EVALUATION OF THE DIFFUSIVE TORTUOSITY BY ANALYZING THE MOLECULAR THERMAL MOTION DISPLACEMENT

by

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Molecular thermal motion is a very meaningful process. Plenty of useful information can be extracted from molecular travel displacement. In this paper, a kerogen model with a random and complex pore network is constructed. Based on the molecular thermal motion process, the diffusive tortuosity caused by the confined pore network is investigated by the molecular dynamics simulations. The influence of thermodynamic parameters on the diffusive tortuosity is carefully studied. The results showed that the diffusive tortuosity ranges from 1.57 to 2.70 depending on the pressure. However, with the variation of temperature and porosity, the diffusive tortuosity has a little change, mainly distributed from 1.79 to 1.95. The thermal diffusive tortuosity of the complex pore network is successfully calculated by analyzing molecular thermal motion property.

Key words: thermal motion, diffusion, tortuosity, nanopore

Introduction

All molecules of substances are in constant random thermal movement, which is highly related to the thermodynamic state. Although this process is extremely complex, the plenty of useful information still can be extracted from the molecular thermal motion process. The diffusive tortuosity, which can be obtained from this process, was discussed by computer simulation and experiment tests [1]. It provides a solution to describe the sinuous degree of the flow path rather than directly obtain the streamlines from the complex and amorphous porous media. However, the focus on the transportation of gases in large scale, and the thermal diffusive tortuosity in small scale (e.g. nanopores network in kerogen) is rarely reported [2, 3]. This is mainly due to the lack of effective tools and appropriate theoretical models.

The Nuclear Magnetic Resonance (NMR) is a potential instrument for evaluating the

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complex structure with pores in nanometers [2]. Nevertheless, the kerogen structure is still not fully understood owing to the difficulty of the isolating kerogen without the destroying the intra-kerogen pores [3]. The FIB-SEM to get the detail information of the pores at the size higher than 5 nm was reported in [4]. The molecular dynamics provides a new opportunity to extract the structure information through statistics and to analyze the velocity and displacement of the molecular thermal motion.

In the other hand, it is difficult to find an appropriate thermal diffusion model to describe the anomalous diffusion [5, 6]. For the diffusive tortuosity, the square of the ratio between bulk phase diffusion coefficient and thermal diffusive coefficient in a porous medium were discussed in [7]. The equivalent thermal diffusion coefficient to take the molecule-molecule and molecule-wall collision into consideration was presented in [8]. The molecular dynamics (MD) is a comprehensive technology that can be used to exploit the thermodynamic information of a complex system. It has the advantage to evaluate the diffusive tortuosity of kerogen model in [4].

Thermal diffusion property and adsorption ability were sensitive to the thermodynamic parameters (see [9]). The aime of the paper is to structure a kerogen model with an amorphous structure and complex pore network and to investigate the influence of porosity, temperature, and pressure on the molecular thermal motion. Moreover, the diffusive tortuosity values under different conditions are calculated and the relationship between the diffusive tortuosity and the thermal state is discussed.

Models and methods

Due to the lighter molecular mass and weak adsorption ability, helium is usually used as the probe gas to study the property of the molecular thermal motion. The kerogen model in an amorphous structure is constructed with the 56 type-II kerogen fragments [10]. The density stabilizes at 1.034 g/cm³ with a box size at 6.78×6.78×6.78 nm (Fig. 1). In the simulations, the CVFF force field is employed to describe the interaction amonig the kerogen atoms [11]. The force field parameters of gases and kerogen used in this study are same to other researches [11, 12]. The van der Waals interactions are calculated with Lennard-Jones potential. During the equilibration stage, two dummy particles are inserted into the kerogen model to create some pores inside the kerogen models. Both Grand Canonical Monte Carlo (GCMC) simulations and molecular dynamics simulations are used to detect the property of the thermal diffusion [11].

![Fig. 1 Kerogen structure obtained from the equilibrated process](image-url)
The porosity ($\phi$) and pore size distribution of the models are analyzed with the Python code. The atoms and empty space are integrated into a binary array and the specific method in [12]. With the use of the ratio between molecular thermal motion in bulk phase and inside the pore network, the diffusive tortuosity ($\tau_d$) in nanoscale can be expressed as [7-9]:

$$\tau_d^2 = \phi \frac{D_e}{(1 + R) \times D_{self}}$$

(1)

where $R$ is used to describe the influence of adsorption ability on diffusive tortuosity obtained from [13], $D_e$ is the equivalent thermal diffusion coefficient, $D_{self}$ is the actual diffusion coefficient in the pore network, and $\phi$ is the porosity of the model.

**Result and discussion**

**Pore size distribution**

The porosity and pore size distribution has a close relationship to the molecular thermal motion process. To obtain kerogen models with different porosity, two dummy particles with different sizes ($\sigma = 1.0$, 1.5, and 2.0 nm) are added into the kerogen model during the equilibration stage. After the equilibration, the dummy particles are removed from the kerogen model. The pore structure information is extracted from the equilibrated kerogen model. With different dummy particles, the corresponding porosities of kerogen are increasing with the dummy particles sizes, as shown in Figs. 2a-c.

![Fig. 2 Pore network caused with different dummy particles: (a) $\sigma = 1.0$ nm, (b) 1.5 nm, (c) 2.0 nm, (d) the corresponding pore size distribution profiles detected with helium](image)

The average pore size can be calculated by the probability detected with helium. As is shown in Fig. 2d, the pores size distribution is not changed dramatically, but the micropores increase with the porosity when the pore size smaller than 1 nm. Using these dummy particles is more likely to
create small pores, which has been discussed and verified in other paper [14]. Large pores are main from the anisotropy of the kerogen composition and molecular structure. The kerogen is known as an amorphous structure, which has a complex pore network and the wide pore size distribution varying from a few angstroms to the nanometers. The gases usually travel in a much more complex paths when the gases move from one side to another side.

Effect of porosity on thermal motion displacement

In order to investigate the thermal motion process, the number of gases that fit the pore network should be determined first. The adsorption capacities of the models are evaluated with GCMC simulations at 330 K and 20 MPa. The total adsorption capacities increase with the porosity just as the prediction (Tab. 1) due to the higher pore volume (Fig. 3a). Later, the final kerogen structure exported from the GCMC simulation is used as the initial structure to do further simulation. The thermal diffusion behavior of the gases in the kerogen can be described with the Einstein’s law of diffusion. The corresponding thermal diffusive coefficients ($D_{self}$) can be calculated with the mean squared displacement (MSD) [9], e.g.,

$$D_{self} = \frac{1}{2Bt} \frac{1}{N} \sum_{i=1}^{N} [r_i(t) - r_i(0)]^2$$

where $N$ represents the number of gases inside kerogen, $B$ equals to 3 at here in the 3D pore system, and $r_i(t)$ is the position vector of gases at the time of $t$. The thermal diffusion property of helium in models is outputted for 5 ns with a time interval ($\Delta t$) at 1 fs (Fig. 3b). The first 2 ns are used to bring the system into thermal equilibrium and the final 3 ns are used as production time.

Fig. 3 (a) Adsorption amount of He in kerogen model at 330 K and 20 MPa, (b) MSDs of He in these three models are obtained by analyzing the molecular thermal motion displacement

A good linear relationship between the MSD and the simulation time is obtained, and the thermal diffusive coefficients are calculated as $5.45 \times 10^{-09}$ m$^2$/s, $6.67 \times 10^{-09}$ m$^2$/s, and $6.7 \times 10^{-09}$ m$^2$/s, respectively. According to Eq. 1, the diffusive tortuosity is 1.898, 1.779, and 1.86. Therefore, the molecular thermal motion process is not sensitive to porosity. A minor change of porosity cannot make a big influence on the molecular thermal motion displacement. Based on the study of the tortuosity of kerogen in [15], the tortuosity of kerogen is around 1.26 to 2.99. According to the present model, the diffusive tortuosity (from 1.7 to 1.9) is reasonable, which is consistent with other research [15].
Tab. 1 Diffusive tortuosity of kerogen models obtained by MD simulations

<table>
<thead>
<tr>
<th>Dummy Particle Size</th>
<th>Adsorption Number</th>
<th>Diffusion coefficient m²/s</th>
<th>Porosity % (1+R)</th>
<th>Diffusive Tortuosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 nm</td>
<td>315</td>
<td>0.0453</td>
<td>15</td>
<td>1.691</td>
</tr>
<tr>
<td>1.5 nm</td>
<td>337</td>
<td>0.0445</td>
<td>16</td>
<td>1.659</td>
</tr>
<tr>
<td>2.0 nm</td>
<td>342</td>
<td>0.0424</td>
<td>16.6</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Effect of temperature on thermal motion displacement

In the micro-scale, the diffusive tortuosity is no longer an intrinsic property. Thus, it may also change with the temperature, probe molecular size, and mass, which has been discussed by the previous paper [16]. In this section, the effect of temperature on the molecular thermal motion displacement is discussed. The Knudsen number ranges from 0.42 to 0.49, indicating that the transportation of the gas in this model belongs to the transition regime (Tab. 2). The effect of pore wall on the molecular thermal motion should also be considered. Same to the previous section, the adsorption capacities in different temperatures are obtained from the GCMC simulation (Fig. 4a). The results showed that the adsorption capacity decrease with temperature. This is the result of an equilibrium between the molecular thermodynamic motion and pore adsorption potential.

Fig. 4 (a) Effect of temperature on adsorption capacity of He, (b) total MSD of He and its component in x/y/z directions, (c) effect of temperature on helium thermal diffusive ability, (d) relationship between the adsorption capacity and temperature, and the corresponding diffusive tortuosity

The original model used to study the thermal diffusion property is exported from the GCMC simulation. In the simulation, MSD is recorded every 1000 fs. Taking the helium at 300 K as an example, the molecular thermal motion displacement is not the same to each other, but in an order of Z-axis > X-axis > Y-axis (Fig. 4b). This is mainly caused by the anisotropic structure. According to
the MSD, the diffusive tortuosity is obtained from the Eq. 1. It shows that the thermal diffusion coefficients increase with temperature (from 300 to 350 K) (Fig. 4c). However, the diffusive tortuosity values at different temperatures are nearly the same, and the differences between the diffusive tortuosity values are smaller than the systemic error (Fig. 4d). Thus, the effect of the temperature on the calculation of diffusive tortuosity is weak.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Adsorption amount</th>
<th>Kn</th>
<th>$D_{self} \times 10^9$ (m$^2$/s)</th>
<th>$D_e \times 10^7$ (m$^2$/s)</th>
<th>$(1+R)$</th>
<th>Diffusive Tortuosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>365</td>
<td>0.423</td>
<td>4.77</td>
<td>1.97</td>
<td>1.73</td>
<td>1.86</td>
</tr>
<tr>
<td>310</td>
<td>344</td>
<td>0.437</td>
<td>5.52</td>
<td>2.05</td>
<td>1.68</td>
<td>1.79</td>
</tr>
<tr>
<td>320</td>
<td>334</td>
<td>0.451</td>
<td>5.32</td>
<td>2.13</td>
<td>1.69</td>
<td>1.86</td>
</tr>
<tr>
<td>330</td>
<td>315</td>
<td>0.465</td>
<td>5.45</td>
<td>2.21</td>
<td>1.69</td>
<td>1.90</td>
</tr>
<tr>
<td>340</td>
<td>305</td>
<td>0.480</td>
<td>5.38</td>
<td>2.29</td>
<td>1.67</td>
<td>1.95</td>
</tr>
<tr>
<td>350</td>
<td>292</td>
<td>0.494</td>
<td>6.15</td>
<td>2.37</td>
<td>1.65</td>
<td>1.87</td>
</tr>
</tbody>
</table>

Effect of pressure on thermal motion displacement

The pressure is another important factor affecting the molecular thermal motion process in micropores or macropores. According to the GCMC simulations, the adsorption amount of CH$_4$ increases very fast with pressure (Fig. 5a). In the lower pressure, most of the gases are adsorbed on the pore surface. With the increase of pressure, the ratio between adsorbed gases and free gases is reduced due to the limited adsorbed sites, but the bulk phase density increase with pressure. Therefore, the adsorption impact factor ranges from 1.73 to 1.61 when the pressure is set as 5 to 20 MPa (Tab. 3).

![Fig. 5](image-url)
As the pressure increases, the probability of collisions between molecules in the bulk phase can be characterized by the molecular mean free path (MFP) (Tab. 3). The mean free path reduces with the pressure suggesting that they have more chance to collide with each other when they transport from one side to another side. Therefore, in confined nanopores, the collision between molecules becomes the dominant factor. Moreover, the thermal diffusion displacement changes a little characterized with MSD (shown in Figs. 5b-c), which result in the real diffusion coefficients locating in the range of $5.21\times10^{-9}$ to $6.13\times10^{-9}$ m$^2$/s. Thus, the diffusive tortuosity reduces from 2.7 to 1.57 when the pressure increase from 5 to 30 MPa. Compared with the bulk phase, more gases adsorb on the pore wall at a lower pressure. The gas has more chance to collide with the pore wall. Consequently, the molecules receive a higher thermal motion resistance from the pore wall and travel a more sinuous path. As a result, the diffusive tortuosity decreases with pressure (Fig. 5d).

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>Adsorption amount</th>
<th>MFP (nm)</th>
<th>$Kn$</th>
<th>$D_{eqy} \times 10^{-9}$ (m$^2$/s)</th>
<th>$D_e \times 10^{-7}$ (m$^2$/s)</th>
<th>$1+R$</th>
<th>Diffusive Tortuosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>86</td>
<td>2.94</td>
<td>1.86</td>
<td>5.38</td>
<td>4.53</td>
<td>1.73</td>
<td>2.70</td>
</tr>
<tr>
<td>10</td>
<td>165</td>
<td>1.47</td>
<td>0.931</td>
<td>5.21</td>
<td>4.37</td>
<td>1.68</td>
<td>2.47</td>
</tr>
<tr>
<td>15</td>
<td>242</td>
<td>0.735</td>
<td>0.621</td>
<td>6.13</td>
<td>3.25</td>
<td>1.69</td>
<td>1.96</td>
</tr>
<tr>
<td>20</td>
<td>315</td>
<td>0.98</td>
<td>0.465</td>
<td>5.45</td>
<td>2.61</td>
<td>1.69</td>
<td>1.90</td>
</tr>
<tr>
<td>25</td>
<td>383</td>
<td>0.588</td>
<td>0.372</td>
<td>5.87</td>
<td>1.93</td>
<td>1.67</td>
<td>1.71</td>
</tr>
<tr>
<td>30</td>
<td>435</td>
<td>0.490</td>
<td>0.310</td>
<td>6.02</td>
<td>1.72</td>
<td>1.61</td>
<td>1.57</td>
</tr>
</tbody>
</table>

**Conclusions**

In this work, the diffusive tortuosity of complex pore network was calculated by the molecular thermal motion displacement based on the molecular dynamic simulation. The Knudsen number from 0.31 to 1.86 means that the molecular thermal motion in the kerogen is in the transition flow region. The variation of the pressure has a great influence on molecular thermal motion displacement, mainly caused by the thickened gas molecular. From 5 MPa to 30 MPa, the diffusive tortuosity ranges from 1.57 to 2.70. The diffusion tortuosity also changes with the porosity and temperature, but the variation of diffusion tortuosity is lower than the systemic error. The calculated diffusive tortuosity is in the range of 1.79 to 1.95.

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**Nomenclatures**

$D_e$ – equivalent diffusion coefficient, [m$^2$/s]  
$D_0$ – diffusion coefficient in bulk phase, [m$^2$/s]
\( D_{\text{self}} \) – effective diffusion coefficient, [m\(^2\)/s]  
\( T \) – temperature, [K]  
\( N \) – number of statistical particles, [-]  
\( V \) – volume, [m\(^3\)]  
\( R \) – adsorption factor, [-]  
\( \tau \) – tortuosity, [-]  
\( r_i(t) \) – molecular position at time \( t \), [m]  
\( r_i(0) \) – molecular initial position, [m]  
\( \Delta t \) – time interval, [s]  
\( \lambda \) – molecular mean free path, [m]  
\( \phi \) – porosity, [-]  

References