Apparent permeability prediction of organic shale with generalized lattice Boltzmann model considering surface diffusion effect

Junjian Wang^{a,b}, Li Chen^{c,b}, Qinjun Kang^{b,*}, Sheik S Rahman^a

^a*School of Petroleum Engineering, University of New South Wales, Sydney, NSW, Australia, 2033*

^b*Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM, USA, 87545*

^c*Key Laboratory of Thermo-Fluid Science and Engineering of MOE, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shanxi, China, 710049*

Abstract

Gas flow in shale is associated with both organic matter (OM) and inorganic matter (IOM) which contain nano-pores ranging in size from a few to hundreds of nano-meters. In addition to the non-continuum effect which leads to an apparent permeability of gas higher than the intrinsic permeability, the surface diffusion of adsorbed gas in organic pores also can influence the apparent permeability through its own transport mechanism. In this study, a generalized lattice Boltzmann model (GLBM) is employed for gas flow through the reconstructed shale matrix consisting of OM and IOM. The Expectation-Maximization (EM) algorithm is used to assign the pore size distribution to each component, and the dusty gas model (DGM) and generalized Maxwell-Stefan model (GMS) are adopted to calculate the apparent permeability accounting for multiple transport mechanisms including viscous flow, Knudsen diffusion and surface diffusion. Effects of pore radius and pressure on permeability of both IOM and OM as well as effects of Langmuir parameters on OM are investigated. The effect of total organic content and distribution on the apparent permeability of the reconstructed shale matrix at different surface diffusivity is also studied. It is found that the influence

*Corresponding author at: Earth and Environmental Sciences Division, LANL, Los Alamos, NM 87545

Email address: qkang@lanl.gov (Qinjun Kang)

of pore size and pressure on the apparent permeability of organic matter is affected by the surface diffusion of adsorbed gas. Moreover, surface diffusion plays a significant role in determining apparent permeability and the velocity distribution of shale matrix.

Keywords: shale gas, lattice Boltzmann method, surface diffusion

1. Introduction

Shale gas reservoirs contain a significant proportion of hydrocarbon energy, and the successful exploitation of such resource plays an increasingly important role in meeting world's demand for natural gas. Organic shale is known to be fine grained sedimentary rocks consisting of inorganic matter (IOM) and organic matter (OM) with pore sizes ranging from nano- to meso- scale[1][2], in each component of which are involved different flow mechanisms[3]. In the literature, gas flow on nano- to micro-scale in shale is often referred to as rarefied gas flow[4], where the mean free path of gas is comparable to the characteristic length of the micro-pores or throats. Gas flow in shale matrix usually leads to a deviation from the continuum theory[5]. Moreover, previous studies have confirmed that the amount of adsorbed gas constitutes about 20%-80% of the total gas in place of shale gas reservoir[6][7][8], and the surface diffusion of adsorbed gas is an important transport mechanism in these reservoirs[9][10]. A physics-based understanding of gas transport mechanism in shale including non-continuum behaviours and surface diffusion is essential for the development of accurate descriptive transport simulators to predict fluid flow and transport in shale.

For decades, the problem of modelling gas transport in narrow pores and confined spaces in shale has attracted considerable attention among petroleum engineers. Generally speaking, two approaches have been proposed to describe the gas transport and to calculate apparent permeability of organic shale. The first approach is to modify the non-slip boundaries in continuum model by accounting for slip boundary conditions. Beskok and Karniadaki[11] derived a unified Hagen-Poiseuille-type formula to take account of slip flow, transition flow and free molecular flow. Later, Civan[12] and Florence et al.[13] proposed different forms of rarefaction coefficient in Beskok-Karniadaki model. Xiong et al.[14] introduced a capillary model by adding the mass transfer of adsorbed gas into Beskok-Karniadaki empirical equation to study the impact of the adsorbed gas and surface diffusion on

gas apparent permeability. The second approach is the superposition of various transport mechanisms. Javadpour[3] combined slip flow and Knudsen diffusion into gas flux equation and derived an equation for apparent permeability. Freeman et al.[15] applied dusty gas model (DGM) to account for Knudsen diffusion in shale gas reservoir. Singh et al.[4] combined viscous flow with Knudsen diffusion in their non-empirical apparent permeability model(NAP), and validated the model with previous experimental data. The results show that the NAP can be used for Kn less than unity. Wu et al.[9] further proposed two weighted factors for viscous flow and Knudsen diffusion, respectively. The surface diffusion was also considered in their apparent permeability model.

The limitation of the application of analytical or semi-analytical models to gas flow in porous media is that the pore structure is usually relatively simple, such as capillaries[3][4][14]. Such simplification might produce erroneous results because the pore structures in shale are very complex, as detected by well-established characterization techniques such as SEM[1][16]. To improve this, different pore-scale models have been proposed to link the micro-structure of the porous media with fluid flow characteristics. Among them, the lattice Boltzmann (LB) method has gone through significant improvements over the past years and has become a viable and efficient substitute for conventional N-S solvers in many flow problems especially porous flow and multiphase flow[17]. Because of its inherent kinetic nature, the LB method has attracted huge interest in its extension to simulating micro-gaseous flows, and tremendous efforts have been made to advance the LBM since 2002[18][19][20]. With the implementation of appropriate slip boundary conditions and/or effective relaxation time, the LBM was successfully extended for simulation of gaseous flows in slip flow and transition flow regimes, and these LBM approaches have been applied to study gas transport in shale gas reservoir[21][22][23]. However, because of the complexity of boundary conditions, most of the applications of the slip-based LBM are limited to single channel or bundle of channels[23]. Recently, Chen et al.[20][24] proposed a LB model based on the Dusty gas model (DGM) to predict the apparent permeability of shales with complex porous structures, where the complexity of the slip boundary conditions are avoided. Very recently, Chen et al.[25] improved the generalized lattice Boltzmann model (GLBM) proposed by Guo and Zhao[26] for fluid flow through porous media by including the Klinkenberg effect, and performed several simulations based on heterogeneous shale matrix with natural fractures, organic matter and inorganic minerals[25][27].

69 In this study, we present a novel adaptation of the GLBM with slip ef-
70 fect proposed by Guo and Zhao[26] and Chen et al.[25] for micro-gas flow
71 in 2-dimensional (2-D) porous shale with surface diffusion further consid-
72 ered. The novelty of the present study is the use of the DGM-generalized
73 Maxwell-Stefan (GMS) approach to calculate the local permeability taking
74 the adsorbed gas and surface diffusion into account. The rest of the paper is
75 as follows. The mathematical and numerical models for predicting apparent
76 permeability of organic shale is introduced in Section 2, and the validation of
77 numerical models is also shown in this section. In section 3, firstly the per-
78 meability of IOM and OM are discussed, and then the effects of component
79 distribution and organic content on apparent permeability of reconstructed
80 shale sample are analyzed. Finally, some conclusions are drawn in section 4.

81 2. Model description

82 2.1. Dusty gas model and generalized Maxwell-Stefan model

83 The transport of non-adsorbable gas through porous media is in gen-
84 eral caused by concentration or pressure gradients. It has been confirmed
85 experimentally and mathematically that the corresponding fluxes can be cal-
86 culated with high accuracy using the DGM or Knudsen-like theory[28]. How-
87 ever, most recent studies indicate that the above applications have failed to
88 model the gas transport in the presence of the adsorbed gas[29]. To take
89 account of the adsorbed gas effect, Krishna and co-workers[30][31] extended
90 the Maxwell-Stefan formulation in the spirit of the DGM by introducing a
91 generalized Maxwell-Stefan model (GMS) for surface diffusion of adsorbed
92 gas(See Fig. 1). With the premise that the DGM appropriately describes
93 the transport in the “quasi-bulk” phase located in the pore space whereas
94 the GMS describes gas molecular transport at the surface, the total molar
95 flux is expressed by:

$$N_{total} = N_{DGM} + N_{GMS}, \quad (1)$$

96 where N_{DGM} is the contribution to the flux from the DGM ($mol \cdot m^{-2} \cdot s^{-1}$), in
97 which adsorption and surface diffusion is ignored, and N_{GMS} is the contribu-
98 tion from the GMS for surface diffusion ($mol \cdot m^{-2} \cdot s^{-1}$). Detailed descriptions
99 of DGM and GMS are given in the next two subsections, respectively.

Figure 1: Schematic diagram of gas transport in organic pores of shale matrix based on DGM-GMS model proposed by Krishna and co-workers[30][31] (a) Gas transport mechanisms in organic pores (b) Conceptual models for different gas transport

2.1.1. Dusty gas model

The DGM is based on the combination of the Maxwell-Stefan diffusion equations and the characteristics of mass transfer in porous media. The basic idea of DGM is to consider the solid as a dummy species of infinite mass, which is constrained by unspecified external forces and has zero drift velocity. For a single species i in a n -component mixture the following flux equation of the DGM holds[32]:

$$-\frac{P}{RT}\nabla x_i - \frac{x_i}{RT}\left(1 + \frac{K_0}{\eta D_{K,i}}P\right)\nabla P = \sum_{j=1, j \neq i}^n \frac{x_j N_i - x_i N_j}{\varepsilon/\tau D_{ij}^0} + \frac{N_i}{D_{K,i}}, \quad (2)$$

where P is pressure (P_a), R is the universal gas constant ($8.314 J \cdot K^{-1} \cdot mol^{-1}$), T is temperature (K), η is dynamic viscosity ($kg \cdot m^{-1} \cdot s^{-1}$), x_i is the molar fraction of species i , D_{ij}^0 is the binary molecular diffusivity in gas phase (m^2/s), and ε/τ is the ratio of porosity to tortuosity. The Knudsen diffusivity

111 $D_{k,i}$ of species i is defined as:

$$D_{K,i} = \frac{4}{3}K_c\sqrt{\frac{8RT}{\pi M_i}}, \quad (3)$$

112 where M_i is the Molecular weight of species i (kg/mol). In the case where
 113 the pore space is assumed to have a diameter d_p (m), the values of Knudsen
 114 coefficient, K_c and the permeability of the porous medium quantifying the
 115 viscous flux, K_0 can be related as[33]:

$$K_c = \frac{8}{d_p}K_0 = \frac{\varepsilon}{\tau} \frac{d_p}{4}. \quad (4)$$

116 If the system contains only one species, Eq. 2 can be simplified as:

$$N_{DGM} = -\frac{1}{RT}(D_K + \frac{K_0}{\eta}P)\frac{\partial P}{\partial r}. \quad (5)$$

117 2.1.2. Generalized Maxwell-Stefan Model

118 The GMS model is based on the assumption that the movement of species
 119 is caused by a driving force balanced by the friction that the moving species
 120 experience both from each other and from their surroundings. The diffusion
 121 of adsorbed species satisfies[31]:

$$-\frac{\theta_i(1-\varepsilon)}{RT}\nabla\mu_i = \sum_{j=1, j \neq i}^n \frac{\theta_j N_i^s - \theta_i N_j^s}{\rho_p q_{sat} D_{ij}^s} + \frac{N_i^s}{\rho_p q_{sat} D_i^s}, \quad (6)$$

122 where μ_i is the chemical potential of i (J/mol), θ_i is the fractional coverage, ρ_p
 123 is the density of particle or solid skeleton (kg/m^3), q_{sat} is the saturation sur-
 124 face concentration (mol/m^3), D_{ij}^s is the Maxwell-Stefan counter-sorption dif-
 125 fusivity (m^2/s), and D_i^s is the Maxwell - Stefan diffusivity of species i (m^2/s).
 126 The surface fluxes N_i^s of the diffusing adsorbed species are defined as:

$$N_i^s = (1-\varepsilon)q_{sat}\theta_i\mathbf{u}_i, \quad (7)$$

127 where $\mathbf{u}_i$ is species velocity (m/s). Assuming equilibrium between the sur-
 128 face and the bulk phase, the following relationship for the surface chemical
 129 potential μ_i of species i holds:

$$\mu_i = \mu_i^0 + RT\ln(f_i), \quad (8)$$

130 where μ_i^0 is the chemical potential in the chosen standard state and f_i is the
 131 fugacity of species i in the bulk fluid mixture (P_a). For not too high system
 132 pressures, the component partial pressures, P_i , can be used instead of the
 133 component fugacity. Then the surface chemical potential gradients can be
 134 expressed in terms of the gradients of the surface occupancies by introduction
 135 of the matrix of thermodynamics factors:

$$\frac{\theta_i}{RT} \nabla \mu_i = \sum_{j=1}^n \Gamma_{ij} \nabla \theta_j, \quad (9)$$

136 and the elements of thermodynamic matrix Γ can be expressed as:

$$\Gamma_{ij} \equiv \theta_i \frac{\partial \ln P_i}{\partial \theta_j}. \quad (10)$$

137 Assuming that the Langmuir equation to be valid and the adsorption
 138 equilibrium to be established, the fractional coverage θ_i can be written in
 139 terms of the Langmuir parameters:

$$\theta_i = \frac{q_i}{q_{sat}} = \frac{b_i P_i}{1 + \sum_{j=1}^n b_j P_j}, \quad (11)$$

140 where b_i is the Langmuir constant (P_a^{-1}), $q_i = q_{m,i}/(1 - \varepsilon)$ is the solid volume
 141 dependent adsorbed phase concentration (mol/m^3), and $q_{m,i}$ is the equilib-
 142 rium mass dependent loading which is measured during the Langmuir ad-
 143 sorption experiment (mol/m^3).

144 Based on Eq. 6 and Eq. 9, for a single component surface diffusion, the
 145 molar flux of surface diffusion is:

$$N_{GMS} = (1 - \varepsilon) q_{sat} \frac{D_s}{1 - \theta} \nabla \theta, \quad (12)$$

146 where D_s is the Maxwell-Stefan surface diffusivity (m^2/s). The Langmuir
 147 equation (Eq. 11) can be simplified to:

$$\theta = \frac{q}{q_{sat}} = \frac{bP}{1 + bP}. \quad (13)$$

148 Based on Eq. 13, the gradient of the adsorbed phase concentration can
 149 be further expressed in terms of the partial pressure gradient as follows:

$$\frac{\partial q}{\partial r} = q_{sat} \frac{b}{(1 + bP)^2} \frac{\partial P}{\partial r}, \quad (14)$$

150 where r represents the pore radius (m). Substituting Eq. 14 to Eq. 12, the
 151 surface diffusion flux in terms of partial gradient satisfies:

$$N_{GMS} = (1 - \varepsilon)q_{sat} \frac{bD_s}{1 + bP} \frac{\partial P}{\partial r}. \quad (15)$$

152 For a single gas species the combination of the DGM (Eq. 5) and the
 153 GSM (Eq. 15) results in the total flux:

$$N_{total} = N_{DGM} + N_{GMS} = -\left(\frac{1}{RT}(D_K + \frac{K_0}{\eta}P) + (1 - \varepsilon)q_{sat} \frac{bD_s}{1 + bP}\right) \frac{\partial P}{\partial r}, \quad (16)$$

154 and the apparent permeability, k_{app} satisfies:

$$m_{total} = N_{total}M\pi\left(\frac{d_p^2}{4}\right) = \rho_g\pi\left(\frac{d_p^2}{4}\right) \frac{K_{app}}{\eta} \frac{\partial P}{\partial r}, \quad (17)$$

155 where m_{total} is the total mass flow rate (kg/s). As the surface diffusion of
 156 adsorbed gas only happens in organic matter, substituting Eq. 5 into Eq.
 157 17, the apparent permeability of inorganic matter is:

$$K_{app,iom} = \frac{\eta M}{\rho_g} \left(\frac{1}{RT} (D_K + \frac{K_{0,iom}}{\eta}P) \right), \quad (18)$$

158 and with Eq. 16 and Eq. 17, the apparent permeability of organic matter is:

$$K_{app,om} = \frac{\eta M}{\rho_g} \left(\frac{1}{RT} (D_K + \frac{K_{0,om}}{\eta}P) + (1 - \varepsilon)q_{sat} \frac{bD_s}{1 + bP} \right). \quad (19)$$

159 2.2. Expectation-Maximization (EM) algorithm

160 The pore size distribution of shale matrix is a combination of the pore size
 161 distributions within the IOM and OM. The range of pore sizes, however, is
 162 different in the two components, with pores in the OM an order of magnitude
 163 smaller than those in the IOM[34]. Therefore, the pore structures in the
 164 OM and IOM need to be distinguished. Then gas flow with and without
 165 surface diffusion of adsorbed gas can be simulated using the GMS and DGM,
 166 respectively.

167 Current nitrogen adsorption tests indicate that the pore size distributions
 168 in shale usually satisfy double-mode distributions[35] and the assumption
 169 of Gaussian distribution for probability distribution function (PDF) of pore
 170 size in rocks has been reported in several studies[34][36]. Under the Gaussian

171 mixtures model(GMM) assumption, the Expectation-Maximization (EM) al-
 172 gorithm used by Naraghi and Javadpour[34] is applied here to obtain the pore
 173 size distribution in both the IOM and OM. The EM algorithm is an iterative
 174 algorithm that starts from the initial estimation of parameters and proceeds
 175 to iteratively update those parameters until the convergence is reached. Each
 176 iteration consists of an Expectation-step and a Maximization-step.

177 2.2.1. Expectation step

178 In the expectation step, the probability that data point i belongs to clus-
 179 ter j can be calculated using the following:

$$w_j^{(i)} = \frac{g_j(x)\Phi_j}{\sum_{l=1}^k g_l(x)\Phi_l}, \quad (20)$$

180 where $w_j^{(i)}$ is the probability that example i belongs to cluster j , k is the
 181 number of clusters, Φ_j is the fraction of the dataset belonging to cluster j ,
 182 and $g_j(x)$ is the probability density function of a multivariate Gaussian which
 183 satisfies:

$$g_j(x) = \frac{1}{\sqrt{(2\pi)^n |\Sigma_j|}} e^{\frac{1}{2}(x-\mu_j)^T \Sigma_j^{-1} (x-\mu_j)}, \quad (21)$$

184 where x is the input vector, n is the input vector length, Σ_j is the covariance
 185 matrix for cluster j , and μ_j is the mean of cluster j .

186 2.2.2. Maximization step

187 In the Maximization step, the cluster covariances and means based on the
 188 probabilities calculated in the Expectation step are calculated. The updated
 189 parameters are expressed in the following equations:

$$\Phi_j^{(new)} = \frac{1}{m} \sum_{i=1}^m w_j^{(i)}, \quad (22)$$

$$\mu_j^{(new)} = \frac{\sum_{i=1}^m w_j^{(i)} x^{(i)}}{\sum_{i=1}^m w_j^{(i)}}, \quad (23)$$

$$\sum_j^{(new)} = \frac{\sum_{i=1}^m w_j^{(i)} (x^{(i)} - \mu_j)(x^{(i)} - \mu_j)^T}{\sum_{i=1}^m w_j^{(i)}}. \quad (24)$$

190 *2.3. Generalized lattice Boltzmann model*

191 Nithiarasu et al.[37] proposed a generalized N-S equation for isothermal
192 incompressible fluid flow in porous media which can be expressed as follows:

$$\nabla \cdot \mathbf{u} = 0, \quad (25)$$

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \left(\frac{\mathbf{u}}{\varepsilon} \right) = -\frac{1}{\rho} \nabla(\varepsilon P) + v_e \nabla^2 \mathbf{u} + \mathbf{F}, \quad (26)$$

193 where $\mathbf{u}$ and P are the volume-averaged velocity and pressure, respectively.
194 v_e is an effective viscosity equals to the shear viscosity of fluid v times the
195 viscosity ratio J ($v_e = vJ$). In the present study, ε is assumed to be the
196 effective porosity that is responsible for gas flow, and “dead-end” pores are
197 not included. $\mathbf{F}$ represents the total body force due to the presence of the
198 porous media and other external forces, which is given by:

$$\mathbf{F} = -\frac{\varepsilon v}{K} \mathbf{u} - \frac{\varepsilon F_\epsilon}{\sqrt{K}} |\mathbf{u}| \mathbf{u} + \varepsilon \mathbf{G}, \quad (27)$$

199 where $\mathbf{G}$ is the external force, F_ϵ is the geometric function and K is the local
200 permeability. To incorporate the effects of Knudsen diffusion and surface
201 diffusion, Eq. 27 is modified by substituting K with apparent permeability
202 K_{app} based on the idea proposed by Chen et al[25]. Without considering the
203 nonlinear drag force term as the flow rate is extremely small in shale matrix,
204 the body force is given by:

$$\mathbf{F} = -\frac{\varepsilon v}{K_{app}} \mathbf{u} + \varepsilon \mathbf{G}, \quad (28)$$

205 and K_{app} can be calculated based on Eq. 18 and Eq. 19 for IOM and OM,
206 respectively.

207 To solve the generalized N-S equation, Guo and Zhao[26] proposed a
208 generalized LBE as follows:

$$f_i(\mathbf{x} + \mathbf{e}_i \Delta t, t + \Delta t) - f_i(\mathbf{x}, t) = -\frac{1}{\tau} [f_i(\mathbf{x}, t) - f_i^{eq}(\mathbf{x}, t)] + \Delta t F_i, \quad (29)$$

209 where $f_i(\mathbf{x}, t)$ is the distribution function for the particle with velocity $\mathbf{e}_i$ at
210 position $\mathbf{x}$ and time t , Δt is the time increment, and τ is the relaxation time.
211 In two dimensional and nine velocity ($D2Q9$) model, the discrete velocity $\mathbf{e}_i$

is defined as $\mathbf{e}_1=(0, 0)$, $\mathbf{e}_2 = -\mathbf{e}_4=(1, 0)c$, $\mathbf{e}_3 = -\mathbf{e}_5=(0, 1)c$, $\mathbf{e}_6 = -\mathbf{e}_8=(1, 1)c$, $\mathbf{e}_7 = -\mathbf{e}_9=(-1, 1)c$. In three dimensional and nineteen velocity (*D3Q19*) model, the discrete velocity $\mathbf{e}_i$ is defined as $\mathbf{e}_i=(0, 0, 0)c$ (for $i = 0$); $\mathbf{e}_i=(\pm 1, 0, 0)c$, $(0, \pm 1, 0)c$, $(0, 0, \pm 1)c$ (for $i=2, 3, \dots, 7$); $\mathbf{e}_i=(\pm 1, \pm 1, 0)c$, $(\pm 1, 0, \pm 1)c$, $(0, \pm 1, \pm 1)c$ (for $i=8, 9, \dots, 19$), where $c = \Delta x / \Delta t$ is the lattice speed.

The equilibrium distribution functions f^{eq} are defined as the following form with the porosity effect considered:

$$f_i^{eq} = w_i \rho \left[1 + \frac{3}{c^2} (\mathbf{e}_i \cdot \mathbf{u}) + \frac{9}{2\varepsilon c^4} (\mathbf{e}_i \cdot \mathbf{u})^2 - \frac{3}{2\varepsilon c^2} \mathbf{u}^2 \right], \quad (30)$$

where w_i is the weighting factor. In *D2Q9* model, $w_i = 4/9$ (for $i = 1$), $w_i = 1/9$ (for $i=2, 3, 4, 5$), and $w_i = 1/36$ (for $i=6, 7, 8, 9$). In *D3Q19* model, $w_i = 1/3$ (for $i = 1$), $w_i = 1/18$ (for $i=2, 3, \dots, 7$), and $w_i = 1/36$ (for $i=8, 9, \dots, 19$). The force term F_i is calculated as:

$$F_i = w_i \rho \left(1 - \frac{1}{2\tau} \right) \left[\frac{3}{c^2} (\mathbf{e}_i \cdot \mathbf{F}) + \frac{9}{\varepsilon c^4} (\mathbf{e}_i \cdot \mathbf{u}) (\mathbf{e}_i \cdot \mathbf{F}) - \frac{3}{c^2} (\mathbf{u} \cdot \mathbf{F}) \right], \quad (31)$$

and the fluid velocity $\mathbf{u}$, density ρ and the kinematic viscosity are defined as:

$$\rho = \sum_i f_i, \quad (32)$$

$$\rho \mathbf{u} = \sum_i f_i \mathbf{e}_i + \frac{\Delta t}{2} \rho \mathbf{F}, \quad (33)$$

$$v_e = c_s^2 (\tau - 0.5) \Delta t. \quad (34)$$

where $c_s = c / \sqrt{3}$.

Due to the quadratic nature of Eq. 33, the velocity $\mathbf{u}$ can be given explicitly by:

$$\mathbf{u} = \frac{\mathbf{v}}{c_0 + \sqrt{c_0^2 + c_1 |\mathbf{v}|}}, \quad (35)$$

where $\mathbf{v}$ is a temporal velocity defined as:

$$\rho \mathbf{v} = \sum_i f_i \mathbf{e}_i + \frac{\Delta t}{2} \varepsilon \rho \mathbf{G}, \quad (36)$$

and the two parameters c_0 and c_1 are given by:

$$c_0 = \frac{1}{2} \left(1 + \varepsilon \frac{\Delta t}{2} \frac{v}{K_{app}} \right), \quad (37)$$

$$c_1 = \varepsilon \frac{\Delta t}{2} \frac{F_\epsilon}{\sqrt{K_{app}}}. \quad (38)$$

In the simulation of gas flow through a porous system, the GLBM model can be employed by simply replacing the usual computational lattices with porous lattices in the domain occupied by the porous medium in both 2-D and 3-D situations[38]. In this study, the porosity remains the same in each component, and each porous lattice in the simulation domain is characterized by a pore radius based on the pore size distribution in OM and IOM. The local K_{app} and its components such as K_0 or $K_{Knudsen}$ of every computational lattice are calculated based on Eqs. 18 and 19, and the permeability of the porous structure is obtained by applying Darcy's law to the entire domain based on the velocity field. The advantages of the above GLB model are as follows: Firstly, the modelling of pore space and the impermeable solid can be achieved by assigning porosity as unity and by assigning the drag force as infinity, respectively. Hence, the GLBM can account for the pore connectivity. Secondly, without invoking any boundary conditions, it can automatically simulate the interfaces between different components in shale matrix with spatially variable porosity and pore size distribution. Finally, different nodes in the shale matrix are fully accounted for and the Knudsen diffusion as well as surface diffusion can be easily considered in the model. For more details of the generalized N-S equation with slippage effect and the LB model, one can refer to our previous work[25][27].

3. Validation

3.1. Validation of DGM-GMS

It is not an easy task to evaluate the accuracy of DGM-GMS model in simulating gas flow in organic shale as there is an insufficient experimental data available in the literature. However, some experimental studies were proposed to verify the feasibility of DGM-GMS in modelling gas transport in mesoporous solids such as silicas and aluminas in the presence of adsorption fields. In this study, the experimental data of Carbon dioxide flowing through the porous Vycor glass membrane under temperature 293K and 343K[33] were used here to validate the formulation to calculate the apparent permeability of organic matter with surface diffusion considered(Eq. 19). The structure properties and geometry of the Vycor membrane are shown in Table 1.

Table 1: Structure properties of the Vycor membrane

Inner membrane radius r_1 (mm)	3.9
Outer Membrane radius r_2 (mm)	5
Membrane length L (mm)	100
Apparent density ρ_a (g/cm^3)	1.472
skeleton density ρ_p (g/cm^3)	2.057
Porosity	0.2842
The ratio of porosity to tortuosity ε/τ	0.03

263 The CO_2 adsorption isotherms were modelled by Langmuir equation, and
 264 the obtained parameters are given in Table 2.

Table 2: Langmuir parameter of CO_2

T (K)	$D_s(m^2/s)$	$q_{sat}(mol/m^3)$	$b(P_a^{-1})$
293K	2.2×10^{-9}	3135	0.467×10^{-5}
343K	2.8×10^{-9}	2255	0.191×10^{-5}

265 Experimental data and calculations of total molar flow rate, N_{total} are
 266 given in Fig. 2 and Fig. 3. It can be seen that the simulation results based
 267 on DGM-GMS match reasonably well with experimental observations, with
 268 the deviations below 15%. As predicted by theory a slight decrease of the
 269 permeation data was observed for increasing pressure at different tempera-
 270 tures. It can also be concluded from Fig. 2 and Fig. 3 that for the given
 271 experimental conditions, the surface transport was only slightly smaller than
 272 the transport in the bulk phase, and the DGM without surface diffusion will
 273 lead to a significant underestimation of the permeation (see dash lines in
 274 Fig. 2 and 3). Noteworthy, although the solid properties, the adsorption and
 275 surface diffusion properties of Vycor glass are different from those of organic
 276 shale samples, the validation still can confirm that DGM-GMS in which the
 277 surface diffusion is considered can provide a better estimation of gas flow
 278 compared to the models without considering surface diffusion.

Figure 2: Permeation of carbon dioxide through Vycor at 293K. The data denoted by the solid squares were reported by Tuchlenski et al.[33].

Figure 3: Permeation of carbon dioxide through Vycor at 343K. The data denoted by the solid squares were reported by Tuchlenski et al.[33].

279 3.2. Validation of EM algorithm

280 To validate the accuracy of the EM algorithm for classifying pore size dis-
 281 tribution in each component, a two-cluster Gaussian Mixture with different
 282 mean pore sizes (μ) and standard deviations (σ) are tested. The parameters
 283 of two clusters and the calculated results are listed in Table 3. The compar-
 284 ison is shown in Fig. 4. The simulation results estimated based on the EM
 285 algorithm are comparable to the original data.

Table 3: Parameters of test clusters

	$\mu(nm)$	$\sigma(nm)$	Fraction	$\mu_{EM}(nm)$	$\sigma_{EM}(nm)$	$Fraction_{EM}$
Set 1	10	1	0.25	9.8848	0.9886	0.2418
Set 2	20	4	0.75	19.6846	4.0804	0.7582

Figure 4: PDF of two clusters with different mean pore sizes and standard deviations

286 4. Results and Discussion

287 Different from the previous studies which focus on the influence of poros-
 288 ity, tortuosity and adsorption phenomenon[4][27][39], this study details the
 289 surface diffusion phenomenon. The $D2Q9$ model is employed due to its sim-
 290 plicity and efficiency. Firstly the GLBM is used to simulate the K_{app} of

both the IOM and OM, and then the base case data of an Eagle Ford Shale sample[34] are applied to analyze the K_{app} of reconstructed shale. The external body force is calculated according to $G = \Delta P/L/\rho$, and the extrapolated pressure boundary conditions[40] are applied to the left and right boundaries of the simulation domain to specify the inlet and outlet pressure respectively. Periodic boundary conditions are applied to the top and bottom boundaries parallel to the flow direction. The conversion from lattice units to physical units is given in the following way. The unit of length is given by the lattice resolution δx , the unit of time, δt , is derived from the kinematic viscosity. Considering that the kinematic viscosity has the dimensions of length squared over time, we have:

$$v_{phy} = v\delta x^2/\delta t, \quad (39)$$

where the kinematic viscosity in lattice unit can be calculated using Eq. 34 and the kinematic viscosity in physical unit is calculated using a open software called Peace Software. And then the scaling for other parameters such as velocity and permeability can be obtained based on δx and δt .

4.1. Permeability of IOM and OM

Based on Eq. 18 and Eq. 19, it is evident that K_{app} of the IOM and the OM depend both on pressure and pore radius. $K_{app,om}$ also depends on the gas adsorption properties. In this section, the change of K_{app} with P and r both in OM and IOM as well as the variation of $K_{app,om}$ with Langmuir parameters are discussed. The porosity remains constant in each component and each lattice is given a pore radius based on the pore size distribution which is assumed to be Gaussian.

4.1.1. Permeability of IOM

Fig. 5 shows the variation of $K_{app,iom}$ and the ratio of $K_{app,iom}$ to intrinsic permeability, $K_{0,iom}$ with the mean pore radius of IOM, and the input parameters are listed in Table 4. Based on Fig. 5, one can observe that with the increase of the mean pore radius, $K_{app,iom}$ increases, so does its rate of change. $K_{app,iom}/K_{0,iom}$ and its slope, however, decrease with the increase of mean pore radius. When the mean pore radius approaches 100nm, the gas flow becomes continuum, and $K_{app,iom}$ approximately equals K_0 . The simulation results clearly show the effect of Knudsen diffusion on the gas transport in IOM, especially when pore radius is smaller than 100nm. Also

Table 4: Input parameters of IOM

Inlet pressure P_{in} (MPa)	22
Outlet pressure P_{out} (MPa)	20
Viscosity of Methane at outlet ($10^{-6} Pa \cdot s$)	18.231
Tortuosity of IOM	2
Porosity of IOM	0.04
Length $\times$ Width ($cm \times cm$)	3.2×1.6

the deviation of $K_{app,iom}$ from $K_{0,iom}$ indicates that the permeability of IOM
in shale will be underestimated if the Knudsen diffusion is ignored.

Figure 5: Variation of $K_{app,iom}$ and $K_{app,iom}/K_{0,iom}$ with mean pore radius, r . $P_{in} = 22MPa$ and $P_{out} = 20MPa$.

Fig. 6 shows the variation of $K_{app,iom}$, $K_{0,iom}$, and $K_{Knudsen,iom}$ with the
average pressure, where $K_{0,iom}$ and $K_{Knudsen,iom}$ are components from vis-
cous flow (intrinsic permeability) and Knudsen diffusion, respectively. The
average radius is 2 nm and the standard deviation is 0.25 nm. As can be
seen in Fig. 6, as the average pressure increases, the intrinsic permeability
does not change, but $K_{Knudsen,iom}$ (and hence $K_{app,iom}$) decreases. This re-
sult is important for shale gas production, as the reservoir is depleted and

the reservoir pressure decreases, $K_{app,iom}$ deviates from the intrinsic permeability owing to high contribution of Knudsen diffusion at zones with low pressures, and gas transport in these zones therefore is predominantly controlled by Knudsen diffusion. Fig.6 also indicates that permeability of IOM is a function of reservoir pressure, and the permeability must be considered as a dynamic reservoir parameter and updated accordingly as the reservoir is being depleted.

Figure 6: Variation of $K_{app,iom}$ and its components with average pressure. The average pore radius is 2 nm, and the average pressure is calculated based on $(P_{in} + P_{out})/2$.

Similar dependencies on pore sizes and pressure have been observed by other studies considering conductivity of a single channel[41] and bundle of channels or nanopore networks[42].

4.1.2. Permeability of OM

Adsorbed gas and surface diffusion in OM are drawing more attention recently. Various studies have confirmed that the adsorption can change $K_{app,om}$ of shale matrix and the surface diffusion is an important transport mechanism at reservoir conditions[4][43]. In some treatments, the surface diffusion is considered as an extra flux in capillary models[21][14][39]. However the sensitivity of permeability to adsorption and surface diffusion are seldom

mentioned. In others, the adsorbed gas is modelled by taking some pore space and therefore reducing the local pore size[27][44][7]. In other words, if adsorbed gas is assumed to pre-exists in OM, the intrinsic permeability will increase with the decrease in pressure because the desorbed gas will release some pore space[4]. Nonetheless, no consensus on the volume occupied by adsorbed gas exists in these treatments[14][44][39], also the contribution of the surface diffusion is ignored. In this study, with the introduction of DGM-GMS model, the effect of surface diffusion on $K_{app,om}$ can be easily considered, and based on the assumption that the total flux N_{total} is the sum of N_{DGM} and N_{GMS} , the ambiguity in the adsorption layer thickness can be avoided. As mentioned above, the contribution of surface diffusion is affected by parameters regarding the Langmuir adsorption model and the surface diffusivity. Therefore, the model parameter values of adsorbed gas and surface diffusivity for the following sensitivity analysis were carefully collected from the reported data. Specifically, b and q_{sat} were collected from the previous Langmuir isothermal of shale samples and the results are presented in Table 5. Based on data in Table 5, a range of b from 0.125 to $1MPa^{-1}$ (b^{-1} from 1 to $8MPa$) and a range of $q_{sat,k}$ from 1000 to $8000mol/m^3$ are used for discussion in this study. For the determination of Langmuir volume q_{sat} , data were treated with caution as the definition and unit of q_{sat} vary from one study to another. For instance, Eq. 40 is used to obtain $q_{sat,k}$ if $q_{sat,b}$ is presented in the literature.

$$q_{sat,k} = \frac{q_{sat,b}\rho_b}{(1 - \varepsilon)TOC} \frac{\rho_{CH_4}}{M_{CH_4}}, \quad (40)$$

where TOC is the volume fraction of the kerogen content, $q_{sat,k}$ is the mole volume of methane divided by the volume of kerogen skeleton (mol/m^3), and $q_{sat,b} = V/m_b$ is the volume of methane divided by the bulk mass of shale sample (m^3/kg).

Table 5: Langmuir constant given by different authors[45][46][47][48][49][50][51][52]

Reference	Sample	T (K)	1/b(MPa)	$q_{sat,k}(mol/m^3)^\dagger$
Zhang et al.[45]	Woodford	309	3.57	3011.25
		324	4.76	
		339	7.69	
	Green river	309	6.67	2516.12
		324	7.69	
Mengal & Wattenbarger[46]	Barnett	- -	4.48	1817.57
Boulis et al.[47]	Marcellus	322	3.58	3606.23
Zuber et al.[48]	New Albany	- -	2.84	3340.08
Rexer et al.[49]	Bornholm	300	1.65	7321.88
		303	1.68	6943.75
		308	1.50	6256.25
		318	1.68	5981.25
		338	2.30	5809.57
		358	2.60	5190.63
		373	2.60	4468.75
		398	3.06	3781.25
		423	3.10	3162.50
		448	2.83	2475.00
Heller & Zoback[50]	Barnett	313	4.00	3595.83
	Eagleford	313	4.79	613.81
	Marcellus	313	3.84	1367.77
Etminan et al.[51]	- -	323	6.14	3214.62
Hu[52]	Barnett 1	309	2.94	2319.89
		324	4.00	
		339	4.76	
		349	5.26	
	Barnett 2	309	1.59	3315.13
		324	2.38	
		339	3.13	
		349	4.00	

[†] When the properties of TOC is not given in the literature, the $q_{sat,k}$ is calculated based on the assumption that the TOC , the porosity of Kerogen and the density of OM are 0.2, 0.2 and $1.65 \times 10^3 kg/m^3$, respectively.

The surface diffusion diffusivity can be measured in forms of self-diffusivity

378 D_{self} , Maxwell-Stefan diffusivity D_s or Fickian diffusivity D_f . From Table
 379 6 it can be seen that $D_f > D_s > D_{self}$. The D_f of organic shale given by
 380 Kang et al.[53] is from 1.55×10^{-7} to $8.8 \times 10^{-6} m^2/s$, and by Akkutlu and
 381 Fathi[54] is from 8.3×10^{-8} to $8.8 \times 10^{-6} m^2/s$. D_{self} of organic shale given
 382 by Zhai et al.[55] is between 9.43×10^{-9} and $11.62 \times 10^{-9} m^2/s$ and by Yuan
 383 et al.[56] is from 2.38×10^{-9} to $9.96 \times 10^{-9} m^2/s$. Wu et al.[10] proposed an
 384 empirical equation to determine D_s of methane based on the experimental
 385 data of methane-activated carbon:

$$D_s = (8.29 \times 10^{-7}) T^{0.5} \exp\left(-\frac{\Delta H^{0.8}}{RT}\right), \quad (41)$$

386 where ΔH is the isosteric adsorption heat, ranging from 12000 to 16000 J/mol
 387 at 338.7K, and D_s ranges from 6.72×10^{-6} to $7.96 \times 10^{-6} m^2/s$. In a most
 388 recent study, Wu et al.[57] made a detailed summary of surface diffusivity
 389 of various gas under different circumstances (see Table 4 in the Ref.[57]),
 390 and extremely high surface diffusivity which is larger than $1 \times 10^{-6} m^2/s$
 391 has been observed in the literature[58][59]. Based on these data, considering
 392 the specific values of surface diffusivity of shale samples are still not clear
 393 and more experiments will likely be done in the future, in this study we
 394 choose to cover a wide range of Maxwell-Stefan diffusivity to take account of
 395 more cases, and D_s from 1×10^{-9} to $1 \times 10^{-5} m^2/s$ is used for the following
 396 discussions.

Table 6: Comparison of different diffusivity[60]

Self-diffusion diffusivity	$D_{self} \approx D_0(1 - \theta)$
Maxwell-Stefan diffusivity	$D_s \approx D_0$
Fickian diffusivity	$D_f = \frac{D_0}{1-\theta}$

397 Fig. 7 shows the variation of $K_{app,om}$ and $K_{app,om}/K_{0,om}$ with r . D_s , q_{sat}
 398 and b are set to be $5 \times 10^{-7} m^2/s$, $4000 mol/m^3$ and $0.25 MPa^{-1}$, respectively.
 399 The other inputs are the same as that listed in Table 4. $K_{app,om}$ without
 400 considering the surface diffusion is also listed in the figure for comparison.
 401 From Fig. 7 it can be seen that, the trend of $k_{app,om}$ and $k_{app,om}/k_{0,om}$ is
 402 similar to that of IOM. In large pores, both Knudsen diffusion and surface
 403 diffusion can be ignored, and $K_{app,om}$ equals $K_{0,om}$. Fig. 7 also shows that the
 404 surface diffusion is the primary flow mechanism in nano-pores, and significant
 405 underestimation of permeability can be observed if the surface diffusion is

406 ignored when the average pore radius is less than 10 nm. Wu et al.[10]
 407 reported that the contribution of surface diffusion to the shale gas mass
 408 transfer can be up to 92.95% when pore radius is smaller than 2nm. The
 409 results presented in Fig. 7 agree well with that presented by Wu et al.[10],
 410 and the value of $K_{app,om}/K_{0,om}$ can be larger than 10 at $r < 2nm$ when
 411 surface diffusion is considered.

Figure 7: Variation of $K_{app,om}$ and $K_{app,om}/K_{0,om}$ with mean pore radius, r of organic matter at $D_s = 5 \times 10^{-7} m^2/s$, $q_{sat} = 4000 mol/m^3$ and $b = 0.25 MPa^{-1}$. $P_{in} = 22 MPa$ and $P_{out} = 20 MPa$.

412 Fig. 8 illustrates $K_{app,om}$ and its components estimated based on DGM-
 413 GMS under different average pressure conditions. The average radius used
 414 in this case is 2 nm with a standard deviation of 0.25 nm. The other inputs
 415 are the same as those of Fig. 7. Fig. 8 shows that the surface diffusion de-
 416 creases linearly with the increasing pressure, and the contribution from both
 417 Knudsen diffusion and surface diffusion becomes almost negligible when the
 418 pressure reaches a high level. However, the surface diffusion is the dominant
 419 mass transport mechanism in OM at low pressures, and $K_{app,om}$ accounting
 420 for surface diffusion can be several times larger than that without considering
 421 it. Similar to $K_{app,iom}$, $K_{app,om}$ is sensitive to pressure and deviates further
 422 from the intrinsic permeability at lower pressure. It is typically believed that
 423 the shale gas production quickly declines from an initial high production rate

424 which results from the free gas in major fractures in the first years, followed
 425 by a long tail which is controlled by accessibility of small pores of shale ma-
 426 trix that may last 20 years or more[61]. The increase of K_{app} with decreasing
 427 pressure in both OM and IOM shown in this study explains why the conven-
 428 tional continuum models using the intrinsic permeability underestimate the
 429 production rate at the later stage. This phenomenon has been confirmed by
 430 the earlier numerical simulation studies, and more details can be found from
 431 Ref.[61][62][63].

Figure 8: Variation of $K_{app,om}$ and its components with average pressure at $D_s = 5 \times 10^{-7} m^2/s$, $q_{sat} = 4000 mol/m^3$ and $b = 0.25 MPa^{-1}$. The average pore radius, $r = 2 nm$, and standard deviation, $\sigma = 0.25 nm$.

432 Fig. 9 depicts $K_{app,om}$ with different Langmuir parameters. D_s is set
 433 to be $5 \times 10^{-7} m^2/s$, the average radius is $11 nm$, and σ is $0.25 nm$. To
 434 represent the reservoir condition, the inlet pressure is set to be $22 MPa$, and
 435 the outlet pressure is $20 MPa$. As can be seen in Fig. 9, $K_{app,om}$ is linearly
 436 increasing with the increase of q_{sat} and the decrease of b^{-1} . This is because
 437 based on Langmuir model(Eq. 13), a larger q_{sat} or b induces a larger amount
 438 of adsorbed gas at a certain pressure, and therefore leads to a higher surface
 439 flux. Also, the influence of b on $K_{app,om}$ is becoming obvious with the increase
 440 of q_{sat} . The results of Fig. 9 further emphasizes the impact of adsorbed gas
 441 on gas flow in OM.

Figure 9: Variation of $K_{app,om}$ with Langmuir parameters at $D_s = 5 \times 10^{-7} m^2/s$. $P_{in} = 22MPa$ and $P_{out} = 20MPa$, the average pore radius, $r = 11nm$ and $\sigma = 0.25nm$.

442 The above results confirm that the flow patterns of OM differ from that
 443 of IOM, and the gas flow in OM is more complicated than that in IOM.
 444 Moreover, the variation of K_{app} with pore radius suggests that the pore sizes
 445 corresponding to each components should be considered, and the usage of
 446 the mean pore size could be erroneous. In the following sections, the analysis
 447 based on reconstructed shale matrix consisting of both OM and IOM are
 448 performed to estimate the variation of K_{app} with component distribution
 449 and content.

450 4.2. Effects of the component distribution

451 The pore size distribution of reconstructed shale sample is obtained by
 452 nitrogen intrusion test of the Eagle Ford Shale reported by Naraghi and
 453 Javadpour[34]. As can be seen in Fig. 10, an evidenced bimodal trend exists
 454 in the shale sample. With a hypothesis that the pore radius of OM is smaller
 455 than that of IOM, pore size distributions in OM and IOM are extracted from
 456 Fig. 10 by using EM algorithm and are presented in Table 7.

Figure 10: Pore-size distribution of the Eagle Ford Shale sample[34]

Table 7: Properties of pore size distributions in OM and IOM, μ and σ are mean and standard deviation of the log transform of the pore size shown in Fig. 10

Region	$\mu(\text{nm})$	$\sigma(\text{nm})$	Fraction
OM	0.4	0.18	0.56
IOM	1.4	0.44	0.44

Based on the model parameters, the pore size distribution in different OM and IOM regions can be found. In order to study the effect of the distribution of each component on K_{app} , four cases are considered(See Fig. 11). In case 1, the OM and the IOM are placed parallel to the flow direction. In case 2 and case 3, gas passes through the OM and the IOM in sequence. In case 4, the OM and the IOM are randomly distributed in the simulation domain. At a given pore size distribution and component distribution, since the EM algorithm is a stochastic process, one will get different realizations of pore sizes with each run. Therefore, For each case, multiple realizations of the same pore size distribution are generated randomly into different data sets based on the parameters listed in Table 7. The other inputs are listed in Table 8.

Table 8: Input parameter for gas flow in shale matrix

$P_{in}(MPa)$	0.2
$P_{out}(MPa)$	0.1
$q_{sat} (mol/m^3)$	4000
$D_s (m^2/s)$	1×10^{-8}
$b (MPa^{-1})$	0.25
Tortuosity	2
Porosity of IOM	0.02
Porosity of OM	0.04
Length $\times$ Width ($\mu m \times \mu m$)	16×8

469 The simulation results of K_{app} for different component distributions are
 470 listed in Fig. 12. It can be seen that for each case, different data sets give
 471 rise to almost identical results, which demonstrates the numerical accuracy
 472 of the current LB model. Comparing all four cases, it can be seen that the
 473 influence of the component distribution on K_{app} is not significant, and K_{app}
 474 approximately ranges from 0.0845 mD to 0.0856 mD . Nevertheless, within
 475 this small range of K_{app} , case 3 and case 2 determine the upper and lower
 476 bounds of K_{app} , respectively. It has been pointed out that gas becomes more
 477 rarefied in smaller pores under lower pressure. As the mean pore radius
 478 of OM is roughly 3 times smaller than that of IOM, accumulation of OM
 479 near the outlet (case 3) where the pressure is lower will increase the gas
 480 rarefaction, leading to a higher K_{app} . Conversely, when OM is accumulating
 481 near the inlet (case 2), the gas rarefaction in OM pores is less significant due
 482 to the high pressure.

Figure 11: Structure of reconstructed 2-D shale matrix (length $\times$ width = $16 \times 8 \mu m$). The region in red is OM, and the region in blue is IOM. The properties of OM and IOM are listed in Table 7 and Table 8. To obtain the K_{app} , $P_{in} = 0.2 MPa$ and $P_{out} = 0.1 MPa$ are applied on the left and right boundaries of the simulation domain, respectively. Periodic boundary conditions are applied to the top and bottom boundaries.

Figure 12: K_{app} of 2-D reconstructed shale images with different structures that is shown in Fig. 11. For each case, multiple realizations of the same pore size distribution are generated randomly into different data sets.

4.3. Effects of the total organic content (TOC)

To study the effects of TOC on permeability of shale, the shale matrix is constructed based on the pore size distributions listed in Table 7 with the TOC varying from 0.2 to 0.8. The structures of the shale matrix are shown in Fig. 13, and the pore size distributions within both OM and IOM are assumed to remain constant during the simulation which are the same as that listed in Table 8.

Figure 13: The structure of shale matrix with different TOC (length $\times$ width = $16 \times 8 \mu m$). The region in red is OM, and the region in Blue is IOM. The properties of OM and IOM are listed in Table 7 and Table 8. To obtain the K_{app} , $P_{in} = 0.2 MPa$ and $P_{out} = 0.1 MPa$ are applied on the left and right boundaries of the simulation domain, respectively. Periodic boundary conditions are applied to the top and bottom boundaries.

As have been discussed in previous sections, K_{app} is influenced by the Langmuir adsorption properties and the surface diffusivity, therefore the variation of K_{app} with different D_s are analyzed and the simulation results are presented in Fig. 14. Fig. 14 shows that the apparent permeability can be enhanced or reduced with the increase of TOC, which depends on variations in surface diffusion of adsorbed gas under different conditions. Without surface diffusion or when the surface diffusion is negligible, K_{app} decreases with TOC as OM has smaller pores. A similar phenomenon has been observed by Naraghi and Javadpour[34] based on their stochastic permeability model for shale gas systems. With the increase of D_s , the contribution of surface diffusion to total flux is becoming more pronounced, and therefore the negative

501 impact of small pore radius on K_{app} is gradually compensated. In current
 502 simulation study, when D_s is larger than $1 \times 10^{-8} m^2/s$, the permeability
 503 starts to increase with TOC.

Figure 14: Variation of K_{app} with TOC based on the structure shown in Fig. 13.

504 The distributions of velocity magnitude ($\sqrt{\mathbf{u}^2}$) in the reconstructed shale
 505 matrix with different TOC at $D_s = 1 \times 10^{-9} m^2/s$ and $D_s = 1 \times 10^{-5} m^2/s$
 506 are shown in Figs. 15 and 16, respectively. In consistent with the results
 507 shown in Fig. 14, the velocity magnitude decreases with TOC at low surface
 508 diffusivity as OM has smaller pores, and increase with TOC at high surface
 509 diffusivity as surface diffusion is predominant. Moreover, the results of Fig.
 510 15 show that the gas flow in reconstructed shale sample is similar to that
 511 of the rarefied gas flow, and the velocity increases from inlet to outlet when
 512 surface diffusion is small (the velocity distribution of rarefied gas flow can
 513 be found from Refs.[64]). However, at high surface diffusivity and in the
 514 situation that the surface diffusion of adsorbed gas provides a significant
 515 mass flux in addition to the Knudsen diffusion and the convection flow, some
 516 predominant pathways are formed with the increase of TOC, and the dynamic
 517 similarity of rarefied gas flow and nano-/micro domains breaks down. The
 518 velocity distribution again emphasizes the significance of surface diffusion to
 519 gas flow in organic shale.

Figure 15: Velocity distribution of reconstructed 2-D organic shale structure (length $\times$ width = $16 \times 8 \mu m$) with different TOC for the case $D_s = 10^{-9} m^2/s$. $P_{in} = 0.2 MPa$ and $P_{out} = 0.1 MPa$ are applied on the left and right boundaries of the simulation domain, respectively. Periodic boundary conditions are applied to the top and bottom boundaries.

Figure 16: Velocity distribution of reconstructed 2-D organic shale structure (length $\times$ width = $16 \times 8 \mu m$) with different TOC for the case $D_s = 10^{-5} m^2/s$. $P_{in} = 0.2 MPa$ and $P_{out} = 0.1 MPa$ are applied on the left and right boundaries of the simulation domain, respectively. Periodic boundary conditions are applied to the top and bottom boundaries.

520 5. Conclusion

521 In this study, a generalized lattice Boltzmann algorithm for gas flow sim-
522 ulation through porous shale matrix and the DGM-GMS model are employed
523 to estimate K_{app} that includes the surface diffusion effect. Numerical simula-
524 tions of gas flow in reconstructed shale matrix containing the organic matter
525 and inorganic matter have been carried out.

526 Unlike the intrinsic permeability, K_{app} of the shale matrix is a dynamic
527 parameter and should be adjusted as the pressure decreases in a reservoir.
528 Permeability of the IOM increases with the increase of pore radius and the
529 decrease of pressure. Permeability of the OM shows a similar trend with pres-
530 sure and pore radius to that of the IOM. Moreover, surface diffusion in the
531 OM can have a more important role than Knudsen diffusion and convection
532 flow in determining the apparent permeability at low pressure and in pores
533 smaller than $10nm$. Furthermore, permeability shows strong dependence on
534 the value of Langmuir parameters and surface diffusivity, which is still not
535 well understood.

536 Simulation results of reconstructed shale matrix show that the apparent
537 permeability is influenced by the distribution of OM and IOM, as well as the
538 pore size distribution corresponding to each component. The TOC plays a
539 more significant role in the determination of K_{app} , and its effect depends on
540 the surface diffusivity of adsorbed gas.

541 The present study emphasizes that the surface diffusion in OM needs to
542 be considered for an accurate determination of the apparent permeability,
543 especially for very small pores at low pressure. The proposed LBM is shown
544 to be an effective simulation tool in determining the apparent permeability
545 of organic shale and in revealing gas transport mechanisms in shale matrix.
546 In future studies, K_{app} based on the real shale sample will be analyzed.

547 6. Acknowledgement

548 The authors would like to acknowledge the support from SCOPE, UNSW
549 and the LDRD program of LANL. J.W. would like to acknowledge the finan-
550 cial support from the China Scholarship Council (CSC). J.W. also thanks the
551 suggestions from Prof. Andreas Seidel-Morgenstern, Max Planck Institute
552 for Dynamics of Complex Technical Systems, Magdeburg. L.C. would also
553 like to acknowledge the support from National Nature Science Foundation
554 of China (No. 51406145, 51136004), and Q.K. would also like to acknowledge
555 the support from a DOE oil & gas project.

- 556 [1] R. G. Loucks, R. M. Reed, S. C. Ruppel, D. M. Jarvie, Morphology, gen-
557 esis, and distribution of nanometer-scale pores in siliceous mudstones of
558 the mississippian barnett shale, *Journal of sedimentary research* 79 (12)
559 (2009) 848–861.
- 560 [2] C. H. Sondergeld, K. E. Newsham, J. T. Comisky, M. C. Rice, C. S.
561 Rai, et al., Petrophysical considerations in evaluating and producing
562 shale gas resources, in: *SPE Unconventional Gas Conference*, Society of
563 Petroleum Engineers, 2010.
- 564 [3] F. Javadpour, D. Fisher, M. Unsworth, et al., Nanoscale gas flow in shale
565 gas sediments, *Journal of Canadian Petroleum Technology* 46 (10).
- 566 [4] H. Singh, Nonempirical apparent permeability of shale, *Unconventional*
567 *Resources Technology Conference (URTEC)*, 2013.
- 568 [5] G. Karniadakis, A. Beskok, N. Aluru, *Microflows and nanoflows: fun-*
569 *damentals and simulation*, Vol. 29, Springer, 2006.
- 570 [6] Y.-S. Wu, J. Li, D. Ding, C. Wang, Y. Di, et al., A generalised frame-
571 work model for the simulation of gas production in unconventional gas
572 reservoirs, *SPE Journal* 19 (05) (2014) 845–857.
- 573 [7] Z.-Z. Li, T. Min, Q. Kang, Y.-L. He, W.-Q. Tao, Investigation of
574 methane adsorption and its effect on gas transport in shale matrix
575 through microscale and mesoscale simulations, *International Journal of*
576 *Heat and Mass Transfer* 98 (2016) 675–686.
- 577 [8] T. Wu, D. Zhang, Impact of adsorption on gas transport in nanopores,
578 *Scientific Reports* 6.
- 579 [9] K. Wu, Apparent permeability for gas flow in shale reservoirs coupling
580 effects of gas diffusion and desorption, *Unconventional Resources Tech-*
581 *nology Conference (URTEC)*, 2014.
- 582 [10] K. Wu, X. Li, C. Wang, W. Yu, Z. Chen, Model for surface diffusion
583 of adsorbed gas in nanopores of shale gas reservoirs, *Industrial & Engi-*
584 *neering Chemistry Research* 54 (12) (2015) 3225–3236.
- 585 [11] A. Beskok, G. E. Karniadakis, Report: a model for flows in channels,
586 pipes, and ducts at micro and nano scales, *Microscale Thermophysical*
587 *Engineering* 3 (1) (1999) 43–77.

- 588 [12] F. Civan, Effective correlation of apparent gas permeability in tight
589 porous media, *Transport in porous media* 82 (2) (2010) 375–384.
- 590 [13] F. A. Florence, J. Rushing, K. E. Newsham, T. A. Blasingame, et al.,
591 Improved permeability prediction relations for low permeability sands,
592 in: *Rocky Mountain Oil & Gas Technology Symposium*, Society of
593 Petroleum Engineers, 2007.
- 594 [14] X. Xiong, D. Devegowda, M. Villazon, G. German, R. F. Sigal, F. Civan,
595 et al., A fully-coupled free and adsorptive phase transport model for
596 shale gas reservoirs including non-darcy flow effects, in: *SPE Annual
597 Technical Conference and Exhibition*, Society of Petroleum Engineers,
598 2012.
- 599 [15] C. Freeman, G. Moridis, T. Blasingame, A numerical study of microscale
600 flow behavior in tight gas and shale gas reservoir systems, *Transport in
601 porous media* 90 (1) (2011) 253–268.
- 602 [16] M. E. Curtis, R. J. Ambrose, C. H. Sondergeld, et al., Structural char-
603 acterization of gas shales on the micro-and nano-scales, in: *Canadian
604 Unconventional Resources and International Petroleum Conference*, So-
605 ciety of Petroleum Engineers, 2010.
- 606 [17] L. Chen, Q. Kang, Y. Mu, Y. He, W. Tao, A critical review of the
607 pseudopotential multiphase lattice boltzmann model: Methods and ap-
608 plications, *International Journal of Heat and Mass Transer* 76 (2014)
609 210–236.
- 610 [18] X. Nie, G. D. Doolen, S. Chen, Lattice-boltzmann simulations of fluid
611 flows in mems, *Journal of Statistical Physics* 107 (1-2) (2002) 279–289.
- 612 [19] Z. Guo, B. Shi, T. Zhao, C. Zheng, Discrete effects on boundary con-
613 ditions for the lattice boltzmann equation in simulating microscale gas
614 flows, *Physical Review E* 76 (5) (2007) 056704.
- 615 [20] L. Chen, L. Zhang, Q. Kang, H. S. Viswanathan, J. Yao, W. Tao,
616 Nanoscale simulation of shale transport properties using the lattice
617 boltzmann method: permeability and diffusivity, *Scientific reports* 5.

- 618 [21] J. Ren, P. Guo, Z. Guo, Z. Wang, A lattice boltzmann model for sim-
619 ulating gas flow in kerogen pores, *Transport in Porous Media* 106 (2)
620 (2015) 285–301.
- 621 [22] E. Fathi, Lattice boltzmann method for simulation of shale gas transport
622 in kerogen, *SPE Journal* 18 (1) (2013) 27–37.
- 623 [23] J. Wang, L. Chen, Q. Kang, S. S. Rahman, The lattice boltzmann
624 method for isothermal micro-gaseous flow and its application in shale
625 gas flow: a review, *International Journal of Heat and Mass Transfer* 95
626 (2016) 94–108.
- 627 [24] L. Chen, Q. Kang, R. Pawar, Y.-L. He, W.-Q. Tao, Pore-scale predic-
628 tion of transport properties in reconstructed nanostructures of organic
629 matter in shales, *Fuel* 158 (2015) 650–658.
- 630 [25] L. Chen, W. Fang, Q. Kang, J. D. Hyman, H. S. Viswanathan, W.-Q.
631 Tao, Generalized lattice boltzmann model for flow through tight porous
632 media with klinkenberg’s effect, *Physical Review E* 91 (3) (2015) 033004.
- 633 [26] Z. Guo, T. Zhao, Lattice boltzmann model for incompressible flows
634 through porous media, *Physical Review E* 66 (3) (2002) 036304.
- 635 [27] L. Chen, Q. Kang, Z. Dai, H. S. Viswanathan, W. Tao, Permeability
636 prediction of shale matrix reconstructed using the elementary building
637 block model, *Fuel* 160 (2015) 346–356.
- 638 [28] R. E. cunningham, R. Williams, *Diffusion in gases and porous media*,
639 springer, 1980.
- 640 [29] S. K. Bhatia, M. R. Bonilla, D. Nicholson, Molecular transport in
641 nanopores: a theoretical perspective, *Physical Chemistry Chemical*
642 *Physics* 13 (34) (2011) 15350–15383.
- 643 [30] R. Krishna, Problems and pitfalls in the use of the fick formulation
644 for intraparticle diffusion, *Chemical Engineering Science* 48 (5) (1993)
645 845–861.
- 646 [31] R. Krishna, J. Wesselingh, The maxwell-stefan approach to mass trans-
647 fer, *Chemical Engineering Science* 52 (6) (1997) 861–911.

- 648 [32] E. A. Mason, A. Malinauskas, Gas transport in porous media: the dusty-
649 gas model, Vol. 17, Elsevire, 1983.
- 650 [33] A. Tuchlenski, P. Uchytíl, A. Seidel-Morgenstern, An experimental
651 study of combined gas phase and surface diffusion in porous glass, Jour-
652 nal of Membrane Science 140 (2) (1998) 165–184.
- 653 [34] M. E. Naraghi, F. Javadpour, A stochastic permeability model for the
654 shale-gas systems, International Journal of Coal Geology 140 (2015)
655 111–124.
- 656 [35] A. Al Hinai, R. Rezaee, L. Esteban, M. Labani, Comparisons of pore size
657 distribution: A case from the western australian gas shale formations,
658 Journal of Unconventional Oil and Gas Resources 8 (2014) 1–13.
- 659 [36] M. Kutílek, L. Jendele, K. P. Panayiotopoulos, The influence of uniax-
660 ial compression upon pore size distribution in bi-model soils, Soil and
661 Tillage Research 86 (1) (2006) 27–37.
- 662 [37] P. Nithiarasu, K. Seetharamu, T. Sundararajan, Natural convective heat
663 transfer in a fluid saturated variable porosity medium, International
664 Journal of Heat and Mass Transfer 40 (16) (1997) 3955–3967.
- 665 [38] J. Gao, H. Xing, Z. Tian, H. Muhlhaus, Lattice boltzmann modeling and
666 evaluation of fluid flow in heterogeneous porous media involving multiple
667 matrix constituents, Computers & Geosciences 62 (2014) 198–207.
- 668 [39] H. Sun, J. Yao, D.-y. Fan, C.-c. Wang, Z.-x. Sun, Gas transport mode
669 criteria in ultra-tight porous media, International Journal of Heat and
670 Mass Transfer 83 (2015) 192–199.
- 671 [40] F. Verhaeghe, L.-S. Luo, B. Blanpain, Lattice boltzmann modeling of
672 microchannel flow in slip flow regime, Journal of Computational Physics
673 228 (1) (2009) 147–157.
- 674 [41] F. Javadpour, et al., Nanopores and apparent permeability of gas flow
675 in mudrocks (shale and siltstone), Journal of Canadian Petroleum Tech-
676 nology 48 (08) (2009) 16–21.
- 677 [42] A. Sakhaee-Pour, S. Bryant, et al., Gas permeability of shale, SPE
678 Reservoir Evaluation & Engineering 15 (04) (2012) 401–409.

- 679 [43] D. Do, K. Wang, Dual diffusion and finite mass exchange model for
680 adsorption kinetics in activated carbon, *AICHE journal* 44 (1) (1998)
681 68–82.
- 682 [44] A. M. Allan, G. Mavko, The effect of adsorption and knudsen diffusion
683 on the steady-state permeability of microporous rocks, *Geophysics* 78 (2)
684 (2013) D75–D83.
- 685 [45] T. Zhang, G. S. Ellis, S. C. Ruppel, K. Milliken, R. Yang, Effect of
686 organic-matter type and thermal maturity on methane adsorption in
687 shale-gas systems, *Organic Geochemistry* 47 (2012) 120–131.
- 688 [46] S. A. Mengal, R. A. Wattenbarger, et al., Accounting for adsorbed gas
689 in shale gas reservoirs, in: *SPE Middle East Oil and Gas Show and*
690 *Conference*, Society of Petroleum Engineers, 2011.
- 691 [47] A. Boulis, R. Jayakumar, F. Lalehrokh, H. Lawal, et al., Improved
692 methodologies for more accurate shale gas assessments, in: *SPE Amer-*
693 *icas Unconventional Resources Conference*, Society of Petroleum Engi-
694 neers, 2012.
- 695 [48] M. D. Zuber, J. R. Williamson, D. G. Hill, W. K. Sawyer, J. H. Frantz Jr,
696 et al., A comprehensive reservoir evaluation of a shale reservoir-the new
697 albany shale, in: *SPE Annual Technical Conference and Exhibition*,
698 Society of Petroleum Engineers, 2002.
- 699 [49] T. F. Rexer, M. J. Benham, A. C. Aplin, K. M. Thomas, Methane
700 adsorption on shale under simulated geological temperature and pressure
701 conditions, *Energy & Fuels* 27 (6) (2013) 3099–3109.
- 702 [50] R. Heller, M. Zoback, Adsorption of methane and carbon dioxide on gas
703 shale and pure mineral samples, *Journal of Unconventional Oil and Gas*
704 *Resources* 8 (2014) 14–24.
- 705 [51] S. R. Etminan, F. Javadpour, B. B. Maini, Z. Chen, Measurement of
706 gas storage processes in shale and of the molecular diffusion coefficient
707 in kerogen, *International Journal of Coal Geology* 123 (2014) 10–19.
- 708 [52] H. Hu, Methane adsorption comparison of different thermal maturity
709 kerogens in shale gas system, *Chinese Journal of Geochemistry* 33 (4)
710 (2014) 425–430.

- 711 [53] S. M. Kang, E. Fathi, R. J. Ambrose, I. Y. Akkutlu, R. F. Sigal, et al.,
712 Carbon dioxide storage capacity of organic-rich shales, *Spe Journal*
713 16 (04) (2011) 842–855.
- 714 [54] I. Y. Akkutlu, E. Fathi, et al., Multiscale gas transport in shales with
715 local kerogen heterogeneities, *SPE Journal* 17 (04) (2012) 1–002.
- 716 [55] Z. Zhai, X. Wang, X. Jin, L. Sun, J. Li, D. Cao, Adsorption and diffusion
717 of shale gas reservoirs in modeled clay minerals at different geological
718 depths, *Energy & Fuels* 28 (12) (2014) 7467–7473.
- 719 [56] W. Yuan, Z. Pan, X. Li, Y. Yang, C. Zhao, L. D. Connell, S. Li, J. He,
720 Experimental study and modelling of methane adsorption and diffusion
721 in shale, *Fuel* 117 (2014) 509–519.
- 722 [57] K. Wu, X. Li, C. Guo, C. Wang, Z. Chen, et al., A unified model for
723 gas transfer in nanopores of shale-gas reservoirs: Coupling pore diffusion
724 and surface diffusion, *SPE Journal*.
- 725 [58] M. Okazaki, H. Tamon, R. Toei, Interpretation of surface flow phe-
726 nomenon of adsorbed gases by hopping model, *AIChE Journal* 27 (2)
727 (1981) 262–270.
- 728 [59] Y. Horiguchi, R. Hudgins, P. Silveston, Effect of surface heterogeneity
729 on surface diffusion in microporous solids, *The Canadian Journal of*
730 *Chemical Engineering* 49 (1) (1971) 76–87.
- 731 [60] H. Ramanan, S. M. Auerbach, Modeling jump diffusion in zeolites: I.
732 principles and methods, in: *Fluid Transport in Nanoporous Materials*,
733 Springer, 2006, pp. 93–125.
- 734 [61] R. S. Middleton, J. W. Carey, R. P. Currier, J. D. Hyman, Q. Kang,
735 S. Karra, J. Jiménez-Martínez, M. L. Porter, H. S. Viswanathan, Shale
736 gas and non-aqueous fracturing fluids: Opportunities and challenges for
737 supercritical co 2, *Applied Energy* 147 (2015) 500–509.
- 738 [62] H. Darabi, A. Eftehad, F. Javadpour, K. Sepehrnoori, Gas flow in ultra-
739 tight shale strata, *Journal of Fluid Mechanics* 710 (2012) 641–658.
- 740 [63] Y.-S. Wu, J. Li, D. Ding, C. Wang, Y. Di, et al., A generalized frame-
741 work model for the simulation of gas production in unconventional gas
742 reservoirs, *SPE Journal* 19 (05) (2014) 845–857.

- 743 [64] E. B. Arkilic, M. A. Schmidt, K. S. Breuer, Gaseous slip flow in long
744 microchannels, *Microelectromechanical Systems, Journal of* 6 (2) (1997)
745 167–178.