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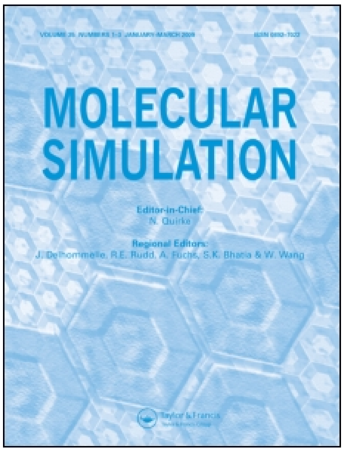

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SIMULATION PERFORMANCE OF A NON-EQUILIBRIUM MOLECULAR DYNAMICS METHOD USING DENSITY DIFFERENCE AS DRIVING FORCE

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The simulation performance of two NEMD algorithms, the constant density difference (DD) and the constant chemical potential difference (CPD) methods, has been compared in fluctuations of molar flux for He and CH_4 permeation across the ZSM-5 membrane. The CPD method and the DD method are found to give almost the same performance; however, the former seems slightly superior to the latter in terms of low fluctuations of molar flux though the former needs more CPU time than the latter. An advantage of the DD method is that it can simulate the mixed-gas permeation through a membrane under the specification of high and low pressures and the composition of feed gas. It is shown that the density profile of permeating gas could provide important information about the relative resistance at the entrance, inside, and exit regions for permeation.

Keywords: Non-equilibrium molecular dynamics; gas permeation; zeolite membrane; helium; methane

INTRODUCTION

Much attention has been drawn on studies of membrane separation mechanisms at a molecular level since high performance inorganic membranes suitable for gas separations have been developed during a decade [1, 2]. Gas permeation is essentially a non-equilibrium phenomenon since it occurs

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when different pressures are applied on two sides of a membrane. Direct molecular dynamics (MD) simulation of membrane permeation, therefore, requires two regions at different pressures or densities, which give a driving force for molecular transport (diffusion and flow) across a membrane. The grand canonical ensemble Monte Carlo (GCMC) method is suitable for maintaining a region to be at constant chemical potential or a constant density. The specification of two sub-regions at different chemical potentials (or densities) yielded a new type of non-equilibrium molecular dynamics (NEMD) methods: the dual control volume grand canonical ensemble MD (DCV-GCMD) method proposed by Heffelfinger and Swol [3], a grand canonical MD (GCMD) method by MacElroy [4], a GCMD method by Cracknell, Nicholson and Quirke [5], and the grand canonical ensemble NEMD (μVT-NEMD) method by Furukawa *et al.* [6, 7].

The DCV-GCMD method of Heffelfinger and Swol [3] was first applied to simulate the counter-diffusion in a mixed-gas and later it was used to simulate permeation of light gases across a zeolite (ZSM-5) membrane by Pohl *et al.* [8]. In the latter paper, two membranes and two couples of control regions were arranged in mirror image in order to meet the periodic boundary condition. The control regions were manipulated at each time step so as to keep the regions to be at specified chemical potentials, which resulted in density fluctuation in each region. In this case, the chemical potential difference (CPD) was a driving force for gas permeation. The GCMD methods of MacElroy [4] and Cracknell *et al.* [5] also used two control regions which were kept at specified chemical potentials as in the case of the DCV-GCMD method. The μVT-NEMD method of Furukawa *et al.* [6, 7] was applied to simulate the permeation of the Lennard-Jones fluids through slit-shaped pore membranes by keeping the densities in two control regions at specified values; therefore, density difference (DD) was a driving force for gas permeation. They also paid attention to the mirror-image arrangement of two membranes in a simulation cell to meet the periodic boundary condition. The basic concept of the mirror-image arrangement was first suggested by Hafskjold *et al.* [9, 10] in their simulation of thermal diffusion in fluids.

In the present work, two types of the NEMD simulations, the density difference (DD) and the chemical potential difference (CPD) as a driving force, have been conducted to investigate permeation of pure and mixed Lennard-Jones gases across the pure silica ZSM-5 membrane and some comparisons of the performance of the two methods will be given in terms of fluctuations of flux and the applicability to mixed-gas permeation.

SIMULATION METHOD AND MODELS

Figure 1 shows a schematic diagram of the simulation cell, which has a mirror-image arrangement of pure silica ZSM-5 membranes, H-regions, and L-regions to meet the periodic boundary condition.

The size of ZSM-5 model crystals used in this work is as follows: $XL_{\mathrm{mem}} = 4.0\,\mathrm{nm}$, $YL = 6.7\,\mathrm{nm}$, and $ZL = 6.0\,\mathrm{nm}$. The cell length XL is 34.5 nm long and the lengths of H- and L-regions are set at 4.0 nm. It is noted that the fluid-phase regions shown in Figure 1 are drawn extraordinarily short compared with the size of ZSM-5 membrane. The 010 surface is chosen as the permeation surface, which means that the straight channels are located parallel to the permeating direction.

The number densities of the H- and L-regions (ρ_{H}, ρ_{L}) are kept constant at specified values by monitoring the number of particles in each region with the help of μVT-MC algorithm for creation or destruction attempts [11]. The specified values of ρ_{H} and ρ_{L} are calculated from the temperature (T) and the pressures (P_{H}, P_{L}) through the ideal gas law. The number densities are directly related to the configurational part of chemical potentials at the H- and L-regions, $\mu_{\mathrm{H}}^{\mathrm{conf}}$ and $\mu_{\mathrm{L}}^{\mathrm{conf}}$, which are required in the μVT-MC algorithm.

$$\mu^{\mathrm{conf}}/kT = \ln \rho \tag{1}$$

The creation attempts for a test molecule located at random positions are accepted with probability

$$P_{\mathrm{acc}}^{\mathrm{cr}} = \min\left[1, \frac{z^{\mathrm{conf}}V}{N+1}\exp\left(-\frac{\Delta U}{kT}\right)\right] \tag{2}$$

where $z^{\mathrm{conf}} (= \exp(\mu^{\mathrm{conf}}/kT) = \rho)$ is the configurational absolute activity, ΔU is the difference in potential energy, V is the volume of H-region or L-region, and N is the number of molecules in the volume V. The destruction attempts for a molecule that is randomly chosen among the molecules in the volume V are accepted with probability

$$P_{\mathrm{acc}}^{\mathrm{dest}} = \min\left[1, \frac{N}{z^{\mathrm{conf}}V}\exp\left(-\frac{\Delta U}{kT}\right)\right] \tag{3}$$

For a binary gas mixture of mole fraction y_{A} and y_{B}, z^{conf} is extended to $z_{\mathrm{A}}^{\mathrm{conf}} = y_{\mathrm{A}}\rho$ or $z_{\mathrm{B}}^{\mathrm{conf}} = y_{\mathrm{B}}\rho$ for component A or B, and N becomes N_{A} or N_{B}, respectively. In the L-region where the total number density of a mixed-gas

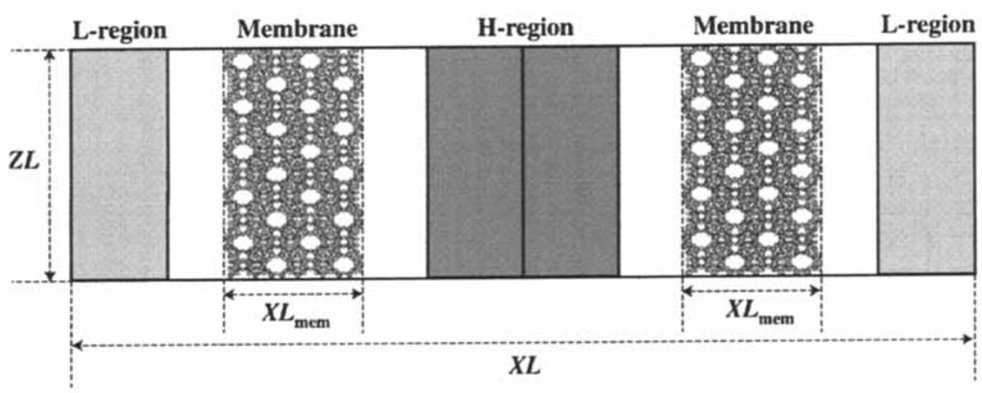

FIGURE 1 Schematic diagram of a simulation cell for the μVT-NEMD method.

is specified without knowledge of the composition, only the destruction attempts for molecules randomly chosen can be tried with probability $P_{\rm acc}^{\rm dest}$ given in Eq. (3), in which N is taken as the total number of molecules and $z^{\rm conf}$ the specified total number density ρ.

In the case of the DD driving force method, the μVT-MC operations are conducted only when the number densities in the H- and L-regions deviate from the specified values while in the case of the CPD driving force method they are consecutively done with a fixed number of trials (for example, 64) of creation/destruction at each time step. Therefore, the DD method would save the CPU time compared with the CPD method. Another important advantage of the DD driving force method is that it can calculate the mixed-gas permeation by specifying the feed-side pressure ($P_{\rm H}$) and the permeate-side pressure ($P_{\rm L}$) as well as the feed-gas composition (y) and the temperature (T). The composition of the permeate gas can be determined after a simulation, not before the simulation, since the separation is effective through permeation across the membrane. In the DD driving force scheme, the total density of the L-region, $\rho_{\rm L}$, can be calculated from the values of $P_{\rm L}$ and T through the ideal gas law. Therefore, the total number of molecules in the L-region is the target manipulation by using the destruction attempts only and the permeate-gas composition (x) is obtained automatically.

It is noted here that the DD driving force method is based upon a plausible hypothesis that the behavior of an MD system whose number of molecules is kept at N confined in a control region V may resemble that of the regular MD system characterized by the NVT ensemble. An additional comment is that the chemical potential of the NVT ensemble can be determined from the number density of the system and the temperature.

The arrangement of the simulation cell is almost the same as that of Pohl *et al.* [8] except the size of pure silica ZSM-5 crystals. The size that Pohl *et al.*, used was 4.0 nm in the membrane thickness and 20 nm × 16 nm in the cross-section. The membrane thickness is the same as that used in the present work, but their cross-sectional area of the crystals is 8 times larger than that of the present work, which indicates that they treated approximately 8 times more molecules in their simulation cell.

The helium (He) and methane (CH_4) are selected as permeating molecules. The Lennard-Jones (L-J) potential model is used for interactions between molecule–molecule and molecule–oxygen atoms comprising the zeolite. The L-J potential parameters (ε and σ), and operational variables, T, $P_{\rm H}$, and $P_{\rm L}$, are taken from the article of Pohl *et al.* [8]: $T = 300\,{\rm K}$, $P_{\rm H} = 2.0\,{\rm MPa}$, and $P_{\rm L} = 0.15\,{\rm MPa}$. The L-J parameters used are listed in Table I. The cross parameters are calculated from the Lorentz-Berthelot mixing rules.

TABLE I The L-J parameters used in this work

Molecule	$\sigma[nm]$	$\varepsilon/k\ [K]$
He	0.26	10
CH_4	0.38	148
O	0.30	230

The leap-frog method of Verlet [11] was used for the NEMD calculations. The molecular velocities were rescaled independently in three directions after every 20 steps so as to keep the temperature of molecules in subcells to be at a specified value (T). The details of the NEMD algorithm are given elsewhere [7, 12]. The time step used in the present work is 5 fs for both He and CH_4 while Pohl *et al.*, used 2.9 fs for He and 9 fs for CH_4. In the simulation, 500,000 steps were discarded and the next 1,000,000 steps were used for averaging. It is noteworthy that about one tenth smaller steps were reported by Pohl *et al.* [8] in order to reach a steady state in their simulations. The fact that approximately 8 times more molecules were present in their simulation cell might result in smaller time steps to reach a steady state.

RESULTS AND DISCUSSION

Figure 2 shows snapshots for permeation of pure gases, He and CH_4. The number density of He molecules inside the membrane is lower than that in the upper gas region, while the inside number density of CH_4 molecules is much higher than in the gas region due to adsorption in the cavities that are formed at intersections of straight and zigzag channels.

Number Density Profiles

Figure 3 shows the ensemble-averaged density profiles of He and CH_4. The thick lines in Figures 3a and 3b represent the profiles of gases permeating under the density difference across the membrane while the thin lines represent the density profiles when both sides of the membrane are filled with the feed gas.

The density profiles inside the membrane have four peaks where their locations correspond to the cavities. The features of the four peaks for He and CH_4 are quite different. In Figure 3a, the thick line inside the membrane decreases stepwise toward the permeating direction, which indicates that

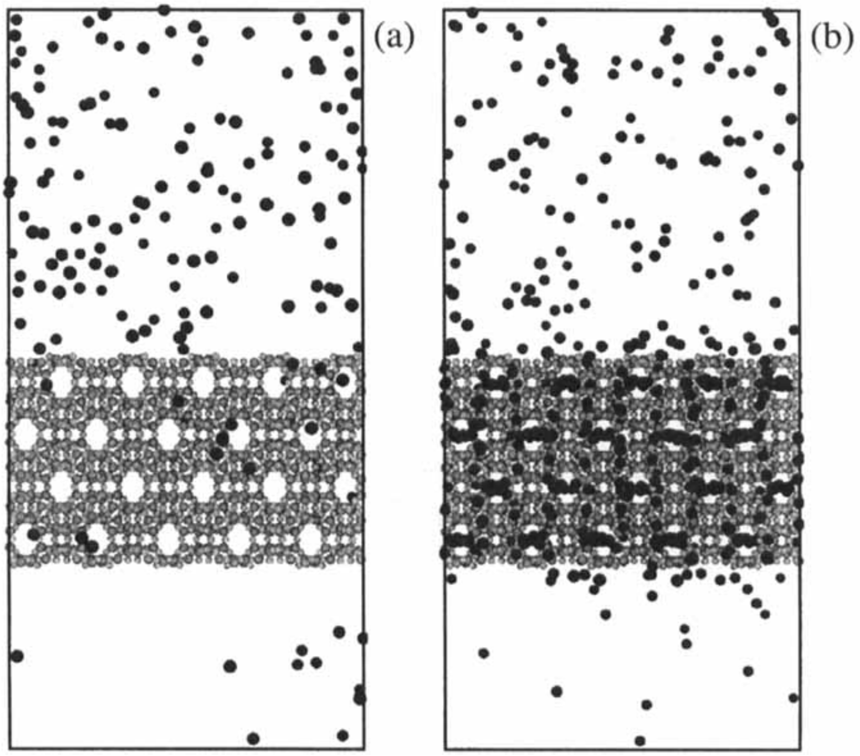

FIGURE 2 Snapshots for permeation of pure gases; (a) He, (b) CH_4.

the permeation of He is controlled by the inside permeation resistance consisting of stochastic processes of molecular migration from cavity to cavity through straight channels. The permeation resistance at the entrance and exit region may be almost the same as that of one cavity unit.

On the other hand, in Figure 3b, the thin line and the thick line inside the membrane are completely indentical, which indicates that the CH_4 molecules inside the membrane are in equilibrium with the feed gas. In other words, the permeation resistance for CH_4 across a thin (4.0 nm) membrane exists only at the exit, *i.e.*, a molecular migration step from the last cavity to the outside surface or an evaporation step from the outside surface to the L-region must be the largest resistance compared to the entrance and inside resistance for migration through cavities. The physical significance of the density profiles inside the membrane as mentioned above has not been clearly described before.

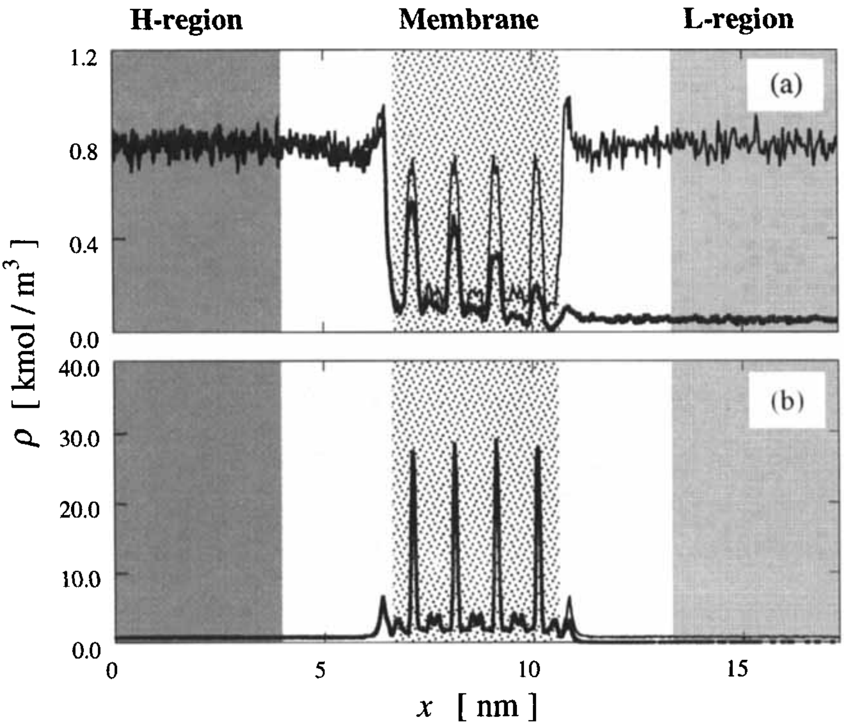

FIGURE 3 The ensemble-averaged density profiles for (a) He and (b) CH_4.

Fluctuations in Permeation Flux

Figure 4 shows the block-averaged molar flux (J) for He against the blocks each of which consists of 10^4 time steps.

An instantaneous molar flux is calculated from the number density (ρ) multiplied by the molecular velocity (v) in the whole region except the H- and L-regions. The upper curve calculated under the constant density difference (DD) shows slightly larger fluctuations than the lower curve calculated under the constant chemical potential difference (CPD). It would be worthy of expense to manipulate creation/destruction operations at each time step to obtain a lower fluctuation. In the case of CH_4, both the DD and CPD methods provide almost the same features in molar fluctuations at a low level.

CPU Times

Table II shows a comparison of CPU times required to compute 100,000 steps starting from the same conditions (number of molecules, their

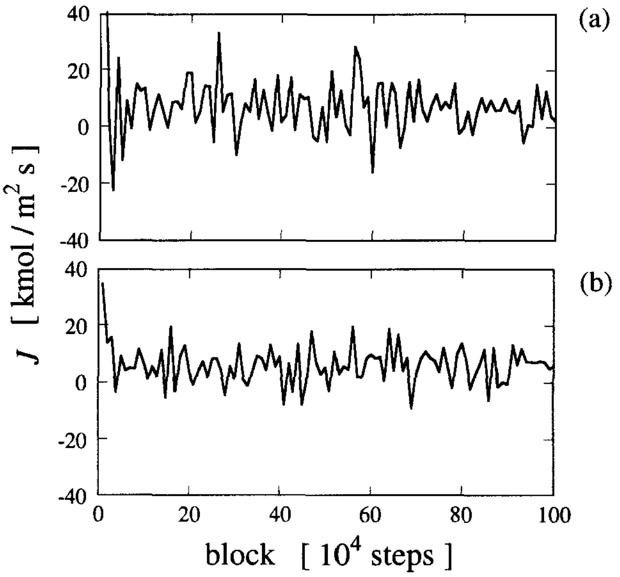

FIGURE 4 The block-averaged fluxes for He against the number of blocks; (a) DD method, (b) CPD method.

TABLE II Comparison of CPU times* for 100,000 time steps

Driving force	*CPU time* [*sec*]
DD	2330
CPD	2780

* by a COMPAQ Alpha 21264-533 MHz.

locations and initial velocities) obtained after a dynamically steady state had reached.

The DD method is found to be 19% faster than the CPD method. In honesty, we expected that the DD method would be much faster than the CPD method; however, the major part of CPU time is devoted to the calculations of pair potentials (or forces) between molecules and wall atoms. Therefore, the DD method would be more efficient in the case of simulations of transport phenomena in fluids.

Mixed-gas Permeation

Figure 5 shows profiles of the ensemble-averaged molar fluxes (J) for pure gases (solid lines) and for an equimolar mixed-gas (dotted lines) under the same total pressures at the H- and L-regions.

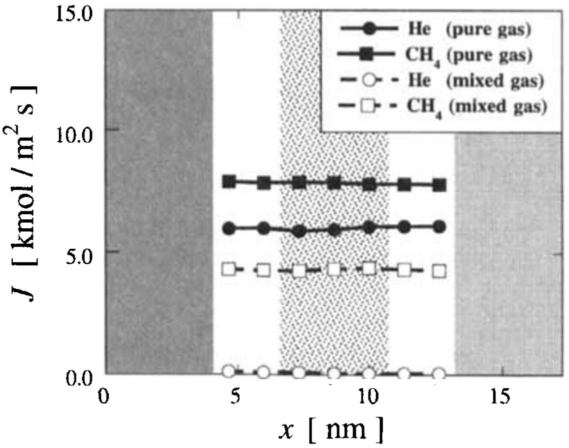

FIGURE 5 Profiles of the ensemble-averaged fluxes for pure gases (solid lines) and for an equimolar mixed-gas (dotted lines).

The profiles are nearly horizontal, which indicates that the simulations reached dynamically stationary states. The flux of pure CH_4 is slightly higher than that of He and the flux of CH_4 for the mixed-gas is smaller than that of pure CH_4 since the partial pressure of CH_4 for the mixed-gas is half the pressure of pure CH_4. It is interesting to see that the permeation of He is almost prohibited by CH_4 in the mixed gas, which is ascribed to the strong adsorption of CH_4 in ZSM-5, *i.e.*, CH_4 molecules occupy the cavities near the feed side and He molecules are unable to enter the membrane at the feed side.

Comparisons of Permeability

In Table III, comparisons are made for permeability of He and CH_4 obtained in this work (DD and CPD) and that reported by Pohl *et al.* (CPD). The permeability ($\hat{P}$) is calculated as

$$\hat{P} = J L_{\mathrm{mem}} / (P_{\mathrm{H}} - P_{\mathrm{L}}) \tag{4}$$

where L_{mem} is the membrane thickness.

For pure He and CH_4, the values of permeability obtained from different driving forces are essentially the same. We can also conclude that the values of permeability obtained in the present work are almost the same as those from different research group.

It is worthy of noting that the simulated values of permeability for CH_4 may have no physical significance for the comparison with experimental

TABLE III Permeability [10^{-12} mol m/m^2 s Pa] for pure and mixed-gases

	Pure gas		*Mixed-gas*	
	He	CH_4	*He*	CH_4
DD	13	17	nd[†]	20
CPD	12 14[*]	17 18[*]		

[*] Pohl *et al.* [8].
[†] not detected.

values since the calculated permeation flux is perfectly controlled by the exit-side reistance for permeation. In Table III, the permeability for an equimolar mixed-gas is also given.

The permeability of component i for mixed-gas permeation is calculated as

$$\hat{P}_i = J_i L_{\text{mem}}/(y_i P_{\text{H}} - x_i P_{\text{L}}) \tag{5}$$

where y_i and x_i are the mole fractions in the feed side and exit side, respectively. The observed flux of He was nearly zero, which indicates that He molecules were blocked by CH_4 molecules. It is noted that the permeability of CH_4 for the equimolar mixed-gas slightly increases compared to that for pure gas since adsorption coefficient (ratio of the amount adsorbed to the partial pressure) of CH_4 increases at a low partial pressure in the case of the Langmuir type adsorption.

CONCLUSIONS

Two types of the NEMD simulations, the density difference (DD) and the chemical potential difference (CPD) as a driving force, were conducted for permeation of pure and mixed Lennard-Jones gases across the ZSM-5 membrane. The simulation performance of the two methods is found to be almost the same; however, the CPD method might be considered to have slight superiority to the DD method in terms of low fluctuations of molar flux though the former needs a little more CPU time than the latter. It has been demonstrated that the DD method has an advantage to simulate the mixed-gas permeation through a membrane under the specification of high and low pressures and the composition of feed gas. It is also pointed out that the density profile of permeating gas inside the membrane could provide us with important information about the relative resistance at the entrance, inside, and exit regions for permeation.

Acknowledgements

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