분자 전산 모사를 통한 멤브레인 기체 투과 현상 예측

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Prediction of Gas Permeation Phenomena in a Membrane System using Molecular Dynamics Simulation

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Abstract

Amorphous silica membrane is prepared and non-adsorbed gas permeation is permeated using molecular dynamics (MD) simulation. The permeation is observed and the permeability of each gas is estimated from the number of permeated molecules. It is compared with experimental data and the macroscopic equation of membrane system. In this study, helium and nitrogen are passed through a silica membrane. The permeability is evaluated for various operation conditions. For helium gas, Knudsen diffusion is followed in a low pressure region. The permeability agrees with experimental values. And viscous flow is shown in a high pressure region. In case of nitrogen gas, Knudsen diffusion is a major separation mechanism. The permeability of both gases decreases with temperature.

Introduction

Recently, much attention is given to the porous inorganic membranes as it has many advantages - good stability for high temperature and corrosive atmosphere. Generally, silica membrane are suitable for gas separation. Many membrane preparation methods and its applications are developed theoretically and experimentally[1-3].

The transport properties in inorganic membranes have an influence on the permeation phenomena of gas molecules. Performances of membrane are evaluated from them. And many parameters affect the transport phenomena in the inorganic membrane. As the permeation phenomena occurrs at the molecule scale, it is difficult to find the proper separation mechanism through experiments and theoretical approaches because both physical and chemical conditions affect diffusion behavior. Besides, physical and chemical properties are very difficult to measure and analyze for microporous membranes. There is no systematic way to determine the transport mechanism of an inorganic membrane system.

Takaba et. al.[4] simulated the gas permeation of amorphous silica membrane under the conventional canonical ensemble. They observed the number of permeated molecule and estimated the separation mechanism roughly. But, they did not analyze and compare the permeation parameters for various operation conditions.

In the present study, amorphous silica membrane is prepared and non-adsorbed gas molecules are passed through a synthesized silica membrane using canonical MD method. And the proper separation mechanism is found out from the permeation molecules and parameters.

Governing Equation

Let the total force of molecule i interacted with molecule j $\boldsymbol{F}_i$, then $\boldsymbol{F}_i$ can be described as:

$$\boldsymbol{F}_i = \sum_j \sum_\beta \sum_\alpha \boldsymbol{f}_{i\alpha j\beta} \tag{1}$$

where, $\boldsymbol{f}_{i\alpha j\beta}$ is the force exerted by atom β in molecule j on atom α in molecule i.

Total force can be written by Newton's equation of motion.

$$M_i \boldsymbol{R}_i'' = \boldsymbol{F}_i \tag{2}$$

It is possible to calculate $\boldsymbol{f}_{i\alpha j\beta}$ by the gradient of potential function. If $\phi_{i\alpha j\beta}(\boldsymbol{r}_{i\alpha j\beta})$ is the potential energy between atom β in molecule j and atom α in molecule i, $\boldsymbol{f}_{i\alpha j\beta}$ can be expressed as following formula:

$$\begin{aligned} U &= \sum_i \sum_{j>i} \sum_\alpha \sum_\beta \phi_{i\alpha j\beta}(\boldsymbol{r}_{i\alpha j\beta}) \\ \boldsymbol{f}_{i\alpha j\beta} &= -\nabla \phi_{i\alpha j\beta}(\boldsymbol{r}_{i\alpha j\beta}) \end{aligned} \tag{3}$$

Transport Equation and Permeability

Many transport phenomena exist in a membrane system. Gas transport through a membrane can divided into some mechanisms - Knudsen diffusion, viscous flow, continuum diffusion, and surface diffusion. These mechanisms affect the gas phase flux. The flux can be expressed from Dusty Gas Model[5].

$$\frac{p}{RT}\nabla x_i + \left(\frac{x_i}{RT} + \frac{x_i}{D_{Kn,i}}\frac{B_0}{\eta}\frac{p_{ave}}{RT}\right)\nabla p = \sum_{l=0}^{n}\frac{x_i N_l - x_l N_i}{D_{il}^{eff}} - \frac{N_i}{D_{Kn,i}} \tag{4}$$

where, $\boldsymbol{D}_{Kn,i}$, η, $\boldsymbol{B}_0$, and $\boldsymbol{D}_{il}^{eff}$ represent Knudsen diffusion coefficient, viscosity, viscous flow parameter, and effective diffusion coefficient, respectively. Surface diffusion occurs parallel to the gas phase transport and its contribution can simply be added to the gas phase flux[6]:

$$N_i^{(tot)} = N_i^{(gas)} + N_i^{(surf)} \tag{5}$$

In the present study, non-adsorbed gas is permeated so that surface diffusion does not occur. And continuum diffusion can be neglected because pure gas is permeated through membrane. For gas phase, the transport equation can be obtained as:

$$N_i = -\frac{1}{RT}\left(D_{Kn,i} + \frac{B_0}{\eta}p_{ave}\right)\nabla p \tag{6}$$

The permeability indicates the relationship between gas phase flux and pressure gradient. It is defined in equation (7).

$$F_i = \frac{1}{RT}\left(D_{Kn,i} + \frac{B_0}{\eta}p_{ave}\right) \tag{7}$$

The number of permeated molecules during time t can be written as an integral form:

$$A\int_0^t N_i ds = -\int_0^t F_i \nabla p ds \tag{8}$$

Permeability Estimation

In this research, the number of permeated molecules is analyzed using simulation. Simulation is carried out until the equilibrium is reached. And the simulation results are compared with those from equation (8). The permeability is estimated through least square method. It can be formulated as a simple optimization problem. We can find out the permeability that is suitable for the simulation results.

$$MIN_{F_i} \sum_{k=0}^{eq}(n_{sim}(k) - n_{cal}(k))^2 \tag{9}$$

Membrane System

The simulation system has the following dimensions: 70 Å×70 Å×200 Å. α-cristobalite is relaxed during 10 ps and it is changed to the amorphous structure. Born-Mayer-Huggins potential[7] is used during simulation. And drilling the membrane forms a pore of the membrane. A stabilization process is carried out for 10 ps. But, the obtained membrane contains some unsaturated oxygen and silicon atoms that have less coordination compared to bulk atoms. Typical silica membrane contains hydroxyl groups at unsaturated branches. They

occur from manufacturing processes. Consequently, hydrogen atoms and hydroxyl groups are added to unsaturated oxygen and silicon atoms, respectively. Finally, the membrane is again stabilized during 10 ps. The thickness and pore diameter of membrane is 50 Å and 25 Å, respectively.

In the simulation of gas permeation, gas molecules are placed in a region and the other region maintains vacuum initially. Helium and nitrogen gas are permeated in the synthesized membrane until the system is in equilibrium. Lennard-Jones potential and Morse potential[8] are used to describe the intermolecular interaction and bond stretching of a nitrogen molecule.

Results and Discussion

1. Helium Permeation

Figure 1 and 2 show the permeability with average pressure and temperature, respectively. Knudsen diffusion dominates the flow in a low pressure region and viscous flow is a major transport mechanism in a high pressure region. The kinetic diameter of helium gas is much smaller than the pore diameter so that molecules are passed through membrane easily. High pressure results in large average pressure and it leads the permeability to be large. And the collision among molecules is more important than the interaction between pore wall and gas molecules. Viscous flow plays a role of transport phenomena in the high pressure region.

In figure 2, permeability decreases with temperature. The mean free path decreases with temperature and this phenomena make the permeability reduced. The slope of estimates is similar with that of Knudsen diffusion.

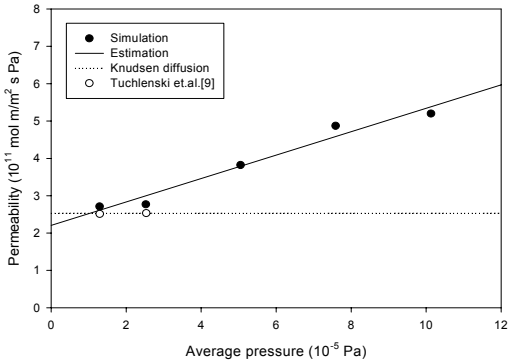

Figure 1 Permeability of helium with pressure (T = 300 K)

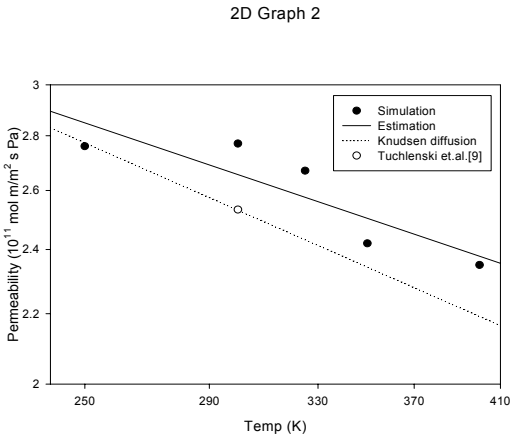

Figure 2 Permeability of helium with temperature (P_{ave} = 2.5 atm)

2. Nitrogen Permeation

Figure 3 illustrates the permeability of nitrogen gas with average pressure. The permeability is not changed significantly with average pressure. The average pressure does not affect the permeability. Knudsen diffusion dominates on the transport phenomena. The size of nitrogen gas molecule is a forth of the pore diameter. The interaction between wall and gas molecules should be considered in the permeation process and it leads the average pressure not to change permeability rapidly.

The permeability of nitrogen gas with temperature is shown in figure 4. It is reduced as temperature increases. The permeation matches up to Knudsen diffusion in a low temperature region. But, the permeability is smaller than that of Knudsen diffusion in high temperature ranges. It is confirmed that another transport phenomena happens to nitrogen permeation in

these ranges.

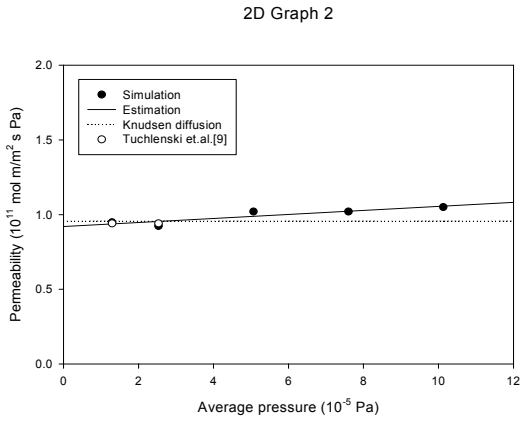

Figure 3 Permeability of nitrogen with pressure (T = 300 K)

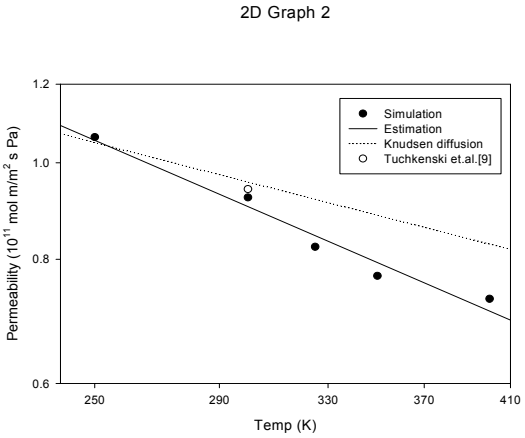

Figure 4 Permeability of nitrogen with temperature (P_{ave} = 5 atm)

Conclusion

In the present study, amorphous silica membrane was synthesized and helium and nitrogen gas was passed through the synthesized membrane system using MD simulation. The permeability was calculated from the number of permeated molecules and it was compared with the experimental data and the macroscopic equation of membrane system.

For helium gas, Knudsen diffusion was followed in a low pressure region. Viscous flow occurred in a high pressure region. It was confirmed that the permeability decreased with temperature and that it showed the similar trend of Knudsen diffusion.

The permeation of nitrogen followed Knudsen diffusion with a pressure change. The permeability was reduced with temperature. It agreed with that of Knudsen diffusion in a low temperature region. However, it became smaller in high temperature ranges. It could be confirmed that another transport phenomena happened to nitrogen permeation in these ranges.

Acknowledgement

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