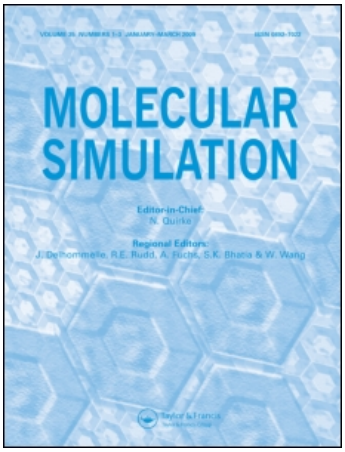

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DEVELOPMENT OF DUAL ENSEMBLE MONTE CARLO PROGRAM AND ITS APPLICATION TO THE CO_2/N_2 SEPARATION

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A novel Monte Carlo simulation named as Dual Ensemble Monte Carlo (DEMC) method is developed for the investigation of the membrane separation process. In this method the spatial combination of Grand Canonical MC and Canonical MC techniques is employed. The DEMC method can be used to calculate the separation factor at a specific chemical potential gradient. At first, a check on the accuracy of the DEMC method is made by generating gas density gradient between two reservoir regions. Thereafter, we applied this method to CO_2/N_2 gas separation by inorganic membranes and calculated the separation factor dependence on the size of micropore in membranes.

Keywords: Monte Carlo method; separation; inorganic membrane

1. INTRODUCTION

A new molecular dynamics (MD) method named as grand canonical molecular dynamics (GCMD) method was recently developed. With its aim one can establish the steady state of the chemical potential gradient in the system. This was used to perform the simulation of the steady state of the flow dynamics [1–5]. In problems of permeation through a membrane, such as a membrane separation, the situation is under the condition of existing

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chemical potential gradient. Such GCMD methods are very suitable for the simulation of a membrane separation. However, the computational time in the GCMD calculations are particularly high for the systems that include the membranes strongly interacting with the gas molecules.

In general, gas separation by an inorganic porous membrane can be described by four transport mechanisms [6]: Knudsen diffusion, surface diffusion, capillary condensation and molecular sieving. The Knudsen diffusion mechanism gives relative permeation rates that are equal to the inverse square root ratio of the molecular weights of the gases. This mechanism can be applied when the mean free path of the molecules is greater than the pore diameter, and collisions of the molecules with the pore walls occur more frequently than the collisions between diffusion molecules. The molecular sieving mechanism is based on the molecular size difference and permits only the species that have a diameter smaller than that of the pore to diffuse. By decreasing the pore size and increasing the interaction between the molecules and the membrane wall, other transport mechanism can appear. For strong adsorption, the molecules diffuse and adsorb on the pore wall, making the transport of a surface diffusion. Besides, with a high pore occupancy, accumulation of the molecules in the pore leads to the capillary condensation mechanism. The capillary condensation and the surface diffusion mechanisms are based on the affinity differences of molecules where the diffusion selectivity favors the molecule with the strongest affinity to the membrane surface.

These last two mechanisms can be considered as a suitable mechanisms which can be utilized for the separation system of molecules of similar molecular weight and size, like CO_2/N_2 mixture. In application of an inorganic membrane to the separation of CO_2 from CO_2/N_2 mixture, the selective permeation of carbon dioxide was observed and it was presumed that carbon dioxide molecules adsorbed in narrow pores have obstructed the penetration of nonadsorptive nitrogen molecules [7]. In such a system, it was considered that the ratio of adsorption amount and the resulted separation factor can be evaluated by Monte Carlo calculation since the affinity difference of the molecules to the membrane is the dominant factor to determine the separation property, instead of the difference of the diffusivity. We developed a novel Monte Carlo simulation method, Dual Ensemble Monte Carlo (DEMC), to calculate the separation factor at a specific chemical potential gradient in the membrane separation. We also applied this method to the separation process in mixture of carbon dioxide and nitrogen and evaluated the separation factor for the inorganic membrane.

2. METHOD

The DEMC method employs the grand canonical (μ VT) ensemble Monte Carlo method (GCMC) in combination with usual canonical Monte Carlo technique. The geometry of the system is given in Figure 1. In the DEMC, the system is separated into three regions. Chemical potentials in two distinct regions, indicated as area 1 and area 3 in Figure 1, correspond to two different reservoirs' regions. They were maintained with high and with low chemical potentials by the usual GCMC algorithm [8], respectively. The movements of gas molecules were attempted in the manner of usual NVT ensemble MC [8] in all areas. The periodic boundary conditions were applied to x- and y-directions. These directions are perpendicular to the flow direction. The molecules moved to outside of the simulation box in z-direction (flow direction) were immediately deleted. The density in area 3 is maintained at 0 by deleting all molecules entered this area. Thus the flow of gas between the two reservoirs through a membrane is investigated. Equilibration is permitted in order to achieve a steady state. The time for equilibration depends on the permeability of the membrane. Properties of the system were calculated only when steady state is achieved.

The simulation cell has the following dimensions: $x = 25.267$ Å, $y = 25.267$ Å, $z = 84.224$ Å. The length of areas 1 and 3 toward $+0$ z-direction is 25.267 Å, and counted from the each end of the cell.

The gas–gas and gas-membrane interactions were modeled by the Lennard-Jones potential and carbon dioxide and nitrogen molecules were simplified to the sphere. The parameters are summarized in Table I. The epsilon parameters between gas and membrane have been determined so that carbon dioxide has stronger affinity for the membrane than that of

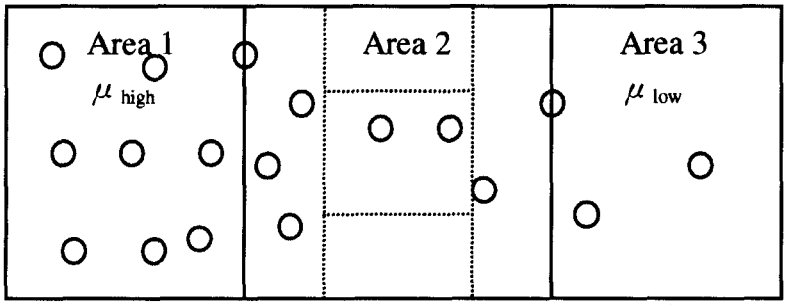

FIGURE 1 Schematic diagram of the DEMC method.

TABLE I Parameters employed in this simulation

	$\varepsilon/k[K]$	$\sigma[\AA]$
CO_2	225.3	3.794
N_2	71.4	3.798
CO_2-Mg	550	2.281
CO_2-O	550	2.459
N_2-Mg	85	2.282
N_2-O	85	2.461

nitrogen, and this difference is sufficient to achieve high separation ratio [9]. The cutoff distances for all pair interactions are 2.5σ.

The maximum displacement parameter is adjusted in such a way that the ratio of the number of the accepted displacements to the total number of displacements is equal to 50% [8]. We used the same maximum displacement parameter for each component and also applied the same dr(max) parameter to all molecules in all areas.

The translational displacement trials are applied to all molecules in one MC step. Hence, the ratio of the number of the displacement trials of two components is equal to the ratio of the number of each molecule in the simulation cell at each MC step.

We employed MgO membrane model with sizes of micropore of 6, 11 and 19 Å. This membrane is located at the center of z-direction. These models are different only in the size of the diameter of the micropore. The CG images are shown in Figure 2. The thickness of these membranes is 15 Å and the membrane atoms were fixed during the simulation. The separation factor was calculated from the ratio of the number of carbon dioxide molecules to that of nitrogen molecules which have been deleted in area 3 after achieving the steady state.

3. RESULTS AND DISCUSSION

At first, we calculated the density profile along the flow direction at various degrees of the chemical potential gradient for the case of single gas component system. Figure 2 shows the density profile of nitrogen along the flow direction at 573 K in three cases. In the case 1, the absolute activities in areas 1 and 3 are equal each to other. Since the absolute activity is the function of a chemical potential, the chemical potentials are also equal each to other in these two regions. Hence, the case 1 corresponds to the system with no chemical potential gradient. The density profile of the case 1 shown in Figure 3 is flat. This result indicates that the DEMC program worked as

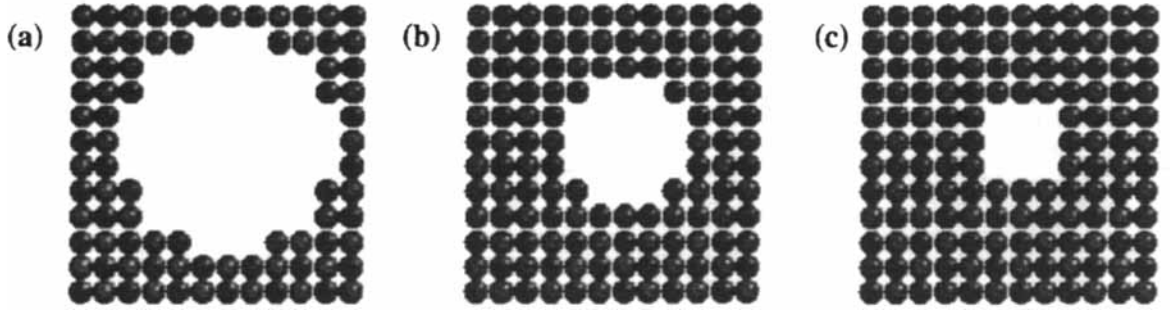

FIGURE 2 The CG image of MgO membrane models viewed from the z-direction. Pore diameter: (a) 19 Å; (b) 11 Å; (c) 6 Å.

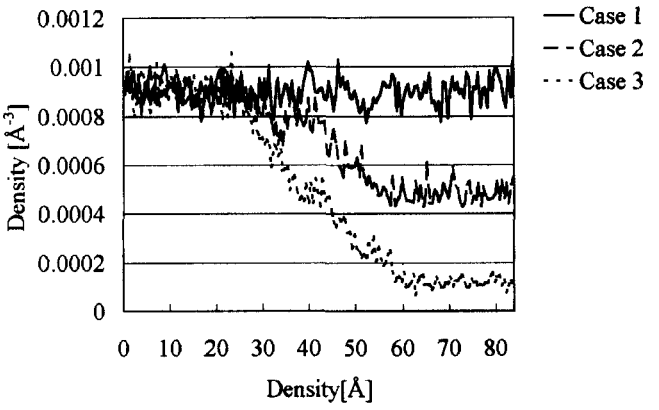

FIGURE 3 Density profile along flow direction.

expected. In the cases 2 and 3, the absolute activities in area 1 are equal to that of the case 1, while the absolute activities in the area 3 are lower than that of the case 1. The case 2 corresponds to the gentle chemical potential gradient and the case 3 corresponds to the steep chemical potential gradient. In the cases 2 and 3, the density profile in the areas 1 and 3 are flat. This indicates that the procedure of creation and deletion of gas molecules in this program is reliable. Also in the area 2, density decreases linearly in the cases 2 and 3. From this result it was suggested that reliable chemical potential gradient can be produced by the DEMC.

In the next step, the DEMC program is applied to CO_2/N_2 separation process by an inorganic membrane. All simulations were performed at 573 K. Figures 4(a), 4(b), 4(c) show the density profiles of gas components toward a flow direction by the membrane having a micropore size of 19, 11, and 6 Å, respectively. The density profile shown in Figure 4 is determined as follows. We divided the simulation cell in the flow direction into the sub-cells in 1 Å width and calculated the density in each sub-cell in order to estimate the density profile along the flow direction. The density in each sub-cell was defined by (the average number of the molecules in the sub-cell)/(the effective volume of the sub-cell). The effective volume was determined from the total space by excluding the space occupied by the membrane atoms. Hence the effective volume in the region where the membrane atoms exist is equal to the pore volumes. In all of these figures, two remarkable peaks exist. The peak around $z = 34$ Å corresponds to the gas adsorption on a membrane surface, whereas the peak around $z = 57$ Å correspond to the gas adsorption on a permeate side of the surface. The magnitude of the peak on the feed side is

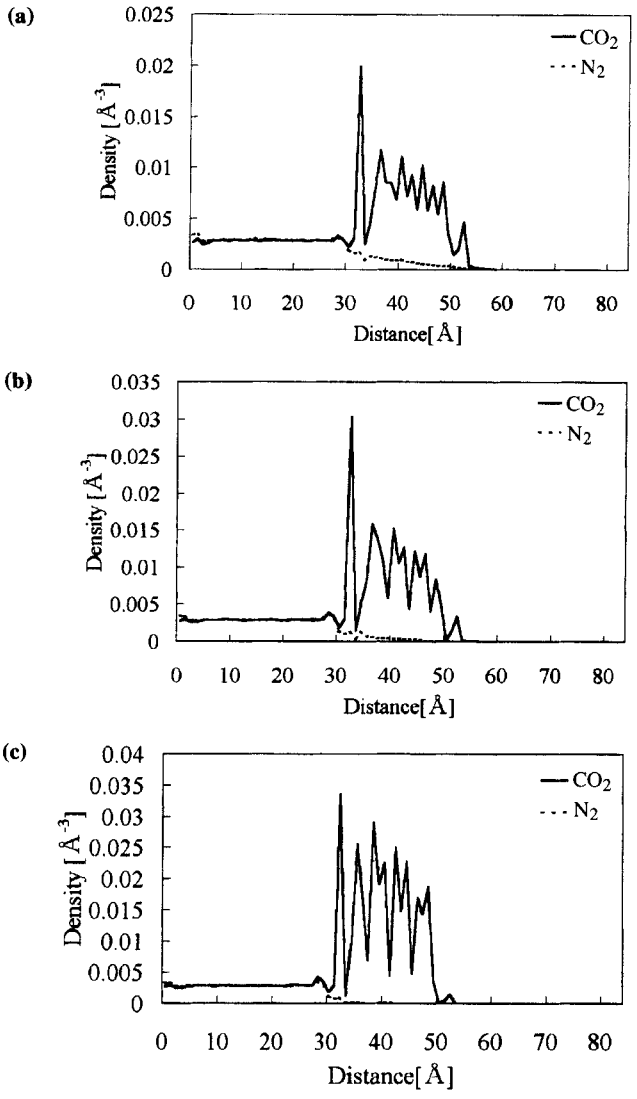

FIGURE 4 Density profile of CO_2 and N_2 in porous membranes with various pore diameters along the flow direction. Pore diameter: (a) 19 Å; (b) 11 Å; (c) 6 Å.

higher than that of the permeate side. The densities on the feed side and permeate side increase as the pore diameter decreases. The carbon dioxide density in a micropore region (approximately $z = 34-54$ Å) is higher than in case of nitrogen. This implies the existence ratio of carbon dioxide in the membrane due to the difference in a gas molecule affinity to the membrane.

The density profile of carbon dioxide in membrane region shows periodic fluctuation although the profile of nitrogen monotonically decreases. The distance of each peaks is almost equal to the pore surface periodicity in other words, to the Mg—O bond length.

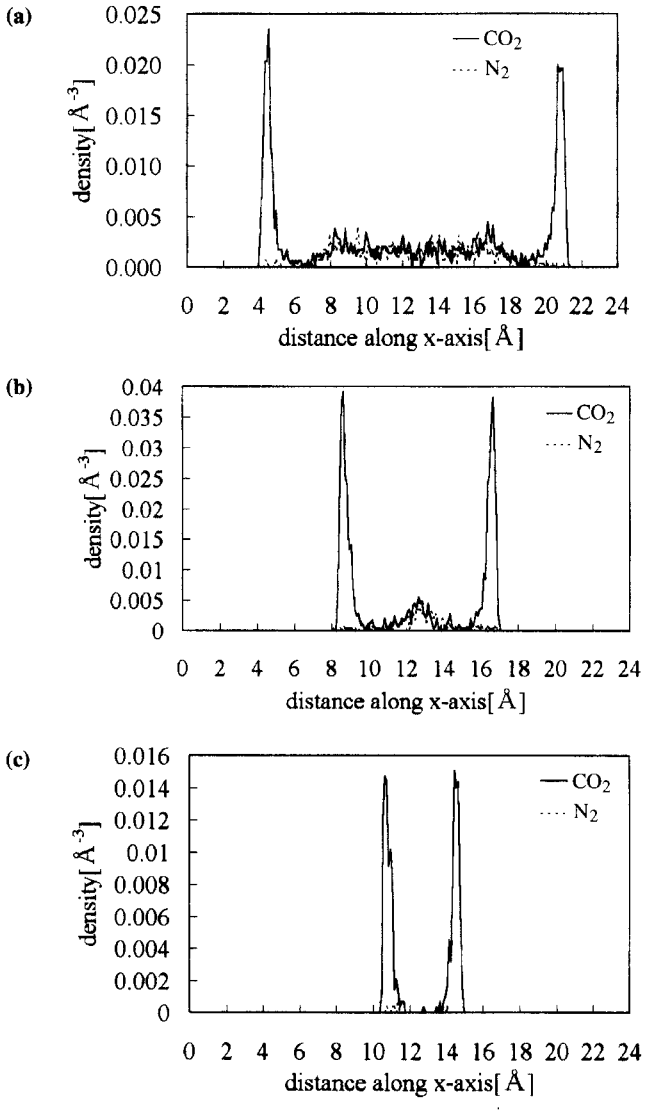

FIGURE 5 Density distribution of CO_2 and N_2 inside the pores with different diameters along the *x*-axis. Pore diameter: (a) 19 Å; (b) 11 Å; (c) 6 Å.

We also made an analysis of the density distribution along the x-axis (which is perpendicular to the flow direction) and the result of this analysis is shown in Figures 5(a), 5(b) and 5(c). These figures correspond to the case when the pore diameters equal to 6, 11 and 19 Å, respectively. The density distribution along the x-axis shown in Figure 5 is defined by (the number of the molecules in the sub-cell)/(the volume of the sub-cell). For the calculation of the density distribution along the x-axis, the sub-cell width toward the y-axis is restricted to 2 Å and the sub-cells are placed at the center of the y-axis. The width of a sub-cell toward the x-axis is 0.1 Å. In all these figures, two strong peaks of the carbon dioxide exist. These two peaks indicate that the gas adsorption on the pore surface take place. As the pore diameter becomes smaller, the value of the peaks becomes larger. In the case of pore diameters equal to 6 and 11 Å, not only carbon dioxide but also nitrogen molecules are located around the center of the micropore. In case of a micropore diameter of 19 Å, the nitrogen molecules are almost absent, and only the carbon dioxide molecules exist near the pore wall.

Finally, we evaluated the temperature dependence of the separation factor. Table II shows the separation factors and existence ratios for various pore diameters in CO_2/N_2 separation process. From Table II one can see that when the pore diameter becomes smaller, the separation factor and the existence ratio become larger.

This result can be interpreted as follows. Because the difference in affinity to the membrane between carbon dioxide and nitrogen molecules, carbon dioxide preferably adsorbed at the pore wall for all sizes of pores as shown in Figures 5(a), (b) and (c). However carbon dioxide density in the center of the pore is roughly the same as that of the nitrogen in the cases of pore diameters of 19 and 11 Å. In the case of 19 Å, the separation factor is small compared to the existence ratio in the membrane. The reason is that the adsorbed layer represents a substantial amount of carbon dioxide in the pore and the adsorbed layer is much less mobile than the gas phase in the pore. In the case of 6 Å, the gas phase almost doesn't exist, and hence the separation factor almost matches the existence ratio.

TABLE II Separation factors and existence ratios for various pore diameters in CO_2/N_2 separation process

Pore diameter [Å]	*Separation factor* (CO_2/N_2)	*Existence ratio in the membrane* (CO_2/N_2)
19	1.8	10.5
11	6.6	26.4
6	240.0	354.0

4. CONCLUSIONS

We have successfully developed a novel Monte Carlo method named as Dual Ensemble Monte Carlo (DEMC) for the gas separation by the membrane. The accuracy of the DEMC method was verified by studying nitrogen single component system.

We also applied the DEMC method to the CO_2/N_2 separation process with the inorganic membranes and evaluated the separation factor dependence on the size of the micropore. It was shown that as the pore diameter becomes smaller, the separation factor and the existence ratio of two gas components in membrane become larger. It was attributed to the difference in affinity to a membrane between the carbon dioxide and N_2 molecules, which leads to the selective condensation of carbon dioxide inside the pore.

From the analysis of the pore size dependence on the separation factor, it was found that the pore diameter becomes smaller, the separation factor and the existence ratio of carbon dioxide to nitrogen in membrane become larger and the separation factor becomes closer to the existence ratio. The reason is that the adsorbed layer represents a substantial amount of carbon dioxide in the pore with larger pore size and the adsorbed layer is much less mobile than the gas phase in the pore. In the case of much narrower pore, the gas phase almost doesn't exist and the separation factor almost matches the existence ratio.

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