Numerical Study on Gas Transport in Shale Kerogen with Adsorption Effect Using LBM

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Abstract. Gas transport and storage mechanism in gas reservoirs with complex pore size distribution play a key role in gas production. In the nano-scale, during the process of density disturbance caused by depressurization development, notable output gas collides with the wall as they convey along the channel. The continuum assumption of fluid flow is therefore invalid, and taking the influence of particles to collide with solid walls into account is necessary. The effective viscosity and slip boundary conditions were introduced in the simulation. Meanwhile, because of the adsorption effect is one of the most important intrinsic properties of shale, the impact of surface adsorption on the solid wall by using Langmuir adsorption kinetics was also involved in our investigation. In this work, a unified LB model was developed for gas multiple transports and surface adsorption in nanopores. In the model, the double distribution function was employed for a coupled bulk flow and gas diffusion model. The model is valid within the range of the continuum regime to the transition regime and has been verified by the analytical solution and the results of some previously published works. The results show that (1) the driven force of the fluid, the combination coefficient of slippage and the Knudsen number of the flow have an impact on the adsorption rate, (2) adsorption effect only directly influence the local small region of the solid surface, and the induced concentration gradient makes the global concentration variation, (3) once acting the surface adsorption on the boundary, the flux falls more significant as Knudsen number increases.

1. Introduction
During past decades, the production of shale gas has achieved great success and shows wonderful potential. The Shale reservoir is composed of the organic and inorganic portion, and the organic part is the major area for gas production and storage. The pore and pore throat size of the organic portion is usually less than conventional gas reservoirs, and mainly including microporous (<2 nm), mesoporous (2~50 nm) [1], and macroporous (>50nm), and the average pore diameter less than 10 nm [2].

Currently, the LBM study for gas transport of shale gas in kerogen involves two important subjects. The first one is how to capture a gas-solid interfacial slip. Phenomena of gas slippage near the solid wall were first demonstrated by Klinkenberg [3] when he discusses the permeability of porous media under steady-state and laminar flow condition. He supposes the existence of a layer, namely, the Knudsen layer, adjacent to the solid wall, and only consider the molecules-wall interactions. Nevertheless, Klinkenberg’s formulation is invalid in the transition flow region, because of both molecule-molecule
and molecule-wall interactions are playing a relevant role under the situation. In traditional fluid mechanics, the non-slip velocity scheme of the solid boundary corresponding to the continuum flow regime serves as the boundary condition. However, the assumption of continuum flow, as previously stated, is failing to work for the storage condition of shale gas. Great efforts have been devoted to developing accurate and efficient boundary schemes for catching the gas-solid interfacial slip. Another subject is the description of the gas diffusion problem. For LBM simulation of a two-dimensional (2D) case, it is a common practice to utilize an additional distribution function for advection-diffusion. Due to the advection-diffusion equation does not involve second-order velocity terms \(O(u^2)\), it is sufficient to keep the terms of \(O(u)\) in the equilibrium distribution function only [4]. As a result, the common D2Q9 velocity model can be simplified to a D2Q5 model.

In this work, the double distribution function involving the D2Q9 velocity model for fluid flow and the D2Q5 velocity model for diffusion was employed. And both the Knudsen effect and the surface adsorption effect were taken into consideration in the simulation. To investigate the transport mechanism of shale gas in kerogen, flow performance of a real gas steady flow model and a complex pressure-driving flow is studied.

2. Lattice Boltzmann Method

In this work, the transport of shale gas in kerogen is considered as fluid bulk flow and mass transfer in organic nanopores, which can be described by a double distribution LB function.

Since the standard LB method only valid under the assumption of the Navier-Stokes equations, the effective viscosity is introduced to establish the LB model for real gas (non-ideal gas) flow in the microchannel. The effective viscosity [5-7] and the corresponding relaxation time can be defined as

\[
\mu_e = \mu_0 / (1 + aKn), \quad \tau_f = \frac{1}{2} + \frac{hKn}{6\pi(1+aKn)}
\]

Where \(H\) is the height of the channel, \(a = a_0/a_\infty\), and \(a = 2\).

It is important to adopt an efficient slip boundary scheme for catching gas slippage in the gas-solid interfacial. Thus, the combined bounce-back/specular-reflection boundary condition (CBBSR) is adopted for slip boundary condition within the framework of LB method [8-10], e.g. the treatment of bottom wall can be given as

\[
\begin{align*}
    f_2 &= f_4 \\
    f_5 &= rf_7 + (1-r)f_8 \\
    f_6 &= rf_8 + (1-r)f_7
\end{align*}
\]

Where the left part of the above equations is the post-collision distribution function of the wall, the parameter \(r\) is the combination coefficient which represents the degree of slippage effect, e.g. \(r = 0\) indicates bounce-back scheme, namely, non-slip boundary, \(r = 1\) is the specular-reflection scheme and theoretically corresponds to the full slip boundary, \(A_1 = (1 - 0.1817\sigma)\), \(a_\sigma = (2 - \sigma)/\sigma\).

With the consideration of mass conservation, the boundary model proposed by Kang [11] was employed for the mass transfer system with surface adsorption

\[
\sum_a g_a e_a = Cu - D_s \nabla C, \quad D_s \frac{\partial C}{\partial t} + \frac{\partial N}{\partial t} = k_a C(N_m - N) - k_d N
\]

Where \(D_s\) is the diffusion coefficient of shale gas in pores, and can be obtained by experiment, \(k_a\) and \(k_d\) are the constant adsorption and desorption rates, respectively, \(N_m\) is the adsorption capacity, \(N\) is the adsorbed amount of solid surface.
3. Results and discussion

3.1. Steady flow with the periodic boundary condition

Generally, the Knudsen number is a position-dependent parameter in complex flow at the nano-scale, while it is acceptable to simplify a complex flow to a steady flow in a small local region. In steady flow, we can assume that the Knudsen number Kn remains constant along the entire channel due to the variation of density and temperature in the channel can be ignored [8]. Therefore, the periodic boundary condition is employed for inlet and outlet boundaries. Besides, the other two types of boundary conditions, namely, the slip boundary condition and the Langmuir adsorption kinetics boundary condition, are implemented for fluid bulk flow and mass transfer of the solid wall, respectively. The size of the microchannel is set to $100 \times 100$. Other input parameters as shown in Tab.1.

The adsorption efficiency, which is influenced by the different transport mechanisms, is investigated by varying the pressure gradient, slip combination coefficient, and Knudsen number. In the simulation, the bottom wall is acted as an adsorptive sink, whereas the upper wall remains non-adsorptive as a control group. These simulation results in Fig.1a show that when the pressure gradient of the system is larger, the adsorption effect on the solid surface reaches the equilibrium state more quickly. It makes sense that a greater pressure gradient will certainly boost the convection-diffusion motion. On the contrary, the trend under different slip combination coefficient or Knudsen number oppositely makes the tendency, as shown in Fig.1b and Fig.1c. It is well known that the slip combination coefficient determines the approach of gas molecules collides with the boundary and the slip velocity on the boundary. Therefore, the adsorption rate is in proportion to the slip velocity, and when $r=1$, namely, the non-slip boundary condition, reaching a minimum value. Normally, a small Knudsen number mean pore size at the smaller scale, and it makes the adsorption effect more efficient. The adsorption rate is relatively low with $Kn=0.4$. The greatest adsorption amount (the equilibrium adsorption amount) can be calculated by the typical isothermal Langmuir adsorption equation. Hence, $N_{\text{max}}=2.8235$, is given in this case.

| Simulation parameters for the steady gas flow |
|-----------------------------------------------|
| $L \times H$ | $F_x$ | $\sigma$ | $C_0$ | $D_s$ | $N_m$ | $k_a$ | $k_d$ |
| 100 \times 100 | $10^{-4}$ | 1 | 1 | 1/6 | 3 | 0.015 | 0.001 |

The difference of concentration distribution with adsorption effect and without adsorption effects are presented in Fig.2. In this section, the adsorption boundary condition is employed for the bottom wall, and for comparison, the upper wall is treated as the zero-concentration flux condition with a non-adsorption effect. In general, the concentration difference between the upper wall and bottom wall is not normally visible because the surface adsorption zone is rather smaller than the entire field, and the concentration change due to the adsorption effect is not large enough compared to the concentration within the system. Therefore, only the concentration near the bottom wall is retained in Fig. 2a and the value of other places are set to zero. A clear difference is observed in the bottom wall compared with the overall concentration distribution, including the amount of the upper wall. Fig.2b gives information about the concentration distribution near the bottom wall in detail by adjusting the view scope. The contour distributions show that the concentration at the bottom wall is larger than the surrounding place which can be attributed to that the adsorption effect making the gas molecules gathering together in the bottom surface.

For further discussion, the line graph of Fig.2c demonstrates the diverse concentration distribution of a particular position, namely, $x=L/2$, on discrete time steps. As is shown in the graph, from $y=0$ to $y=H$, five concentration distribution groups ($t=2000, 3000, 4000, 5000, 8000$) experience a similar pattern. Each of the groups grows up slightly between $y=0$ and $y=H/2$, reaching the maximum value,
and then declines in an alike way. This trend comes from the influence of the parabolic velocity distribution of channel flow.

On the other hand, the distributions on different time steps are experiencing a totally different tendency. The first time steps see a rise in the concentration difference between the upper wall and the bottom wall, with the difference reaching its peak at $t=3800$, after that, the number falls in the next time steps. Besides, the concentration of the intact region increases gradually to 1.

Fig.2d depicts the predicted time history of concentration difference between $y=0$ and $y=H$ under an entire adsorption process, where $Kn = 2k/\sqrt{\pi}$. The concentration difference $\Delta C$ remains zero for a short time at $t=0$ due to the gas molecules have not arrived. Then, the value of $\Delta C$ experiences a sudden increase as time passes, and the rate drops when $Kn$ rises. Resulting from the assumption of monolayer adsorption of Langmuir adsorption theory, there will be a peak in the process. Besides, with the $Kn$ increases, the greatest value of the concentration difference can reach will be smaller. We will witness a sharp decrease in the next time, up to 0.1, the rate falls with $Kn$, but after that, the rate increases for $Kn$. The difference will finally reach zero, meanwhile, the concentration distribution of the bottom wall will back to consistent with the upper wall.

Figure 1. Comparison of absorption rate by varying the pressure gradient, slip combination coefficient and Knudsen number, respectively

Figure 2. Comparing of concentration distribution under adsorption effect.
3.2. Gas flow in a long microchannel with pressure boundary condition

To connect with the complex fluid flow of shale gas in kerogen, we proposed a non-steady flow model by pressure-driving in a long microchannel with the ratio of the length to the height \( L/H = 100 \). The grid is \( 2000 \times 20 \), other input parameters as shown in Tab.2. The local Knudsen number is calculated by \( K_n = K_{n,\text{out}}p_{\text{out}}p(x) \), where \( K_{n,\text{out}} \) and \( p_{\text{out}} \) are the Knudsen number and pressure at the outlet, respectively, \( p(x) \) is the pressure along the centerline of the channel.

In this section, we investigate the influence of Knudsen effect on velocity along microchannel at the first step. Both the Knudsen effect and surface adsorption on the boundary is taken into consideration. The parameters for the simulation are listed in Table.2.

| \( L \times H \) | \( p_{\text{in}} \) | \( p_{\text{out}} \) | \( \sigma \) | \( C_0 \) | \( D_s \) | \( N_m \) | \( k_a \) | \( k_d \) |
|-----------------|----------------|----------------|-------|--------|--------|--------|--------|--------|
| \( 2000 \times 20 \) | 2 | 1 | 0.93 | 1 | 1/6 | 3 | 0.015 | 0.001 |

Fig.3a illustrates the impact of the Knudsen effect on the mass flux, where the dimension flux is calculated by \( Q = \int_0^H C \, dy / \int_0^H C_0 \, dy \). Throughout the period, each of the flux increases dramatically from the initial state, reaching a peak around 0.5, then hovers at it. But for the upward trend, there is a noticeable difference between them. The flux on the continuum regime \((K_n<0.001)\) reaches the highest value at first, the rate of mass transfer without adsorption effect achieves full development decreases from \( K_{n,\text{out}}=0.025 \) onward. This tendency is similar to the one with the adsorption effect, only the rate fasts a little. On the other side, the effect of surface adsorption on total mass flux is shown in Fig.3b. The dimensionless flux \( S \) is normalized by \( S = m/m_c \), where \( m = \sum (\int_0^H C \, dy) \) is the total flux of mass transfer with adsorption effect or without adsorption effect, respectively, and \( m_c \) is the flux under the continuum regime. We can learn that the mass flux saw a moderate drop as the \( K_{n,\text{out}} \) goes up, and without the impact of surface adsorption, the flux is a bit less. The above results suggest that the adsorption effect can slow down the rate of mass transfer, and reduce the mass flux of gas transport.

**Fig. 3** Comparing of velocity profile along the microchannel and the normalized mass flux at the outlet.

4. Conclusion and future work

The value of pore scale in kerogen under typical initial reservoir conditions indicates that the gas transport belongs to the slip flow regime or transition flow regime. It means Darcy’s law is invalid. Thus, a new numerical model that is available for treating non-Darcy effect should be proposed. In this paper, a Bosanquet-type effective viscosity is introduced to the LBM, and the second-order slip boundary condition is implemented to capture the Knudsen layer and simulate gas flow in kerogen. For the mass diffusion, which should not be neglected on shale gas flow in nanopores, an additional advection-diffusion equation has been employed, besides, the surface adsorption effect is taken into account. The
model has been validated by some typical benchmarks, and we found that the slippage effect causes non-negligible velocities on the pore wall, and was in good agreement with the analytical solution and the previous works, e.g. MRT-LBM, DSMC, and PI-DSMC. Simulation results show that the adsorption rate increases when the pressure gradient grows, on the contrast, as the slippage coefficient or the Knudsen number rises, the adsorption rate will drop. With the effect of surface adsorption, the concentration near the boundary will witness a time-independent change, and the variation tendency will follow the Knudsen number. Besides, the adsorption effect will slow down the rate of flow achieve full development, and decrease the total mass flux.

People are paying greater attention to the desorption effect in the shale gas production, and the study of proposing a numerical model which considers the desorption-diffusion-convection process is our future work.

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