A pore structure based real gas transport model to determine gas permeability in nanoporous shale

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ABSTRACT: Gas flows in the forms of multiple transport mechanisms in shale nanoporous media with complex pore structure and different pore types. Laboratory pressure pulse decay technique is often applied to measure gas permeability but the current gas permeability interpretation model is mostly based on the homogeneous macro scale model while the influence of pore structure on real gas transport is neglected. In this study, a novel pore structure based real gas transport model is proposed to determine gas permeability in nanoporous shale combining laboratory pressure pulse decay technique with pore network simulation. The laboratory pressure pulse decay process is simulated in a virtual system based on the similarity principle which contains upstream vessel, downstream vessel, and core sample. The core sample is constructed by a series of connected pore networks and the sizes of pores and throats in each location of the pore network are randomly assigned according to laboratory measured pore size distribution. Gas transport mechanisms inside the core sample consider viscous flow, Knudsen diffusion, surface diffusion and real gas effect. At each time step, the upstream vessel pressure decreases and the downstream vessel pressure increases until the upstream vessel pressure and downstream vessel pressure become equal. The simulated pressure drop versus time curve is obtained and is applied to fit the laboratory measured pressure drop data by repeating core sample construction and pressure pulse decay process. The proposed model is applied to measure gas permeability of Sichuan basin, Longmaxi formation shale core sample. The results indicate that the predicted value based on the proposed model matches well with the
experimental measured pressure drop data. The proposed model is used to study the influences of test gas type and pore size on gas permeability. When the average organic pore radius is less than 20nm, helium tested permeability overestimates at least 40% of the methane permeability.

Keywords: gas permeability; pressure pulse decay; pore network model; pore structure; test gas

1. Introduction

Shale is the typical porous media with large amounts of nanopores [1]. The heterogeneities of shale nanoporous media are expressed in terms of complex pore structure and different pore types. Because shale pore size approaches to the molecular mean free path, the gas flow deviates from viscous flow [2] and the flow regime is conventionally subdivided according to the Knudsen number, the ratio of molecular mean free path to the pore radius. Loucks et al. [3] categorised pore types in shale into three types: interparticle mineral pores, intraparticle mineral pores and intraparticle organic-matter pores. Intraparticle organic-matter pores are referred to as organic pores and the other two types of pores are referred to as inorganic pores in our study. Organic pores represent the pores inside the organic matter (kerogen) and are also named as kerogen pores. An organic-rich pore has a large specific surface area and the organic matter can adsorb a significant amount of gas molecules [4]. Surface diffusion takes place within the adsorbed gas to enhance the transport of gas molecules along molecular concentration gradients [5]. In order to assess gas flow ability in nanopores, Civan [6] developed apparent gas permeability models based on the Knudsen number. Song et al. [7] considered the influence of different pore types on apparent gas permeability. Javadpour et al. [2,8,9] and Singh [10,11] developed apparent gas permeability models based on superposition of Knudsen diffusion and slip flow. While gas transport mechanisms are considered in apparent gas permeability model, conventional apparent gas permeability model is based on homogeneity assumption and neglects the influences of organic matter spatial distribution, pore size distribution on gas flow ability. The heterogeneity of shale pore structure is neglected and therefore predicted permeability of shale sample is not reliable. Kou et al. [12] proposed a convective–
diffusive transport model including the capillary wall effects and studied steady-state transport in the network of nanocapillaries using a multi-scale theoretical approach. F. K. Alafnan and Akkutlu [13] extended the pore network modeling approach to describe the interaction between organic materials and single crack from which a coupling flow exchange term that can be used in continuum modeling of shale matrix dynamics is developed. Recent advances in high-resolution imaging technology and so-called digital core analysis approach have made it possible to characterise pores and solids in porous material [14]. Using such pore-structure models, numerical simulations can be carried out to predict transport and mechanical properties [15].

Currently two approaches are applied to measure permeability of porous media namely indirect and direct method. The indirect method involves steady state permeability and unsteady state permeability measurements. Permeability obtained from the direct approach is based on the homogeneous correlation method like the Carman–Kozeny or Hagen–Poiseuille equations. For shale with strong heterogeneities and nanoscale pore size, permeability is dependent on gas transport mechanisms, pore size spatial distribution and reservoir properties (pore pressure, temperature) and therefore the direct method is not applicable. The traditional steady state flow permeability measurement is extremely time consuming for shale core samples and is not practical because of the instrumentation requirements for measuring extremely small pressure drops or flow rates. The unsteady state method namely pressure pulse decay method measures the decay of upstream pressure and the increase in downstream pressure and has been used extensively to estimate permeability of shale samples [16]. The slope of pressure gradient change versus time is used to estimate the permeability [17] and the measured permeabilities order can reach as low as $10^{-12}$ D [18–20]. CUI et al. [18] improved the pressure pulse decay technique to consider the influence of adsorption on effective permeability by correcting effective porosity in homogeneous macro scale model. Akkutlu et al. [21] developed dual porosity model to incorporate the influences of organic and inorganic pores and randomized maximum likelihood method was applied to analyze pressure drop data. However, the above mentioned pulse decay data interpretation models are homogeneous model based on the porosity and the influences
of pore size spatial distribution and different pore types on gas flow are neglected [22]. Furthermore, the gas permeability is not pressure dependent during derivation of the analytical solutions of the gas permeability. Attempts have been made to put more and more shale pore structure characteristic information into the pressure pulse decay data interpretation. Naraghi et al. [23] constructed ensemble-based stochastic model conditioned to total organic content (TOC) and the characteristics of pore-size distributions in organic and inorganic matrix.

The purpose of this study is to develop a pore structure based real gas transport model to determine shale gas permeability combining laboratory pressure pulse decay technique with pore network simulation. In Section 2, the laboratory pressure pulse decay process is simulated in a virtual system based on the similarity principle which contains upstream vessel, downstream vessel, and core sample. In Section 3, gas flow models for different gas types and solution method are introduced. In Section 4, the proposed approach is applied to measure gas permeability of Sichuan basin, Longmaxi formation shale core sample and is compared with available model from the literature. This is followed by a section of conclusion.

2. Physical model description

The shale core sample in Fig. 2(a) is gathered from Sichuan basin, Longmaxi shale formation. The porosity of the studied shale is 6.5% and the studied shale sample mainly contains pores and solids. Parameters used in pulse-decay experiment are shown in Table 1. The laboratory pressure pulse decay process is simulated in a virtual system in Fig. 3 based on the similarity principle which contains upstream vessel, downstream vessel, and core sample. A 3D pore-solid shale model in Fig. 4 (a) is generated stochastically using Multiple-Point Statistics (MPS) method [24] from a 2D binary SEM image in Fig. 2(b) acquired on a polished thin-section of the shale core sample. The resolution of the SEM image is 400 ×400 pixels and the pixel size of the SEM image taken is 20 nm×20 nm. From the generated 3D model, pore structure mid axis in Fig. 4 (b) is extracted from the pore space based on mid axis method, where each intersection of skeletons is designated as a centre for a spherical pore node and connected pore centres is replaced by a circular cylinder of infinitesimal radius. The
sizes of pores and throats in each location of the pore topology are randomly assigned according to laboratory measured pore size distribution in Fig. 5. The core sample is constructed by connecting a series of same pore networks obtained from above mentioned procedure and the physical length of the simulated core sample is the same as that of the laboratory core sample. It should be mentioned that the throat size is smaller than the size of two connect pores during randomly assigning process. The upstream volume $V_{up}$ and downstream volume $V_{down}$ are given in Eq.(1) and Eq.(2) based on the similarity principle according to the ratio of simulated core sample volume $V_{core_sim}$ to the laboratory core sample volume $V_{core_lab}$.

$$V_{up} = V_{up_{lab}} \frac{V_{core_sim}}{V_{core_lab}} \quad (1)$$

$$V_{down} = V_{down_{lab}} \frac{V_{core_sim}}{V_{core_lab}} \quad (2)$$

$$V_{core_{sim}} = l_x l_y L_{core} \quad (3)$$

Where $l_x, l_y$ are the length of simulated core sample and reconstructed shale digital core in $x$ direction and $y$ direction, respectively (m), $L_{core}$ is the length of laboratory core sample (m).

3. Numerical method

3.1 Gas flow models for different gas types

For nonadsorbing gas like helium, gas flows in the forms of viscous flow and Knudsen diffusion [25]. Gas flow regimes are identified by the Knudsen number, the ratio of the mean free path of gas molecules and the radius of a capillary. The mean free path for real gas can be expressed by Eq.(4) [26]. Real gas property for helium is obtained from the experimental data given in Seibt et al. work [27].

$$\lambda = \sqrt{\frac{\pi ZRT}{2M}} \frac{\mu}{p_o} \quad (4)$$

Where $Z$ is gas compressibility factor, dimensionless, $R$ is the ideal gas constant, 8.314 J/(K·mol), $T$ is temperature (K), $M$ is gas molecular weight (g/mol), $\mu$ is the gas viscosity (Pa·s), $p_o$ is the pore pressure (Pa).
The Knudsen number can be written as [28]:

\[ K_n = \frac{\lambda}{r} \]  (5)

Where \( r \) is the pore radius (m). Gas flow conductance for helium and methane in consideration of viscous flow and Knudsen diffusion can be written as [28,29]:

\[ g = \frac{\pi r^4 f(Kn)}{8 \mu l} \]  (6)

Where \( l \) is the capillary length (m) and the flow condition function \( f(Kn) \) is given by [30]:

\[ f(Kn) = (1 + \alpha K_n)(1 + \frac{4K_n}{1 - \beta K_n}) \]  (7)

The parameter \( \alpha \) in Eq.(7) is a dimensionless rarefaction coefficient, which can be written as [30]:

\[ \alpha = \frac{128}{15\pi^2} \tan^{-1}[4.0K_n^{0.4}] \]  (8)

Though the slip coefficient \( \beta = -1 \) initially can only be applied to a slip flow condition, evidence based on comparisons of the model with the Direct Simulation Monte Carlo and Boltzmann solutions [30] showed that \( \beta = -1 \) is valid within the full range of flow regimes.

For methane, gas flows in the forms of viscous flow and Knudsen diffusion in inorganic pores while surface diffusion also takes place in organic pores. Detailed derivations of methane flow conductance in organic pores is given in Appendix A. The resultant conductance for a cylinder-shaped organic pores are given in Eq.(9).

\[ g_{or} = \frac{\pi r_{eff, or}^4}{8 \mu l} f(Kn) + \frac{1}{l} \frac{M}{\rho} D_s C_{amax} \frac{d\theta}{dp} \pi (r^2 - r_{eff, or}^2) \]  (9)

Where \( r_{eff, or} \) is the effective capillary radius (m), \( \rho \) is the gas density (kg/m\(^3\)), \( D_s \) is the surface diffusion coefficient (m\(^2\)/s), \( C_{amax} \) is the maximum adsorbed gas concentration inside the nanoporous organic matter (mol/m\(^3\)).

According to Eq.(6), gas permeability for a single pore in consideration of viscous flow and Knudsen diffusion can be written as:

\[ k_{He, free} = \frac{r^2}{8} f(Kn) \]  (10)
According to Eq. (9), gas permeability for a single pore in consideration of free gas and adsorbed gas flow can be given as:

\[ k_{\text{free+adsorb}} = \frac{8 \mu_l d^2}{\pi r^2} f(Kn) + \frac{M}{\rho D_c \alpha_{\text{max}}} \frac{d\theta}{dp} \left( 1 - \left( \frac{r_{\text{eff,or}}}{r} \right)^2 \right) \]  

(11)

### 3.2 Simulation of pressure pulse decay process

At initial condition, the upstream pressure \( P_u \) is higher than the downstream pressure \( P_d \). Gas flows from the upstream vessel to the downstream vessel through the connected pore networks. The upstream pressure decreases and downstream pressure increases until the two pressures become equal. The number of connected pore networks is shown in Eq. (12). Because the connected pore networks are supposed to be the same, the pressure drop in each pore network is shown in Eq. (13). For the first pore network that is in contact with the upstream vessel, the inlet and outlet pressure are shown in Eq. (14) and Eq. (15), respectively.

\[ n_{\text{porenet}} = \frac{L_{\text{core}}}{l_z} \]  

(12)

\[ \Delta p = \frac{P_u^k - P_d^k}{n_{\text{porenet}}} \]  

(13)

\[ P_{\text{inlet}} = P_u^k \]  

(14)

\[ P_{\text{outlet}} = P_u^k - \Delta p \]  

(15)

Where \( l_z \) is the length of reconstructed shale digital core in \( z \) direction (m), \( P_u^k \) and \( P_d^k \) are the upstream pressure and downstream pressure at \( k \) time step, respectively (Pa).

Gas flow inside this pore network is calculated by Eq. (16)-Eq. (19). The calculated gas flux at each time step in Eq. (19) is used to update the upstream and downstream pressure by Eq. (20) and Eq. (21). Then the updated upstream and downstream pressure is used to update the inlet and outlet pressure in Eq. (14) and Eq. (15). The simulation continues until upstream and downstream pressure become equal.

\[ \sum_{j=1}^{N} Q_{ij} = 0 \]  

(16)
where $Q_{ij}$ is the gas flux between pore $i$ and pore $j$ (m$^3$/s), $p_i$ and $p_j$ are the pore pressure in pore $i$ and pore $j$, respectively (Pa), $g_{ij}$ is the gas flow conductance between pore $j$ and pore $i$ (m$^3$/Pa·s), $L_i$, $L_j$, $L_t$ are the length of pore $i$ and pore $j$ and the throat that connects pore $i$ and pore $j$, respectively (m), $g_i$, $g_j$, $g_t$ are the gas flow conductance of pore $i$, pore $j$ and the throat that connect pore $i$ and pore $j$ respectively (m$^3$/Pa·s), $N_{inlet}$ is the number of the inlet pores, $Q_{inlet}$ is the gas flux in inlet pores (m$^3$/s).

$$\Delta V_g = \frac{V_{up}(P_u^{k+1} - P_u^k)}{-Q_{total}\Delta t}$$

$$\Delta V_g = \frac{V_{down}(P_d^{k+1} - P_d^k)}{Q_{total}\Delta t}$$

Where $c_g$ is the coefficient of isothermal compressibility (MPa$^{-1}$), $\Delta t$ is the time step (s). In order to match with experimental pressure pulse decay data, a suitable pore network should be generated and the proposed algorithm is presented in Fig. 6 as follows:

1. Laboratory measured pore size distribution and extracted pore structure mid axis are the basic input data and are applied to generate the pore network model.
2. The upstream and downstream vessel volume is set based on the similarity principle shown in Eq.(1) and Eq.(2). The upstream and downstream pressure is the same as the laboratory used upstream and downstream pressure.
3. Pore and throat size in each location of the pore structure mid axis is assigned according to the laboratory measured pore size distribution.
4. The pressure pulse decay process is simulated and the upstream and downstream pressure drop versus time is calculated.
5. The laboratory measured pressure drop data is compared with simulated pressure drop data. If the simulated pressure drop data match with the experimental data, the simulation stops and Eq.(22) is used to calculate the pore network permeability. If the
simulated pressure drop data doesn’t match with the experimental data, go back to step (3).

\[ k_{app} = \frac{\mu l}{A \Delta p} \sum_{i=1}^{N_{net}} Q_{inlet} \]

Where \( A \) is the area of simulated core sample cross section (m²).

4. Results and discussion

4.1 Model simulation results and validation

The generated pore network to simulate pressure pulse decay process is shown in Fig. 7. The throat size is not shown in the pore network related figures to save computer visualization memory. Fig. 8 shows pressure pulse decay model simulation results compared with experimental data. The simulated pressure pulse decay curve matches well with experimental data. The pressure drop distribution in Fig. 9 is used to calculate gas permeability in Eq.(22) and the permeability value is \( 9.5 \times 10^{-6} \) μm². In order to validate our model, we compare our model with Javadpour et al’s model using available data from the literature [23]. Detailed model comparison parameters are given in Table 2. The 3D shale digital core is reconstructed based on the binarized Eagle Ford Shale SEM image [31] in Fig. 10 and pore structure mid axis is extracted from the pore space based on mid axis method. Note that the pore spaces are divided into organic and inorganic region in Javadpour et al’s model [23]. Therefore the pore network construction differs from the above mentioned procedure in Section 3.2. The pore nodes and bonds of the pore network are randomly partitioned into organic and inorganic regions. A radius is drawn randomly from the respective organic and inorganic pore-size distributions in Table 3, for every randomly-selected pore node or bond, over all pore elements. Note that each element is assigned with a suitable radius so that none of the pore nodes overlaps with any other one in space, and for any bond its radius is always smaller than those of the adjacent pore nodes it connects to. The total organic pore nodes and bonds volume is regulated to occupy the 12% of the total pore volume to represent the value of volumetric TOC. The pore type distribution on the pore pore structure mid axis is shown in Fig. 11.
Fig. 12 and Fig. 13 show the generated pore network and the pressure drop distribution at the first time step respectively. Model simulation results are compared with experimental data and Javadpour et al’s model results in Fig. 14. The calculated gas permeabilities based on our model and Javadpour et al’s model are $1.2 \times 10^{-7}$ μm$^2$ and $1.07 \times 10^{-7}$ μm$^2$, respectively. It should be noted that Javadpour et al’s model pressure pulse data fitting results are better than our model fitting results. The reasons can be attributed into two aspects. First, due to the heterogeneity of the shale formation, the SEM image used to reconstruct 3D shale digital core and pore network can not reflect the pore structure characteristic of the specific shale sample and SEM images in Javadpour et al’s work. Second, Javadpour et al’s model [23] can give good fitting results by optimizing the value of tortuosity and fractal dimension.

4.2 Influence of test gas type and pore size on gas permeability

Helium transports by viscous flow and Knudsen diffusion in shale nanopores and is not influenced by the pore type [32]. However, for methane in organic pores, free gas flows in the forms of viscous flow and Knudsen diffusion while adsorbed gas also contributes to the gas flow by surface diffusion along molecular concentration gradients [33]. Therefore the laboratory measured gas permeability by helium may not accurately describe the methane flow ability. The helium and methane permeabilities in a single pore at different pore radii are calculated by Eq.(10) and Eq.(11). Concrete model parameters are given in Table 4. Fig. 15 shows the $k_{\text{He}}/k_{\text{CH}_4}$ versus pore radius at 13.45 MPa, 273.15K. It is can be seen that when the pore radius is larger than 200 nm, $k_{\text{He}}/k_{\text{CH}_4}$ stays close to 1. When the pore radius is smaller than 200 nm, $k_{\text{He}}/k_{\text{CH}_4}$ is larger than 1 and notably increases with the decrease of pore radius. This can be attributed to the fact that the mean free path for helium obtained from Eq.(4) is larger than that for methane and therefore Kn for helium is larger than that for methane. The larger value of Kn for helium gives a larger value of flow condition function $f(\text{Kn})$ and causes the helium permeability is larger than the methane permeability even when the surface diffusion of the adsorbed gas is considered.

We further calculate the methane/helium permeability on the pore network. Similar to the pore network model construction procedure in model comparison with Javadpour
et al’s model, the pore nodes and bonds of the pore network are partitioned into organic and inorganic regions. A radius is drawn randomly from the respective organic and inorganic pore-size distributions, for every randomly-selected pore node or bond, over all pore elements. Each element is assigned with a suitable radius so that none of the pore nodes overlaps with any other one in space, and for any bond its radius is always smaller than those of the adjacent pore nodes it connects to (see Fig. 1). The organic and inorganic pore size distribution is taken from Table 3. Concrete model parameters are given in Table 4. Helium and methane single phase flow is simulated and gas permeabilities are calculated for helium and methane respectively. In order to study the influence of pore size on helium and methane permeabilities, the radius of every pore and throat in the pore network is rescaled by factor $\delta$ in Eq. (23) to generate a series of pore networks with different average pore radius. The value of $\delta$ ranges from 0.2 to 5 and the corresponding average pore radius ranges from 3.86 nm to 96.6 nm. For each pore network model, the ratio of helium permeability and methane permeability $k_{He}/k_{CH4}$ is calculated. Fig. 17 shows that $k_{He}/k_{CH4}$ significantly increases with the decrease of average pore radius. When the average pore radius is less than 20 nm, helium tested permeability overestimates at least 40% of the methane permeability.

$$r_{rescale} = r\delta$$

5. Conclusion

In this work, we proposed a pore structure based real gas transport model to determine gas permeability in nanoporous media combining laboratory pressure pulse decay technique with pore network simulation. The core sample was constructed by a series of same connected pore networks. The sizes of pores and throats in each location of the pore network were randomly assigned according to laboratory measured pore size distribution. At each time step, the upstream vessel pressure decreased and the downstream vessel pressure increased until the upstream vessel pressure and downstream vessel pressure become equal. The simulated pressure drop versus time curve was obtained and was applied to fit the laboratory measured pressure drop data by repeating core sample construction process and pressure pulse decay process. The
The proposed model was validated by the experimental data and compared with available published model. We extended our model to study the influence of test gas type and pore size on gas permeability. The results show that when the average pore radius is less than 20 nm, at least 40% of the methane permeability is overestimated if helium is applied to estimate gas flow ability. Our analysis results highlight the importance to consider the gas property, pore type and structure characteristic when estimating the shale gas permeability. We didn’t consider the influence of natural fracture on gas flow in the proposed model because the studied core sample mainly contains pores and solids. However, gas flow in complex fracture-matrix interaction system must be considered for fracture-developed shale samples. In addition, the heterogeneity of shale nanoporous media is confined to the pore scale in this work by repeating the same pore network model and studies have shown that shale exhibits heterogeneities at multi-scale levels. A more general model incorporating the influence of natural fracture and multi-scale heterogeneities will be addressed in future work.

Appendix A

In this Appendix, the conductance for organic pores, as defined in Eq. (9) is developed by considering several factors. First, gas adsorption and desorption are considered to define an effective radius for a pore as they affect both free gas flow and surface diffusion. Then the combined viscous flow and Knudsen diffusion to the total flux is established, plus the surface diffusion of adsorbed gas in organic pores.

Influence of adsorption/desorption on capillary radius

At the typical shale gas reservoir condition, there is a consensus that the Langmuir monolayer adsorption model may adequately capture shale gas adsorption behaviours [36]. For this reason, this model is considered in this work. Let the coverage be defined as the ratio of the adsorption volume to the Langmuir volume, and then gas coverage of a real gas can be expressed as [37]:

\[ \theta = \frac{p_o/Z}{p_L + p_o/Z} \]  

(24)

Where \( p_L \) is Langmuir pressure (Pa). Adsorbed gas molecules on the pore surface reduce the pore space available to the remaining gas molecules for flow. Under the
assumption of a homogenous loading of adsorbed gas molecules on the surface, the
effective capillary radius can be expressed as [37]:
\[ r_{\text{eff, or}} = r - d_m \theta \]  
(25)
Where \( d_m \) is gas molecular diameter (m).

**Real gas property**
The modified van der Waals (vdW) EoS developed by Mahmoud [38] for determining
the gas compressibility factor \( Z \) (Eq.(28)) is valid over a wide pressure range.
\[ P_{pr} = \frac{P}{P_c} \]  
(26)
\[ T_{pr} = \frac{T}{T_c} \]  
(27)
\[ Z = (0.702e^{-2.5T_{pr}})P_{pr}^2 - 5.524e^{-2.5T_{pr}}P_{pr} + 0.044T_{pr}^2 - 0.164T_{pr} + 1.15 \]  
(28)
Where \( P_c \) is critical pressure, \( 4.6045 \times 10^6 \) (Pa), \( T_c \) is critical temperature, \( 190.56 \) (K),
\( P_{pr} \) is pseudo reduced pressure, \( T_{pr} \) is pseudo reduced temperature.

Lee et al. [39] developed an empirical gas viscosity model for natural gases that has
been adopted for the confined pores to determine gas viscosity and density as follows:
\[ K = \frac{(9.379 + 0.01607M)T^{1.5}}{(209.2 + 19.26M + T)} \]  
(29)
\[ X = 3.448 + \frac{986.4}{T} + 0.01009M \]  
(30)
\[ Y = 2.447 - 0.2224X \]  
(31)
\[ \mu = \left(1 \times 10^{-4}\right)K \exp\left(X \rho^Y\right) \]  
(32)
\[ \rho = 1.4935 \times 10^{-3} \frac{P_oM}{ZT} \]  
(33)

**Free gas transport**
The Knudsen number in organic pore can be written as
\[ K_n = \frac{\lambda}{r_{\text{eff, or}}} \]  
(34)
According to Eq.(6), free gas flow conductance can be written as:
Surface diffusion of adsorbed gas

Surface diffusion of adsorbed gas molecules has long been considered as one of the key transport mechanisms in organic pores because of the large amount of adsorbed gas in organic shales. It can be modelled as a the general diffusion process, using the molar flow rate per unit area of the concentration gradient within the adsorbed monolayer as developed in [40]. Based on Hwang and Kammermeyer’s model [41], the surface diffusion coefficient for methane (when gas coverage is zero) can be expressed as [42]:

\[ D_{s0} = 8.29 \times 10^{-7} T^{0.5} \exp\left(-\frac{\Delta H^{0.8}}{RT}\right) \]  

(36)

In Eq.(36), the isosteric adsorption heat \( \Delta H \) is a function of gas coverage, according to Nodzeriski et al. work [43], the isosteric adsorption heat and gas coverage have a linear relationship and can be given as:

\[ \Delta H = \gamma \theta + \Delta H(0) \]  

(37)

Where \( \Delta H(0) \) is the isosteric adsorption heat at zero gas coverage (J/mol), \( \eta \) is the fitting coefficients of isosteric adsorption heat (J/mol). The surface diffusion coefficient in Eq.(36) is obtained under a low pressure condition by theory and experiments, and is a function of gas molecular weight, temperature, and gas activation energy, isosteric adsorption heat and independent of pressure [41]. In order to describe the gas surface diffusion in nanopores of shale gas reservoirs under a high pressure condition, the influence of gas coverage on surface diffusion needs to be considered. Chen et al. [44] used the kinetic method to calculate the surface diffusion coefficient:

\[ D_s = D_{s0} \frac{(1 - \theta) + \frac{\kappa}{2} \theta(2 - \theta) + \{H(1 - \kappa)\}(1 - \kappa) \frac{\kappa}{2} \theta^2}{(1 - \theta + \frac{\kappa}{2} \theta)^2} \]  

(38)

\[ H(1 - \kappa) = 0, \kappa \geq 1; 1, 0 \leq \kappa \leq 1 \]  

(39)

\[ \kappa = \frac{K_0}{K_m} \]  

(40)
Where $\kappa_b$ is rate constant for blockage in surface diffusion, $\kappa_m$ is rate constant for forward migration in surface diffusion, $\kappa$ is ratio of the rate constant for blockage to the rate constant for forward migration, $H(1-\kappa)$ is Heaviside function, dimensionless. When $\kappa_m > \kappa_b$, surface diffusion occurs. When $\kappa_m > \kappa_b$, surface diffusion occurs. When $\kappa_m < \kappa_b$, gas molecules are blocked and surface diffusion stops. Adsorbed gas flow conductance can be written as [37]:

$$g_{\text{surface}} = \frac{1}{l} \left( \frac{M}{\rho} D_s C_{\text{a max}} \frac{d\theta}{d\rho} \pi \left( r^2 - r_{\text{eff,or}}^2 \right) \right)$$  \hspace{1cm} (41)

$C_{\text{a max}}$ can be expressed as [45]:

$$C_{\text{a max}} = \frac{C_{\text{max}}}{\varepsilon_{ks}}$$  \hspace{1cm} (42)

Where $C_{\text{max}}$ is the maximum adsorbed gas concentration inside the total core sample (mol/m$^3$), $\varepsilon_{ks}$ is the total organic grain volume per total grain volume, dimensionless.

The surface diffusion incurred conductance in Eq.(41) is appended to that of the free gas flow in organic pore, Eq.(35) to give Eq.(9).

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networks in mudrocks and a descriptive classification for matrix-related


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Table 1 Core sample and pressure data used in pulse-decay experiment.

<table>
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<th>Parameter</th>
<th>Value</th>
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</tbody>
</table>

Fig. 2. Shale core sample used in this study (a) core sample (b) binarized SEM image of the shale core sample (black represents pore phase while white represents matrix).

Fig. 3. Physical model of simulated pressure pulse decay process.
Fig. 4. Reconstructed shale pore structure (a) Reconstructed 3D $400 \times 400 \times 400$ $(l_x \times l_y \times l_z: 8 \mu m \times 8 \mu m \times 8 \mu m)$ shale digital core by MPS (red represents solid phase, blue represents pore phase) (b) Extracted pore structure mid axis by mid axis method (red points represents the location of pore while white line represents the location of throat).

Fig. 5. Laboratory measured pore radius distribution.
Fig. 6. The flowchart of the proposed methodology to determine shale gas permeability from simulation of pressure decay process.
Fig. 7. Generated pore network from simulation of pressure decay process.

Fig. 8. Model simulation results compared with experimental data.
Fig. 9. Pressure drop distribution on the generated pore network at the first time step.

Table 2 Core sample and pressure data adapted from Javadpour et al. work [23] for model comparison.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core length $L_{core}$, in m</td>
<td>0.0615</td>
</tr>
<tr>
<td>Core diameter $d_c$, in m</td>
<td>0.038</td>
</tr>
<tr>
<td>Upstream pressure $P_u$, in MPa</td>
<td>13.79</td>
</tr>
<tr>
<td>Upstream vessel volume $V_{up}$, in m$^3$</td>
<td>$30 \times 10^{-6}$</td>
</tr>
<tr>
<td>Downstream pressure $P_d$, in MPa</td>
<td>13.1</td>
</tr>
<tr>
<td>Downstream vessel volume $V_{down}$, in m$^3$</td>
<td>$30 \times 10^{-6}$</td>
</tr>
<tr>
<td>Volumetric TOC</td>
<td>12%</td>
</tr>
<tr>
<td>Temperature $T$, in K</td>
<td>293</td>
</tr>
<tr>
<td>Gas type</td>
<td>Nitrogen</td>
</tr>
</tbody>
</table>

Fig. 10. Eagle Ford Shale (a) binarized SEM image, the resolution of the SEM image is $300 \times 300$ pixels and the pixel size of the SEM image taken is 48 nm$\times$48 nm. (b)
reconstructed 3D 300 voxel×300 voxel×300 voxel (14.4μm×14.4μm×14.4μm) shale
digital core by MPS (Red represents solid phase, blue represents pore phase).

**Fig. 11.** Pore type distribution on the pore structure mid axis (red points represent
organic pore location while blue points represents inorganic pore location).

**Table 3** Organic and inorganic pore size distribution taken from Javadpour et al.
work[23]: \( \text{ave} \) and \( \sigma \) are mean and standard deviation of the log transform of the pore
size.

<table>
<thead>
<tr>
<th>Pore type</th>
<th>ave</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic pore size</td>
<td>0.4</td>
<td>0.18</td>
</tr>
<tr>
<td>Inorganic pore size</td>
<td>1.4</td>
<td>0.44</td>
</tr>
</tbody>
</table>
Table 4 Parameters used for single pore and pore network flow simulations.

<table>
<thead>
<tr>
<th>Reservoir properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature $T$, in K</td>
<td>293.15</td>
</tr>
<tr>
<td>Pore pressure $p_o$, in MPa</td>
<td>13.45</td>
</tr>
<tr>
<td>Pressure gradient $dp/dx$, in MPa/m</td>
<td>0.1</td>
</tr>
<tr>
<td>Total organic grain volume per total grain volume $\varepsilon_{ks}$</td>
<td>0.12</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Methane properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir pressure $p_L$, in MPa</td>
<td>13.789514</td>
</tr>
<tr>
<td>Maximum adsorbed gas concentration $C_{max}$, in mol/m$^3$</td>
<td>328.7</td>
</tr>
<tr>
<td>Isosteric adsorption heat at zero gas coverage $\Delta H(0)$, in J/mol</td>
<td>16000</td>
</tr>
<tr>
<td>Fitting coefficients of isosteric adsorption heat $\gamma$, in J/mol</td>
<td>$-4186$ [34]</td>
</tr>
<tr>
<td>Ideal gas constant $R$, in J/(mol·K)</td>
<td>8.314</td>
</tr>
<tr>
<td>Ratio of the rate constant for blockage to the rate constant for forward migration $\kappa$</td>
<td>0.5 [35]</td>
</tr>
<tr>
<td>Molecular weight $M_g$, in kg/mol</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Fig. 12. Generated pore network to simulate pressure pulse decay process and match the experimental data [23].
Fig. 13. Pressure drop distribution on the generated pore network at the first time step for model comparison.

Fig. 14. Different model simulation results compared with experimental data (a) our model (b) Javadpour et al’s model [23].
Fig. 15. $k_{He}/k_{CH4}$ at different pore radii.

Fig. 16. Generated shale pore network model with random organic pore nodes and throats (red represents the location of organic pores and throats while blue represents the location of inorganic pores and throats).
Fig. 17. $k_{\text{He}}/k_{\text{CH}_4}$ versus average pore radius at different rescaled factor $\delta$. 

Average pore radius of the pore network at different $\delta$/m