Pore-scale prediction of transport properties in reconstructed nanostructures of organic matter in shales

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Abstract

Size, morphology and distributions of pores in organic matter of shale matrix are discussed based on high resolution images from experiments in the literature. 250 nanoscale structures of the organic matter are then reconstructed by randomly placing pore spheres with different diameters and overlap tolerances. Effects of porosity, the mean diameter and the overlap tolerance on void space connectivity and pore size distribution are studied. Furthermore, a pore-scale model based on the lattice Boltzmann method developed in a previous study is used to predict the Knudsen diffusivity and permeability of the reconstructed organic matter. The simulation results show that the mean pore diameter and overlap tolerance significantly affect the transport properties. The predicted Knudsen effective diffusivity is compared with Bruggeman equation and it is found that this equation underestimates the tortuosity. A modified Bruggeman equation is proposed based on the simulation results. The predicted intrinsic permeability is in acceptable agreement with Kozeny-Carman (KC) equation. In addition, the apparent permeability is determined based on Knudsen diffusivity and intrinsic permeability predicted. The apparent permeability is compared with that obtained with various correlations in the literature. Knudsen's correlations match best with our numerical results and are recommended for calculating the apparent permeability.

Keyword: Shale; Organic matter; Knudsen diffusion; Permeability; Diffusivity; Lattice Boltzmann method

1. Introduction

Over the past decades, advanced techniques such as horizontal drilling and multi-stage hydraulic fracturing greatly promote the exploitation of shale gas from fine grained sedimentary rocks called shale or mudstone [1]. With hydraulic fracturing, both shale matrix and fracture systems exist inside the shale gas reservoirs [2]. Consequently, four kinds of porous systems can be identified in shale reservoirs after hydraulic fracturing, including hydraulic fractures, natural fractures, pores in the inorganic minerals, and pores in the organic matter [3-5]. Morphology of these porous systems at different scales is not well understood, which is very important for characterizing the storage, transport and production of shale gas in shale reservoirs.

Shale matrix is composed of organic matter and inorganic minerals such as clay, quartz, calcite and pyrite [6-12]. The organic matter is the source of shale gas and plays an important role in shales. It adsorbs gas as well as stores free gas (shale gas is also stored in other porous systems mentioned above). The weight percentage of the organic matter in shales, called total organic content (TOC), is an important indicator of the gas reserve. It is found that the amount of both adsorbed gas and free gas increases as the TOC increases [3]. Pores are widely observed in the organic matter, which are dominantly of nanoscale, with diameters in the range of a few nanometers to a few hundred nanometers [6]. In some shale plays, most pores in the shale matrix are associated with organic matter [6], and the permeability of the organic matter is of great importance for shale gas transport from the matrix to the fracture network [3]. The organic matter can be considered as an entirely separate porous system that is distinct from surrounding inorganic matter, which greatly affects the petrophysical properties of shale matrix [8]. Due to nanoscale characteristics of the shale matrix, Darcy law, which is widely adopted in the conventional formation, cannot realistically describe the variety of the relevant flow regimes other than the viscous flow, such as slip flow and Knudsen diffusion [13-17].

To date, petrophysical properties of shale matrix remain poorly understood, which is of significant importance for revealing the transport mechanisms as well as economically assessing the storage of shale gas in shale reservoirs [8]. Advanced experimental techniques have been employed to observe the

nanoscale structures of shale matrix [6-12]. Particularly, scanning electron microscopy (SEM) combined with focused ion beam (FIB) milling allows one to directly visualize the nanoscale structures of shales on high quality flat surfaces [8]. It has been revealed that TOC, pore morphology, porosity and pore size can differ remarkably between shale plays and even in the same play [3, 6-9]. This scenario further complicates the investigation of petrophysical properties of shale matrix.

In our previous studies [18], we developed a nanoscale numerical model based on the lattice Boltzmann method (LBM) to study Knudsen diffusion and fluid flow in shale structures reconstructed from shale samples in Sichuan Basin of China. We also developed a representative elementary volume (REV)-scale generalized LB model for fluid flow through tight porous media with slippage [19]. In the present study, we further apply the LB model developed in [18] to study Knudsen diffusion and gas flow in the organic matter. The present study differs from our previous study [18] in two aspects. First, while previous study was about shale matrix, the emphasis in this study is on transport phenomena in the organic matter. The organic matter is an integral constituent of shale, and very recently pores in the organic matter have been suggested to be an important component of the pore network in shale matrix [3, 6, 8]. Understanding transport processes and properties of organic matter is critical, because in the organic matter considerable amount of shale gas is stored (free gas in nanopores, adsorbed gas on walls of nanopores and dissolved gas in solid organic matter) and several important physicochemical processes take place (solid diffusion, desorption and Knudsen diffusion) [13]. Second, compared with our previous study [18] where only four porous structures were generated, as many as 250 porous structures of the organic matter are reconstructed to conduct comprehensive sensitivity investigations of effects of porosity, pore diameter and pore overlap on the pore connectivity, tortuosity and transport properties of the organic matter. Because the existence of abundant nanopores in the organic matter greatly affects the shale gas generation, migration and production, a separate study to explore the gas transport mechanism in and predict the effective transport properties of the organic matter is warranted.

The remaining of the present work is arranged as follows. We first describe the reconstruction processes of the geometries of the organic matter in Section 2. The numerical method for predicting

transport properties is introduced in Section 3. Then, in Section 4 structure characterization of the reconstructed structures is performed including porosity, pore size distribution and void space connectivity. Predicted effective Knudsen diffusivity and intrinsic permeability are also presented in this section. Then apparent permeability is determined based on the predicted transport properties, and are compared with existing correlations in the literature. Finally some conclusions are drawn in Section 5.

2. Reconstruction of the organic matter

Very recently FIB-SEM technique allows visualization of the nanoscale structures of shales on high quality flat surfaces [3, 6-12], which has provided new insights in the nanoscale structures of the kerogens. It is found that organic matter usually presents as discrete grains in the shale matrix surrounded by inorganic matter [6]. The pore structures in the organic matter are really complex, which are affected by several factors including maturity, organic composition and late localized compaction [6, 9, 12]. Consequently, even answers to the porosity are elusive. Loucks et al. reported a range of porosity 0%~30% in the organic matter of Barnett shales, North Texas [6], while Sondergeld et al. [8] reported a porosity of 50%. The morphology of the nanopores in the organic matter is also diverse, including round, ellipsoidal, triangular, prolate, polyhedral and irregular shapes [6, 8]. Nanopores are generally nonequant to some degree [6]. The pore size is in a wide range, from a few nanometers to a few hundred nanometers [3, 6-8]. The distributions of the pores also cannot be generalized, nevertheless in most cases the pores are quite randomly and uniformly distributed [6, 8].

In the present study, we assume that the void space in the kerogen can be described by uniformly distributed spheres. This assumption is based on the experimental observations (Figs. 5-6 in [6]; Fig. 19 in [8]; Fig. 9 in [7]). The general scheme to reconstruct the organic matter is to randomly place pores with spherical shape into the computational domain. Certain parameters required to be specified before the reconstructions are porosity ε , the radius of each sphere d , the probability for the spheres to overlap p_0 and the overlap tolerance ζ . The overlap tolerance, defined as the volume of the overlapping region of a

sphere with another sphere to its total volume, determines the maximum overlapping volume. The structure generation algorithm is described as follows [20]:

1) The first pore sphere is generated in the computational domain. Random number generators are employed to determine its centers and diameter;

2) A random number generator is employed to determine whether or not the next sphere is allowed to overlap with existing pore spheres in the computational domain. Further, a random number generator is used to generate sphere centers and diameter of a trial pore. a) If the pore sphere is required to overlap with existing spheres, it must overlap with an existing sphere and the overlapping portion should be less or equal to the overlap tolerance; b) otherwise, it can be separated from other spheres, or if it overlaps with any existing spheres, the overlapping portion cannot exceed the overlap tolerance;

3) Repeating Step 2 until the specified porosity has been achieved.

The diameter of pore spheres follows a uniform distribution ($\langle d \rangle - 15\text{nm}$, $\langle d \rangle + 15\text{nm}$), with $\langle d \rangle$ the mean diameter chosen as 30nm, 45 nm and 60 nm. The porosity ranges between 0.1 and 0.55, with an interval of 0.05, based on the experimental results of Loucks et al. [6] and Sondergeld et al. [8]. ξ is set as 0.1, 0.2 and 0.3, respectively. The structure reconstruction algorithm relies on a random process. Therefore, the geometry as well as the properties might vary from one generated structure to another even if the input parameters are identical. To consider such variability, it is necessary to generate several geometries from the same set of input parameters. In the present study, five structures are generated for each configuration. Consequently, totally 250 nanoscale structures of organic matter are reconstructed (Only $\langle d \rangle = 45\text{nm}$ is considered for different ξ values). A 3D representation of a geometry is given in Fig. 1 as an example with $\langle d \rangle = 45\text{nm}$, $\xi = 0.2$ and $\epsilon = 0.4$. The computational domain is a cube with size of $L_x \times L_y \times L_z$ with $L_x = L_y = L_z = 300\text{nm}$, and is discretized by $200 \times 200 \times 200$ lattices, leading to a resolution of 1.5nm per lattice. As shown in Fig.1, the pore spheres with different sizes are randomly distributed in the domains, and most of them are overlapped with each other. Loucks et al. [6] experimentally observed that narrow throats with diameter peak of 10~15nm between larger pores help to connect the void space in the organic matter (Fig. 6 in [6]). High resolution backscattered electrons (BSE) images of a region of

kerogen in Horn River provided by Curtis et al. [7] (Fig. 9 in [7]) also shows that the organic matter contains both large and small pores; and large pores are perforated with numerous smaller pores. In our reconstructed structures, the overlapping regions with smaller pore size can be considered as “narrow throats” or “small pores” which connect the large pore spheres. Changing the overlapping tolerance can control the size of the throats. Obviously, such overlapping is critical for the connectivity between large pore spheres as well as the transport processes in the organic matter. [Note that the reconstruction method here is not a general one for various pore types in the organic matter, but is specific for the pore morphology of large spherical pores connected by smaller pores widely observed in experiments \[6, 7\].](#)

3. The lattice Boltzmann method

During the past few decades, the LBM has developed into a powerful technique for simulating fluid flow and transport processes and is particularly successful in applications involving interfacial dynamics and complex geometries [21-25]. In the present study, intrinsic permeability and effective Knudsen diffusivity of the organic matter are numerically predicted using the LBM. For fluid flow, the multi-relaxation-time (MRT) model [26, 27] (See Ref. [18] for more details) is adopted in the present study to simulate fluid flow in the reconstructed organic matter. Pressure gradient is applied along the flow direction while other four boundaries are fully periodic. For mass transport, in our previous study [18] a LB mass transport model was developed for simulating Knudsen diffusion where the effects of the local pore diameter are taken into account. The key idea of this model is adopted a pore diameter dependent collision time (relaxation time is related to diffusivity in the LB mass transport model, See Ref. [18] for more details) for each pore node. This LB mass transport model is adopted in the present study to study the Knudsen diffusion in the organic matter. Besides, D3Q19 lattice model is adopted due to the complex structures studied [28-30]. Concentration gradient is applied along x direction while y and z directions are fully periodic. [Zero flux boundary condition is applied at the pore walls.](#)

Intrinsic permeability, which only depends on the porous structures and is not affected by the flow condition, is calculated based on the Darcy's Law [31] after the flow field is obtained using the MRT-LBM with no-slip boundary condition on the fluid-solid surface [31]

$$J_d = -\frac{\rho k_d}{\mu} \nabla p \quad (1)$$

where the flow flux J_d equals to $\rho \langle u \rangle$ with $\langle u \rangle$ as the volume-averaged fluid velocity along flow direction. The effective Knudsen diffusivity $D_{K,eff}$ along the x direction is calculated by

$$D_{K,eff} = \frac{(\int_0^{L_y} \int_0^{L_z} (D_K \frac{\partial C}{\partial x})|_{L_x} dydz) / L_y L_z}{(C_{in} - C_{out}) / L_x} \quad (2)$$

where C_{in} and C_{out} is the inlet and outlet concentration, respectively. $|_{L_x}$ means local value at $x=L_x$.

In the LBM framework, the simulation variables are in lattice units instead of physical units. The physical variables such as permeability k_p and diffusivity D_p (subscript “p” denotes “physical space”) can be calculated from the quantities in lattice system (subscripted by L) by the following expression

$$\frac{D_p}{\Delta x_p^2 / \Delta t_p} = \frac{D_L}{\Delta x_L^2 / \Delta t_L}, \quad \frac{k_p}{\Delta x_p^2} = \frac{k_L}{\Delta x_L^2} \quad (3)$$

Δx_p and Δt_p are unity in the LBM. After the computational domain is defined and discretized, the physical length of a lattice Δx_p can be determined.

Details of the validation can be found in our previous study [18], and are not repeated here for brevity.

4. Results and discussion

4.1 Characteristics of the nanoscale structures

Porosity and pore size distribution (PSD) of the organic matter are critical for both gas storage and flow quantification. Porosity studied ranges in 0.1~0.55, as mentioned in Section 2 based on the experiments [6, 8]. A 13 direction averaging method [18, 20] is adopted to determine the pore size of each pore cell in the reconstructed organic matter. Fig. 2 shows the PSD for the reconstructed structures with

$\langle d \rangle = 45\text{nm}$ and $\xi = 0.1$ for different porosities. The PSD for all the cases is unimodal and can be approximately described as a normal distribution. Both the mean and the standard deviation go up as the porosity increases.

Since shale gas transports through the connected pores in the organic matter, connectivity of the void space is therefore very important. For the reconstructed structures of the organic matter, “transport” and “dead” pore cells are distinguished using the connected phase labeling algorithm [18]. The connectivity of void space is defined as the ratio of the number of “transport” cells to the total pore cells. Fig. 3(a) plots the connectivity of the reconstructed structures for different porosities with $\xi = 0.1$. First, the connectivity increases as the porosity increases. At lower porosity, there are fewer spheres in the organic matter, which are sparsely distributed and are less likely to be connected with each other. Second, the discrepancy of the connectivity between different samples of the same porosity becomes larger as the porosity reduces. For the cases with $\langle d \rangle = 45\text{nm}$, when the porosity is lower than 0.15, all the pores are dead for the reconstructed structures, while for the porosity greater than 0.4, the connectivity is almost unity, meaning all the pores are “transport”. This is because fewer pores under lower porosity result in larger fluctuation of the void space. Finally, it can be seen that a higher diameter results in lower connectivity and larger discrepancy of the connectivity. The pores become to be connected when the porosity is greater than 0.15 for $\langle d \rangle = 30\text{nm}$, while for the structures with $\langle d \rangle = 60\text{nm}$, the minimum porosity rises to 0.25. This is because under the same porosity, there are less pore spheres in the organic matter for a higher diameter. Fig. 3(b) displays the effects of overlapping tolerance ξ , where all the cases are with $\langle d \rangle = 45\text{nm}$. It can be seen that as ξ increases, the connectivity decreases and the discrepancy of the connectivity goes up. This is because the pore spheres tend to aggregate under a higher overlap tolerance. On the whole, the results indicate that to obtain better inner-connected void space in the organic matter, both the pore size and the overlapping tolerance should be lower, especially under a low porosity.

4.2 Effective Knudsen diffusivity

Fig. 4 shows the concentration distribution within the organic matter with mean diameter of 45nm, porosity of 0.4 and overlap tolerance of 0.2. Based on the concentration field obtained, the effective diffusivity can be calculated using Eq. (2). Fig. 5(a) shows the effective diffusivity vs porosity for the organic matter with pore spheres of different mean diameter $\langle d \rangle$. In the figure, the overlap tolerance is 0.1 and the diffusivity is normalized by a reference diffusivity $D_{K,ref} = 1.31 \times 10^{-5} \text{ m s}^{-2}$, which is the Knudsen diffusivity with $d=60\text{nm}$ and $T=323$ according to our previous work [18]. The mean diameter greatly affects the effective diffusivity. Generally, a larger mean diameter generates a higher diffusivity. This is because larger spheres results in higher local Knudsen diffusivity. For the same porosity, larger pore spheres lead to higher fluctuation of the structures, thus result in higher discrepancy of diffusivity. Fig. 5(b) displays the effects of overlap tolerance on the effective Knudsen diffusivity, where the mean diameter $\langle d \rangle = 45\text{nm}$. The overlapping region is crucial for the connection of void space as well as the transport processes. As can be seen from Fig. 5(b), a higher overlap tolerance can enhance the mass transport. This is because the local transport within the overlapping region is the limiting factor, because the local pore size is smaller compared with that in the bulk pore spheres. The lower the overlap tolerance is, the smaller the overlapping region is, and hence the lower the local diffusivity is. The discrepancy for samples with the same input parameters increases as the overlap tolerance rises, which is because the pore spheres are more likely to aggregate with a larger overlapping tolerance. Finally, the predicted Knudsen diffusivity ranges from $10^{-9} \text{ m}^2 \text{ s}^{-1}$ to $10^{-6} \text{ m}^2 \text{ s}^{-1}$. To the best of our knowledge, there are no experiments particularly devoted to measure the diffusivity within the organic matter. Javadpour et al. reported a diffusivity of $4 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ in a shale sample [13] (The TOC and the distributions of the organic matter in the shale sample are not mentioned). Their measured value is in the range of our numerically predicted values.

Bruggeman equation has been widely used in the macroscopic models to calculate the effective diffusivity

$$D_{\text{eff}} = D \frac{\varepsilon}{\tau} \quad (4)$$

where τ is the tortuosity of a porous medium, and is set as $\tau = \varepsilon^{-0.5}$ in Bruggeman equation, leading to effective transport properties as a pure function of the volume fraction, namely, $D_{\text{eff}} = D\varepsilon^\alpha$ with $\alpha=1.5$ [32]. Although Bruggeman equation has been widely adopted, it was determined empirically from sphere packed porous media with high porosities, which therefore cannot reflect the complex structures of shales with lower porosities. As can be seen in Fig. 5, the Bruggeman equation greatly overestimates the effective diffusivity. Following the relationship $D_{\text{eff}} = D\varepsilon^\alpha$, it is found that α ranges 2.8~4.0 for the organic matter with different pore diameter and overlap tolerance based on our nanoscale simulation results; and the lower the porosity and the overlap tolerance are, the higher the α . This implies as the porosity and overlap tolerance decrease, the void space within the organic matter becomes more tortuous. Bruggeman equation greatly underestimates the tortuosity in organic matter, especially for lower porosity. Our numerical simulation results show that in the future macroscopic modeling, a higher α in the range of 2.8~4.0 is recommended to use in Bruggeman equation. Fig. 5 also shows the revised Bruggeman equation with $\alpha=2.8$ and 4.0, respectively. As shown in the Figure, they are in good agreement with values predicted by our simulations.

4.3 Intrinsic Permeability

Fig. 6 shows pressure and velocity vector distributions within the reconstructed organic matter with mean diameter of 45nm, porosity of 0.4 and overlap tolerance of 0.2. It can be seen that fluid pathway within the porous structures is very tortuous, and in the overlap region flow is relatively strong. Fig. 7(a) shows the intrinsic permeability vs porosity for organic matter with pore spheres of different mean diameter $\langle d \rangle$ where the overlap tolerance is 0.1, while Fig. 7(b) shows that for different tolerance with $\langle d \rangle=45$ nm. Similar to that of effective diffusivity, the intrinsic permeability increases as the porosity, mean pore diameter and overlap tolerance are increased. The intrinsic permeability predicted ranges $10^{-21}(10^{-6}\text{mD}) \sim 10^{-17}(10^{-2}\text{mD}) \text{ m}^2$. Also, there are no experiments particularly devoted to measure the permeability within the organic matter. Javadpour et al. [13] measured 152 shale samples from nine

reservoirs, and reported that a permeability peak at around 5.4×10^{-5} mD, and the permeability of 90% samples is less than 1.5×10^{-4} mD. Wang and Reed [3] plotted together the permeability of shales in north American with porosity of 0~0.1, and found that the permeability ranges from 1×10^{-12} mD to 1×10^{-2} mD. Our predicted intrinsic permeability of the organic matter is consistent with their studies.

The most adopted empirical relationship for predicting permeability is the KC equation [33]

$$k_d = A \frac{\varepsilon^3}{(1 - \varepsilon)^2} \quad (5)$$

with A is the KC constant and is set as $d^2 / 180$ for packed-spheres porous media, where d is the diameter of the solid spheres. Note that in the present study, the spheres represent the void space rather than the solid phase; nevertheless, in both cases, the permeability will increase as d increase for the same porosity. Hence, in the present study, Eq. (5) is still employed to predict the intrinsic permeability of the reconstructed organic matter with d chosen as the mean diameter $\langle d \rangle$ of the pore spheres. As shown in Fig. 7, the values of permeability predicted by KC equation present acceptable agreement with that obtained from our nanoscale simulations, especially for lower porosity.

4.4 Apparent permeability

Gas slippage phenomenon occurs when the mean free path of the gas is comparable to the character length of the domain. Klinkenberg [34] found that the gas permeability (apparent permeability) through a tight porous medium is higher than liquid permeability (intrinsic permeability), which is due to the slip of gas molecules on the solid surface. He proposed a first-order correlation for calculating the apparent permeability (gas permeability)

$$k_a = k_d f_c, f_c = \left(1 + \frac{b_k}{P}\right), \frac{b_k}{P} = \frac{4c\lambda}{r} \approx 4Kn \quad (6)$$

where f_c is the correction factor and P is the pressure. k_d is the aforementioned intrinsic permeability (See Section 4.3), which only depends on the porous structures of a porous medium and is not affected by the operating condition and fluid properties. b_k is the Klinkenberg's slippage factor, which depends on the

molecular mean free path λ , character pore size of the porous media r and the pressure [34]. Kn is Knudsen number, defined as the ratio between gas mean free path to the pore size. Based on Eq. (6), various expressions of b_k have been proposed in the literature, as listed in Table 1. Heid et al. [35] and Jones and Owens [36] proposed similar expressions relating b_k to k_d . Sampath and Keighin [37] and Florence et al. [38] developed a different form by relating b_k to k_d/ε . Klinkenberg's correlation is of first-order accuracy. Beskok and Karniadakis [39] developed a second-order correlation, and Civan [40] proposed a simplified expression for the rarefaction coefficient in [39]. This second-order correlation is also listed in Table 1.

In shale matrix, the transport behaviors of shale gas are combined results of viscous flow and Knudsen diffusion [13-16]. In our previous study, based on the dusty gas model (DGM), considering the total flux through a porous media as a combined results of viscous flow and Knudsen diffusion [41, 42], the following correlation for apparent permeability is derived [18]

$$k_a = k_d f_c, \quad f_c = \left(1 + \frac{D_{k,eff} \mu}{k_d P}\right) \quad (7)$$

In our previous studies [18], we have demonstrated that, for gas transport in a cylinder, the correction factor predicted by Eq. (7) agrees well with the Beskok and Karniadakis-Civan's correlation in a wide range of Kn , while the Klinkenberg's correlation greatly underestimates the correction factor for high Kn [43]. A new approach was thus proposed based on Eq. (7) to predict the apparent permeability of shale matrix [18]. That is, one can predict the intrinsic permeability and the Knudsen diffusivity of a porous medium, and then use Eq. (7) to determine the apparent permeability [18].

Fig. 8(a) shows the correction factor of the reconstructed organic matter predicted by our LB simulations. Pressure and temperature are set as 2500 psi (≈ 17236893 Pa) and 323K, under which the dynamic viscosity is 1.73×10^{-5} Pa s. In Fig. 8(a), as the mean pore diameter decreases or the overlap tolerance reduces, the correction factor becomes larger, indicating that the Knudsen diffusion plays a more significant role compared to viscous flow. Most of values of the correct factor are in the range of 1.3~2 with intrinsic permeability in the range of $2 \times 10^{-4} \sim 10^{-2}$ md. Particularly, for the case with

$\langle d \rangle = 30 \text{ nm}$ and tolerance $= 0.1$, values of the correction factor for low porosities with low permeabilities are greater than 10 and would be as high as 50, implying that the dominant transport mechanism is Knudsen diffusion.

Fig. 8(b) shows the comparisons between our simulation results and that predicted by various correlations. For the correlations listed in Table 1, porosity and intrinsic permeability obtained from our simulations are used to calculate b_k , and further to determine f_c based on Eq. (6). For Klinkenberg's correlation and Beskok and Karniadakis-Civan's correlation, Kn is required to calculate f_c . Mean free path is calculated by $\mu/p/(\pi RT/2M)^{0.5}$. The character pore size r of the reconstructed organic matter is not easy to be obtained. In the present study, the following expression proposed by Herd et al. is used to calculate r [35]

$$r = 8.886 \times 10^{-2} (k / \varepsilon)^{0.5} \quad (8)$$

The units of r and k are nm and mD, respectively. After r is determined, Kn can be calculated which can be further adopted in Klinkenberg's correlation and Beskok and Karniadakis-Civan's correlation to calculate f_c . As can be seen from Fig. 8(b), the correlations of Heid et al. and Jones and Owens greatly underestimate the correction factor. When calculating b_k by further taking the effects of porosity into consideration, the agreement between our simulation results and the correlations (Correlation of Sampath and Keighin's and correlation of Florence et al.) becomes better. The best agreement is observed for the Klinkenberg's correlation and Beskok and Karniadakis-Civan's correlation, both of which are based on the Knudsen number. Following Ziarani and Aguilera [43], the two correlations based on Knudsen number is called Knudsen's correlation. By comparing different correlations with data from Mesaverde formation, Ziarani and Aguilere [43] concluded that the Knudsen's correlations perform the best. Our results are in line with that of Ziarani and Aguilere. While Ziarani and Aguilere found that Knudsen's correlations underestimate the apparent permeability for low permeability shales, it can be observed in Fig. 8(b) that Knudsen's correlations still match with the simulation results even under low permeability. Therefore, based on Ref. [43] as well as the present study, Knudsen's correlations combined with Eq. (8)

are recommended to calculate the apparent permeability for organic matter. The consistence between our simulation results and experimental results in [43] suggests that our numerical model may be an efficient and effective alternative approach to evaluate apparent permeability of organic matter, given the difficulty in experimentally conducting permeability measurement for low-permeability porous media. Additionally, since both the effective Knudsen diffusivity and intrinsic permeability can be easily predicted using the standard LB models, our approach avoids directly solving slip flow in complex pore structures using LB slip flow models involving complicated slip boundary conditions and local viscosity-relaxation time relationships.

5. Conclusion

In this work, Knudsen diffusion and fluid flow through the organic matter in shale matrix are simulated using the LB models developed in our previous work. Based on the experimental observations in the literature, the nanoscale structures of the organic matter are reconstructed using a random sphere overlapping tolerance method. 250 samples of organic matter are reconstructed with different pore diameter, overlap tolerance and porosity. Effective Knudsen diffusivity and intrinsic permeability are numerically predicted based on the concentration and velocity fields obtained from the LB simulation, and are compared with the values calculated by the empirical equations. An equation, which considers the total flux as a combining result of viscous flow and Knudsen diffusion, is used to determine the apparent permeability. The calculated apparent permeability is also compared with various empirical correlations in the literature. The main conclusions of the present study are as follows.

1. The connectivity of the void space in the organic matter increases as the porosity increases. Under the same porosity, the connectivity of void space reduces as the pore diameter increases or the overlap tolerance increases.
2. The predicted Knudsen diffusivity ranges from $10^{-9} \text{ m}^2 \text{ s}^{-1}$ to $10^{-6} \text{ m}^2 \text{ s}^{-1}$. Bruggeman equation greatly underestimates the tortuosity of the organic matter. Following the relationship $D_{\text{eff}} = D\varepsilon^\alpha$, based on the

pore-scale simulation results in the present study, α in the range of 2.8~4.0 is recommended for calculating the effective diffusivity in the organic matter. The lower the porosity and the overlap tolerance are, the higher the α is, indicating more tortuous void pathways in the organic matter.

3. The predicted intrinsic permeability ranges $10^{-21}(10^{-6}\text{mD}) \sim 10^{-17}(10^{-2}\text{mD}) \text{ m}^2$. The Kozeny-Carman (KC) equation can be adopted to roughly estimate the intrinsic permeability of the organic matter for low or moderate porosities.

4. Transport behaviors of shale gas in the organic matter are combined results of viscous fluid flow and Knudsen diffusion, which can be described by Eq. (7). Apparent permeability of the organic matter can be calculated based on the effective Knudsen diffusivity and intrinsic permeability. The correlations of only using intrinsic permeability to calculate the Klinkenberg's slippage factor (correlations of Heid et al. and Jones and Owens) greatly underestimates the apparent permeability. Correlations further taking into consideration the effects of porosity (Correlation of Sampath and Keighin's and correlation of Florence et al.) can improve the prediction. The Knudsen's correlations (Klinkenberg's correlation and Beskok and Karniadakis-Civan's correlation) match the best with our numerical simulations, in line with the experimental study in the literature [43]. Therefore, Knudsen's correlations are recommended to calculate the apparent permeability of the organic matter.

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Figure caption

Fig. 1 A reconstructed geometry with mean diameter of 45 nm, porosity of 0.4 and overlap tolerance of 0.2. The green spheres are the pore spheres. The computational domain is a cube with size of 300×300×300nm, and is discretized by 200×200×200 lattices, leading to a resolution of 1.5 nm per lattice.

Fig. 2 The PSD for the reconstructed organic matters with $\langle d \rangle = 45\text{nm}$ and $\xi = 0.1$ for different porosities

Fig. 3 The connectivity of void space for different reconstructed organic matters: (a) effects of pore sphere diameter, and (b) effects of overlap tolerance

Fig. 4 Concentration distribution within the reconstructed organic matter with mean diameter of 45 nm, porosity of 0.4 and overlap tolerance of 0.2

Fig. 5 Effective Knudsen diffusivity for the reconstructed organic matters: (a) effects of pore sphere size, and (b) effects of overlap tolerance. The diffusivity is normalized by the Knudsen diffusivity with $d = 60$ nm and $T = 323$ K. The predicted Knudsen diffusivity ranges from $10^{-8} \text{ m}^2 \text{ s}^{-1}$ to $10^{-6} \text{ m}^2 \text{ s}^{-1}$. Revised Bruggeman equation with α ranges 2.8~4.0 are in good agreement with values predicted by our simulations

Fig. 6 Pressure and velocity vector distributions within the reconstructed organic matters with mean diameter of 45 nm, porosity of 0.4 and overlap tolerance of 0.2.

Fig. 7 Intrinsic permeability for the reconstructed organic matters: (a) effects of pore sphere size, and (b) effects of overlap tolerance. The intrinsic permeability predicted ranges $10^{-21}(10^{-6}\text{mD}) \sim 10^{-17}(10^{-2}\text{mD}) \text{ m}^2$. The value of permeability predicted by KC equation presents acceptable agreement with that obtained from our nanoscale simulations.

Fig. 8 The correction factor between apparent permeability and intrinsic permeability: (a) the correction factor based on the numerical results, and (b) comparison between the numerical results and existing empirical corrections

Table 1. Various empirical correlations in the literature

Literature	b_k	units
Heid et al., 1950, [35]	$11.419(k_d)^{-0.39}$	b_k : psi, k_d : mD
Jones and Owens, 1980 [36]	$12.639(k_d)^{-0.33}$	
Sampath and Keighin, 1982 [37]	$13.85(k_d/\varepsilon)^{-0.53}$	
Florence et al., 2007 [38]	$\beta(k_d/\varepsilon)^{-0.5}$ Membrane: $\beta=32.766$	
Beskok and Karniadakis-Civan's correlation [39-40]		
$f_c = (1 + \alpha(Kn)Kn) \left[1 + \frac{4Kn}{1 + Kn} \right], \alpha(Kn) = \frac{1.358}{1 + 0.170Kn^{-0.4348}}$		

Fig1

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