joyner-Halenda technique to compute most of the fluid volume contained in clay mesopores.

- Kaolinite clay ($74.43 \text{ cm}^3/\text{g}$) hosts the highest amount of N_2 adsorbed at STP followed by montmorillonite ($65.08 \text{ cm}^3/\text{g}$), chlorite ($21.01 \text{ cm}^3/\text{g}$) and illite ($16.59 \text{ cm}^3/\text{g}$) has the least capacity. In the same vein, the pore capacity to store fluid and average pore size assessed at 77.4 K follow a similar pattern and increase with aluminum and clay contents.
- Kerogen is a highly tortuous confined porous medium. A realistic kerogen structure can be formed from single kerogen macromolecules through molecular dynamics simulation.
- Gaussian distribution function showed that kerogen structure is log-normally distributed, exhibits a unimodal pore profile and best describes a characteristic pore size in circular pores geometry.
- However, MD calibration showed that the representative pore size in circular kerogen geometry is best obtained with Gaussian PSD or $2.4Vp/Sp$ (not perfectly spherical) while Song 2020 model gives better estimate for slit pores equiv. pore radius.
- During typical depletion when there is a reduction in the internal gas pressure, ultramicropores ($\sim 4\text{-}7 \text{ \AA}$) are more prone to pore compressibility compared to around $7\text{-}20 \text{ \AA}$ owing to their lower closure pressure.
- Methane recovery from kerogen is believed to be controlled by self-diffusivity. The degree of tortuosity reduces the methane diffusion coefficient from the theoretically calculated value.

- Kerogen exerts some attraction forces on methane, causing physi- and chemisorption. Sorption effects impose an additional barrier on methane self-diffusivity.
- The high estimate of gas diffusion tortuosity in the literature is mainly attributed to the sorbed layer, a gas storage mode in shale which is desorbed and contribute to production during typical depletion span.
- Sorption mechanism in tortuous cylindrical pores resembles absorption while slitpores is adsorption. Adsorbed layer effect diminished with increase slitpores sizes, while absorption density ratio is marginally affected by increase in micropores sizes.
- Furthermore, absorption and adsorption mechanisms had a relatively more pronounced effect on self-diffusion at low pressure (around <10 Mpa or 1500 psi) because of non-Fickian effect relative to Fick regime that occurs at higher pressure.
- Adsorption thermodynamic revealed that kerogen follows multisite Langmuir model and type I isotherm
- Diffusion tortuosity after correcting for the sorbed gas is within a close proximity to the range of 2.0 to 3.6, and represents real kerogen geometry factor.
- Multiphysics-based effective diffusion model was proposed and validated by computationally generated data. The equation is accurate in predicting effective diffusion in different kerogen type II-A, II-C and II-D configurations and over a wide range of gas pressure.
- A new apparent permeability model was developed to update and improve the accuracy of the organic flux components. In the validation process, the proposed

model agreed reasonably well with the experimental data and had better predictability of oxygen's molar flux through macropore-sized tubes, as compared to the Knudsen diffusion and forced viscous Hagen-Poiseuille flow (K/HP) analytical and Javadpour models. Interestingly, it tests relatively well with mesoporous kerogen permeability data. A comparison of the performances of the new multi-physics and existing models showed that the apparent and surface permeability predictions were within the prevailing uncertainty bands. In other words, the descriptions of the relative contributions of the fluxes and total fluxes were within a possible range.

- The sensitivity studies revealed that the role of surface diffusion in the apparent gas permeability expanded substantially as the pore size decreased. Specifically, diffusion in adsorbed layers of gas was found to constitute more than 50% of the apparent permeability in that range of pore sizes for pressures below 10 MPa and 5.0 MPa in micropores and mesopores, respectively. At higher pressures, there was a crossover of dominance from surface diffusion to viscous flux. The influence of the Darcy scale flow was notable as the pore size increased.
- Viscous flux based on the Darcy law was determined to be valid for describing the total flux in a material that contains mainly macropores (> 50 nm pore sizes). At the same time, increased intermolecular interactions were found, as compared to molecule-wall collisions. Thus, the assumption of a continuum flow regime should only be considered valid at extremely high pressures, above 10 MPa in the mesopores considered in the present study. Molecular diffusions such as surface and pore diffusion were negligible at elevated pressure conditions.

- Decoupling the adsorption effect when calculating the self-diffusivity could significantly overestimate the total permeability. Although pore diffusion permeability is reduced with increased diffusion tortuosity, the apparent permeability and non-Darcy correction factor for gas in 0.6 nm pores (on average) were unaffected by the micropore structure parameter, except at pressures above 10 MPa.
- In 50 nm and 235 nm pores, the total diffusion permeability was negligible relative to the Darcy flow in the slip regime. However, there was a notable influence of the adsorption equilibrium factor, particularly in the slip, transition, and Knudsen diffusion regimes, and interestingly, the overall contributions of the surface layer and pore diffusion increased as the pore size decreased, and that increase was in the same order from the slip to Knudsen regime.
- The deviation of gas permeability from the Darcy flow in shale and ultra-tight rocks was found to be higher across all transport regimes when the influence of the adsorption forces on pore and surface diffusion flux was considered. Thus, reservoir management strategies must consider these dynamics throughout the life cycle of a gas field asset.
- Finally, a new framework for production forecast modeling in hydraulic fractured shale gas reservoirs by coupling the traditional Darcian pressure diffusion with molecular diffusion through an apparent permeability model was introduced. The production rate is sensitive to the compaction effect on apparent permeability. Discounting the pore compaction leads to variation in the production rate by up to 32% in the cases considered in this study.

- The contribution of the mass flux from the organic matter is sensitive to the local heterogeneity of the organic matter and the sorption capacity. Up to one-third additional cumulative production rate was observed for the high self-diffusivity case. The findings reported in this study highlight the range of organic matter characteristics where non-Darcian molecular flux becomes relevant. Low sorption capacity, and highly heterogeneous tight organic matter may have negligible contribution to the overall production during typical production span.

9.2 Recommendations

Natural gas contains mainly methane gas; however, some gas fields produce associated condensates or liquid fractions of C_2 and C_3 . Therefore, there is a need to understand how the phase behavior is affected by micropores over the reservoir pressure depletion span. Besides, the workflows introduced from micropores to hydraulic fractures macropores in this research can be extended to other trending studies. Consequently, the recommendations are as follows:

- Study the effect of phase behavior changes, such as critical pressure and temperature shifts in shale gas nanopores on Gaussian production rate forecast.
- Extend the study to methane/ethane/ CO_2 / H_2O system to investigate the diffusion in kerogen with this study as basis knowledge and propose a multicomponent self-diffusivity model.
- Improve the new multiphysics forward simulation algorithm to integrate complex fracture geometry and multiphase fluid system. Consequently, validate the approach with a CMG/Eclipse commercial simulator by history matching rate and

pressure with real field data.

- Heat production forecast from hydraulic fractured geothermal reservoir using temperature transient analysis.
- Modeling hydrogen storage in depleted organic-rich shale gas reservoirs.
- Develop a tensor-based stress transient model for 2D and 3D modeling of uplift/subsidence during simultaneous supercritical CO₂ storage and natural gas production.

Nomenclature

$A_m = 0.162 \text{ nm}^2$ is nitrogen molecule surface area at 77 K

c_{BET} BET isotherm fitting constant

N_A Avogadro's number ($6.022 \times 10^{22} \frac{\text{number}}{\text{mol}}$)

p^o Standard pressure of N₂ gas ~1.02 bar at 77.4 K

p/p^o Relative pressure of N₂ gas between 0.001~0.995 and 77.4 K

r Pore radius (m)

$R = 8.314 \text{ J/Kmol}$ is universal gas constant

S_{BET} Total specific surface area (m²/g)

S_{ext} Non – micropores specific surface area

S_{mic} Micropores specific surface area

t_{ads} Statistical thickness of adsorbed layer (Å)

T Temperature (K)

V_{ads} Total volume of adsorbed N₂ gas at $p/p^o = 0.001\sim 0.995$ and 77.4 K (m³/kg)

V_m Monolayer adsorption capacity (cm³/g)

V_{mic} Micropore filling volume
 V_{mol} Molar volume (m^3/mol)
 α Shape factor of the gas/liquid interface during adsorption
 ΔH_m Heat of gas condensation
 γ Surface tension of liquid nitrogen (N/m)
 $D_{x,eff}$ = effective or self diffusion coefficient in the x – direction
 $D_{y,eff}$ = effective or self diffusion coefficient in the y – direction
 $D_{z,eff}$ = effective or self diffusion coefficient in the z – direction
 D_{Fick}, D_F = Fick's diffusion coefficient, m^2/s
 $D_{Knudsen}$ = Knudsen diffusivity coefficient, m^2/s
 $D_{eff\ K,cir}$ = *Effective* Knudsen diffusivity coefficient in circular geometry, m^2/s
 $D_{eff\ K,squ}$ = *Effective* Knudsen diffusivity coefficient in square geometry, m^2/s
 $D_{transition}$ = transition diffusivity coefficient, m^2/s
 D_{eff} = effective diffusion coefficient, m^2/s
 $D_{eff,cir}$ = Effective diffusion coefficient in circular geometry, m^2/s
 $D_{eff,squ}$ = Effective diffusion coefficient in square geometry, m^2/s
 D_s = surface diffusion of adsorbed gas, m^2/s
 D_o = bulk phase diffusion coefficient, m^2/s
 d = pore size, m
 d_m = gas molecular diameter, m
 D_f = surface roughness factor, $2 \leq D_f \leq 3$
 E^{LJ}, E^{NB} = Lennard Jones potential energy or non – bonded LJ potential energy
 E^C = Coulomb potential energy
 f_i = fugacity, Pa
 f_i = ideal fugacity, Pa

G_{ijk} = binary array of the 3D grid

Kn = dimensionless Knudsen number

k_{∞} = liquid permeability, m^2

k_B = Boltzmann constant, J/K

M = gas molar mass, kg/mol

M_{ker} = kerogen molecular mass, kg/mol

m_{ker} = mass of condensed kerogen structure, kg

N_A = Avogadro number ($1/mol$)

N_a = number of kerogen structures

N_{am} = *Gibbs* number of adsorbed molecules from simulation (dimensionless)

N_{total} = *total* number of moles of molecules (mol)

n_{excess} = excess adsorption amount, mol

$\hat{n}_{excess}$ = Specific excess adsorption amount, mol/kg

n = absolute adsorption amount per adsorbent, $mole$

N_x = number of grid numbers in the x – direction

N_y = number of grid number in the y – direction

N_z = number of grid number in the z – direction

n_{ads}^{Gibbs} = *amount of adsorbed number*

n_L = maximum adsorbed capacity for the adsorbent, mol

$\hat{n}_L$ = Maximum adsorbed capacity for the adsorbent, mol/kg

$P(r_s)$ = pore radius distribution

p = pore pressure, Pa

p_L = *Langmuir* pressure, Pa

$\bar{r}_{eff}$ = Effective pore radius

$\bar{r}_{eff,cir}$ = Effective pore radius in circular geometry

$\bar{r}_{eff,squ}$ = Effective pore radius in square geometry

R = universal gas constant, $J/K.mol$

r_{ij} = distance between the sphere center and particles

r_s = sphere radius

T = temperature, K

V_{pore} = volume of pores, m^3

V_{total} = volume of total kerogen box model, m^3

V_{ads} = adsorbed phase volume, m^3

$\alpha(Kn)$ = rarefaction coefficient

β = Adsorption impact factor, ($\beta \geq 0$)

σ = molecular diameter, m

λ = mean free path, m

ε/k_B = bond energy, K

ε_0 = dielectric constant, Fm^{-1}

μ_i = chemical potential, J/mol

μ_{io} = ideal chemical potential, J/mol

ρ_{bulk} = bulk gas density, mol/m^3

ρ_{ker} = kerogen density, kg/m^3

$\rho_{He,b}$ = bulk density of helium gas, mol/m^3

τ_d = diffusion tortuosity

$\tau_{d,geo}$ = Diffusion tortuosity in circular or square geometry

$\tau'_{d,geo}$ = Diffusion tortuosity adsorption effect free in circular or square geometry

τ_e = electrical tortuosity

τ_g = geometric tortuosity

τ_h = hydraulic tortuosity

ϕ = porosity

$\hat{\phi}_i$ = fugacity coefficient

Δt = time interval

References

- [1] Wang Z, Krupnick A. A retrospective review of shale gas development in the United States: What led to the boom? *Econ Energy Environ Policy* 2015;4:5–17. doi:10.5547/2160-5890.4.1.zwan.
- [2] Hill RJ, Jarvie DM, Zumberge J, Henry M, Pollastro RM. Oil and gas geochemistry and petroleum systems of the Fort Worth Basin. *Am Assoc Pet Geol Bull* 2007. doi:10.1306/11030606014.
- [3] Strapoc D. Biogeochemistry of Coal-Bed Methane. *Annu Rev Earth Planet Sci* 2010.
- [4] U.S. Energy Information Agency. Annual Energy Outlook 2019 with projections to 2050. *Annu Energy Outlook 2019 with Proj to 2050* 2019;44:1–64.
- [5] Vanorio T, Mukerji T, Mavko G. Emerging methodologies to characterize the rock physics properties of organic-rich shales. *Lead Edge (Tulsa, OK)* 2008;27:780–7. doi:10.1190/1.2944163.
- [6] Vasileiadis M, Peristeras LD, Papavasileiou KD, Economou IG. Transport Properties of Shale Gas in Relation to Kerogen Porosity. *J Phys Chem C* 2018;122:6166–77. doi:10.1021/acs.jpcc.8b00162.
- [7] Yu H, Xu H, Fan J, Zhu YB, Wang F, Wu H. Transport of Shale Gas in Microporous/Nanoporous Media: Molecular to Pore-Scale Simulations. *Energy and Fuels* 2021;35:911–43. doi:10.1021/acs.energyfuels.0c03276.
- [8] Chen C, Hu D, Westacott D, Loveless D. Nanometer-scale characterization of microscopic pores in shale kerogen by image analysis and pore-scale modeling. *Geochemistry, Geophys Geosystems* 2013;14:4066–75. doi:10.1002/ggge.20254.
- [9] Passey QR, Bohacs KM, Esch WL, Klimentidis R, Sinha S. From oil-prone source rock to gas-producing shale reservoir - Geologic and petrophysical characterization of unconventional shale-gas reservoirs. *SPE Middle East Oil Gas Show Conf MEOS, Proc* 2013;1:6–34.
- [10] Ambrose RJ, Hartman RC, Diaz-Campos M, Akkutlu IY, Sondergeld CH. Shale

gas-in-place calculations Part I: New pore-scale considerations. SPE J 2012;17:219–29. doi:10.2118/131772-PA.

- [11] Curtis ME, Ambrose RJ, Sondergeld CH, Rai CS. Structural characterization of gas shales on the micro- and nano-scales. Soc Pet Eng - Can Unconv Resour Int Pet Conf 2010 2010;3:1933–47.
- [12] Aljamaan H, Ross CM, Kovscek AR. Multiscale imaging of gas adsorption in shales. Soc Pet Eng - SPE Unconv Resour Conf 2017 2017:541–66. doi:10.2118/185054-ms.
- [13] Chen L, Zhang L, Kang Q, Viswanathan HS, Yao J, Tao W. Nanoscale simulation of shale transport properties using the lattice Boltzmann method: Permeability and diffusivity. Sci Rep 2015;5:8089. doi:10.1038/srep08089.
- [14] Vernik L, Nur A. Ultrasonic velocity and anisotropy of hydrocarbon source rocks. Geophysics 1992;57:727–35. doi:10.1190/1.1443286.
- [15] Dasani D, Wang Y, Tsotsis TT, Jessen K. Laboratory-Scale Investigation of Sorption Kinetics of Methane/Ethane Mixtures in Shale. Ind Eng Chem Res 2017;56:9953–63. doi:10.1021/acs.iecr.7b02431.
- [16] Etminan SR, Javadpour F, Maini BB, Chen Z. Measurement of gas storage processes in shale and of the molecular diffusion coefficient in kerogen. Int J Coal Geol 2014;123:10–9. doi:10.1016/j.coal.2013.10.007.
- [17] Sui H, Yao J. Effect of surface chemistry for CH₄/CO₂ adsorption in kerogen: A molecular simulation study. J Nat Gas Sci Eng 2016;31:738–46. doi:10.1016/j.jngse.2016.03.097.
- [18] Zhao T, Li X, Zhao H, Li M. Molecular simulation of adsorption and thermodynamic properties on type II kerogen: Influence of maturity and moisture content. Fuel 2017;190:198–207. doi:10.1016/j.fuel.2016.11.027.
- [19] Huang L, Ning Z, Wang Q, Qi R, Zeng Y, Qin H, et al. Molecular simulation of adsorption behaviors of methane, carbon dioxide and their mixtures on kerogen: Effect of kerogen maturity and moisture content. Fuel 2018;211:159–72. doi:10.1016/j.fuel.2017.09.060.
- [20] Li J, Zhou S, Gaus G, Li Y, Ma Y, Chen K, et al. Characterization of methane adsorption on shale and isolated kerogen from the Sichuan Basin under pressure up to 60 MPa: Experimental results and geological implications. Int J Coal Geol 2018;189:83–93. doi:10.1016/j.coal.2018.02.020.
- [21] Zhang Y, Shao D, Yan J, Jia X, Li Y, Yu P, et al. The pore size distribution and its relationship with shale gas capacity in organic-rich mudstone of Wufeng-Longmaxi Formations, Sichuan Basin, China. J Nat Gas Geosci 2016;1:213–20. doi:10.1016/j.jnggs.2016.08.002.
- [22] Ji W, Song Y, Jiang Z, Chen L, Wang P, Liu Q, et al. Micro-nano pore structure

characteristics and its control factors of shale in Longmaxi Formation, southeastern Sichuan Basin. *Shiyou Xuebao/Acta Pet Sin* 2016. doi:10.7623/syxb201602004.

- [23] Gou Q, Xu S, Hao F, Yang F, Zhang B, Shu Z, et al. Full-scale pores and micro-fractures characterization using FE-SEM, gas adsorption, nano-CT and micro-CT: A case study of the Silurian Longmaxi Formation shale in the Fuling area, Sichuan Basin, China. *Fuel* 2019;253:167–79. doi:10.1016/j.fuel.2019.04.116.
- [24] AYLMOORE LAG, QUIRK JP. THE MICROPORE SIZE DISTRIBUTIONS OF CLAY MINERAL SYSTEMS. *J Soil Sci* 1967. doi:10.1111/j.1365-2389.1967.tb01481.x.
- [25] Afagwu C, Abubakar I, Kalam S, Al-Afnan SF, Awotunde AA. Pressure-transient analysis in shale gas reservoirs: A review. *J Nat Gas Sci Eng* 2020;78:103319. doi:10.1016/j.jngse.2020.103319.
- [26] Javadpour F, Ettehadtavakkol A. Gas Transport Processes In Shale. *Fundam. Gas Shale Reserv.*, 2015. doi:10.1002/9781119039228.ch11.
- [27] Jones FO, Owens WW. Laboratory study of low-permeability gas sands. *SPE Repr Ser* 1999. doi:10.2118/7551-pa.
- [28] Florence FA, Rushing JA, Newsham KE, Blasingame TA. Improved permeability prediction relations for low-permeability sands. *Soc Pet Eng - Rocky Mt Oil Gas Technol Symp* 2007 2007:290–307.
- [29] Kazemi M, Maleki H, Takbiri-Borujeni A. Molecular dynamics study of transport and storage of methane in kerogen. *SPE East Reg Meet* 2016;2016–Janua:13–5. doi:10.2118/184058-MS.
- [30] Hou Y, He S, Wang J, Harris NB, Cheng C, Li Y. Preliminary study on the pore characterization of lacustrine shale reservoirs using low pressure nitrogen adsorption and field emission scanning electron microscopy methods: A case study of the Upper Jurassic Emuerhe Formation, Mohe basin, northeastern Ch. *Can J Earth Sci* 2015. doi:10.1139/cjes-2014-0188.
- [31] Chen S, Han Y, Fu C, Zhang han, Zhu Y, Zuo Z. Micro and nano-size pores of clay minerals in shale reservoirs: Implication for the accumulation of shale gas. *Sediment Geol* 2016. doi:10.1016/j.sedgeo.2016.06.022.
- [32] Jiao K, Yao S, Liu C, Gao Y, Wu H, Li M, et al. The characterization and quantitative analysis of nanopores in unconventional gas reservoirs utilizing FESEM-FIB and image processing: An example from the lower Silurian Longmaxi Shale, upper Yangtze region, China. *Int J Coal Geol* 2014. doi:10.1016/j.coal.2014.03.004.
- [33] Klaver J, Desbois G, Littke R, Urai JL. BIB-SEM pore characterization of mature and post mature Posidonia Shale samples from the Hils area, Germany. *Int J Coal*

Geol 2016. doi:10.1016/j.coal.2016.03.003.

- [34] Zhou S, Yan G, Xue H, Guo W, Li X. 2D and 3D nanopore characterization of gas shale in Longmaxi formation based on FIB-SEM. *Mar Pet Geol* 2016. doi:10.1016/j.marpetgeo.2016.02.033.
- [35] Liu K, Ostadhassan M, Zhou J, Gentzis T, Rezaee R. Nanoscale pore structure characterization of the Bakken shale in the USA. *Fuel* 2017;209:567–78. doi:10.1016/j.fuel.2017.08.034.
- [36] Tang X, Jiang Z, Jiang S, Wang P, Xiang C. Effect of Organic Matter and Maturity on Pore Size Distribution and Gas Storage Capacity in High-Mature to Post-Mature Shales. *Energy and Fuels* 2016;30:8985–96. doi:10.1021/acs.energyfuels.6b01499.
- [37] Yang C, Zhang J, Han S, Xue B, Zhao Q. Classification and the developmental regularity of organic-associated pores (OAP) through a comparative study of marine, transitional, and terrestrial shales in China. *J Nat Gas Sci Eng* 2016;36:358–68. doi:10.1016/j.jngse.2016.10.044.
- [38] Zhang Y, He Z, Jiang S, Lu S, Xiao D, Chen G, et al. Factors Affecting Shale Gas Accumulation in Overmature Shales Case Study from Lower Cambrian Shale in Western Sichuan Basin, South China. *Energy and Fuels* 2018;32:3003–12. doi:10.1021/acs.energyfuels.7b03544.
- [39] Pollard WG, Present RD. On gaseous self-diffusion in long capillary tubes. *Phys Rev* 1948;73:762–74. doi:10.1103/PhysRev.73.762.
- [40] Tesson S, Firoozabadi A. Methane Adsorption and Self-Diffusion in Shale Kerogen and Slit Nanopores by Molecular Simulations. *J Phys Chem C* 2018;122:23528–42. doi:10.1021/acs.jpcc.8b07123.
- [41] Liu P, Harder E, Berne BJ. On the calculation of diffusion coefficients in confined fluids and interfaces with an application to the liquid-vapor interface of water. *J Phys Chem B* 2004;108:6595–602. doi:10.1021/jp0375057.
- [42] Swami V, Settari A. A Pore Scale Gas Flow Model for Shale Gas Reservoir 2012:5–7. doi:10.2118/155756-ms.
- [43] Ji L, Zhang T, Milliken KL, Qu J, Zhang X. Experimental investigation of main controls to methane adsorption in clay-rich rocks. *Appl Geochemistry* 2012;27:2533–45. doi:10.1016/j.apgeochem.2012.08.027.
- [44] Kwon O, Herbert BE, Kronenberg AK. Permeability of illite-bearing shale: 2. Influence of fluid chemistry on flow and functionally connected pores. *J Geophys Res Solid Earth* 2004;109:1–13. doi:10.1029/2004JB003055.
- [45] Yaalon DH. Mineral Composition of the Average Shale. *Clay Miner* 1962. doi:10.1180/claymin.1962.5.27.05.

- [46] Choo KY, Bai K. Effects of bentonite concentration and solution pH on the rheological properties and long-term stabilities of bentonite suspensions. *Appl Clay Sci* 2015;108:182–90. doi:10.1016/j.clay.2015.02.023.
- [47] Ahmed HM, Kamal MS, Al-Harthi M. Polymeric and low molecular weight shale inhibitors: A review. *Fuel* 2019;251:187–217. doi:10.1016/j.fuel.2019.04.038.
- [48] Moore DM, Reynolds RC j. X-Ray Diffraction and the Identification and Analysis of Clay Minerals, second edition. 1997. doi:10.1038/srep26532.
- [49] Worden RH, Griffiths J, Wooldridge LJ, Utley JEP, Lawan AY, Muhammed DD, et al. Chlorite in sandstones. *Earth-Science Rev* 2020;204:103105. doi:10.1016/j.earscirev.2020.103105.
- [50] Brigatti MF, Galán E, Theng BKG. Structure and Mineralogy of Clay Minerals. vol. 5. 2013. doi:10.1016/B978-0-08-098258-8.00002-X.
- [51] Choo KY, Bai K. Effects of bentonite concentration and solution pH on the rheological properties and long-term stabilities of bentonite suspensions. *Appl Clay Sci* 2015;108:182–90. doi:10.1016/j.clay.2015.02.023.
- [52] Avadiar L, Leong YK, Fourie A. Physicochemical behaviors of kaolin slurries with and without cations-Contributions of alumina and silica sheets. *Colloids Surfaces A Physicochem Eng Asp* 2015;468:103–13. doi:10.1016/j.colsurfa.2014.12.019.
- [53] Jin Z, Firoozabadi A. Methane and carbon dioxide adsorption in clay-like slit pores by Monte Carlo simulations. *Fluid Phase Equilib* 2013;360:456–65. doi:10.1016/j.fluid.2013.09.047.
- [54] Ross DJK, Marc Bustin R. The importance of shale composition and pore structure upon gas storage potential of shale gas reservoirs. *Mar Pet Geol* 2009;26:916–27. doi:10.1016/j.marpetgeo.2008.06.004.
- [55] El Ouahabi M, Daoudi L, Fagel N. Mineralogical and geotechnical characterization of clays from northern Morocco for their potential use in the ceramic industry. *Clay Miner* 2014. doi:10.1180/claymin.2014.049.1.04.
- [56] Hubert F, Caner L, Meunier A, Lanson B. Advances in characterization of soil clay mineralogy using X-ray diffraction: From decomposition to profile fitting. *Eur J Soil Sci* 2009;60:1093–105. doi:10.1111/j.1365-2389.2009.01194.x.
- [57] Środoń J. Chapter 12.2 Identification and Quantitative Analysis of Clay Minerals. *Dev Clay Sci* 2006;1:765–87. doi:10.1016/S1572-4352(05)01028-7.
- [58] Mattioli M, Giardini L, Roselli C, Desideri D. Mineralogical characterization of commercial clays used in cosmetics and possible risk for health. *Appl Clay Sci* 2016;119:449–54. doi:10.1016/j.clay.2015.10.023.
- [59] Zhong H, Yang T, Yin H, Lu J, Zhang K, Fu C. Role of Alkali type in chemical

- loss and ASP-flooding enhanced oil recovery in Sandstone formations. *SPE Reserv Eval Eng* 2020;23:431–45. doi:10.2118/191545-PA.
- [60] Zhao Y, Han C, Sun Y, Danesh NN, Liu T, Gao Y. Nano- to micro-pore characterization by synchrotron radiation SAXS and nano-CT for bituminous coals. *Front Earth Sci* 2021;15:189–201. doi:10.1007/s11707-021-0889-6.
 - [61] Loucks RG, Reed RM, Ruppel SC, Jarvie DM. Morphology, Genesis, and Distribution of Nanometer-Scale Pores in Siliceous Mudstones of the Mississippian Barnett Shale. *J Sediment Res* 2009;79:848–61. doi:10.2110/jsr.2009.092.
 - [62] Tang Y, Hou C, He Y, Wang Y, Chen Y, Rui Z. Review on Pore Structure Characterization and Microscopic Flow Mechanism of CO₂ Flooding in Porous Media. *Energy Technol* 2021;9. doi:10.1002/ente.202000787.
 - [63] Downs RT, Hall-Wallace M. The American Mineralogist crystal structure database. *Am Mineral* 2003. doi:10.5860/choice.43sup-0302.
 - [64] Hillier S. Quantitative Analysis of Clay and other Minerals in Sandstones by X-Ray Powder Diffraction (XRPD). 2009. doi:10.1002/9781444304336.ch11.
 - [65] Dunn PJ, Peacor DR, Ramik RA, Su SC, Rouse RC. Franklinfurnaceite, a Ca-Fe³⁺-Mn³⁺-Mn²⁺ zincosilicate isotypic with chlorite, from Franklin, New Jersey. *Am Mineral* 1987;72:812–5.
 - [66] Worden RH, Griffiths J, Wooldridge LJ, Utley JEP, Lawan AY, Muhammed DD, et al. Chlorite in sandstones. *Earth-Science Rev* 2020;204:103105. doi:10.1016/j.earscirev.2020.103105.
 - [67] Bailey SW, Lister JS. Structures, compositions, and X-ray diffraction identification of dioctahedral chlorites. *Clays Clay Miner* 1989;37:193–202. doi:10.1346/CCMN.1989.0370301.
 - [68] RULE A, RADKE F. Baileychlore, the Zn end member of the trioctahedral chlorite series. *Am Mineral* 1988;73:135–9.
 - [69] Krivovichev S V., Armbruster T, Organova NI, Burns PC, Seredkin M V., Chukanov N V. Incorporation of sodium into the chlorite structure: The crystal structure of glagolevite, Na(Mg,Al)₆[Si₃AlO₁₀](OH,O)₈. *Am Mineral* 2004. doi:10.2138/am-2004-0727.
 - [70] Ahmed HM, Kamal MS, Al-Harthi M. Polymeric and low molecular weight shale inhibitors: A review. *Fuel* 2019;251:187–217. doi:10.1016/j.fuel.2019.04.038.
 - [71] Aringhieri R. Nanoporosity characteristics of some natural clay minerals and soils. *Clays Clay Miner* 2004. doi:10.1346/CCMN.2004.0520604.
 - [72] Luo P, Zhong N, Khan I, Wang X, Wang H, Luo Q, et al. Effects of pore structure and wettability on methane adsorption capacity of mud rock: Insights from mixture

- of organic matter and clay minerals. *Fuel* 2019;251:551–61. doi:10.1016/j.fuel.2019.04.072.
- [73] Kuila U, Prasad M. Specific surface area and pore-size distribution in clays and shales. *Geophys Prospect* 2013. doi:10.1111/1365-2478.12028.
- [74] Tompsett GA, Krogh L, Griffin DW, Conner WC. Hysteresis and scanning behavior of mesoporous molecular sieves. *Langmuir* 2005;21:8214–25. doi:10.1021/la050068y.
- [75] Wang X, Cheng H, Chai P, Bian J, Wang X, Liu Y, et al. Pore Characterization of Different Clay Minerals and Its Impact on Methane Adsorption Capacity. *Energy and Fuels* 2020;34:12204–14. doi:10.1021/acs.energyfuels.0c01922.
- [76] Xiong J, Liu K, Liu X, Liang L, Zeng Q. Molecular simulation of methane adsorption in slit-like quartz pores. *RSC Adv* 2016;6:110808–19. doi:10.1039/c6ra22803h.
- [77] Fan E, Tang S, Zhang C, Guo Q, Sun C. Methane sorption capacity of organics and clays in high-over matured shale-gas systems. *Energy Explor Exploit* 2014;32:927–42. doi:10.1260/0144-5987.32.6.927.
- [78] Hwang J, Pini R. Supercritical CO₂ and CH₄ Uptake by Illite-Smectite Clay Minerals. *Environ Sci Technol* 2019;53:11588–96. doi:10.1021/acs.est.9b03638.
- [79] Cheng AL, Huang WL. Selective adsorption of hydrocarbon gases on clays and organic matter. *Org. Geochem.*, 2004. doi:10.1016/j.orggeochem.2004.01.007.
- [80] Ji L, Zhang T, Milliken KL, Qu J, Zhang X. Experimental investigation of main controls to methane adsorption in clay-rich rocks. *Appl Geochemistry* 2012;27:2533–45. doi:10.1016/j.apgeochem.2012.08.027.
- [81] Hu X, Deng H, Lu C, Tian Y, Jin Z. Characterization of CO₂/CH₄ Competitive Adsorption in Various Clay Minerals in Relation to Shale Gas Recovery from Molecular Simulation. *Energy and Fuels* 2019;33:8202–14. doi:10.1021/acs.energyfuels.9b01610.
- [82] Li W, Pang X, Snape C, Zhang B, Zheng D, Zhang X. Molecular Simulation Study on Methane Adsorption Capacity and Mechanism in Clay Minerals: Effect of Clay Type, Pressure, and Water Saturation in Shales. *Energy and Fuels* 2019;33:765–78. doi:10.1021/acs.energyfuels.8b03462.
- [83] Wang Z, Zhang Y, Guo P, Liu H, Liao H. A novel method to calculate the gas adsorption of mixed minerals. *SN Appl Sci* 2020;2:1–9. doi:10.1007/s42452-020-2072-1.
- [84] Jin Z, Firoozabadi A. Methane and carbon dioxide adsorption in clay-like slit pores by Monte Carlo simulations. *Fluid Phase Equilib* 2013;360:456–65. doi:10.1016/j.fluid.2013.09.047.

- [85] Zhang J, Clennell MB, Liu K, Pervukhina M, Chen G, Dewhurst DN. Methane and Carbon Dioxide Adsorption on Illite. *Energy and Fuels* 2016;30:10643–52. doi:10.1021/acs.energyfuels.6b01776.
- [86] Chen G, Lu S, Zhang J, Xue Q, Han T, Xue H, et al. Research of CO₂ and N₂ Adsorption Behavior in K-Illite Slit Pores by GCMC Method. *Sci Rep* 2016;6:1–10. doi:10.1038/srep37579.
- [87] Titiloye JO, Skipper NT. Monte Carlo and molecular dynamics simulations of methane in potassium montmorillonite clay hydrates at elevated pressures and temperatures. *J Colloid Interface Sci* 2005;282:422–7. doi:10.1016/j.jcis.2004.08.131.
- [88] Tian Y, Yan C, Jin Z. Characterization of Methane Excess and Absolute Adsorption in Various Clay Nanopores from Molecular Simulation. *Sci Rep* 2017;7:1–21. doi:10.1038/s41598-017-12123-x.
- [89] Xu R, Prodanović M, Landry C. Pore-Scale Study of Water Adsorption and Subsequent Methane Transport in Clay in the Presence of Wettability Heterogeneity. *Water Resour Res* 2020;56:1–15. doi:10.1029/2020WR027568.
- [90] Em Y, Stoporev A, Semenov A, Glotov A, Smirnova E, Villevald G, et al. Methane Hydrate Formation in Halloysite Clay Nanotubes. *ACS Sustain Chem Eng* 2020;8:7860–8. doi:10.1021/acssuschemeng.0c00758.
- [91] Kou R, Alafnan SFK, Akkutlu IY. Multi-scale Analysis of Gas Transport Mechanisms in Kerogen. *Transp Porous Media* 2017;116:493–519. doi:10.1007/s11242-016-0787-7.
- [92] Jin Z, Firoozabadi A. Thermodynamic modeling of phase behavior in Shale media. *SPE J* 2016;21:190–207. doi:10.2118/176015-PA.
- [93] Sun J, Liu Z, Cao D. A permeation model of shale gas in cylindrical-like kerogen pores at geological conditions. *Chem Eng Sci* 2019;207:457–63. doi:10.1016/j.ces.2019.06.048.
- [94] Kazemi M, Takhiri-Borujeni A. Non-equilibrium molecular dynamics simulation of gas flow in organic nanochannels. *J Nat Gas Sci Eng* 2016;33:1087–94. doi:10.1016/j.jngse.2016.05.068.
- [95] Castez MF, Winograd EA, Sánchez VM. Methane Flow through Organic-Rich Nanopores: The Key Role of Atomic-Scale Roughness. *J Phys Chem C* 2017;121:28527–36. doi:10.1021/acs.jpcc.7b09811.
- [96] Furukawa S ichi, Nitta T. Non-equilibrium molecular dynamics simulation studies on gas permeation across carbon membranes with different pore shape composed of micro-graphite crystallites. *J Memb Sci* 2000;178:107–19. doi:10.1016/S0376-7388(00)00483-X.
- [97] MacElroy JMD, Boyle MJ. Nonequilibrium molecular dynamics simulation of a

- model carbon membrane separation of CH₄/H₂ mixtures. *Chem Eng J* 1999;74:85–97. doi:10.1016/S1385-8947(99)00056-X.
- [98] Meyer JC, Geim AK, Katsnelson MI, Novoselov KS, Booth TJ, Roth S. The structure of suspended graphene sheets. *Nature* 2007;446:60–3. doi:10.1038/nature05545.
- [99] Liang T, Zou YR, Zhan ZW, Lin XH, Shi J, Peng P. An evaluation of kerogen molecular structures during artificial maturation. *Fuel* 2020;265:116979. doi:10.1016/j.fuel.2019.116979.
- [100] Pan S, Wang Q, Bai J, Chi M, Cui D, Wang Z, et al. Molecular Structure and Electronic Properties of Oil Shale Kerogen: An Experimental and Molecular Modeling Study. *Energy and Fuels* 2018;32:12394–404. doi:10.1021/acs.energyfuels.8b03307.
- [101] Hackley PC, Lünsdorf NK. Application of Raman Spectroscopy as Thermal Maturity Probe in Shale Petroleum Systems: Insights from Natural and Artificial Maturation Series. *Energy and Fuels* 2018;32:11190–202. doi:10.1021/acs.energyfuels.8b02171.
- [102] Liu Y, Zhu Y, Chen S, Wang Y, Song Y. Evaluation of Spatial Alignment of Kerogen in Shale Using High-Resolution Transmission Electron Microscopy, Raman Spectroscopy, and Fourier Transform Infrared. *Energy and Fuels* 2018;32:10616–27. doi:10.1021/acs.energyfuels.8b02591.
- [103] Ungerer P, Collett J, Yiannourakou M. Molecular modeling of the volumetric and thermodynamic properties of kerogen: Influence of organic type and maturity. *Energy and Fuels* 2015;29:91–105. doi:10.1021/ef502154k.
- [104] Wang X, Huang X, Lin K, Zhao Y. The Constructions and Pyrolysis of 3D Kerogen Macromolecular Models: Experiments and Simulations. *Glob Challenges* 2019;3:1900006. doi:10.1002/gch2.201900006.
- [105] Sheng M, Li G, Huang Z, Tian S, Shah S, Geng L. Pore-scale modeling and analysis of surface diffusion effects on shale-gas flow in Kerogen pores. *J Nat Gas Sci Eng* 2015;27:979–85. doi:10.1016/j.jngse.2015.09.033.
- [106] Kang SM, Fathi E, Ambrose RJ, Akkutlu IY, Sigal RF. Carbon Dioxide Storage Capacity of Organic-Rich Shales 2011.
- [107] Rexer TFT, Benham MJ, Aplin AC, Thomas KM. Methane adsorption on shale under simulated geological temperature and pressure conditions. *Energy and Fuels* 2013;27:3099–109. doi:10.1021/ef400381v.
- [108] Thomas MM, Clouse JA. Primary migration by diffusion through kerogen: III. Calculation of geologic fluxes. *Geochim Cosmochim Acta* 1990;54:2793–7. doi:10.1016/0016-7037(90)90013-B.
- [109] Xiong J, Liu X, Liang L, Zeng Q. Adsorption of methane in organic-rich shale

- nanopores: An experimental and molecular simulation study. *Fuel* 2017;200:299–315. doi:10.1016/j.fuel.2017.03.083.
- [110] Fathi E, Akkutlu IY. Multi-component gas transport and adsorption effects during CO₂ injection and enhanced shale gas recovery. *Int J Coal Geol* 2014;123:52–61. doi:10.1016/j.coal.2013.07.021.
- [111] Gonciaruk A, Hall MR, Fay MW, Parmenter CDJ, Vane CH, Khlobystov AN, et al. Kerogen nanoscale structure and CO₂ adsorption in shale micropores. *Sci Rep* 2021;11:1–13. doi:10.1038/s41598-021-83179-z.
- [112] Yanfeng H, Jingye C, Xiangji D, Xiang W. Research on shale gas transportation and apparent permeability in nanopores. *J Nat Gas Sci Eng* 2017. doi:10.1016/j.jngse.2016.12.032.
- [113] Cai J, Lin D, Singh H, Zhou S, Meng Q, Zhang Q. A simple permeability model for shale gas and key insights on relative importance of various transport mechanisms. *Fuel* 2019;252:210–9. doi:10.1016/j.fuel.2019.04.054.
- [114] Zheng Q, Yu B, Wang S, Luo L. A diffusivity model for gas diffusion through fractal porous media. *Chem Eng Sci* 2012;68:650–5. doi:10.1016/j.ces.2011.10.031.
- [115] Geng L, Li G, Zitha P, Tian S, Sheng M, Fan X. A diffusion–viscous flow model for simulating shale gas transport in nano-pores. *Fuel* 2016;181:887–94. doi:10.1016/j.fuel.2016.05.036.
- [116] Wu K, Li X, Guo C, Wang C, Chen Z. A unified model for gas transfer in nanopores of shale-gas reservoirs: Coupling pore diffusion and surface diffusion. *SPE J* 2016;21:1583–611. doi:10.2118/2014-1921039-PA.
- [117] Beskok A, Karniadakis GE. Report: A model for flows in channels, pipes, and ducts at micro and nano scales. *Microscale Thermophys Eng* 1999;3:43–77. doi:10.1080/108939599199864.
- [118] Shen Y, Pang Y, Shen Z, Tian Y, Ge H. Multiparameter Analysis of Gas Transport Phenomena in Shale Gas Reservoirs: Apparent Permeability Characterization. *Sci Rep* 2018;8:1–14. doi:10.1038/s41598-018-20949-2.
- [119] Ning Y, Jiang Y, Liu H, Qin G. Numerical modeling of slippage and adsorption effects on gas transport in shale formations using the lattice Boltzmann method. *J Nat Gas Sci Eng* 2015;26:345–55. doi:10.1016/j.jngse.2015.06.015.
- [120] Li J. Efficient prediction of gas permeability by hybrid DSBGK-LBM simulations. *Fuel* 2019;250:154–9. doi:10.1016/j.fuel.2019.03.132.
- [121] Saomoto H, Katagiri J. Direct comparison of hydraulic tortuosity and electric tortuosity based on finite element analysis. *Theor Appl Mech Lett* 2015;5:177–80. doi:10.1016/j.taml.2015.07.001.

- [122] Duda A, Koza Z, Matyka M. Hydraulic tortuosity in arbitrary porous media flow. *Phys Rev E - Stat Nonlinear, Soft Matter Phys* 2011;84:1–8. doi:10.1103/PhysRevE.84.036319.
- [123] Espinoza-Andaluz M, Velasco-Galarza V, Romero-Vera A. On hydraulic tortuosity variations due to morphological considerations in 2D porous media by using the Lattice Boltzmann method. *Math Comput Simul* 2020;169:74–87. doi:10.1016/j.matcom.2019.09.017.
- [124] Yu BM, Li JH. A geometry model for tortuosity of flow path in porous media. *Chinese Phys Lett* 2004;21:1569–71. doi:10.1088/0256-307X/21/8/044.
- [125] Lanfrey PY, Kuzeljevic Z V., Dudukovic MP. Tortuosity model for fixed beds randomly packed with identical particles. *Chem Eng Sci* 2010;65:1891–6. doi:10.1016/j.ces.2009.11.011.
- [126] Comiti J, Renaud M. A new model for determining mean structure parameters of fixed beds from pressure drop measurements: application to beds packed with parallelepipedal particles. *Chem Eng Sci* 1989;44:1539–45. doi:10.1016/0009-2509(89)80031-4.
- [127] Garrouch AA, Ali L, Qasem F. Using diffusion and electrical measurements to assess tortuosity of porous media. *Ind Eng Chem Res* 2001;40:4363–9. doi:10.1021/ie010070u.
- [128] Nguyen TT, Demortière A, Fleutot B, Delobel B, Delacourt C, Cooper SJ. The electrode tortuosity factor: why the conventional tortuosity factor is not well suited for quantifying transport in porous Li-ion battery electrodes and what to use instead. *Npj Comput Mater* 2020;6. doi:10.1038/s41524-020-00386-4.
- [129] Tozzi EJ, Lavenson DM, McCarthy MJ, Powell RL. Magnetic resonance imaging to measure concentration profiles of solutes diffusing in stagnant beds of cellulosic fibers. *AIChE J* 2012. doi:10.1002/aic.12578.
- [130] He J, Ju Y, Lammers L, Kulasinski K, Zheng L. Tortuosity of kerogen pore structure to gas diffusion at molecular- and nano-scales: A molecular dynamics simulation. *Chem Eng Sci* 2019;115460. doi:10.1016/j.ces.2019.115460.
- [131] Pisani L. Simple Expression for the Tortuosity of Porous Media. *Transp Porous Media* 2011;88:193–203. doi:10.1007/s11242-011-9734-9.
- [132] Shen L, Chen Z. Critical review of the impact of tortuosity on diffusion. *Chem Eng Sci* 2007;62:3748–55. doi:10.1016/j.ces.2007.03.041.
- [133] Coleman SW, Vassilicos JC. Transport properties of saturated and unsaturated porous fractal materials. *Phys Rev Lett* 2008;100:1–4. doi:10.1103/PhysRevLett.100.035504.
- [134] McDuff RE, Ellis RA. DETERMINING DIFFUSION COEFFICIENTS IN MARINE SEDIMENTS: A LABORATORY STUDY OF THE VALIDITY OF

RESISTIVITY TECHNIQUES. Am J Sci 1979. doi:10.2475/ajs.279.6.666.

- [135] He J, Ju Y, Lammers L, Kulasinski K, Zheng L. Tortuosity of kerogen pore structure to gas diffusion at molecular- and nano-scales: A molecular dynamics simulation. Chem Eng Sci 2020;215:115460. doi:10.1016/j.ces.2019.115460.
- [136] Geng L, Li G, Wang M, Li Y, Tian S, Pang W, et al. A fractal production prediction model for shale gas reservoirs. J Nat Gas Sci Eng 2018;55:354–67. doi:10.1016/j.jngse.2018.04.025.
- [137] Wasaki A, Akkutlu IY. Permeability of organic-rich shale. SPE J., vol. 20, Society of Petroleum Engineers; 2015, p. 1384–96. doi:10.2118/170830-PA.
- [138] Thomas MM, Clouse JA. Primary migration by diffusion through kerogen: I. Model experiments with organic-coated rocks. Geochim Cosmochim Acta 1990;54:2775–9. doi:10.1016/0016-7037(90)90011-9.
- [139] Weissberg HL. Effective Diffusion Coefficient in Porous Media. J Appl Phys 1963. doi:10.1063/1.1729783.
- [140] Beeckman JW. Mathematical description of heterogeneous materials. Chem Eng Sci 1990. doi:10.1016/0009-2509(90)80148-8.
- [141] Thomas MM, Clouse JA. <1-s2.0-001670379090012A-main.pdf> 1990;54:2781–92.
- [142] Elwinger F, Pourmand P, Furó I. Diffusive Transport in Pores. Tortuosity and Molecular Interaction with the Pore Wall. J Phys Chem C 2017;121:13757–64. doi:10.1021/acs.jpcc.7b03885.
- [143] Collell J, Galliero G, Vermorel R, Ungerer P, Yiannourakou M, Montel F, et al. Transport of Multicomponent Hydrocarbon Mixtures in Shale Organic Matter by Molecular Simulations. J Phys Chem C 2015;119:22587–95. doi:10.1021/acs.jpcc.5b07242.
- [144] Vasileiadis M, Peristeras LD, Papavasileiou KD, Economou IG. Modeling of Bulk Kerogen Porosity: Methods for Control and Characterization. Energy and Fuels 2017;31:6004–18. doi:10.1021/acs.energyfuels.7b00626.
- [145] Wu T, Firoozabadi A. Effect of Microstructural Flexibility on Methane Flow in Kerogen Matrix by Molecular Dynamics Simulations. J Phys Chem C 2019;123:10874–80. doi:10.1021/acs.jpcc.8b12328.
- [146] Cussler EL. Diffusion: Mass Transfer in Fluid Systems, 2nd edition. 1997. doi:10.1017/CBO9780511805134.010.
- [147] Mueller R, Zhang S, Klink M, Bäumer M, Vasenkov S. The origin of a large apparent tortuosity factor for the Knudsen diffusion inside monoliths of a samaria-alumina aerogel catalyst: A diffusion NMR study. Phys Chem Chem Phys 2015;17:27481–7. doi:10.1039/c5cp04609b.

- [148] Lavenson DM, Tozzi EJ, McCarthy MJ, Powell RL. Effective diffusivities of BSA in cellulosic fiber beds measured with magnetic resonance imaging. *Cellulose* 2012;19:1085–95. doi:10.1007/s10570-012-9732-2.
- [149] Lemmon EW, Bell IH, Huber ML, McLinden MO. NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP), Version 10.0; Standard Reference Data; National Institute of Standards and Technology: Gaithersburg, MD. NIST Stand Ref Databasev23 2018.
- [150] Collell J, Ungerer P, Galliero G, Yiannourakou M, Montel F, Pujol M. Molecular simulation of bulk organic matter in type ii shales in the middle of the oil formation window. *Energy and Fuels* 2014;28:7457–66. doi:10.1021/ef5021632.
- [151] Yu H, Xu H, Fan J, Wang F, Wu H. Roughness Factor-Dependent Transport Characteristic of Shale Gas through Amorphous Kerogen Nanopores. *J Phys Chem C* 2020;124:12752–65. doi:10.1021/acs.jpcc.0c02456.
- [152] Liu B, Qi C, Zhao X, Teng G, Zhao L, Zheng H, et al. Nanoscale Two-Phase Flow of Methane and Water in Shale Inorganic Matrix. *J Phys Chem C* 2018;122:26671–9. doi:10.1021/acs.jpcc.8b06780.
- [153] Zhang T, Ellis GS, Ruppel SC, Milliken K, Yang R. Effect of organic-matter type and thermal maturity on methane adsorption in shale-gas systems. *Org Geochem* 2012;47:120–31. doi:10.1016/j.orggeochem.2012.03.012.
- [154] Rexer TF, Mathia EJ, Aplin AC, Thomas KM. High-pressure methane adsorption and characterization of pores in posidonia shales and isolated kerogens. *Energy and Fuels* 2014;28:2886–901. doi:10.1021/ef402466m.
- [155] Rexer TF, Mathia EJ, Aplin AC, Thomas KM. Supercritical methane adsorption and storage in pores in shales and isolated kerogens. *SN Appl Sci* 2020;2:1–17. doi:10.1007/s42452-020-2517-6.
- [156] Dang W, Zhang J, Wei X, Tang X, Chen Q, Li Z, et al. Geological controls on methane adsorption capacity of Lower Permian transitional black shales in the Southern North China Basin, Central China: Experimental results and geological implications. *J Pet Sci Eng* 2017;152:456–70. doi:10.1016/j.petrol.2017.03.017.
- [157] Takbiri-Borujeni A, Kazemi M, Sun T, Mansouri-Boroujeni M. Effect of kerogen type and maturity on performance of carbon dioxide storage in shale. *Proc - SPE Annu Tech Conf Exhib* 2017;2040. doi:10.2118/187360-ms.
- [158] Huang L, Ning Z, Wang Q, Zhang W, Cheng Z, Wu X, et al. Effect of organic type and moisture on CO₂/CH₄ competitive adsorption in kerogen with implications for CO₂ sequestration and enhanced CH₄ recovery. *Appl Energy* 2018;210:28–43. doi:10.1016/j.apenergy.2017.10.122.
- [159] Yucel Akkutlu I, Fathi E. Multiscale gas transport in shales with local kerogen heterogeneities. *SPE J* 2012;17:1002–11. doi:10.2118/146422-pa.

- [160] Obliger A, Ulm FJ, Pellenq R. Impact of Nanoporosity on Hydrocarbon Transport in Shales' Organic Matter. *Nano Lett* 2018;18:832–7. doi:10.1021/acs.nanolett.7b04079.
- [161] Xu HY, Yu H, Fan JC, Zhu YB, Wang FC, Wu HA. Two-Phase Transport Characteristic of Shale Gas and Water through Hydrophilic and Hydrophobic Nanopores. *Energy and Fuels* 2020;34:4407–20. doi:10.1021/acs.energyfuels.0c00212.
- [162] Yu H, Xu H, Xia J, Fan J, Wang F, Wu H. Nanoconfined Transport Characteristic of Methane in Organic Shale Nanopores: The Applicability of the Continuous Model. *Energy and Fuels* 2020;34:9552–62. doi:10.1021/acs.energyfuels.0c01789.
- [163] Afagwu C, Abubakar I, Kalam S, Al-Afnan SF, Awotunde AA. Pressure-transient analysis in shale gas reservoirs: A review. *J Nat Gas Sci Eng* 2020;78. doi:10.1016/j.jngse.2020.103319.
- [164] Wu K, Li X, Wang C, Yu W, Chen Z. A model for surface diffusion of adsorbed gas in nanopores of shale gas reservoirs. *Proc Annu Offshore Technol Conf* 2015;1:199–221. doi:10.1021/ie504030v.
- [165] Yu H, Chen J, Zhu YB, Wang FC, Wu HA. Multiscale transport mechanism of shale gas in micro/nano-pores. *Int J Heat Mass Transf* 2017;111:1172–80. doi:10.1016/j.ijheatmasstransfer.2017.04.050.
- [166] Qu ZG, Yin Y, Wang H, Zhang JF. Pore-scale investigation on coupled diffusion mechanisms of free and adsorbed gases in nanoporous organic matter. *Fuel* 2020;260. doi:10.1016/j.fuel.2019.116423.
- [167] Li XZ, Fan JC, Yu H, Zhu YB, Wu HA. Lattice Boltzmann method simulations about shale gas flow in contracting nano-channels. *Int J Heat Mass Transf* 2018;122:1210–21. doi:10.1016/j.ijheatmasstransfer.2018.02.066.
- [168] Yu H, Zhu YB, Jin X, Liu H, Wu HA. Multiscale simulations of shale gas transport in micro/nano-porous shale matrix considering pore structure influence. *J Nat Gas Sci Eng* 2019;64:28–40. doi:10.1016/j.jngse.2019.01.016.
- [169] Yu H, Fan JC, Xia J, Liu H, Wu HA. Multiscale gas transport behavior in heterogeneous shale matrix consisting of organic and inorganic nanopores. *J Nat Gas Sci Eng* 2020;75:103139. doi:10.1016/j.jngse.2019.103139.
- [170] Song W, Yao J, Wang D, Li Y, Sun H, Yang Y. Dynamic pore network modelling of real gas transport in shale nanopore structure. *J Pet Sci Eng* 2020;184. doi:10.1016/j.petrol.2019.106506.
- [171] Chen J, Yu H, Fan J, Wang F, Lu D, Liu H, et al. Channel-width dependent pressure-driven flow characteristics of shale gas in nanopores. *AIP Adv* 2017;7. doi:10.1063/1.4982729.
- [172] Yu H, Fan JC, Chen J, Zhu YB, Wu HA. Pressure-dependent transport

- characteristic of methane gas in slit nanopores. *Int J Heat Mass Transf* 2018;123:657–67. doi:10.1016/j.ijheatmasstransfer.2018.03.003.
- [173] Chen J, Wang FC, Liu H, Wu HA. Molecular mechanism of adsorption/desorption hysteresis: dynamics of shale gas in nanopores. *Sci China Physics, Mech Astron* 2017;60:1–8. doi:10.1007/s11433-016-0335-5.
- [174] Wang S, Javadpour F, Feng Q. Molecular dynamics simulations of oil transport through inorganic nanopores in shale. *Fuel* 2016;171:74–86. doi:10.1016/j.fuel.2015.12.071.
- [175] Fatt I. The Network Model of Porous Media. *Trans AIME* 1956;207:144–81. doi:10.2118/574-g.
- [176] Blunt MJ, Bijeljic B, Dong H, Gharbi O, Iglauer S, Mostaghimi P, et al. Pore-scale imaging and modelling. *Adv Water Resour* 2013;51:197–216. doi:10.1016/j.advwatres.2012.03.003.
- [177] Succi S. Mesoscopic Modeling of Slip Motion at Fluid-Solid Interfaces with Heterogeneous Catalysis. *Phys Rev Lett* 2002;89:1–4. doi:10.1103/PhysRevLett.89.064502.
- [178] Shan X, Yuan XF, Chen H. Kinetic theory representation of hydrodynamics: A way beyond the Navier-Stokes equation. *J Fluid Mech* 2006;550:413–41. doi:10.1017/S0022112005008153.
- [179] Li Q, He YL, Tang GH, Tao WQ. Lattice Boltzmann modeling of microchannel flows in the transition flow regime. *Microfluid Nanofluidics* 2011;10:607–18. doi:10.1007/s10404-010-0693-1.
- [180] Li ZZ, Min T, Kang Q, He YL, Tao WQ. Investigation of methane adsorption and its effect on gas transport in shale matrix through microscale and mesoscale simulations. *Int J Heat Mass Transf* 2016;98:675–86. doi:10.1016/j.ijheatmasstransfer.2016.03.039.
- [181] Klinkenberg LJ. THE PERMEABILITY OF POROUS MEDIA TO LIQUIDS AND GASES "f. n.d.
- [182] Tang GH, Tao WQ, He YL. Gas slippage effect on microscale porous flow using the lattice Boltzmann method. *Phys Rev E - Stat Nonlinear, Soft Matter Phys* 2005;72:1–8. doi:10.1103/PhysRevE.72.056301.
- [183] Boek ES, Zacharoudiou I, Gray F, Shah SM, Crawshaw JP, Yang J. Multiphase-flow and reactive-transport validation studies at the pore scale by use of lattice Boltzmann computer simulations. *SPE J* 2017;22:940–9.
- [184] Xiaoyi H, Li-Shi L. Lattice Boltzmann Model for the Incompressible Navier–Stokes Equation. *J Stat Phys* 1997;884:927–44.
- [185] Moghaddam RN, Jamiolahmady M. Study of slip flow in shale and tight gas

reservoir rocks using lattice Boltzmann method. Soc Pet Eng - SPE Eur Featur 79th EAGE Conf Exhib 2017:927–48.

- [186] Srisutthiyakorn N, Mavko G. The revised Kozeny-Carman equation: A practical way to improve permeability prediction in the Kozeny-Carman equation through pore-size distribution 2017:3811–5. doi:10.1190/segam2017-17750852.1.
- [187] Watari M. Relationship between accuracy and number of velocity particles of the finite-difference lattice Boltzmann method in velocity slip simulations. J Fluids Eng Trans ASME 2010;132:1–11. doi:10.1115/1.4002359.
- [188] Wei B, Hou J, Wu D, Wang H, Liu H. Pore scale simulation of surfactant flooding by Lattice Boltzmann Method. Soc Pet Eng - SPE Int Heavy Oil Conf Exhib 2018, HOCE 2018 2018. doi:10.2118/193660-MS.
- [189] Yang and Huang_1995_LBM.pdf n.d.
- [190] Li Z, Chen T, Ning Y, Zhang K, Qin G. Numerical simulation of waterflooding process using lattice boltzmann method to estimate relative permeability for fractured unconventional reservoirs. SPE Middle East Oil Gas Show Conf MEOS, Proc 2019;2019–March.
- [191] Yang G, Weigand B. Investigation of the Klinkenberg effect in a micro/nanoporous medium by direct simulation Monte Carlo method. Phys Rev Fluids 2018;3:1–17. doi:10.1103/PhysRevFluids.3.044201.
- [192] Yang Y, Yao J, Wang C, Gao Y, Zhang Q, An S, et al. New pore space characterization method of shale matrix formation by considering organic and inorganic pores. J Nat Gas Sci Eng 2015;27:496–503. doi:10.1016/j.jngse.2015.08.017.
- [193] Tokumasu T, Matsumoto Y. Dynamic molecular collision (DMC) model for rarefied gas flow simulations by the DSMC method. Phys Fluids 1999;11:1907–20. doi:10.1063/1.870053.
- [194] Je B. velocity method (= Ic 1963.
- [195] Ho MT, Li J, Wu L, Reese JM, Zhang Y. A comparative study of the DSBGK and DVM methods for low-speed rarefied gas flows. Comput Fluids 2019;181:143–59. doi:10.1016/j.compfluid.2019.01.019.
- [196] Li W, Bousikhane F, Carey JW, Cusatis G. Discrete modeling of the fracture-permeability behavior of shale. 51st US Rock Mech / Geomech Symp 2017 2017;3:2093–100.
- [197] Li J. Direct simulation method based on BGK equation. AIP Conf Proc 2011;1333:283–8. doi:10.1063/1.3562662.
- [198] Li J. Efficiency and stability of the DSBGK method. AIP Conf Proc 2012;1501:849–56. doi:10.1063/1.4769631.

- [199] Li J, Sultan AS. Klinkenberg slippage effect in the permeability computations of shale gas by the pore-scale simulations. *J Nat Gas Sci Eng* 2017;48:197–202. doi:10.1016/j.jngse.2016.07.041.
- [200] Li J, Cai C. Numerical study on thermal transpiration flows through a rectangular channel 2017.
- [201] Li J, Sultan AS. Permeability Computations of Shale Gas by the Pore-Scale Monte Carlo Molecular Simulations 2015:1–10. doi:10.2523/iptc-18263-ms.
- [202] Qian YH, Orszag SA. Lattice bgk models for the navier-stokes equation: Nonlinear deviation in compressible regimes. *Epl* 1993;21:255–9. doi:10.1209/0295-5075/21/3/001.
- [203] Qian YH, Zhou Y. Complete Galilean-invariant lattice BGK models for the Navier-Stokes equation. *Europhys Lett* 1998;42:359–64. doi:10.1209/epl/i1998-00255-3.
- [204] Qian YH, D’Humières D, Lallemand P. Lattice bgk models for navier-stokes equation. *Epl* 1992;17:479–84. doi:10.1209/0295-5075/17/6/001.
- [205] Tian Y, Yu X, Li J, Neeves KB, Yin X, Wu YS. Scaling law for slip flow of gases in nanoporous media from nanofluidics, rocks, and pore-scale simulations. *Fuel* 2019;236:1065–77. doi:10.1016/j.fuel.2018.09.036.
- [206] Aljaberi J, Alafnan S, Glatz G, Sultan AS, Afagwu C. The Impact of Kerogen Tortuosity on Shale Permeability. *SPE J* 2021;26:765–79. doi:10.2118/204469-pa.
- [207] Afagwu C, Alafnan S, Mahmoud MA, Patil S. Permeability model for shale and ultra-tight gas formations : Critical insights into the impact of dynamic adsorption. *Energy Reports* 2021;7:3302–16. doi:10.1016/j.egyr.2021.05.060.
- [208] Arps JJ. Analysis of Decline Curves. *Trans AIME* 1945. doi:10.2118/945228-g.
- [209] Tugan MF, Weijermars R. Variation in b-sigmoids with flow regime transitions in support of a new 3-segment DCA method: Improved production forecasting for tight oil and gas wells. *J Pet Sci Eng* 2020;192:107243. doi:10.1016/j.petrol.2020.107243.
- [210] Lie K-A. An Introduction to Reservoir Simulation Using MATLAB/GNU Octave. 2019. doi:10.1017/9781108591416.
- [211] Alafnan S. Petrophysics of Kerogens Based on Realistic Structures 2021. doi:10.1021/acsomega.1c00018.
- [212] van Harmelen A, Weijermars R. Complex analytical solutions for flow in hydraulically fractured hydrocarbon reservoirs with and without natural fractures. *Appl Math Model* 2018. doi:10.1016/j.apm.2017.11.027.
- [213] Khanal A, Weijermars R. Pressure depletion and drained rock volume near

hydraulically fractured parent and child wells. *J Pet Sci Eng* 2019.
doi:10.1016/j.petrol.2018.09.070.

- [214] Li W, Liu J, Zeng J, Leong YK, Elsworth D, Tian J, et al. A fully coupled multidomain and multiphysics model for evaluation of shale gas extraction. *Fuel* 2020;278:118214. doi:10.1016/j.fuel.2020.118214.
- [215] Micheal M, Xu WL, Xu HY, Zhang JN, Jin HJ, Yu H, et al. Multi-scale modelling of gas transport and production evaluation in shale reservoir considering crisscrossing fractures. *J Nat Gas Sci Eng* 2021;95:104156. doi:10.1016/j.jngse.2021.104156.
- [216] Li H, Yu G, Fang Y, Chen Y, Wang C, Zhang D. Gas production prediction and risk quantification of shale gas reservoirs in Sichuan Basin based on Gauss prediction model and Monte Carlo probability method. *Front Earth Sci* 2022;10:1–14. doi:10.3389/feart.2022.977200.
- [217] Mehana M, Santos JE, Neil C, Carey JW, Guthrie G, Hyman J, et al. Shale fundamentals: Experimental and modeling insights. *Energy Reports* 2022;8:11192–205. doi:10.1016/j.egy.2022.08.229.
- [218] Cai J, Wood DA, Hajibeygi H, Iglaier S. Multiscale and multiphysics influences on fluids in unconventional reservoirs: Modeling and simulation. *Adv Geo-Energy Res* 2022;6:91–4. doi:10.46690/ager.2022.02.01.
- [219] Weijermars R. Production rate of multi-fractured wells modeled with Gaussian pressure transients. *J Pet Sci Eng* 2021;210:110027. doi:10.1016/j.petrol.2021.110027.
- [220] Sayed Hassan M, Villieras F, Gaboriaud F, Razafitianamaharavo A. AFM and low-pressure argon adsorption analysis of geometrical properties of phyllosilicates. *J Colloid Interface Sci* 2006;296:614–23. doi:10.1016/j.jcis.2005.09.028.
- [221] Macht F, Eusterhues K, Pronk GJ, Totsche KU. Specific surface area of clay minerals: Comparison between atomic force microscopy measurements and bulk-gas (N₂) and -liquid (EGME) adsorption methods. *Appl Clay Sci* 2011;53:20–6. doi:10.1016/j.clay.2011.04.006.
- [222] Kariem H, Kiefer T, Hellmich C, Gaggli W, Steiger-Thirsfeld A, Füssl J. EDX/XRD-based identification of micrometer-sized domains in scanning electron micrographs of fired clay. *Mater Struct Constr* 2020;53. doi:10.1617/s11527-020-01531-7.
- [223] Ochieng O. Characterization and classification of clay minerals for potential applications in Rugi Ward, Kenya. *African J Environ Sci Technol* 2016. doi:10.5897/ajest2016.2184.
- [224] Adeniyi FI, Ogundiran MB, Hemalatha T, Hanumantrai BB. Characterization of raw and thermally treated Nigerian kaolinite-containing clays using instrumental

techniques. *SN Appl Sci* 2020;2:1–14. doi:10.1007/s42452-020-2610-x.

- [225] Chen JJ, Sorelli L, Vandamme M, Ulm FJ, Chanvillard G. A coupled nanoindentation/SEM-EDS study on low water/cement ratio portland cement paste: Evidence for C-S-H/Ca(OH)₂ nanocomposites. *J Am Ceram Soc* 2010;93:1484–93. doi:10.1111/j.1551-2916.2009.03599.x.
- [226] Boulingui JE, Nkoumbou C, Njoya D, Thomas F, Yvon J. Characterization of clays from Mezafe and Mengono (Ne-Libreville, Gabon) for potential uses in fired products. *Appl Clay Sci* 2015;115:132–44. doi:10.1016/j.clay.2015.07.029.
- [227] Zaffar M, Lu SG. Pore size distribution of clayey soils and its correlation with soil organic matter. *Pedosphere* 2015;25:240–9. doi:10.1016/S1002-0160(15)60009-1.
- [228] Li W, Lu S, Xue H, Zhang P, Hu Y. Microscopic pore structure in shale reservoir in the argillaceous dolomite from the Jiangnan Basin. *Fuel* 2016;181:1041–9. doi:10.1016/j.fuel.2016.04.140.
- [229] Wilson W, Sorelli L, Tagnit-Hamou A. Automated coupling of NanoIndentation and Quantitative Energy-Dispersive Spectroscopy (NI-QEDS): A comprehensive method to disclose the micro-chemo-mechanical properties of cement pastes. *Cem Concr Res* 2018;103:49–65. doi:10.1016/j.cemconres.2017.08.016.
- [230] Elgamouz A, Tijani N, Shehadi I, Hasan K, Al-Farooq Kawam M. Characterization of the firing behaviour of an illite-kaolinite clay mineral and its potential use as membrane support. *Heliyon* 2019;5:e02281. doi:10.1016/j.heliyon.2019.e02281.
- [231] Qian G, Li Y, Gerson AR. Applications of surface analytical techniques in Earth Sciences. *Surf Sci Rep* 2015. doi:10.1016/j.surfrep.2015.02.001.
- [232] Lei Q, Zhang L, Tang H, Zhao Y, Chen M, Xie C. Describing the Full Pore Size Distribution of Tight Sandstone and Analyzing the Impact of Clay Type on Pore Size Distribution. *Geofluids* 2020;2020. doi:10.1155/2020/5208129.
- [233] Kamal MS, Mahmoud M, Hanfi M, Elkatatny S, Hussein I. Clay minerals damage quantification in sandstone rocks using core flooding and NMR. *J Pet Explor Prod Technol* 2019;9:593–603. doi:10.1007/s13202-018-0507-7.
- [234] Vandenbroucke M, Largeau C. Kerogen origin, evolution and structure. *Org Geochem* 2007;38:719–833. doi:10.1016/j.orggeochem.2007.01.001.
- [235] Okiongbo KS, Aplin AC, Larter SR. Changes in type II Kerogen density as a function of maturity: Evidence from the Kimmeridge clay formation. *Energy and Fuels* 2005;19:2495–9. doi:10.1021/ef050194+.
- [236] Amao AO, Al-Ramadan K, Koeshidayatullah A. Automated mineralogical methodology to study carbonate grain microstructure: an example from oncoids. *Environ Earth Sci* 2016;75:1–11. doi:10.1007/s12665-016-5492-x.

- [237] Afagwu C, Mahmoud MA, Alafnan S, Patil S. Multiscale storage and transport modeling in unconventional shale gas: A review. *J Pet Sci Eng* 2021;109518. doi:10.1016/j.petrol.2021.109518.
- [238] Ross DJK, Marc Bustin R. The importance of shale composition and pore structure upon gas storage potential of shale gas reservoirs. *Mar Pet Geol* 2009;26:916–27. doi:10.1016/j.marpetgeo.2008.06.004.
- [239] Brunauer S, Emmett PH, Teller E. Adsorption of Gases in Multimolecular Layers. *J Am Chem Soc* 1938;60:309–19. doi:10.1021/ja01269a023.
- [240] Sing K. The use of nitrogen adsorption for the characterisation of porous materials. *Colloids Surfaces A Physicochem Eng Asp* 2001;187–188:3–9. doi:10.1016/S0927-7757(01)00612-4.
- [241] Mohammed I, Afagwu CC, Adjei S, Kadafur IB, Jamal MS, Awotunde AA. A review on polymer, gas, surfactant and nanoparticle adsorption modeling in porous media. *Oil Gas Sci Technol* 2020;75. doi:10.2516/ogst/2020063.
- [242] Tian H, Pan L, Zhang T, Xiao X, Meng Z, Huang B. Pore characterization of organic-rich Lower Cambrian shales in Qiannan Depression of Guizhou Province, Southwestern China. *Mar Pet Geol* 2015;62:28–43. doi:10.1016/j.marpetgeo.2015.01.004.
- [243] Rouquerol J, Llewellyn P, Rouquerol F. Is the BET equation applicable to microporous adsorbents? *Stud Surf Sci Catal* 2007. doi:10.1016/s0167-2991(07)80008-5.
- [244] de Boer JH, Lippens BC, Linsen BG, Broekhoff JCP, van den Heuvel A, Osinga TJ. Thet-curve of multimolecular N₂-adsorption. *J Colloid Interface Sci* 1966;21:405–14. doi:10.1016/0095-8522(66)90006-7.
- [245] Coasne B, Gubbins KE, Pellenq RJM. A Grand Canonical Monte Carlo study of adsorption and capillary phenomena in nanopores of various morphologies and topologies: Testing the BET and BJH characterization methods. *Part Part Syst Charact* 2004;21:149–60. doi:10.1002/ppsc.200400928.
- [246] Sing KSW. REPORTING PHYSISORPTION DATA FOR GAS/SOLID SYSTEMS., 1984. doi:10.1002/9783527610044.hetcat0065.
- [247] Barsotti E, Tan SP, Piri M, Chen JH. Capillary-condensation hysteresis in naturally-occurring nanoporous media. *Fuel* 2020;263. doi:10.1016/j.fuel.2019.116441.
- [248] Groen JC, Peffer LAA, Pérez-Ramírez J. Pore size determination in modified micro- and mesoporous materials. Pitfalls and limitations in gas adsorption data analysis. *Microporous Mesoporous Mater* 2003;60:1–17. doi:10.1016/S1387-1811(03)00339-1.
- [249] Barrett EP, Joyner LG, Halenda PP. The Determination of Pore Volume and Area

Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. J Am Chem Soc 1951. doi:10.1021/ja01145a126.

- [250] Li T, Tian H, Chen J, Cheng L. Application of low pressure gas adsorption to the characterization of pore size distribution of shales: An example from Southeastern Chongqing area, China. J Nat Gas Geosci 2016;1:221–30. doi:10.1016/j.jnggs.2016.07.001.
- [251] 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. doi:10.1016/j.coal.2016.01.013.
- [252] Tournassat C, Bourg IC, Steefel CI, Bergaya F. Surface Properties of Clay Minerals. Dev. Clay Sci., 2015. doi:10.1016/B978-0-08-100027-4.00001-2.
- [253] Muhammed NS, Olayiwola T, Elkatatny S, Haq B, Patil S. Journal of Natural Gas Science and Engineering Insights into the application of surfactants and nanomaterials as shale inhibitors for water-based drilling fluid : A review. J Nat Gas Sci Eng 2021;92:103987. doi:10.1016/j.jngse.2021.103987.
- [254] Fatimah I, Narsito, Wijaya K. Effect of aluminium content in aluminium pillared montmorillonite on its surface acidity properties. ITB J Sci 2011;43 A:123–38. doi:10.5614/itbj.sci.2011.43.2.5.
- [255] Yang H, He K, Lu D, Wang J, Xu D, Jin Z, et al. Removal of phosphate by aluminum-modified clay in a heavily polluted lake, Southwest China: Effectiveness and ecological risks. Sci Total Environ 2020;705:135850. doi:10.1016/j.scitotenv.2019.135850.
- [256] Wang J, Chen J, Chen Q, Yang H, Zeng Y, Yu P, et al. Assessment on the effects of aluminum-modified clay in inactivating internal phosphorus in deep eutrophic reservoirs. Chemosphere 2019;215:657–67. doi:10.1016/j.chemosphere.2018.10.095.
- [257] Roshan H, Lv A, Aghighi MA, Sarmadivaleh M, Siddiqui MAQ, van As D, et al. Stabilization of clay-rich interburdens using silica nanoparticles. J Pet Sci Eng 2022;211:110126. doi:10.1016/j.petrol.2022.110126.
- [258] Sadek OM, Reda SM, Al-Bilali RK. Preparation and Characterization of Silica and Clay-Silica Core-Shell Nanoparticles Using Sol-Gel Method. Adv Nanoparticles 2013. doi:10.4236/anp.2013.22025.
- [259] Alperovitch N, Shainberg I, Keren R, Singer MJ. Effect of clay mineralogy and aluminium and iron oxides on the hydraulic conductivity of clay-sand mixtures. Clays Clay Miner 1985. doi:10.1346/ccmn.1985.0330511.
- [260] Muhammed NS, Olayiwola T, Elkatatny S. A review on clay chemistry, characterization and shale inhibitors for water-based drilling fluids. J Pet Sci Eng

2021. doi:10.1016/j.petrol.2021.109043.

- [261] Zhang P, Hu L, Meegoda JN, Gao S. Micro/Nano-pore Network Analysis of Gas Flow in Shale Matrix. *Sci Rep* 2015;5:1–11. doi:10.1038/srep13501.
- [262] Yang K, Li M, Ling NNA, May EF, Connolly PRJ, Esteban L, et al. Quantitative Tortuosity Measurements of Carbonate Rocks Using Pulsed Field Gradient NMR. *Transp Porous Media* 2019;130:847–65. doi:10.1007/s11242-019-01341-8.
- [263] Fu J, Thomas HR, Li C. Tortuosity of porous media: Image analysis and physical simulation. *Earth-Science Rev* 2021;212:103439. doi:10.1016/j.earscirev.2020.103439.
- [264] Wang H, Qu Z, Yin Y, Bai J, Yu B. Erratum to: Review of Molecular Simulation Method for Gas Adsorption/desorption and Diffusion in Shale Matrix (*Journal of Thermal Science*, (2018), 10.1007/s11630-018-1053-9). *J Therm Sci* 2018;27. doi:10.1007/s11630-018-1068-2.
- [265] Plimpton S. Plimpton1995.Pdf. *J Comput Phys* 1995. doi:10.1006/jcph.1995.1039.
- [266] Hoover WG. Canonical dynamics: Equilibrium phase-space distributions. *Phys Rev A* 1985;31:1695–7. doi:10.1103/PhysRevA.31.1695.
- [267] Zhang H, Zeng X, Zhao Z, Zhai Z, Cao D. Adsorption and selectivity of CH₄/CO₂ in functional group rich organic shales. *J Nat Gas Sci Eng* 2017;39:82–9. doi:10.1016/j.jngse.2017.01.024.
- [268] Bhattacharya S, Gubbins KE. Fast method for computing pore size distributions of model materials. *Langmuir* 2006;22:7726–31. doi:10.1021/la052651k.
- [269] Barber CB, Dobkin DP, Huhdanpaa H. The Quickhull Algorithm for Convex Hulls. *ACM Trans Math Softw* 1996;22:469–83. doi:10.1145/235815.235821.
- [270] Edition S. Adsorption and Diffusion in Nanoporous Materials, Second Edition. 2018. doi:10.1201/b22379.
- [271] Universit JC. Molecular Simulation of Shales Organic Matter . par Julien Collell Molecular Simulation of Shales Organic Matter . 2015.
- [272] Sun H, Mumby SJ, Maple JR, Hagler AT. An ab Initio CFF93 All-Atom Force Field for Polycarbonates. *J Am Chem Soc* 1994;116:2978–87. doi:10.1021/ja00086a030.
- [273] Waldman M, Hagler AT. New combining rules for rare gas van der waals parameters. *J Comput Chem* 1993;14:1077–84. doi:10.1002/jcc.540140909.
- [274] Chen G, Lu S, Zhang J, Xue Q, Han T, Xue H, et al. Research of CO₂ and N₂ Adsorption Behavior in K-Illite Slit Pores by GCMC Method. *Sci Rep* 2016;6:1–10. doi:10.1038/srep37579.
- [275] Gasparik M, Bertier P, Gensterblum Y, Ghanizadeh A, Krooss BM, Littke R.

Geological controls on the methane storage capacity in organic-rich shales. *Int J Coal Geol* 2014;123:34–51. doi:10.1016/j.coal.2013.06.010.

- [276] Ju Y, He J, Chang E, Zheng L. Quantification of CH₄ adsorption capacity in kerogen-rich reservoir shales: An experimental investigation and molecular dynamic simulation. *Energy* 2019;170:411–22. doi:10.1016/j.energy.2018.12.087.
- [277] Langmuir I. THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM. *J Am Chem Soc* 1918;40:1361–403. doi:10.1021/ja02242a004.
- [278] Freundlich HMF. Adsorption in solution. *Z Phys Chem* 1906.
- [279] Gibbs JW. The collected works of J. W. Gibbs. 1961.
- [280] Tesson S, Firoozabadi A. Methane Adsorption and Self-Diffusion in Shale Kerogen and Slit Nanopores by Molecular Simulations. *J Phys Chem C* 2018;122:23528–42. doi:10.1021/acs.jpcc.8b07123.
- [281] Kulasinski K, Guyer R, Derome D, Carmeliet J. Water Diffusion in Amorphous Hydrophilic Systems: A Stop and Go Process. *Langmuir* 2015;31:10843–9. doi:10.1021/acs.langmuir.5b03122.
- [282] Gangi AF. Variation of whole and fractured porous rock permeability with confining pressure. *Int J Rock Mech Min Sci* 1978;15:249–57. doi:10.1016/0148-9062(78)90957-9.
- [283] Alafnan SFK, Akkutlu IY. Matrix–Fracture Interactions During Flow in Organic Nanoporous Materials Under Loading. *Transp Porous Media* 2018;121:69–92. doi:10.1007/s11242-017-0948-3.
- [284] Afagwu C, Mahmoud MA, Alafnan S, Patil S. Multiscale storage and transport modeling in unconventional shale gas: A review. *J Pet Sci Eng* 2022;208:109518. doi:10.1016/j.petrol.2021.109518.
- [285] Sun Z, Li X, Liu W, Zhang T, He M, Nasrabadi H. Molecular dynamics of methane flow behavior through realistic organic nanopores under geologic shale condition: Pore size and kerogen types. *Chem Eng J* 2020;398:124341. doi:10.1016/j.cej.2020.124341.
- [286] Afagwu C, Al-Afnan S, Patil S, Aljaberi J, Mahmoud MA, Li J. The impact of pore structure and adsorption behavior on kerogen tortuosity. *Fuel* 2021;303:121261. doi:10.1016/j.fuel.2021.121261.
- [287] Civan F. Effective correlation of apparent gas permeability in tight porous media. *Transp Porous Media* 2010;82:375–84. doi:10.1007/s11242-009-9432-z.
- [288] Wua K, Li X, Guo C, Chen Z. Adsorbed gas surface diffusion and bulk gas transport in nanopores of shale reservoirs with real gas effect-adsorption-mechanical coupling. *Soc Pet Eng - SPE Reserv Simul Symp* 2015 2015;1:210–40.

doi:10.2118/173201-ms.

- [289] Zheng J, Zheng L, Liu HH, Ju Y. Relationships between permeability, porosity and effective stress for low-permeability sedimentary rock. *Int J Rock Mech Min Sci* 2015;78:304–18. doi:10.1016/j.ijrmms.2015.04.025.
- [290] Song W, Yao J, Li Y, Sun H, Zhang L, Yang Y, et al. Apparent gas permeability in an organic-rich shale reservoir. *Fuel* 2016;181:973–84. doi:10.1016/j.fuel.2016.05.011.
- [291] Clarkson CR, Jensen JL, Blasingame TA. Reservoir engineering for unconventional gas reservoirs: What do we have to consider? *Soc. Pet. Eng. - SPE Am. Unconv. Gas Conf.* 2011, UGC 2011, 2011.
- [292] Wei M, Liu J, Elsworth D, Wang E. Triple-porosity modelling for the simulation of multiscale flow mechanisms in shale reservoirs. *Geofluids* 2018;2018. doi:10.1155/2018/6948726.
- [293] Aslanov E, Alafnan SF, Mahmoud M, Abdulraheem A, Aljawad MS. Study of the Mechanical Behavior of Organic Matters Contained in Source Rocks: New Insights into the Role of Bitumen. *ACS Omega* 2022;7:7024–31. doi:10.1021/acsomega.1c06717.
- [294] Curtis ME. Influence of thermal maturity on organic shale microstructure. *Oklahoma Shale Gas Oil Work Oklahoma Geol Surv* 2013.
- [295] Luo P, Zhong N. The role of residual bitumen on the pore structure of organic-rich shales from low to over mature: Insight from shale and coal samples after the hydrous pyrolysis. *Int J Coal Geol* 2020. doi:10.1016/j.coal.2020.103515.
- [296] Han Y, Horsfield B, Wirth R, Mahlstedt N, Bernard S. Oil retention and porosity evolution in organic-rich shales. *Am Assoc Pet Geol Bull* 2017. doi:10.1306/09221616069.
- [297] Bernard S, Horsfield B. Thermal maturation of gas shale systems. *Annu Rev Earth Planet Sci* 2014. doi:10.1146/annurev-earth-060313-054850.
- [298] Hackley PC, Cardott BJ. Application of organic petrography in North American shale petroleum systems: A review. *Int J Coal Geol* 2016. doi:10.1016/j.coal.2016.06.010.
- [299] Alafnan S. The self-diffusivity of natural gas in the organic nanopores of source rocks The self-diffusivity of natural gas in the organic nanopores of source rocks 2022;042004. doi:10.1063/5.0081258.
- [300] Le Page Y, Saxe P. Symmetry-general least-squares extraction of elastic coefficients from ab initio total energy calculations. *Phys Rev B - Condens Matter Mater Phys* 2001;63:1–8. doi:10.1103/PhysRevB.63.174103.
- [301] Mayer B, Anton H, Bott E, Methfessel M, Sticht J, Harris J, et al. Ab-initio

- calculation of the elastic constants and thermal expansion coefficients of Laves phases. *Intermetallics* 2003;11:23–32. doi:10.1016/S0966-9795(02)00127-9.
- [302] Birch F. Velocity of Compressional Waves in Rocks To 10 Kilobars, .2. *J Geophys Res* 1961;66:2199–224.
- [303] Anderson OL. a Simplified Method for Calculating the. *J Phys Chem Solids* 1963;24:909–17.
- [304] Armatas GS. Determination of the effects of the pore size distribution and pore connectivity distribution on the pore tortuosity and diffusive transport in model porous networks 2006;61:4662–75. doi:10.1016/j.ces.2006.02.036.
- [305] Franquet JA, Abass HH. Experimental evaluation of Biot’s poroelastic parameter - Three different methods. *Vail Rocks 1999 - 37th U.S. Symp. Rock Mech.*, 1999.
- [306] Salemi H, Yurikov A, Lebedev M, Behnoudfar P, Rezagholilou A, Iglauer S, et al. A novel approach to determine the Biot’s coefficient using X-ray computed tomography. *Bull Eng Geol Environ* 2021;80:7865–77. doi:10.1007/s10064-021-02405-0.
- [307] Wu T, Firoozabadi A. Mechanical Properties and Failure Envelope of Kerogen Matrix by Molecular Dynamics Simulations. *J Phys Chem C* 2020;124:2289–94. doi:10.1021/acs.jpcc.9b09639.
- [308] Omovie SJ, Castagna JP. Relationships between dynamic elastic moduli in shale reservoirs. *Energies* 2020;13:1–22. doi:10.3390/en13226001.
- [309] Javadpour F. Nanopores and apparent permeability of gas flow in mudrocks (shales and siltstone). *J Can Pet Technol* 2009;48:16–21. doi:10.2118/09-08-16-DA.
- [310] Ziarani AS, Aguilera R. Knudsen’s Permeability Correction for Tight Porous Media. *Trans Porous Media* 2012;91:239–60. doi:10.1007/s11242-011-9842-6.
- [311] Darabi H, Ettihad A, Javadpour F, Sepehrnoori K. Gas flow in ultra-tight shale strata. *J Fluid Mech* 2012;710:641–58. doi:10.1017/jfm.2012.424.
- [312] Singh H, Javadpour F. A New Non-Empirical Approach to Model Transport of Fluids in Shale Gas Reservoirs 2013:1258–73. doi:10.1190/urtec2013-127.
- [313] Guo C, Xu J, Wu K, Wei M, Liu S. Study on gas flow through nano pores of shale gas reservoirs. *Fuel* 2015;143:107–17. doi:10.1016/J.FUEL.2014.11.032.
- [314] CUI X, BUSTIN AMM, BUSTIN RM. Measurements of gas permeability and diffusivity of tight reservoir rocks: different approaches and their applications. *Geofluids* 2009;9:208–23. doi:10.1111/j.1468-8123.2009.00244.x.
- [315] I.J.F. A. Lerman 1979. *Geochemical Processes. Water and Sediment Environments*. viii+481 pp., numerous figs. New York: Wiley. Price £21.00. ISBN

0 471 03263 8. Geol Mag 1980. doi:10.1017/s0016756800030545.

- [316] Ullman WJ, Aller RC. Diffusion coefficients in nearshore marine sediments. *Limnol Oceanogr* 1982. doi:10.4319/lo.1982.27.3.0552.
- [317] Boudreau BP. The diffusive tortuosity of fine-grained unlithified sediments. *Geochim Cosmochim Acta* 1996;60:3139–42. doi:10.1016/0016-7037(96)00158-5.
- [318] Rayleigh, Lord. LVI. On the influence of obstacles arranged in rectangular order upon the properties of a medium . London, Edinburgh, Dublin Philos Mag J Sci 1892. doi:10.1080/14786449208620364.
- [319] Millington RJ. Gas diffusion in porous media. *Science* (80-) 1959. doi:10.1126/science.130.3367.100-a.
- [320] Yue WZ, Tao G. A new non-archie model for pore structure: Numerical experiments using digital rock models. *Geophys J Int* 2013;195:282–91. doi:10.1093/gji/ggt231.
- [321] Iversen N, Jørgensen BB. Diffusion coefficients of sulfate and methane in marine sediments: Influence of porosity. *Geochim Cosmochim Acta* 1993;57:571–8. doi:10.1016/0016-7037(93)90368-7.
- [322] Sweerts JRA, Kelly CA, Rudd JWM, Hesslein R, Cappenberg TE. Similarity of whole-sediment molecular diffusion coefficients in freshwater sediments of low and high porosity. *Limnol Oceanogr* 1991. doi:10.4319/lo.1991.36.2.0335.
- [323] Van Cappellen P, Gaillard JF. Biogeochemical dynamics in aquatic sediments. *Rev Mineral* 1996.
- [324] Dowdy RH, Low PF. Principles of Ion Diffusion in Clays, 1981. doi:10.2134/aspectpub40.c3.
- [325] Koponen A, Kataja M, Timonen J, Kandhai D. Simulations of single-fluid flow in porous media. *Int J Mod Phys C* 1998;9:1505–21. doi:10.1142/S0129183198001369.
- [326] Neale GH, Nader WK. Prediction of transport processes within porous media: Diffusive flow processes within an homogeneous swarm of spherical particles. *AIChE J* 1973. doi:10.1002/aic.690190116.
- [327] Petersen EE. Diffusion in a pore of varying cross section. *AIChE J* 1958;4:343–5. doi:10.1002/aic.690040322.
- [328] Bruggeman DAG. Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen. *Ann Phys* 1935. doi:10.1002/andp.19354160705.

- [329] van Brakel J, Heertjes PM. Analysis of diffusion in macroporous media in terms of a porosity, a tortuosity and a constrictivity factor. *Int J Heat Mass Transf* 1974;17:1093–103. doi:10.1016/0017-9310(74)90190-2.
- [330] Akanni KA, Evans JW, Abramson IS. Effective transport coefficients in heterogeneous media. *Chem Eng Sci* 1987. doi:10.1016/0009-2509(87)80141-0.
- [331] Ho F gau, Striender W. A variational calculation of the effective surface diffusion coefficient and tortuosity. *Chem Eng Sci* 1981. doi:10.1016/0009-2509(81)85003-8.
- [332] Tomadakis MM, Sotirchos S V. Transport properties of random arrays of freely overlapping cylinders with various orientation distributions. *J Chem Phys* 1993. doi:10.1063/1.464604.
- [333] The diffusion of electrolytes in a cation-exchange resin membrane I. Theoretical. *Proc R Soc London Ser A Math Phys Sci* 1955. doi:10.1098/rspa.1955.0234.
- [334] Lucia FJ, Loucks RG. Micropores Development in Carbonate Mud: Early Development and Petrophysics. *Gulf Coast Assoc Geol Soc J* 2013.
- [335] Li P, Jiang Z, Zheng M, Bi H, Chen L. Journal of Natural Gas Science and Engineering Estimation of shale gas adsorption capacity of the Longmaxi Formation in the Upper Yangtze Platform , China 2016;34:1034–43. doi:10.1016/j.jngse.2016.07.052.
- [336] Beskok A, Em Karniadakis G, Trimmer W. Rarefaction and compressibility effects in gas microflows. *J Fluids Eng Trans ASME* 1996;118:448–56. doi:10.1115/1.2817779.
- [337] Tomadakis MM, Sotirchos S V. Ordinary, transition, and Knudsen regime diffusion in random capillary structures. *Chem Eng Sci* 1993;48:3323–33. doi:10.1016/0009-2509(93)80149-K.
- [338] R. Byron Bird Warren E. Stewart Edwin N. Lightfoot, Bird RB, Stewart WE, Lightfoot EN. *Transport Phenomena*, Revised 2nd Edition. John Wiley Sons, Inc 2006.
- [339] Brown GP, Dinardo A, Cheng GK, Sherwood TK. The flow of gases in pipes at low pressures. *J Appl Phys* 1946. doi:10.1063/1.1707647.
- [340] Wu K, Chen Z, Li X, Guo C, Wei M. A model for multiple transport mechanisms through nanopores of shale gas reservoirs with real gas effect-adsorption-mechanic coupling. *Int J Heat Mass Transf* 2016;93:408–26. doi:10.1016/j.ijheatmasstransfer.2015.10.003.
- [341] Chen YD, Yang RT. Concentration dependence of surface diffusion and zeolitic diffusion. *AIChE J* 1991;37:1579–82. doi:10.1002/aic.690371015.
- [342] Geng L, Li G, Zitha P, Tian S, Sheng M. A fractal permeability model for shale

- gas flow through heterogeneous matrix systems. *J Nat Gas Sci Eng* 2016;35:593–604. doi:10.1016/j.jngse.2016.08.033.
- [343] O’Carroll C, Sorbie KS. Generalization of the Poiseuille law for one- and two-phase flow in a random capillary network. *Phys Rev E* 1993. doi:10.1103/PhysRevE.47.3467.
- [344] Guo C, Xu J, Wu K, Wei M, Liu S. Study on gas flow through nano pores of shale gas reservoirs. *Fuel* 2015;143:107–17. doi:10.1016/j.fuel.2014.11.032.
- [345] Dong JJ, Hsu JY, Wu WJ, Shimamoto T, Hung JH, Yeh EC, et al. Stress-dependence of the permeability and porosity of sandstone and shale from TCDP Hole-A. *Int J Rock Mech Min Sci* 2010;47:1141–57. doi:10.1016/j.ijrmms.2010.06.019.
- [346] Alafnan S, Solling T, Mahmoud M. Effect of kerogen thermal maturity on methane adsorption capacity: A molecular modeling approach. *Molecules* 2020;25. doi:10.3390/molecules25163764.
- [347] Afagwu CC, Al-afnan SF, Mahmoud M, Fahd K. SPE-205922-MS The Impact of Kerogen Structure on Shale Permeability : Coupled Molecular Diffusion and Geomechanical Behavior Study 2021.
- [348] Riewchotisakul S, Akkutlu IY. Adsorption enhanced transport of hydrocarbons in organic nanopores. *Proc - SPE Annu Tech Conf Exhib* 2015;2015–Janua:5559–78. doi:10.2118/175107-ms.
- [349] Heller R, Vermylen J, Zoback M. Experimental investigation of matrix permeability of gas shales. *Am Assoc Pet Geol Bull* 2014;98:975–95. doi:10.1306/09231313023.
- [350] Afagwu C, Alafnan S, Mahmoud M, Akkutlu IY. Journal of Natural Gas Science and Engineering Modeling of natural gas self-diffusion in the micro-pores of organic-rich shales coupling sorption and geomechanical effects. *J Nat Gas Sci Eng* 2022;106:104757. doi:10.1016/j.jngse.2022.104757.
- [351] Weijermars R. Diffusive Mass Transfer and Gaussian Pressure Transient Solutions for Porous Media. *Fluids* 2021;6:379. doi:10.3390/fluids6110379.
- [352] Mahmoud MA. Development of a new correlation of gas compressibility factor (Z-factor) for high pressure gas reservoirs. *Soc. Pet. Eng. - North Africa Tech. Conf. Exhib. 2013, NATC 2013, 2013*. doi:10.1115/1.4025019.
- [353] Lee AL, Gonzalez MH, Eakin BE. Viscosity of Methane-n-Decane Mixtures. *J Chem Eng Data* 1966. doi:10.1021/je60030a001.
- [354] Javadpour F, Fisher D, Unsworth M. Nanoscale gas flow in shale gas sediments. *J Can Pet Technol* 2007;46:55–61. doi:10.2118/07-10-06.
- [355] Afagwu C, Alafnan S, Mahmoud MA, Patil S. Permeability model for shale and

ultra-tight gas formations : Critical insights into the impact of dynamic adsorption. *Energy Reports* 2021;7:3302–16. doi:10.1016/j.egyr.2021.05.060.

- [356] Cussler E. *Diffusion: Mass transfer in fluid systems*: Cambridge Univ Pr. View Artic PubMed/NCBI Google Sch 1997.
- [357] Horne RN. *Modeling Pressure-Transient Behavior* 1993:145–52.
- [358] Zimmerman RW. *Pressure Diffusion Equation for Fluid Flow in Porous Rocks*. Imp. Coll. Lect. Pet. Eng., 2018. doi:10.1142/9781786345004_0001.
- [359] Horne R. *Modern Well Test Analysis: A Computer-Aided Approach*. Inc Palo Alto Calif 1995.
- [360] Weijermars R, Afagwu C. Hydraulic diffusivity estimations for US shale gas reservoirs with Gaussian method: Implications for pore-scale diffusion processes in underground repositories. *J Nat Gas Sci Eng* 2022:104682. doi:10.1016/j.jngse.2022.104682.
- [361] Bear J. *Dynamics of Fluids in Porous Media* (Dover Civil and Mechanical Engineering). Publ 1972 Repr 1988 New York NY) by Dover 1972.
- [362] Javadpour F, Singh H, Rabbani A, Babaei M, Enayati S. Gas flow models of shale: A review. *Energy and Fuels* 2021;35:2999–3010. doi:10.1021/acs.energyfuels.0c04381.
- [363] Alafnan S. *The Impact of Pore Structure on Kerogen Geomechanics* 2021;2021.
- [364] Site- FT, Basin M, Texas W. *Gaussian Decline Curve Analysis of Hydraulically Fractured Wells in Shale Plays : Examples from HFTS-1 (Hydraulic* 2022;1.
- [365] Weijermars R, Wang J. Stress reversals near hydraulically fractured wells explained with linear superposition method (LSM). *Energies* 2021. doi:10.3390/en14113256.
- [366] Weijermars R, Wang J, Nelson R. Stress concentrations and failure modes in horizontal wells accounting for elastic anisotropy of shale formations. *Earth-Science Rev* 2020;200:102957. doi:10.1016/j.earscirev.2019.102957.

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C Afagwu, S Alafnan, M Mahmoud, W. Akkutlu (2022). Modeling of natural gas self-
diffusion in the micro-pores of organic-rich shales coupling sorption and
geomechanical effects. Journal of Natural Gas Science and Engineering, 104757

R Weijermars, **C Afagwu** (2022). Hydraulic diffusivity estimations for US shale gas reservoirs with Gaussian method: Implications for pore-scale diffusion processes in underground repositories. *Journal of Natural Gas Science and Engineering*, 104682

C Afagwu, M Mahmoud, S Alafnan, A Alqubalee, A ElHusseiny, S Patil (2022). Pore Volume Characteristics of Clay-Rich Shale: Critical Insight into the Role of Clay Types, Aluminum and Silicon Concentration. *Arabian Journal for Science and Engineering*, 1-17.

C Afagwu, MA Mahmoud, S Alafnan, S Patil (2022). Multiscale storage and transport modeling in unconventional shale gas: A review. *Journal of Petroleum Science and Engineering* 208, 109518.

S Kalam, **C Afagwu**, J Al Jaberi, OM Siddig, Z Tariq, M Mahmoud, ... (2021). A review on non-aqueous fracturing techniques in unconventional reservoirs. *Journal of Natural Gas Science and Engineering* 95, 104223.

C Afagwu, S Al-Afnan, S Patil, J Aljaberi, MA Mahmoud, J Li (2021). The impact of pore structure and adsorption behavior on kerogen tortuosity. *Fuel* 303, 121261.

C Afagwu, S Alafnan, MA Mahmoud, S Patil (2021). Permeability model for shale and ultra-tight gas formations: Critical insights into the impact of dynamic adsorption. *Energy Reports* 7, 3302-3316.

J Aljaberi, S Alafnan, G Glatz, AS Sultan, **C Afagwu** (2021). The impact of kerogen tortuosity on shale permeability. *SPE Journal* 26 (02), 765-779.

C Afagwu, I Abubakar, S Kalam, SF Al-Afnan, AA Awotunde (2020). Pressure-transient analysis in shale gas reservoirs: A review. *Journal of Natural Gas Science and Engineering* 78, 103319.

I Mohammed, **CC Afagwu**, S Adjei, IB Kadafur, MS Jamal, AA Awotunde (2020). A review on polymer, gas, surfactant and nanoparticle adsorption modeling in porous media. *Oil & Gas Science and Technology–Revue d'IFP Energies Nouvelles* 75, 77. |