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Study on Gas Permeability in Nano Pores of Shale Gas Reservoirs

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Abstract

Producing gas from shale gas reservoirs has played an increasingly important role in the volatile energy industry over recent years in North America for considerable volume of natural gas stored in the reservoirs. Unlike conventional gas reservoirs, the gas flow in shale reservoirs is a complex multi-scale flow process and has special flow mechanisms. Most importantly, the shale gas reservoir contains a large portion of nano pores. The study of flow in nano pores is essential for accurate shale gas numerical simulation. However, there is still not a comprehensive study in understanding how gas flows in nano pores.

In this paper, based on the advection-diffusion model, we constructed a new mathematical model to characterize gas flow in nano pores. We derived a new apparent permeability expression based on advection and Knudsen diffusion. Acomprehensive coefficient in characterizing the flow process was proposed. Simulation results were verified against the experimental data for gas flow through nano membranes. By changing the comprehensive coefficient, we found the best candidate for the case of Argon with membrane pore diameter 235 nm. We verified the model using different gases (Oxygen, Argon) and different pore diameters (235 nm, 220 nm). The comparison shows that the new model matches the experimental data very closely. Additionally, we compared our results with experimental data, Knudsen/Hagen-Poiseuille analytical solution, and existing researcher's work. The results show that this study yielded a more reliable solution. For shale gas simulation where gas flowing in nano pores plays a critical role, the results from this work will made the simulation more accurate and reliable.

Introduction

With the growing shortage of domestic and foreign energy, producing gas from shale strata has played an increasingly important role in the volatile energy industry over recent years in North America and is gradually becoming a key component in the world's energy supply (Wang and Krupnick, 2013). A shale gas reservoir is characterized of an organic-rich deposition with extremely low matrix permeability and clusters of mineral-filled "natural" fractures (**Fig.1**). Through experiment analysis on 152 cores of nine reservoirs in North America, Javadpour (2009) found that the permeability of shale bedrock is mostly 54 nd and about 90% are less than 150 nd (Javadpour et al. 2007). Most of the pores' diameter are concentrated in the range of 4 ~ 200 nm (10^{-9} m)(Curtis et al. 2010).

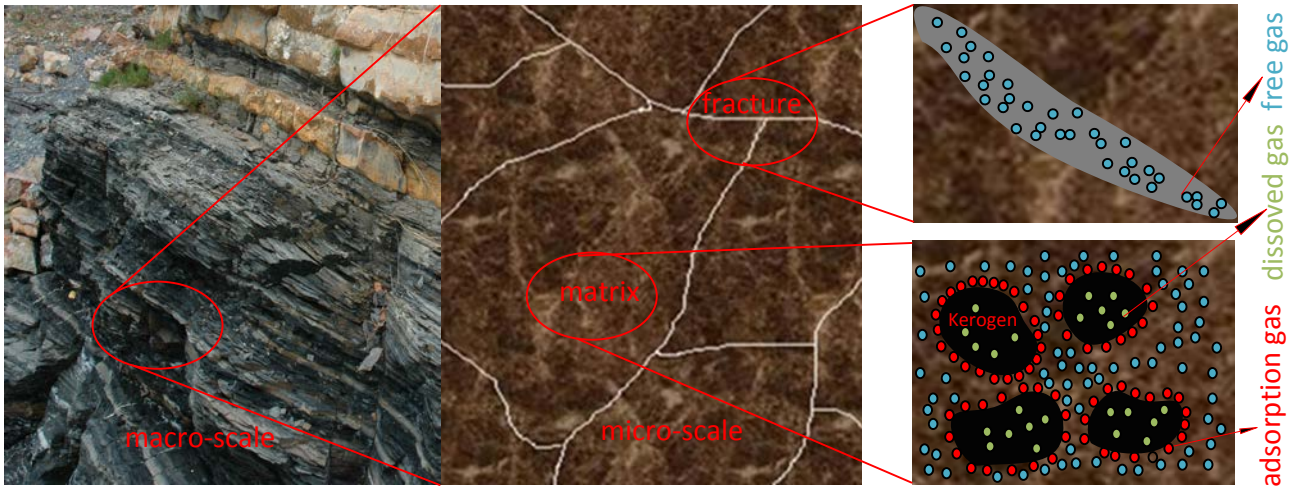

Figure 1: Gas distribution in shale strata from macro-scale to micro-scale. In the fracture there exists free gas and in the matrix free gas and adsorption gas co-exist.

Robert (Loucks et al. 2009) also found that gas shale strata is composed of micro and nanopores, with the majority being nanopores. These facts emphasize the importance of studying how gas flows in nanopores or nanotubes, which will be critical for shale gas simulation and effective commercial production.

Different modeling approaches have been adopted to simulate gas flow in nanotubes: Hornyak et al. used the Lattice-Boltzmann (LB) method to study gas flow(Hornyak et al. 2008); Bird and Bhattacharya et al. tried the molecular dynamics method (MD)(Bhattacharya and Lie, 1991; Bird 1994); Tokumasu and Karniadakis used direct simulation Monte Carlo (DSMC) to study gas flow characteristics(Karniadakis and Beskok, 2002;Tokumasu and Matsumoto, 1999); and Burnett introduced the Burnett equation type method in 1935(Burnett, 1935). However, all of these modeling methods are space and time consuming and when systems are larger than a few microns, it will become impracticable. The situation worsens when attempting to make accurate simulations when the time step and grid size are very small, at which convergence becomes a significant problem. Also, there are some scholars who tried to derive an equation to characterize gas flow law. Beskok and Karniadakis (1999) derived a unified Hagen–Poiseuille-type equation for volumetric gas flow through a single pipe. Klinkenberg (Klinkenberg 1941) introduced the Klinkenberg coefficient to consider the slip effect when gas flows in nanopores. However, the applicability of these methods still needs further investigation and the comparison between these modeling results to real experimental data has also not been provided.

The concept of apparent permeability was first proposed by Javadpour (2009) to simplify the simulation work. In 2009, he proposed the concept of apparent permeability considering Knudsen diffusion, and advection flow (Javadpour, 2009). By this method, the flux vector term can be simply expressed in the form of Darcy equation, which will greatly reduce the computing complexity. Then the concept of apparent permeability was further applied in pore scale modeling for shale gas (Shabro et al. 2011; Shabro et al. 2012). Civan (2010) and Ziarani and Aguilera (2012) derived the expression for apparent permeability in the form of Knudsen number based on a unified Hagen-Poiseuille equation (Beskok and Karniadakis, 1999).

In this paper, using the ADM model(Jinno et al. 1993), we constructed an equation that was derived theoretically and is easy to simulate. A comparison between the simulation result, experimental data, the K/HP analytical solution (Rutherford and Do, 1997) and Javadpour's solution (Javadpour, 2009) shows that the new model's results are more accurate and match more closely with the experimental data provided by Dr. Cruden (Cooper et al. 2003).

Mechanism for gas flow in nanotubes

Here we use Advection-Diffusion Model to characterize gas flow behavior in nano pores, as shown in **Fig.2**. But we do not show the slip flow because we will consider the slip flow in the proposed comprehensive coefficient.

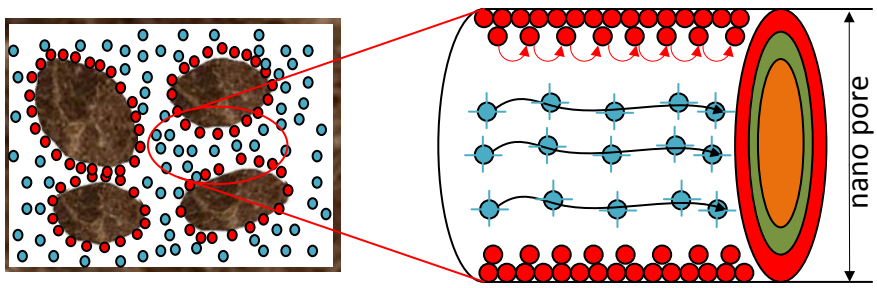

Figure 2: Gas flow mechanisms in a nano pore. Red represents Knudsen diffusion, Purple represents viscous flow.

1. Viscous flow

When the gas mean free path (Stops, 1970) is smaller than the pore diameter, the motion of gas molecules is determined by their collision with each other. Gas molecules collide with the wall less frequently. During this period, there exists viscous flow, which is caused by the pressure gradient between single-component gas molecules. The mass flux of viscous flow can be calculated by the Darcy law, which can be expressed as **Eq. 1** (Kast and Hohenthanner, 2000):

$$N_v = -\frac{\rho_g k_i}{\mu_g}(\nabla p) \tag{1}$$

where N_v is the mass flux caused by viscous flow (kg/(m^2·s)) ,k_i is the intrinsic permeability of the nano capillary(m^2) ,p is the pressure of the nano capillary (Pa), μ_g is the and gas density (kg/ m^3).

2. Knudsen Diffusion

When the diameter of the pore is very small, the mean free path lies relatively close to it. Then, the collision between gas molecules and the wall becomes the dominant effect. The gas mass flux can be expressed by the Knudsen diffusion equation (Kast and Hohenthanner, 2000; Gilron and Soffer, 2002):

$$N_k = -M_g D_k (\nabla C)$$

where $C = \frac{\rho_g}{M_g} = \frac{\overline{p}}{ZRT}$ and $\rho_g = \frac{\overline{p} M_g}{ZRT}$

$$N_k = -M_g D_k (\nabla \cdot (\frac{\overline{p}}{ZRT})) = -\frac{\rho_g D_k (\nabla p)}{\overline{p}} \tag{2}$$

N_k is the mass flux caused by Knudsen diffusion (kg/(m^2·s)) ,C is the gas mole concentration (mol/m^2) ,M_g is the gas molar mass（kg/mol）, D_k is the Kundsen diffusion coefficient (m^2/s), and D_k can be expressed as **Eq. 3** (Florence, Rushing et al. 2007):

$$\begin{aligned} D_k &= \frac{4 k_i c}{2.81708\sqrt{\frac{k_i}{\phi}}}\sqrt{\frac{\pi RT}{2M_g}} \\ &= \frac{4\sigma k_i}{\sqrt{\frac{k_i}{\phi}}}\sqrt{\frac{\pi RT}{2M_g}} \end{aligned} \tag{3}$$

where ϕ_m is the porosity of a single nano capillary, which is equal to 1, R is the gas constant 8.314474 $(m^3 \cdot Pa)/(K \cdot mol)$, M_g is the gas molar mass, T is the temperature (K) and σ is the comprehensive coefficient.

Apparent permeability of gas flow in a nano capillary

As the gas mean free path (Stops, 1970) is changing, when the gas flow in nanotube, there are viscous flow and Knudsen diffusion co-exist. Here we use the Advective-Diffusion Model (ADM) (Jinno et al. 1993) to derive the mass flux:

$$F = N_v + N_k = -\frac{\rho_g k_i}{\mu_g}(\nabla p) - \frac{\rho_g D_k}{\bar{p}}(\nabla p) \tag{4}$$

which we can change to:

$$F = -\frac{\rho_g}{\mu_g} k_i (1 + \frac{b}{\bar{p}})(\nabla p)$$

$$b = \frac{D_k \mu_g}{k_i} \tag{5}$$

Compared with the Darcy law:

$$F = -\frac{\rho_g k_{app}}{\mu_g}(\nabla p) \tag{6}$$

We can obtain:

$$k_{app} = k_i (1 + \frac{b}{\bar{p}}) \tag{7}$$

We can obtain:

$$b = \frac{D_k \mu_g}{k_i} = \frac{\mu_g}{k_i} \cdot \frac{4 k_i \sigma}{\sqrt{\frac{k_i}{\phi}}} \sqrt{\frac{\pi RT}{2M_g}}$$

$$= 4\mu_g \sigma \sqrt{\frac{\pi RT \phi}{2M_g k_i}} \tag{8}$$

So, k_{app} can be expressed as **Eq. 9**:

$$k_{app} = k_i (1 + \frac{b}{\bar{p}}) = k_i \left(1 + \frac{4\mu_g \sigma}{\bar{p}} \sqrt{\frac{\pi RT \phi}{2M_g k_i}} \right) \tag{9}$$

According to the Hagen-Poiseuille equation (Rutherford and Do, 1997), the intrinsic permeability of gas flow in cylinders can be calculated using **Eq. 10**:

$$k_i = \frac{r^2}{8} \tag{10}$$

Additionally, k_{app} can be expressed as **Eq. 11**:

$$k_{app} = k_i (1 + \frac{b}{\bar{p}}) = k_i \left(1 + \frac{4\sigma\mu_g}{\bar{p}} \sqrt{\frac{\pi RT \phi}{2M_g (r^2/8)}} \right)$$

$$= k_i \left(1 + \frac{8\sigma\mu_g}{r\bar{p}} \sqrt{\frac{\pi RT \phi}{M_g}} \right) \tag{11}$$

The mole flux can be expressed as:

$$J = -\frac{P_{avg} k_{app}}{\mu_g M_g ZRT} \nabla P$$
$$= -\frac{P_{avg} k_i}{\mu_g M_g ZRT} \left(1 + \frac{8\sigma\mu_g}{r\,\overline{p}} \sqrt{\frac{\pi RT\phi}{M_g}} \right) \nabla P \tag{12}$$

where k_{app} is the apparent permeability (m^2), b is the Klinkenberg coefficient (Kaluarachchi, 1995; Wu et al. 1998), and σ is the comprehensive coefficient which needs to be fitted. As this equation indicates, the Klinkenberg effect actually is caused by Knudsen diffusion (Gilron and Soffer, 2002).

Model validation and comparison

We then use **Equation 12** to simulate gas flow in the nanotube and compare it to the experimental data provided by Dr. Cruden(Cooper et al. 2003). The experimental data were collected from three kinds of nanotubes, which are listed in **Table 1** (Cooper et al. 2003). The model dimensions and fluid properties are listed in **Table 2**. The simulation model is shown in **Fig. 3**.

Table 1: Nanotube characteristics(Cooper, Cruden et al. 2003).

avg. pore diameter (nm)	avg. pore density ($\times 10^{12}$m^{-2})	porosity
212	8	0.28
235	10.2	0.22
220	7.2	0.27
169	9.4	0.21

Table 2: Model dimensions and fluid properties.

Flow parameters	Nanotube
Length L	60 μm
Diameter D	235 nm, 220 nm
Outlet Pressure P_{out}	4.8kPa
Pressure Drop $\Delta P = P_{in} - P_{out}$	100.0 200.0 300.0 400.0 500.0 600.0 700.0 800.0 900.0 1000.0 1200.0
Absolute Viscosity μ	2.22×10^{-5} *Pa.s*
Gas Molecular Weight	Oxgen (0.032 *kg/mol*), Argon (0.039948 *kg/mol*)
Temperature	300 *K*

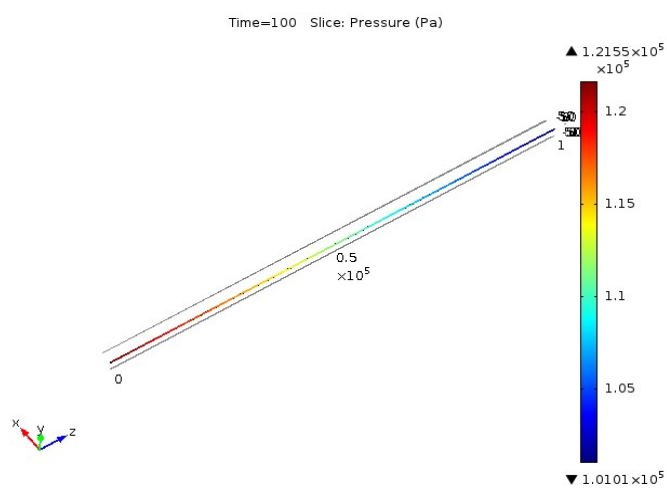

Figure 3: Model for simulating gas flow in nanotubes.

Changing the constant σ will yield different mole fluxes, which is shown in **Fig. 4 (a)**. The best-fitting σ should lie in the range of 0.75 to 0.89. Then, we can more accurately investigate the best-fitting σ, which is shown in **Fig. 4 (b)**. We estimated the best-fitting σ to be 0.82. Then, the new model was tested with the experimental data using different pore diameters and gases.

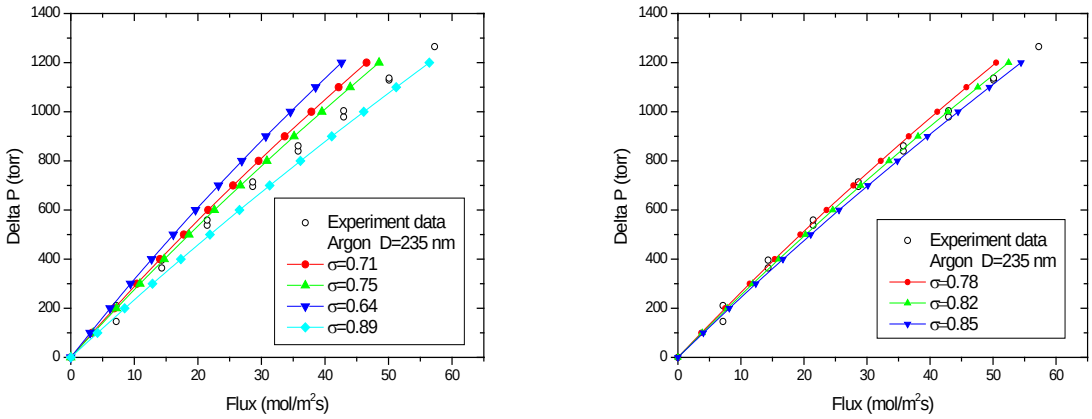

Figure 4: Pressure drop versus flux for different σ, (a) is the left figure and (b) is the right figure.

Model validation

In this part, we will verifiy the model using different gas and pore diameters. As we have derived the best fitting σ using the Argon with pore diameter of 235 nm. For better verifying the model, we will change the gas type and pore diameters to see whether the model still works. First, we will change the gas type from Argon to Oxgen, the pore diameter still keeps 235 nm; second, we will change the pore diameter from 235 nm to 220 nm, but the gas still is Argon. As **Fig. 5** and **Fig. 6** indicate, the best-fitting σ can fit the experimental data under different diameters and gases. **Fig. 6** shows that when the investigated gas is oxygen, the model matches the experimental data perfectly. **Fig. 6** shows that when the diameter is 220 nm, the model still matches the experimental data well. Later, we will compare this new model with the model provided by Javadpour and the theoretical analytical solution when transport is due to a combination of Knudsen diffusion and forced viscous Hagen-Poiseuille flow.

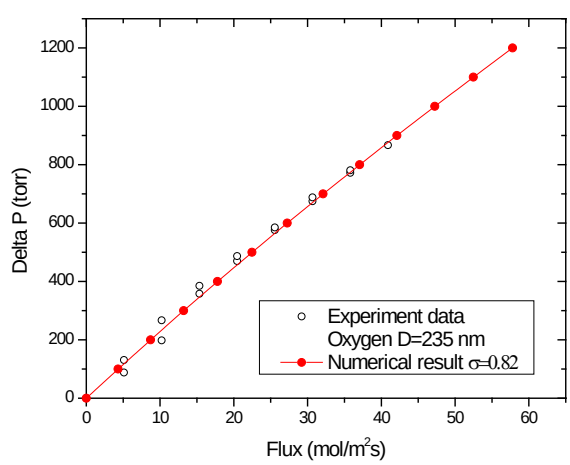

Figure 5: Pressure drop versus flux for oxygen in a nanotube with a diameter of 235 nm.

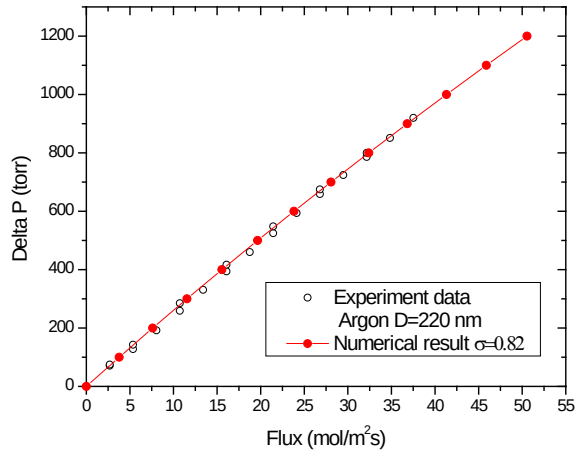

Figure 6: Pressure drop versus flux for argon in a nanotube with a diameter of 220 nm.

Model comparison

We have comparied this new model with the theoretical analytical solution, and some researchers' work. These models include the model provided by Javadpour (2009) and Florence et al. (2007).

The analytical solution is derived when transport is due to a combination of Knudsen diffusion and forced viscous Hagen-Poiseuille flow. The theoretical analytical solution (K/HP Analytical) can be expressed as shown in **Eq. 13**:

$$J = \frac{2rp}{3l}\sqrt{\frac{8RT}{\pi M}\frac{P}{RT}} + \frac{r_p^2}{16\mu l}\frac{P^2}{RT} \tag{13}$$

The first term is the Knudsen diffusion, and the second is the Hagen-Poiseuille flow (Rutherford and Do, 1997). Javadpour(2009) conducted a very thorough study of gas flow in nanopores, deriving a similar formula for gas flow in nanotubes based on Knudsen diffusion and viscous force (Javadpour et al. 2007) as shown in **Eq. 14** and **Eq. 15:**

$$J = -\frac{1}{M_g}\left[\frac{2rM_g}{3000RT}\left(\frac{8RT}{\pi M_g}\right)^{0.5} + F\frac{r^2\rho_{avg}}{8\mu}\right]\nabla P \tag{14}$$

$$F = 1 + \left(\frac{8\pi RT}{M_g}\right)^{0.5}\frac{\mu_g}{P_{avg}r}\left(\frac{2}{\alpha} - 1\right) \tag{15}$$

The apparent permeability provided by Javadpour is as shown in **Eq. 16**:

$$k_{app} = \frac{2r\mu_g M_g}{3000RT\rho_{avg}}\left(\frac{8RT}{\pi M_g}\right)^{0.5} + F\frac{r^2}{8} \tag{16}$$

Florence(Florence et al. 2007) approximated the apparent permeability derived by Beskok and Karniadakis (2002) for $Kn << 1$ under slip flow condition, where Knudsen number is the dimensionless number, defined as the ratio of the molecular mean free path length to pore diameter. It can be expressed as **Eq. 17**:

$$k_{app} = k_i(1 + 4Kn) \tag{17}$$

For a pore diameter of 235 nm, using argon in the simulation, the comparison between our new apparent permeability, Javadpour (2009) and Florence et al. (2007) is presented in **Fig. 7** and **Fig. 8**. The comparison between our new model's numerical solution, experimental data, Javadpour's and the analytical solution is shown in **Fig. 9**.

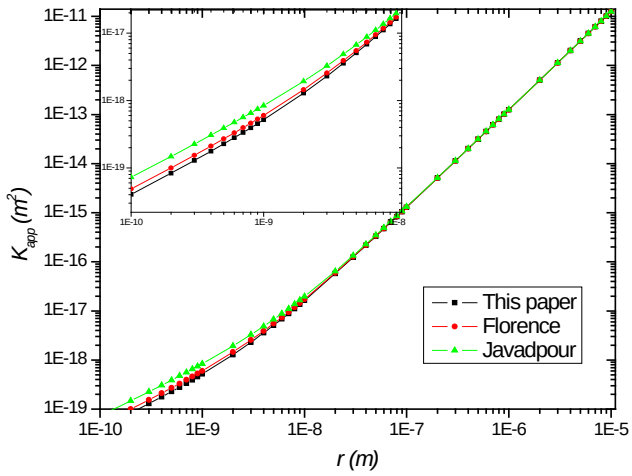

Figure 7: Comparison of Kapp versus radius between new apparent permeability, Florence's and Javadpour's.

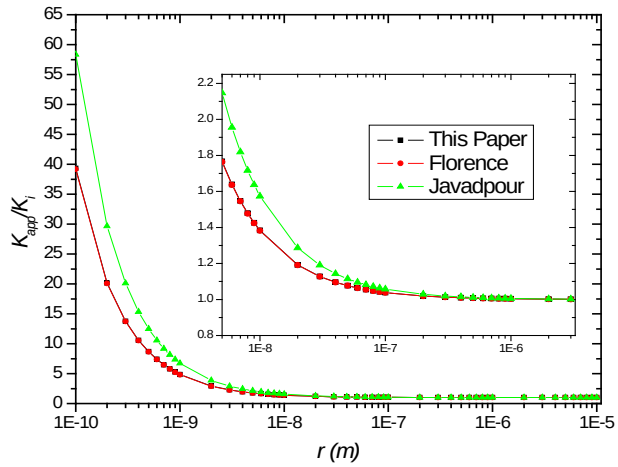

Figure 8: Comparison of K_{app}/K_i versus radius for different methods.

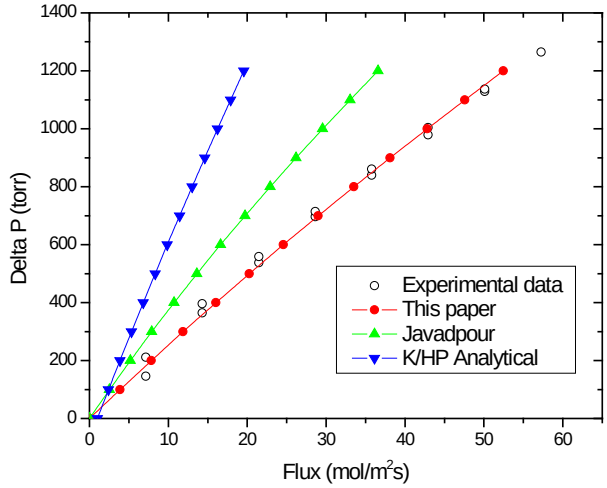

Figure 9: Comparison of pressure difference versus flux between new model, the analytical solution, Javadpour's solution and experimental data.

Fig. 7 indicates that the new model's apparent permeability is closer to the permeability provided by Florence et al. (2007). When compared with Javadpour's solution, there is more divergence. Also, as **Fig. 8** indicates, the value of K_{app}/K_i is nearly the same for Florence's method and the new method presented here. Again, there is some divergence from Javadpour's solution. However, which method is more accurate to characterize gas flow through nano pores needs more consideration because we do not know which method is accurate. So, it is necessary to compare different methods against the experimental data. In **Fig. 9**, different methods have been compared against the experimental data based on the flux.

Fig. 9 clarifies that the solution in this paper is closer to the experimental data compared with the theoretical analytical solution and Javadpour's solution. As can be seen, the K/HP Analytical equation is not reliable when used to characterize the real gas flow because the analytical solution has not considered the slip flow. And also there is some error for Javadpour's method. Furthermore, from **Fig. 9**, we can find that the flux is not increasing proportionally with the pressure difference. This is due to the fact that permeability is actually changing with the average pressure, which is fundamentaly different from Darcy flow where permeability is a constant during the whole process. Also, we can find that in flux computation, different permeability expression will generate results with much difference. This informs us that it is crucial to select the right formulation to compute the apparent permeability for gas flow through nano pores. So, by comparasion, the new method is more reliable and can characterize the gas flow in nanopores more accurately.

Conclusion

In conclusion, we have derived a new mathematical model to characterize gas flow in nanotubes and have used a new formulation to compute the apparent permeability for gas flow in nanopores. By fitting values with the experimental data, the best-fitting value of σ =0.82 was found. Through validation under different gas and pore diameter conditions, the new model was found to match the experimental data well. Additionally, the new model was compared with Javadpour's and the K/HP analytical solution, with results showing that the new model matches best with the experimental data. This work will provide a solid foundation for later study on gas flow in shale strata and numerical simulation in nanotubes.

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Nomenclature

b = Klinkenberg coefficient [$1/Pa$]
C = gas mole concentration [mol/m^2]
D_k = Kundsen diffusion coefficient [m^2/s]
J = mass flux [$kg/(m^2 \cdot s)$]
M_g = the gas mole weight [kg / mol]
N_v = mass flux caused by viscous flow [$kg/(m^2.s)$]
N_k = mass flux caused by Knudsen diffusion [$kg/(m^2.s)$]
k_i = intrinsic permeability of the nano capillary [m^2]
k_{app} = apparent permeability [m^2]
Kn = Knudsen number, which is equal to the ratio of free length to pore diameter [dimensionless]
p = pressure of the nano capillary [Pa]
P_{avg} = average gas pressure [Pa]
P_{in} = inlet pressure [Pa]
P_{out} = outlet pressure [Pa]
r = pore radius [m]
R = universal gas constant [8.314474 $J/(K \cdot mol)$]
T = temperature [K]
Z = compression factor
α = slip coefficient
ρ_g = gas density [kg/m^3]
ϕ_m = the porosity of a single nano capillary, which is equal to 1

σ = comprehensive coefficient

μ_g = gas viscosity [$mPa \cdot s$]

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