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MD simulation studies for effect of membrane structures and dynamics on gas permeation properties through microporous amorphous silica membranes

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Abstract

Imaginary amorphous silica membranes were prepared on a computer and gas permeation simulations were conducted using a dual control plane non-equilibrium molecular dynamics (DCP-NEMD) method. The Melt-Quench technique was employed to prepare various types of imaginary amorphous silica membranes which had different densities (from 1.3 to 2.2 g/cm^3) and different mean pore sizes. Helium was adopted as a permeating gas species and its permeability was calculated at temperatures from 300 to 800 K. The Knudsen diffusion-like temperature dependencies of permeability could be observed for densities below 1.7 g/cm^3, while the activated diffusion for the higher density models. We have also examined the effect of 3-body membrane potential parameters on membrane dynamics and gas permeation properties. The larger thermal vibration of oxygen atoms both in siloxane bonds and silanol groups on membranes could be observed for greater γ_1 parameter in the SW potential function, which might result in the change of activation energy for gas permeation.

Keywords: Molecular dynamics; Silica membrane; Amorphous structure; Gas permeation

1. Introduction

Sol–gel derived microporous amorphous silica membranes are assumed to have small openings formed by network of siloxane bonds (network pore) [1,2]. Small molecules such as helium and hydrogen are able to permeate through network pores, that exist in dense phase occupying the greater part of a silica membrane surface. Therefore, to reveal the amorphous silica structure and gas permeation characteristics of small molecules are important to develop silica based microporous gas separation membranes. Molecular simulations of gas permeation through microporous silica membranes have been already conducted

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by many research groups to obtain useful findings [3–10]. In this work, the effects of silica membrane density and membrane potential parameters on gas permeation properties were examined using molecular dynamics simulations from a microscopic point of view. Some dense amorphous silica membranes were fabricated using the Melt-Quench (MQ) method [11], and the permeation rate of He was calculated using a simple non-equilibrium molecular dynamics simulation technique. The goal of this work is to develop a molecular dynamics simulator which can reproduce gas permeation characteristics on real microporous silica-based membranes.

2. Simulation method

2.1. Preparation of virtual membranes

Our simulation consisted of two steps, that is, a membrane preparation stage and a gas permeation stage. The ideal experimental system used here consisted of a microporous membrane unit and permeating gas molecules. The membrane material was amorphous silica, comprised of silicon and oxygen atoms. In order to simulate an amorphous silica structure, we employed the modified BMH (Born-Mayer-Huggins) pair potential, and the SW (Stillinger-Weber) potential given by Eqs. (1) and (2), respectively [11],

$$\phi_2(r_{ij}) = A_{ij}\exp\left(\frac{-r_{ij}}{\rho}\right) + \frac{z_i z_j e^2}{4\pi\varepsilon_0 r_{ij}}\mathrm{erfc}\left(\frac{r_{ij}}{\beta_{ij}}\right) \quad (1)$$

$$\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \begin{cases} \lambda_i \exp\left(\frac{\gamma_i}{r_{ij}-r_i^c} + \frac{\gamma_i}{r_{ik}-r_i^c}\right)\left(\cos\theta_{jik} - \cos\theta_{jik}^c\right)^2, & r_{ij} < r_i^c \text{ and } r_{ik} < r_i^c \\ 0, \quad r_{ij} \geq r_i^c \text{ or } r_{ik} \geq r_i^c \end{cases} \quad (2)$$

where r_{ij} is the inter-particle separation distance, Z_i the formal ionic charge, A_{ij} and ρ the parameters of the short range repulsive term, and β_{ij} describes the range of Coulombic interactions. Eq. (1) represents a two-body potential for Si–Si, Si–O and O–O atom pairs as a function of inter-particle distance and formal ionic charges. Eq. (2) is a three-body potential for O–Si–O ($i = 1$) and Si–O–Si ($i = 2$) atom bonds as a function of two inter-particle distances r_{ij}, r_{ik} and bond angle θ_{jik}. The potential parameters used in our simulations for the modified BMH potential and the SW potential are summarized in Table 1. An MD cell was started from a cristobalite crystalline structure, which consisted of 256 silicon atoms and 512 oxygen atoms, and was melted at 8500 K. The system was then rapidly cooled to 300 K to give a bulk amorphous silica structure. Various virtual amorphous silica membranes, the densities of which were different from each other, from 1.3 to 2.2 g/cm^3 were prepared. The thickness of resulting membrane unit cells was about 1.5 nm.

2.2. Non-equilibrium molecular dynamics simulation

In order to carry out a non-equilibrium MD simulation under constant pressure, we introduced control planes on boundaries with imaginary gas

Table 1
Modified BMH and SW potential parameters taken from literatures [11,12]

	Si–Si	O–O	Si–O
Modified BMH			
A_{ij} (10^{-16} J)	1.88	1.10	3.00
β_{ij} (nm)	0.234	0.234	0.229
ρ (nm)	0.029	0.029	0.029
	O–Si–O	Si–O–Si	
SW			
λ_i (10^{-18} J)	18.0	0.3	
γ_i (nm)	0.26	0.20	
r_i^c(nm)	0.30	0.26	
cos θ_{jik}	−1/3	−1	

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