



## Invited review

# Gas transport mechanisms, mathematical models, and impact factors in low-permeability rocks: A critical review

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### Abstract:

The study of gas transport in low-permeability rocks is both practical and of significant importance to produce tight rock reservoirs. The presence of nanopores in tight rocks results in distinctly different gas transport mechanisms from those found in conventional reservoirs. Traditional Darcy's law is inadequate for describing gas flow in this context. Instead, various modes of gas transport, such as continuum flow, slip flow, transition flow, and Knudsen diffusion for bulk gas, as well as surface diffusion and adsorption/desorption for adsorbed gas, coexist within these nanopores. This paper mainly focuses on studies of gas transport in nanopores that consider apparent permeability. To begin with, the pore structure characteristics and gas seepage mechanisms in shale are introduced. An overview of the three main methods for measuring apparent permeability including laboratory experiments, numerical simulations, and analytical techniques, is provided. Mathematical models describing gas transport within nanopores are emphasized as a foundational component of apparent permeability measurements. Furthermore, the factors that influence these models are discussed. Upon analyzing the existing models, it is evident that they are diverse and numerous. While these models typically encompass multiple mechanisms and influencing factors related to gas transportation, each model has its specific limitations. Therefore, there is a continued need for the development of more comprehensive and general models. This study offers the most detailed overview of gas transport mechanisms and mathematical models in low-permeability rocks, aiming to support the evaluation and exploitation of tight rock reservoirs.

## 1. Introduction

Unconventional reservoirs have increasingly garnered attention in the oil and gas industries, particularly since the

development of hydraulic fracturing techniques and horizontal well technologies (Peng et al., 2023; Liu et al., 2024; Zhou et al., 2024b). The unconventional reservoir sources are often tight rocks such as tight gas sands, shale, and coal beds,

which can be classified as low-permeability rocks. Fluid in unconventional reservoirs are gas and liquid. The gases are found to exist as bulk gas/free gas, adsorbed gas and dissolved gas (Wang and Yu, 2019; Dai et al., 2020), and the liquid are typically water and oil (Zhang and Wang, 2023). Bulk and adsorbed gas are the main object in an extracting process, and the apparent permeability is a key parameter for describing the production rate of a gas well (Zhang et al., 2018a). Darcy's Law is based on continuous flow theory and may no longer hold for low-permeability rocks (Han et al., 2018; Song et al., 2019; Cai et al., 2024b) because the pore diameters are significantly smaller than those found in conventional reservoirs (Cui et al., 2018; Zhou et al., 2024a). Since Klinkenberg (1941) proposed the definition of apparent permeability, many scholars have devoted efforts to gas transport studies (Wu et al., 2020; Hatami and Walsh, 2022). Although the Klinkenberg model accounts for slippage effects compared to Darcy's Law, it still lacks consideration of other flow mechanisms (Javadpour et al., 2021).

Gas transport mechanisms in nanopores are fundamental and critical for accurately evaluating the apparent permeability. Complex and various flow regimes co-exist in nanopores (Li et al., 2019; Yang et al., 2020). Continuum flow, slip flow, transition flow and Knudsen diffusion are the bulk gas flow regimes (Sun et al., 2015b; Peng, 2021) distinguished by the Knudsen number (Firouzi et al., 2014; Gensterblum et al., 2015). Adsorbed gas flow regimes include surface diffusion and adsorption/desorption (Amann-Hildenbrand et al., 2012). Then the apparent permeability can be derived by combining these mechanisms and modifying the governing equations (Hatami et al., 2022). There are three types of methods for apparent permeability determination: The laboratory experiments, the numerical methods and the analytical methods (Yang et al., 2019; Li et al., 2020b). The laboratory experiments are straightforward methods evolved from conventional reservoir permeability measurements (Gao and Yu, 2018).

Because the unconventional reservoirs are extremely tight with low porosity (Xu et al., 2018; Xiao et al., 2022a), the laboratory experiments are always time-consuming (Hildenbrand et al., 2002) and results from different experiments often exhibit variations. (Darabi et al., 2012; Shen et al., 2018b). The numerical methods can construct three-dimension models; however, they need extensive time for computational calculation (Sun et al., 2015a; Shen et al., 2018a). The analytical methods are convenient and attractive choices for scholars to study gas flow mechanisms through nanopores. Numerous mathematical models have been established and reported based on various gas flow regimes (Cai et al., 2019; Tian et al., 2022). The mathematical models are also the basic calculation methods for laboratory experiments and numerical methods. Though scholars have taken plenty of possible influencing factors to established models, each model has its own limitations (Xiao et al., 2022b). For example, most models define the cross-section shape of nanopores as circular or slit with uniform pore size. The sensitivity analyses also vary across different models. There is a consensus in the literature that shale formations contain both organic matter and clay minerals, with variations in cross-sectional pore struc-

tures across different matrices (Akilu et al., 2021). Moreover, research on the factors influencing apparent permeability in these models needs to be systematically summarized. Despite all this, there is no unified model for gas permeability in nano-porous media that is widely accepted so far (Salama et al., 2017; Zhang et al., 2020). Thus, it is essential to review these models and relevant factors.

The fluid flow mechanisms in tight rocks were first analyzed, followed by a review of the measurement methods for apparent permeability. Finally, the related mathematical models of apparent permeability and their influencing factors were discussed in this study. This review can provide significant guidance and inspiration for future studies on gas permeability in tight rocks.

## 2. Fluid flow mechanisms in nanopores

Fluid flow in extremely tight formations no longer follow the traditional Darcy's law (Zhang et al., 2015; Zhang and Yu, 2016; Sun et al., 2023a). Complicated pore size distributions and various gas existence mechanisms lead to various gas transport mechanisms in shale gas reservoirs (Chen et al., 2015). Fluid flow types in shale reservoirs include the viscous flow, slippage flow, Fick diffusion, Knudsen diffusion, surface diffusion, etc. (Wang et al., 2017; Woignier et al., 2018). Gas transport regimes are clarified in detail because they are the foundation principle of gas permeability in shale, while liquid flow mechanisms are also briefly introduced in this section.

### 2.1 Gas flow

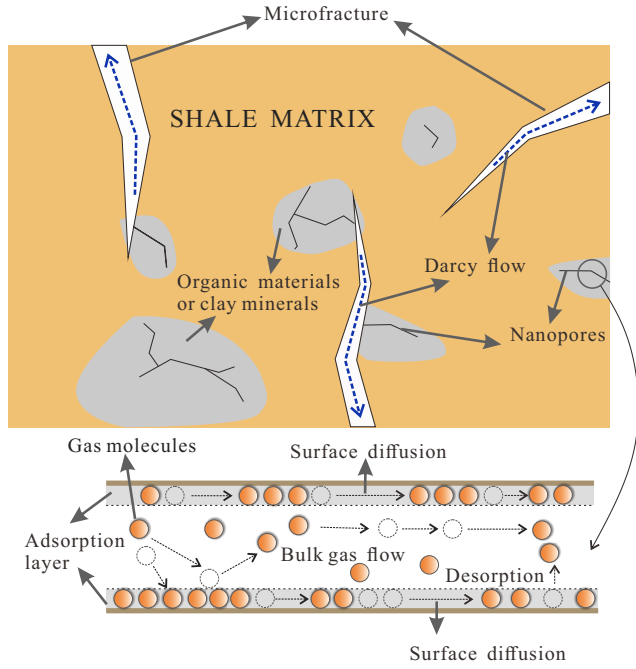
Gas flow mechanisms in shale are intimately linked to the state of gas existence and the size of flow paths. In tight reservoirs, gas primarily exists in three distinct forms: Free gas, adsorbed gas, and dissolved gas (Feng et al., 2020; Wei et al., 2021). Free gas can flow through both macroscopic fractures and microscopic pore networks, while adsorbed gas locates on the walls of inorganic or organic mineral nanopores (Qiu and Zou, 2020). On the other hand, dissolved gas is typically found within the structure of kerogen materials (Fig. 1). A brief overview of the gas flow mechanisms is analyzed in the following section.

#### 2.1.1 Bulk gas

Bulk gas transport mechanisms are always categorized based on a thermodynamic equilibrium parameter-Knudsen number ( $Kn$ ).  $Kn$  is defined as the ratio of the average free path of gas molecules to the characteristic length of nanopores (Zhang et al., 2012). The expression of  $Kn$  can be described as:

$$Kn = \frac{\lambda}{d} \quad (1)$$

where  $\lambda$  is the average free path of gas molecules, m;  $d$  is the characteristic length of nanopores, m. The average free path of gas molecules is defined as follow (Wu et al., 2015a; Li et al., 2017a):



**Fig. 1.** Gas transport mechanisms in shale matrix.

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

where  $\mu$  is the gas viscosity, mPa·s;  $T$  is the formation temperature, K;  $p$  is the formation pressure, Pa;  $R$  is the universal gas constant, dimensionless;  $Z$  is the compressibility factor, dimensionless;  $M$  is the gas molar mass, g/mol.

According to the Knudsen number, there are four different transport mechanisms for bulk gas (Li et al., 2017b). Bulk gas transport mechanisms and corresponding governing equations are shown in Fig. 2. When  $Kn < 0.001$ , gas molecular collisions with each other are significantly stronger than gas molecular collisions with the pore walls, and the gas transport mechanism is defined as continuum flow which can be described by Darcy's law (Cui et al., 2009). Using the diameter of methane molecules as the mean free path of gas molecules, Fig. 3 illustrates the variation of the  $Kn$  with pressure across different pore scales at a temperature of 298 K.

When  $0.001 < Kn < 0.1$ , the velocity of the gas molecules at the wall is no longer zero as collisions between gas molecules and pore walls increase. The gas transport mechanism is characterized as slip flow. Klinkenberg (1941) demonstrated how the slip of gas molecules on solid surfaces affects gas transport and introduced the concept of apparent permeability. It is inversely proportional to pressure:

$$k = k_{\infty} \left( 1 + \frac{b}{p_m} \right) \quad (3)$$

where  $k$  is the apparent permeability, md;  $k_{\infty}$  is the liquid permeability, md;  $b$  is the slope of Klinkenberg straight line, dimensionless; and  $p_m$  is the pore pressure, MPa.

Numerous studies consistently demonstrate that rock with lower permeability exhibits a more pronounced slip effect (Tan et al., 2021; Tian et al., 2021). Three slip models have been proposed as first-order slip, second-order slip and Langmuir slip. As summarized by Feng et al. (2018), the slip velocity

( $u_s$ ) at a pore wall can be described in a first-order slip model:

$$u_s - u_w = \pm C_1 \frac{2 - \sigma}{\sigma} \lambda \left( \frac{\partial u}{\partial n} \right)_s \quad (4)$$

where  $u_w$  is the gas velocity at a solid surface, m/s;  $C_1$  is a first-order slip coefficient,  $\sigma$  is a tangential momentum accommodation coefficient, dimensionless; and  $(\partial u / \partial n)_s$  is the velocity gradient in a direction perpendicular to the solid surface,  $s^{-1}$ .

The second-order slip boundary model is proposed as:

$$u_s - u_w = \pm C_1 \lambda \left( \frac{\partial u}{\partial n} \right)_s - C_2 \lambda^2 \left( \frac{\partial^2 u}{\partial n^2} \right)_s \quad (5)$$

where  $C_2$  is the second-order slip coefficient dimensionless.

The Langmuir slip boundary model considering gas molecules and a solid surface is proposed as:

$$u_s = \theta u_w + (1 - \theta) u_g \quad (6)$$

where  $u_g$  is a reference gas velocity, m/s; and  $\theta$  is the gas coverage ratio on a solid surface, dimensionless.

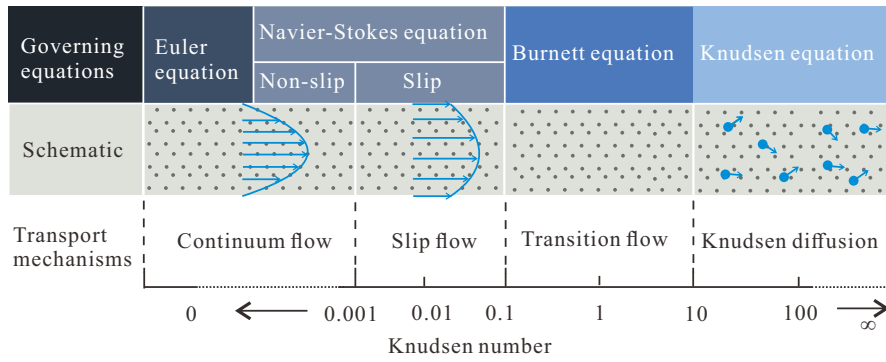
When  $0.1 < Kn < 10$ , the gas molecular collisions with each other are equivalent to the collisions between gas molecules and pore walls. The gas transport mechanism is transition flow described by the Burnett equation. The mathematical results often exhibit low accuracy, making molecular dynamic (MD) simulation and lattice Boltzmann method (LBM) more common ways for describing the transition flow state (Akilu et al., 2021).

When  $Kn > 10$ , gas molecules collide with pore walls more frequently, and the gas transport mechanism is Knudsen diffusion. The Knudsen diffusion coefficient ( $D_k$ ) is a critical parameter expressed as (Zhang et al., 2019):

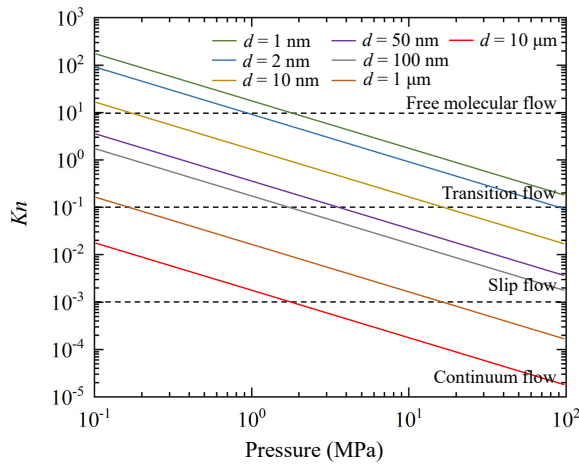
$$D_k = \frac{d}{3} \sqrt{\frac{8RT}{\pi M}} \quad (7)$$

### 2.1.2 Adsorbed gas

The movement mechanisms of adsorbed gas include adsorption/desorption and surface diffusion. Gas adsorption and desorption mainly governed by the van der Waals force in shale nanopores is a physical reversible process of transformation of adsorbed gas and free gas as shown in Fig. 4 (Yu et al., 2016). When a system is considered to reach an adsorption equilibrium, it indicates that gas adsorption and desorption are in dynamic equilibrium. Pore walls provide adsorption sites for free gas molecules. Organic matter and clay minerals with micro-nanopores are the main sites for gas adsorption (Rani et al., 2019; Mudoj et al., 2022). The gas adsorption and desorption process is affected by pressure, temperature, pore size, pore wall roughness, etc. Gas molecules can form mono- or multilayer adsorption formation on pore walls. Monolayer adsorption formation is formed in micro- and mesopores while multilayer formation is always considered to be formed at a high relative pressure condition (Zhou et al., 2018; Klewiah et al., 2020). Most scholars agree with that it is reasonable to analyze gas adsorption/desorption using Langmuir isotherm with an assumption of single layer adsorption formation (Pan et al., 2010; Zhang and Yu, 2022). The Langmuir equation is



**Fig. 2.** Bulk gas transport mechanisms in nanopores and governing equations (Javadpour et al., 2021).



**Fig. 3.** Schematic diagram of Knudsen number changes with pressure and flow regime partitioning.

shown in Eq. (8). The Brunauer-Emmett-Teller theory (Brunauer et al., 1938) is developed based on the Langmuir adsorption theory and is widely used in multilayer adsorption research (Eq. (9)). Adsorption is an exothermic process so that higher temperatures weaken adsorption and promote desorption (Hao et al., 2013; Zhou et al., 2019):

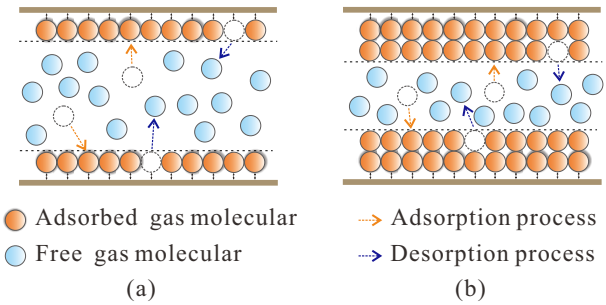
$$V_p = \frac{V_L P}{P_L + P} \quad (8)$$

where  $V_p$  is the adsorbed volume at pressure  $P$ ,  $\text{cm}^3/\text{g}$ ;  $P$  is the pressure of the gas, MPa;  $V_L$  is the Langmuir volume,  $\text{cm}^3/\text{g}$ ; and  $P_L$  is the Langmuir pressure, MPa:

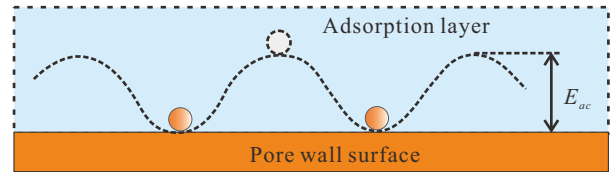
$$\frac{P}{V \left(1 - \frac{P}{P_0}\right)} \cdot \frac{C-1}{CV_m} \cdot \frac{P}{P_0} + \frac{1}{CV_m} \quad (9)$$

where  $P_0$  is the saturation pressure of the gas, MPa;  $V$  is the adsorbed gas volume,  $\text{cm}^3/\text{g}$ ;  $V_m$  is the monolayer adsorption saturation capacity,  $\text{cm}^3/\text{g}$ ; and  $C$  is an appropriate constant which is related to adsorption heat, dimensionless.

Surface diffusion is a process that adsorbed gas molecules migrate derived by a concentration gradient along pore walls in the adsorption phase (Fig. 5). It is a complex physical phenomenon (Spanakos and Rigby, 2020) primarily caused by the interaction between diffusion particles and solid surface,

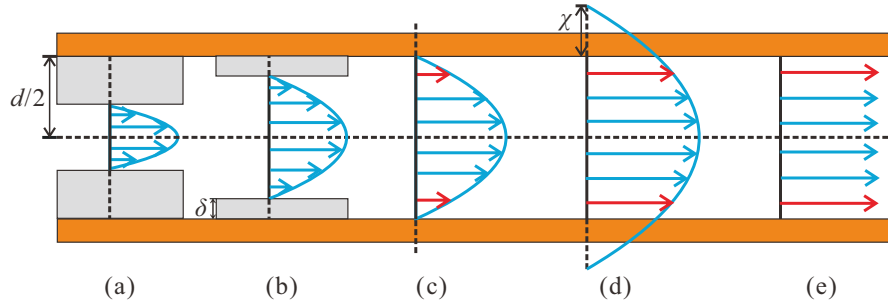


**Fig. 4.** Schematic diagram of adsorption/desorption in nanopores: (a) Monolayer and (b) multilayer.



**Fig. 5.** Schematic diagram of surface diffusion ( $E_{ac}$  is the active energy of surface diffusion).

and also influenced by van der Waal's force, electrostatic force, and direct or indirect interaction forces (Medve and Cerny, 2011; Wu et al., 2015b). The presence of surface diffusion is important to the gas transport in the porous medium, and the apparent permeability can be ten times or even several orders of magnitude higher (Majumder et al., 2005; Holt et al., 2006). Many theories, such as hopping model (Okazaki et al., 1981; Chen and Yang, 1998), hydrodynamic model (Kikkinides et al., 1997; Kainourgiakis et al., 1998) and Fickian model (Kapoor et al., 1989) have been proposed to describe surface diffusion. The hopping model is a widely applied mode, which assumes that an adsorbed gas molecule escapes from an adsorption site and hops to a neighboring adsorption site (Yang et al., 1973; Spanakos and Rigby, 2022). The hopping model is applicable with single layer adsorption and it is actually an activated process of adsorbed gas molecules. Several classical and fundamental hopping models have been established and became the basic research of most subsequent surface diffusion models. Hwang and Kammermeyer (1966) established a surface diffusion analytical model under a low-pressure condition. The surface diffusion coefficient ( $D_s^0$ ) when



**Fig. 6.** Schematic representation of water flow in nanopores with (a) and (b) hydrophilic pore walls, (c) midwetting pore walls, (d) and (e) hydrophobic pore walls adapted from Wu et al. (2017a) ( $\delta$  represents the thickness of multilayer sticking regions and  $\chi$  represents the slip length).

the gas coverage is equal to zero in their model can be expressed as:

$$D_s^0 = \Omega T^m \exp\left(-\frac{E}{RT}\right) \quad (10)$$

where  $\Omega$  is a constant related to the gas molecular weight,  $\text{m}^2/(\text{s}\cdot\text{K}^{0.5})$ ;  $m$  is a constant, dimensionless; and  $E$  is the activation energy, J/mol.

Guo et al. (2008) fitted an empirical expression of the surface diffusion coefficient without consideration of pressure influence based at the expression of Hwang and Kammermeyer (1966) as:

$$D_s^0 = 8.29 \times 10^{-7} T^{0.5} \exp\left(-\frac{\Delta H^{0.8}}{RT}\right) \quad (11)$$

where  $\Delta H$  is the isosteric heat of adsorption,  $\text{KJ} \cdot \text{mol}^{-1}$ .

Their two surface diffusion models are all derived from experimental data but they are not applicable under high pressure conditions. Other classical hopping models for surface diffusion have been established with the consideration of adsorbed gas coverage (Chen and Yang, 1991) and energy heterogeneity (Kapoor et al., 1989; Kapoor and Yang, 1990) as shown in Eqs. (12)-(14). Adsorbed gas surface diffusion is very complicated and can be influenced by pressure, temperature, surface heterogeneity, gas type, etc. Models with consideration of more influence factors need to be established for surface diffusion research:

$$D_s = D_s^0 \frac{(1-\theta) + \frac{\xi}{2}\theta(2-\theta) + [H(1-\xi)](1-\xi)\frac{\xi}{2}\theta^2}{\left(1-\theta + \frac{\xi}{2}\theta\right)^2} \quad (12)$$

$$H(1-\xi) = \begin{cases} 0, & \xi \geq 1 \\ 1, & 0 \leq \xi \leq 1 \end{cases} \quad (13)$$

$$\xi = \frac{\xi_b}{\xi_m} \quad (14)$$

where  $D_s$  is the surface diffusion coefficient,  $\text{m}^2/\text{s}$ ;  $H(1-\xi)$  is the Heaviside function, dimensionless;  $\xi_m$  and  $\xi_b$  are the forward velocity coefficient and blocking velocity coefficient of adsorbed molecules,  $\text{m/s}$ ; and  $\xi$  is the ratio of a blocking velocity coefficient to the forward velocity coefficient, dimen-

sionless.

## 2.2 Liquid flow

Liquid flow mechanism in nanopores is another complex study that gives a brief summary in this section. The interaction between liquid and pore wall mainly influences liquid flow in nanopores. Similar to gas flow, liquid flow in nanopores is also accompanied by slippage on the pore wall (Cui et al., 2022b).

Consequently, some typical studies on liquid flow mechanisms are summarized in Table 1. Wu et al. (2017a) proposed slip models for liquid flow in hydrophilic, mid-wetting and hydrophobic nanopores, and the slip length can be understood clearly. True slip length, apparent slip length and apparent viscosity were taken into account in their study to establish a confined water flow model in nanopores. For hydrophilic pore walls, no-slip boundary conditions and multilayer sticking which are represented as grey regions are shown in Figs. 6(a) and 6(b). For midwetting pore walls, no-slip boundary are shown in Fig. 6(c). Compared to bulk water, the viscosity of water near walls (red arrows) the wall is smaller. For hydrophobic pore walls, the slip boundary exists as shown in Figs. 6(d) and 6(e). By incorporating the fluid slip length measured through atomic force microscopy, Javadpour et al. (2015) calculated the brine permeability in the shale matrix. Based on this, Afsharpoor and Javadpour (2016) developed a liquid flow equation considering slip length and pore shape factors using computational fluid dynamics modeling. The equation can be applied in nanopores without restrictions on cross-section shape and can accommodate slip effect. Different from Afsharpoor and Javadpour's study, Wang et al. (2016a, 2016b) developed fluid flow models through inorganic and organic nanopores containing slip length and apparent viscosity.

By coupling liquid-solid adsorption in organic nanopores with near-wall flow and velocity slip in inorganic nanopores, Zhang et al. (2017) derived a unified apparent fluid permeability model for macroscale oil flow modeling. Fan et al. (2019) established a multiscale liquid flow model based on homogenization theory using molecular dynamics simulation. They coupled slip boundary with Navier-Stokes equation to describe the liquid flow in micropores and then derived a slip-corrected Darcy-like transport model for macroscale pores. Liu

**Table 1.** Liquid flow mechanisms in nanopores.

References	Fluid type	Basic equation	Modeling methods
(Javadpour et al., 2015)	Brine	-	A stochastic model
Afsharpoor and Javadpour (2016)	-	Hagen-Poiseuille equation	Computational fluid dynamic model
Wang et al. (2016a)	Oil and supercritical CO <sub>2</sub>	Poiseuille equation	MD simulation
Wang et al. (2016b)	Oil	Poiseuille equation	MD simulation
Zhang et al. (2017)	Oil	Hagen-Poiseuille equation	MD simulation
Wu et al. (2017a)	Confined water	Hagen-Poiseuille equation	MD simulation and experiments
Fan et al. (2019)	Oil and water	Navier-Stokes equation	MD simulation
Liu et al. (2020)	Oil and water	Poiseuille equation	MD simulation
Zhang et al. (2022)	Oil and water	Poiseuille equation	MD simulation
Xie et al. (2023)	-	Darcy-Brinker-Stokes equation	CT image and 3D digital reconstruction technology
Yang et al. (2024)	Water	-	Mathematical models

et al. (2020) studied the shale oil transport behavior within kerogen nanoslits and discussed the effects of heterogeneous density distributions, different driving forces and temperatures. Zhang et al. (2022) proposed “apparent viscosity” model and “liquid-liquid slip” model based on the static and dynamic phenomena of oil-water two-phase flow in quartz nanopores. Xie et al. (2023) discussed the characteristics of fluid velocity under different deviatoric stresses. Yang et al. (2024) found that solid-liquid interactions significantly influence the fluid flow at the nanoscale as the pore size decreases. As summarized above, fluid slippage is a fundamental factor in nanopores fluid flow, and on this basis other influence factors are then taken into account in studies.

### 3. Apparent permeability determination methods

The permeability determined with gases depends on the nature of gas, which can be defined as apparent permeability (Klinkenberg, 1941). When extrapolated to infinite pressure, the apparent permeability reaches the intrinsic permeability (Eq. (3)) (Li and Horne, 2001, 2004; Gao et al., 2016). Apparent permeability is significantly influenced by factors such as fluid type, fluid saturation, pore structure, pressure, and temperature (Javadpour, 2009; Gao et al., 2021). Shale is a porous medium with a considerable amount of nanopores, and this paper primarily discuss the gas-measured apparent permeability of shale. In the view of measurement means, there are three main methods to determine the apparent permeability: The laboratory experiment, the numerical method and analytical method (Li et al., 2020b).

#### 3.1 Laboratory experiments

The laboratory experiment is considered the most direct method for determining the apparent permeability of dense

rocks, typically involving both steady-state and unsteady-state approaches (Xiao et al., 2022b; Mukherjee and Vishal, 2023). It is widely agreed that the steady-state method is not suitable for measuring permeability in the nano-darcy range (Ma et al., 2016; Mukherjee and Vishal, 2023). The pressure pulse-decay method served as the initial unsteady state technique (Brace et al., 1968).

Furthermore, the pressure pulse-decay method is widely used to measure gas apparent permeability for extremely tight rock (Heller et al., 2014; Sander et al., 2017). The decay of a pressure pulse at the upstream end of a confined core and / or the increase in pressure at the downstream end are measured in pressure pulse-decay experiments (Cui et al., 2009; Yang et al., 2015). Permeability can be calculated from the pressure difference between the inlet and outlet of the rock sample. This method can measure permeability as low as  $10^{-9}$  millidarcies under high confining and pore pressures. But the experimental setup is complicated and the test is considerably time-consuming as long as several months (Cui et al., 2009; Peng and Loucks, 2016).

The Gas Research Institute technique is known as the pressure fall-off method which is first proposed by Luffel et al. (1993). It is a variation of the pulse decay method that determines permeability from drill cuttings or crushed samples, excluding in-situ stress considerations (Luffel and Guidry, 1992; Cui et al., 2009). This method has a simpler experimental setup and is less time-consuming than the pressure pulse-decay method. But it is conducted under a pore pressure that is lower than reservoir pressure and do not consider the Klinkenberg effect (Peng and Loucks, 2016).

The gas expansion technique is modified based on the original GRI technique. The differences are that cylindrical core plugs are used instead of crushed samples and confining pressure is applied in the gas expansion technique (Cui et al., 2009; Peng and Loucks, 2016). Laboratory experiments

are straightforward for permeability determination. The disadvantage is that the results from different experiments are often inconsistent (Naraghi and Javadpour, 2015).

### 3.2 Numerical methods

The numerical methods are visual computational simulation that can provide higher temperature and pressure that consist with actual formation conditions, and reconstruct and simulate microporous media (Sun et al., 2023b; Cai et al., 2024b). MD method, LBM and direct simulation Monte Carlo are particle-based methods that are widely used in numerical simulation.

(1) MD method is built on Newton mechanics to simulate the dynamic information of all molecules in a single cell, which is suitable to simulate the fluid movement in nanoscale porous materials (Yu et al., 2019; Zhao et al., 2022). Many scholars have studied pore structure, gas transport, gas adsorption, gas storage and other fluid flow characterization in nanopores using MD method (Zhai et al., 2014; Chen et al., 2020; Yu et al., 2020). However, the computational cost of MD method is expensive when the pore width is larger than 10 nm, which will limit its application in simulation (Li et al., 2018a).

(2) LBM is a developing and intriguing numerical method that has been widely applied in microscale gas flow regions (Liu et al., 2021; Zhang et al., 2021; Zhao et al., 2023). The Lattice Boltzmann equation (LBE) can be derived directly from the continuous Boltzmann equation, which contains two fundamental terms: Collision and streaming (Cheng et al., 2021). Hence the generalized LBE is also called the multiple relaxation time model which is one of the collision models (Li et al., 2018a). LBE is adept in dealing with complex boundary and simple simulation algorithms. However, the disadvantage of LBE is that it requires reference data like from MD to tune some parameter values (Zhao et al., 2022).

(3) Direct simulation Monte Carlo is a mesoscopic method like LBE between microscopic and macroscopic perspectives tracking the motion of representative particles in physical space to simulate a gas stream probabilistically (Yousefi-Nasab et al., 2022). It is more suitable for modeling dilute gas flows than MD and LBE (Yousefi-Nasab et al., 2022; Zhao et al., 2022). Some new methods in the mechanism of collision and tracking of particles make it useful for investigating of gas flow and permeability in microscale (Ewart et al., 2009; Mohammadmoradi and Kantzas, 2016).

### 3.3 Analytical methods

The analytical methods do not need complex and expensive apparatus as the laboratory experiments and resolve the computational problems faster than the numerical methods. Based on some reasonable assumptions, the analytical methods can help determine the effect of critical factors on gas flow (Wu et al., 2015a; Sun et al., 2018b). The analytical methods can be considered as the most widely used one in the three methods of apparent permeability determination. Scholars can integrate multiple gas flow mechanisms and physical properties altogether according to specific simulation conditions.

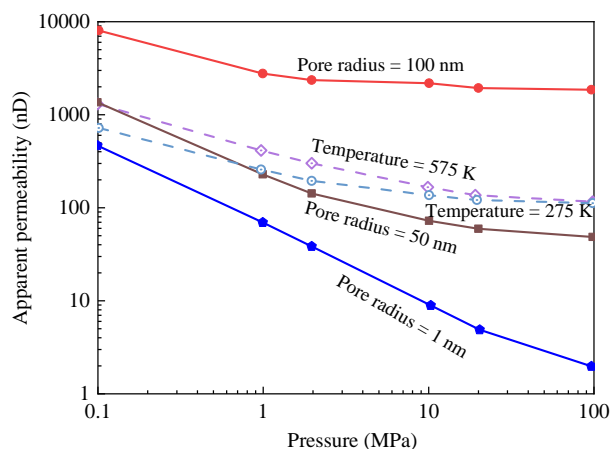
Various mathematical models and relevant research progress in analytical model development have been established which will be reviewed emphatically in section 4.

## 4. Mathematical models and influencing factors

### 4.1 Mathematical models

Mathematical models are the basis of the gas flow and apparent permeability determination in microscale porous medium. There are two types of the models can be concluded. The first type of models modifies the slip boundary condition of the continuity model to account for additional gas transport mechanisms. The second type of models superimposes different gas transport mechanisms by giving them corresponding weight coefficients. The 2<sup>nd</sup>-type models can be divided into two groups: (1) Superimposing gas transport regimes such as slip flow and Knudsen diffusion of bulk gas in inorganic nanopores; (2) combining the gas transport mechanisms within inorganic (bulk gas) and organic nanopore (adsorbed gas) systems to receive a total apparent permeability. Numerous scholars have reviewed models of gas transport (some of these typical models are summarized in Table S1 of Supplementary file).

A model for gas transport in porous media considering slip effect was proposed by Klinkenberg (1941), which can be seen as the basis of type I models. Fick's law is a classical and straightforward approach to gas diffusion which is also a basic law for many models. Stefan-Maxwell equation is an extension of Fick's law for a multicomponent mixture (Baehr, 1990). However, both Fick's law and the Stefan-Maxwell equations are applied to gas diffusion in open spaces and have serious limitations in low permeability porous media (Webb and Pruess, 2003). Then the advective-diffusive model and the dusty-gas model are developed for gas transport in porous media. In the advective-diffusive model, the advection calculated by Darcy's law and the diffusion calculated by Fick's law, slip effects and Knudsen diffusion are linearly added with a corrected Klinkenberg parameter (Abriola and Pinder, 1985; Pruess, 1991). In contrast, the dusty-gas model theoretically evaluates the coupling effects between ordinary diffusion, Knudsen diffusion, and advection (Webb and Pruess, 2003). Bravo (2006) shows that both the advective-diffusive model and the dusty-gas model will underpredict cumulative flow in a homogeneous case with permeability of 1  $\mu\text{D}$  (Freeman et al., 2011). Wu and Persoff (1998) presented a set of new analytical solutions considering slippage effects at low-pressure conditions. Then Beskok and Karniadakis (1999) constructed a model based on a unified Hagen-Poiseuille equation for gas transport in cylindrical capillaries considering all bulk gas flow mechanisms. Based on Beskok and Karniadakis's model: Civan (2010) proposed a model by considering tortuosity, rarefaction factor, porosity, intrinsic permeability and gas slippage; Xiong et al. (2012) presented a model by considering both free gas transport and adsorbed gas surface diffusion; Wang et al. (2017) introduced a real gas transport model by considering monolayer and multilayer adsorption, and surface diffusion and free gas flow. Anderson et al. (2014) modified the slip boundary condition based on a continuous flow model



**Fig. 7.** The variation trend of apparent permeability under different pressures (the solid lines) and temperatures (the dashed lines) referenced from Zhang et al. (2018b, 2018c) and Akilu et al. (2021).

according to experiment data. Though the type I models have developed for a long time, most of them are not really adapted for flow regime at a higher Knudsen number (Barber and Emerson, 2006; Zhang et al., 2012).

The type II models can contain more flow mechanisms and specific influence factors. There are many models have been proposed: Ertekin et al. (1986) developed a model for ideal gas based on Darcy flow and molecular Fickian diffusion. Liu et al. (2002)'s model considered the continuum flow and Knudsen diffusion. Javadpour (2009) proposed a classical model based on the Maxwell theory linearly superposing the continuum flow and Knudsen diffusion. Several modifications of Javadpour's model have been made by other scholars latterly: Azom and Javadpour (2012) proposed a dual-continuum model taking the real gas effect into account; Darabi et al. (2012) modified Javadpour's model by considering the effect of pore wall roughness; Ma et al. (2014) also considered the real gas effect but no combination of different gas transportation mechanisms. Sakhaee-Pour and Bryant (2012) superposed free molecular diffusion and slip flow linearly to put forward a gas transport model. Singh and Javadpour (2013) proposed a model considering advection and diffusion flow under a low Knudsen number condition. Rahmanian et al. (2013) proposed a model by describing the weighted contribution of the continuous flow and Knudsen diffusion. Singh et al. (2013) put forward an apparent permeability model by linearly superposing viscous flow and Knudsen diffusion with no empirical coefficient. Wu et al. (2015a) proposed a model for real gas considering the weight coefficients of slip flow and Knudsen diffusion. Sun et al. (2018a) established a comprehensive non-empirical model for viscous flow through inorganic shale nanopores considering real gas effect, water film thickness and stress dependence. The above models contain various bulk gas transportation regimes but with no consideration of adsorbed gas motion mechanisms. Models superpose both bulk gas and adsorbed gas transportation regimes have come to be proposed. Wu et al. (2016) considered slip flow, Knudsen diffusion and surface diffusion of adsorbed gas to construct a combined model. Li et al. (2017a) established a model com-

bined inorganic and organic nanopores by considering the continuum flow mechanism, and surface diffusion and desorption mechanisms of adsorbed gas. Zhang et al. (2018c) proposed a model by considering viscous flow, Knudsen diffusion of bulk gas, and the surface diffusion of adsorbed gas. Huang et al. (2018)'s permeability model contained viscous flow, slip flow, and Knudsen diffusion of bulk gas, and the surface diffusion of adsorbed gas. Shen et al. (2018b) superposed slip flow and Knudsen diffusion of bulk gas, and surface diffusion and adsorption of adsorbed gas to construct a model for slit nanopores. Obviously, the gas transport models for nanopores have been well established in abundance and only some of them are introduced in this section. However, these models have their own construction premises and limitations so that need to be proposed and used at a suitable condition.

## 4.2 Influencing factors

Gas transport within nanopores is governed by various factors, each contributing significantly to the behavior of gases in tiny spaces. Key elements include pressure and temperature, which are fundamental in determining gas dynamics. Additionally, the distribution of pore sizes is crucial, as it directly affects how gas moves through the nanopores (Cai et al., 2018). The real gas effect, which considers the non-ideal behavior of gases under certain conditions, also plays a vital role (Wu et al., 2017b; Sun et al., 2018b). Stress dependence, which refers to how the physical stress in the surrounding environment impacts gas transport, is another important factor. In addition to these factors, various gas flow mechanisms contribute to the overall transport process (Cai et al., 2019; Zhang et al., 2019). To understand the impact of these diverse factors comprehensively, sensitivity analysis is typically performed once a model is developed. This analysis helps in evaluating and quantifying the influence of each factor on the gas transport within nanopores, providing valuable insights for further research and practical applications.

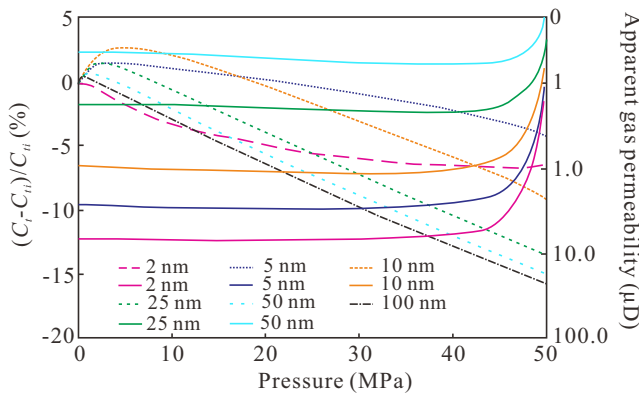
### 4.2.1 Pressure and temperature

The effect of pressure on the apparent permeability is complicated (Cui et al., 2022a). Usually, the apparent permeability increases with decreasing pressure, as shown in Fig. 7 and solid lines in Fig. 9. Other studies indicate that the apparent permeability increases first and then decreases with increasing pressure, as shown in Fig. 8 and dotted lines in Fig. 9. The influence of pressure is intricately connected to both pore size and gas flow mechanisms, resulting in a complex impact on the apparent permeability. At relatively low pressure, an increase in temperature leads to an increase in apparent permeability. However, this temperature effect becomes less pronounced as the pressure rises, especially at high pressures (Akilu et al., 2021).

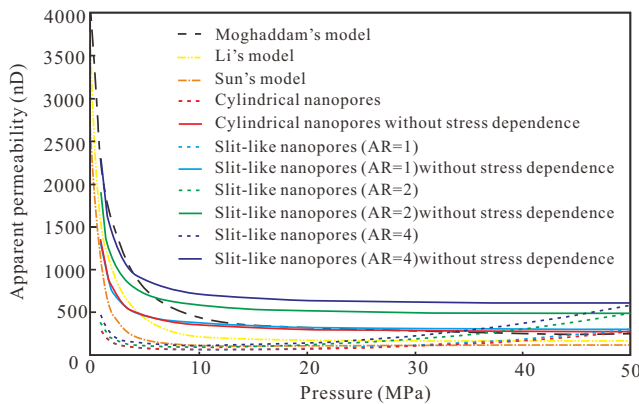
### 4.2.2 Real gas effect

The real gas effect on gas transportation cannot be ignored under high pressure condition and when a gas molecule size is comparable with nanopore width (Yin et al., 2017; Li et al., 2018b). Some study results show that the real gas effect





**Fig. 8.** The real gas effect on total flow conductance and apparent gas permeability referenced from Wu et al. (2016) and Li et al. (2020b) ( $C_t$  is the total real gas flow conductance, s;  $C_{ti}$  is the total ideal gas flow conductance, s; the dashed lines and solid lines represent total flow conductance and apparent gas permeability, respectively).



**Fig. 9.** Effect of stress dependence on the apparent permeability referenced from Moghaddam and Jamiolahmady (2016), Sun et al. (2017, 2018a) and Li et al. (2020b) (AR is the aspect ratio of the inorganic pores, dimensionless).

can increase the gas transport capacity (Wang and Li, 2007; Ma et al., 2014). The real gas effect influences the gas transport process by affecting the molecular mean free path and adsorption capacity. Wu et al. (2016) discussed the real gas effect on surface diffusion, slip flow and Knudsen diffusion. Their research demonstrated that the real gas effect has various impacts on gas transport in nanopores. Specifically, it increases slip flow and Knudsen diffusion by extending the gas molecular mean free path. Under high-pressure conditions, it decreases slip flow due to an increased repulsion between gas molecules. Additionally, it weakens the gas adsorption capacity and results in a decrease in surface diffusion. The consideration of the real gas effect is crucial, as it can lead to an exaggeration of the total flow conductance when omitted (Fig. 8).

#### 4.2.3 Stress dependence

The stress dependence is an important factor (Wang et al., 2017; Feng et al., 2022) as its effect becomes evident when the formation pressure is lower than the initial formation

pressure influencing the entire production process. The apparent permeability will be significantly overestimated when the stress dependence is not considered as shown in Fig. 9. The results also reveal that the effect of stress dependence is higher for slit-like nanopores than cylindrical nanopores.

#### 4.2.4 Water content

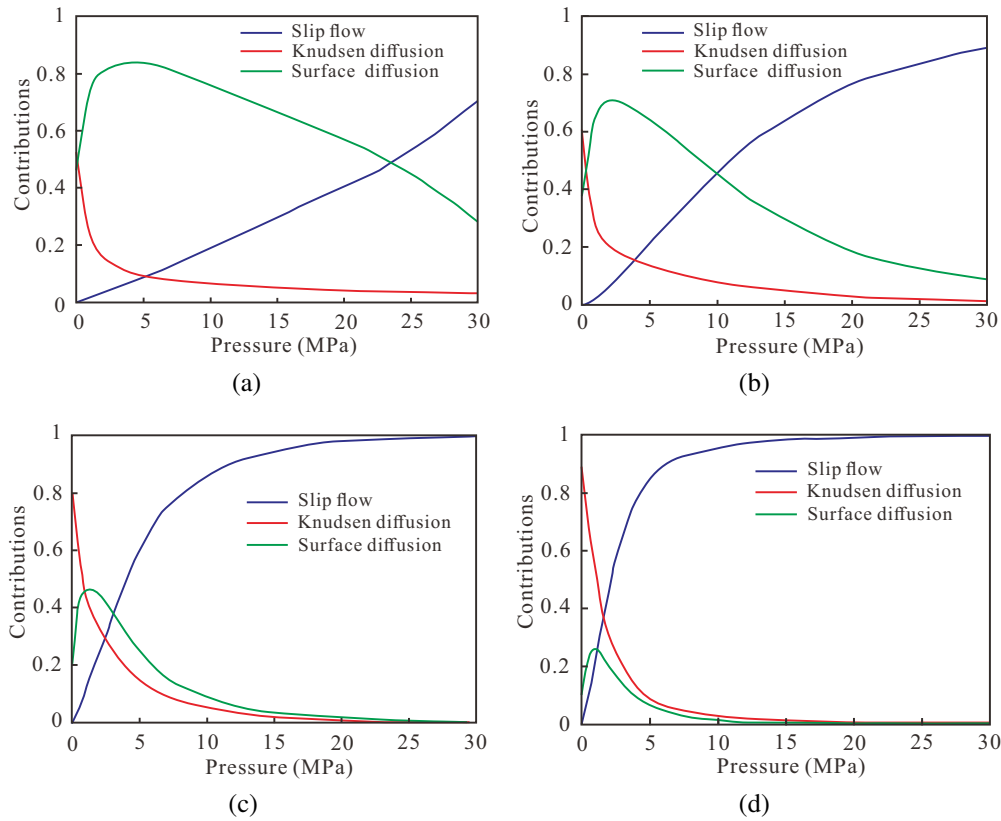
Water can be stored as adsorbed water film at inorganic pore walls through structural and electrostatic forces and hydrogen bonds (Harrington and Horseman, 1999; Fu et al., 2022) or free water in larger pores (Tian et al., 2020; Mu et al., 2024). The existence of water can shrink or block the effect pore size and lead to a decrease in the apparent permeability (Zhang and Yu, 2019; Cai et al., 2024a). Water content in shale has a significant influence on gas transport (Guo and Fall, 2021; Lyu et al., 2022). The apparent permeability decreases with the increasing relative humidity at a certain pressure, with this trend being more pronounced under low-pressure conditions. Although the presence of water can influence the apparent permeability, many studies indicate that it does not significantly affect gas capacity and can often be neglected in most models (Sun et al., 2018a; Akilu et al., 2021).

#### 4.2.5 TOC and pore size distribution

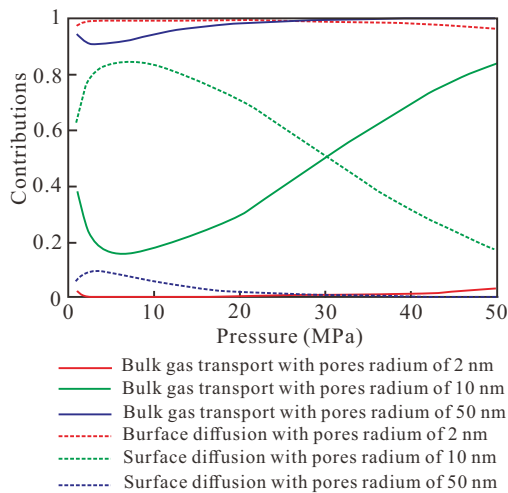
The effect of total organic carbon (TOC) on the apparent permeability is closely related to the gas flow mechanisms (Mu et al., 2023). The total apparent permeability decreases with increasing TOC under higher pressure but increases under lower pressure (Li et al., 2020a). This is because slip flow is the dominant flow mechanism under high pressures and decreases with TOC; while the surface diffusion which usually occurs in organic pores, dominates under low pressures and increases with TOC. Wang et al. (2018) and Naraghi and Javadpour (2015) concluded the effect of pore size distribution on the apparent permeability in organic and inorganic porous media. The behavior of apparent permeability for organic pores varies with pressure conditions: Under higher pressure, there is a noticeable increase in apparent permeability as the standard deviation rises. However, this variation in permeability with standard deviation is minimal under lower pressure conditions. In contrast, the apparent permeability for inorganic pores consistently increases with the standard deviation across all pressure conditions. This distinction highlights the different responses of organic and inorganic pores to pressure changes in terms of their permeability characteristics (Zhang et al., 2020).

#### 4.2.6 Different gas flow mechanisms

As evident from the discussion above, numerous factors that affect apparent permeability are intricately linked to the gas flow mechanisms. Section 4 of this paper provides a comprehensive exploration of various gas flow regimes through microscale porous media. Several scholars have dedicated their research to understanding the contributions of different gas flow mechanisms to the overall apparent permeability. While the critical pressure and pore radius may vary, a prevailing consensus in most studies suggests that surface diffusion of



**Fig. 10.** The contributions of different gas flow mechanisms on apparent permeability referenced from Gao et al. (2021). With pores radius of (a) 10 nm, (b) 20 nm, (c) 50 nm and (d) 100 nm.



**Fig. 11.** The contributions of bulk gas transport and surface diffusion on apparent permeability, referenced from Wang et al. (2018) and Li et al. (2017a).

adsorbed gas predominantly governs total gas flow under conditions of low pressure and larger pore sizes (Figs. 10(a), 10(b) and 11). Conversely, either slip flow or bulk gas flow typically determines the total apparent permeability under conditions of high pressure and larger pore sizes (Figs. 10(c), 10(d) and 11) (Wu et al., 2016; Li et al., 2017a; Gao et al., 2021).

## 5. Conclusions

A comprehensive understanding of gas transport in microscale porous media is vital for the assessment and exploitation of tight rock reservoirs, such as shale gas reservoirs. This review serves as an introduction to gas flow within nanopores, with a focus on gas transport regimes and the existing mathematical models.

Fluid flow mechanisms within nanopores play a pivotal role in determining the permeability of porous media. Section 2.2 provides a detailed introduction to the principles and governing equations governing gas flow mechanisms. The coexistence of diverse gas flow regimes within nanopores forms the theoretical foundation for gas transport models and significantly influences the apparent permeability of nanoporous media.

There are three primary methods for measuring apparent permeability: Laboratory experiments, numerical techniques, and analytical approaches. Among these, analytical methods are the most widely employed for determining apparent permeability. Mathematical models form the theoretical foundation for these apparent permeability measurement methods, especially in the case of analytical methods. They are thoroughly summarized and detailed in section 4.1.

A wide array of models describing gas transport within nanopores that can be broadly classified into two types (as indicated in Supplementary file). Notably, models that combine

various gas transport mechanisms by assigning them corresponding weight coefficients have been extensively reported. Multiple factors, including pressure, temperature, pore size distribution, stress dependence, the real gas effect, and gas flow mechanisms, can influence the establishment and accuracy of these models. Among these factors, gas flow mechanisms are of fundamental importance and require careful consideration when developing a model.

Multiple flow mechanisms and complex influencing factors make difficulties in research of gas transport in low-permeability rocks. Mathematical model is a kind of effective method of gas transport research, and it is crucial to acknowledge that each model possesses specific limitations and hypothetical premises. Thus, the ongoing endeavor to establish more comprehensive and generalized models of gas transportation remains imperative.

## 6. Recommendations and outlook

There are exciting opportunities to advance current methodologies and models in enhancing the study of gas transport mechanisms in nano-porous media, particularly in shale gas reservoirs. Currently, most models use pure gases such as He, CH<sub>4</sub>, and CO<sub>2</sub>, but the real scenario in natural shale gas reservoirs is far more complex, involving a diverse mix of gases. Incorporating realistic gas phases or components that mirror those found in actual reservoirs into the mathematical models can significantly improve the reliability of these models. For example, water and CO<sub>2</sub> are often considered in the study of migration mechanisms in the transport of gas mixture in shales. These multi-gases systems are also included in the micro-simulation study in porous media. This approach promises a more accurate analysis of shale gas transport mechanisms and opens avenues for groundbreaking discoveries in gas extraction and management techniques.

Furthermore, rethinking the assumptions about pore uniformity in current gas transportation models presents another thrilling prospect. Gas transport in nano-porous media is intricately linked to the variations in pore sizes. By integrating a detailed understanding of pore size distributions into these models, researchers can gain deeper insights into the subtleties of gas movement through these complex structures. This could lead to the development of more efficient and environmentally sustainable methods of gas extraction and usage. The shift towards models that reflect the real complexities of shale gas reservoirs not only advances our scientific understanding but also aligns with the growing need for innovative solutions in energy resource management. It makes this field both challenging and exciting for future research endeavors.

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## Supplementary file

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## Conflict of interest

The authors declare no competing interest.

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