Supporting Information for

Trajectory Extending Kinetic Monte Carlo Simulations to Evaluate Pure and Gas Mixture Diffusivities through a Dense Polymeric Membrane

Subhadeep Dasgupta,[†] Arun K.S.,[†] K. Ganapathy Ayappa,[‡] and Prabal K. Maiti[*,†]

†*Department of Physics, Indian Institute of Science, Bangalore, 560012, India*

‡*Department of Chemical Engineering, Indian Institute of Science, Bangalore, 560012, India*

E-mail: maiti@iisc.ac.in

Force field parameters

The interactions involving the gas molecules are modeled using the TraPPE force fields[1] and the 6F-CMSM atoms are modelled using modified Dreiding.[2,3] The values are shown in Table S1.

Table S1: Parameters for LJ potential and atomic charges for gas molecules and 6F-CMSM.

Molecule	Site	σ (Å)	ϵ (K)	q (e)	Bond length (Å)
CMS	H	1.65	7.65	0.056	–
	N_R	3.26	38.95	−0.617	–
	C_3	3.47	47.86	0.059	–
	C_R_r	3.47	47.86	−0.078	–
	C_R	3.47	47.86	−0.078	–
CH_4	CH_4	3.73	148.0	–	–
CO_2	C	2.80	27.0	0.70	$C - O = 1.16$
	O	3.05	79.0	−0.35	
N_2	N	3.31	36.0	−0.482	$N - N = 1.1$
	COM	0.0	0.0	0.964	

Validation of TEKMC algorithm using bulk water simulations

We performed a fully atomistic MD simulation of the bulk water system consisting of 800 SPC/E [4] water molecules using LAMMPS. Initial positions of water molecules were randomly assigned inside the MD box with a constraint that all of them are separated by a threshold distance greater than the bond length of water. Periodic boundary conditions were enforced in all directions. The bulk water system was energetically minimized to remove bad contacts. The minimization comprised of 500 steps of steepest descent followed by 500 steps of conjugate gradient. After the energy minimization, the system was heated to 300 K in steps of 30 K, each for 10 ps, using a Langevin thermostat. [5] The system is next simulated in an NPT ensemble so that the system attains appropriate density at 1 atm pressure. During the NPT run of 1 ns at 300 K temperature and 1 atm pressure, the density of the system reaches equilibrium by varying the MD box boundaries. To maintain a constant pressure of 1 atm, Nosé-Hoover barostat was used with a coupling constant of 2 ps. Finally, we perform a production run for 1 ns in an NVT ensemble. Nosé-Hoover thermostat [6,7] with

a heat bath coupling constant of 1 ps was used to maintain a constant temperature during the production run. The velocity-Verlet scheme was used to do the MD integration with an integration time step of 1 fs. The OH bond was constrained using the SHAKE[8] algorithm. To compute the long-range Coulomb potential, particle-particle particle-mesh Ewald summation method (PPPM)[9] was used with a tolerance of 10^{-5}. The trajectory of water molecules was dumped every 10 ps.

The TEKMC algorithm uses trajectories obtained from the production run to extend the MSD to a longer time scale. Trajectories obtained from the NVT simulation are used by the TEKMC algorithm to extend the MSDs to larger time scales. The timestep between the MD frames analyzed by TEKMC is 10 ps. Hence, the timestep between steps of the random walk is 10 ps. From the 1 ns NVT simulation of SPC/E water, the transition probability matrix is estimated during the first stage of the TEKMC algorithm. We perform 3000 random walks for various grid sizes up to 3 ns and tune the grid size to match with the MSD of MD simulation.

Random walks of TEKMC were extended till 100 ns for these grid sizes. MSD and diffusion coefficient till 0.5 ns obtained from the MD simulation are also shown. Grid size of 0.28 nm best matches the MD data (having the lowest MSE). The exponent α is 1.0, indicating that MSD is linear with time and SPC/E water follows Fickian diffusion in this time scale. From TEKMC, we obtain diffusion coefficient of SPC/E water to be $2.47 \pm 0.15 \times 10^{-5} \, \text{cm}^2 \, \text{s}^{-1}$, in good agreement to the literature value of $2.75 \times 10^{-5} \, \text{cm}^2 \, \text{s}^{-1}$.[10] The diffusion coefficient of bulk water obtained from simulations is subject to finite size effects based on the size of the box and number of molecules.[11] The main goal of our validation was to reproduce the MD obtained MSD by tuning d_{grid} during TEKMC. Once validated, our main focus is on the gas diffusivity inside the ultramicropores. Diffusion in the polymeric membrane is related to the inherent pore size distribution in the membrane which could be influenced by finite size effects. We point out that the polymeric membranes used in this study have been prepared by using extensive compression and decompression cycles which

has shown to reproduce the experimental pore size distribution and adsorption isotherm for this system.[12] The finite size corrected diffusivities may also be obtained by a suitable further tuning of d_{grid}. The self-diffusion coefficient of pure water has been measured to be $2.3 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ at $298\,\mathrm{K}$ from experimental techniques like diaphragm-cell technique[13] or the pulsed-gradient spin echo (PGSE) NMR method.[14]

Probability distribution of gases used for performing TEKMC

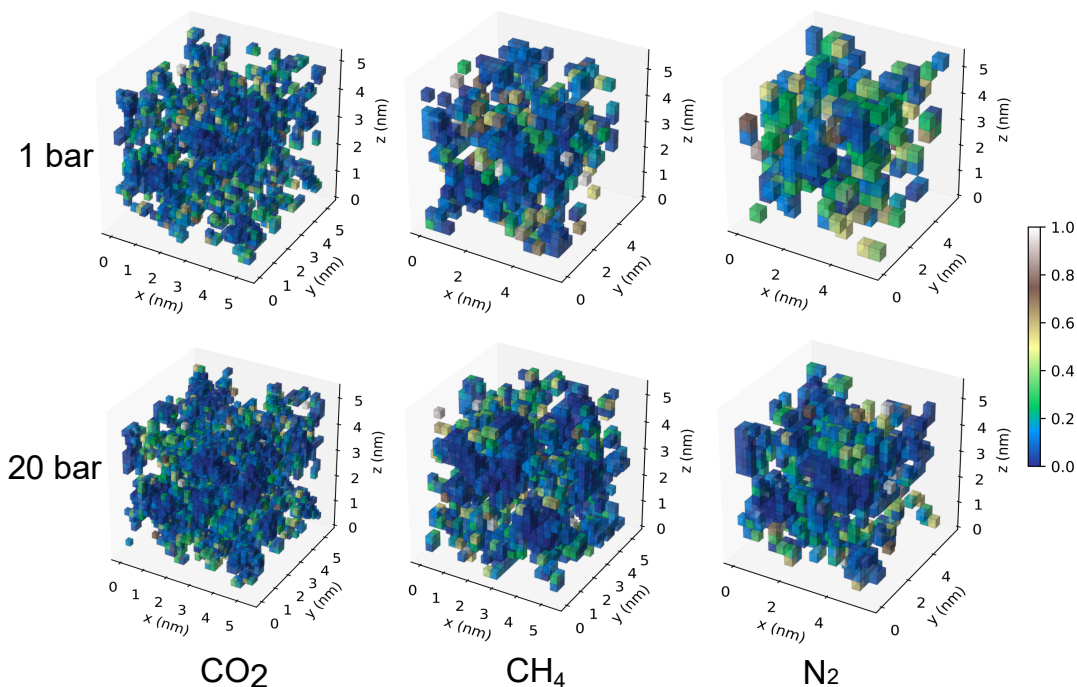
Figure S1: Probability of survival in a voxel for pure gas systems at two pressure values. The size of the voxel corresponds to the optimum d_{grid} per system.

Binary component diffusion inside 6F-CMSM

We perform MD simulations of binary gas mixtures inside 6F-CMSM corresponding to different pressure conditions. The obtained trajectories are then extended till $5\,\mathrm{\mu s}$ to obtain

CO₂   CO₂   CO₂

CH₄   CH₄   N₂
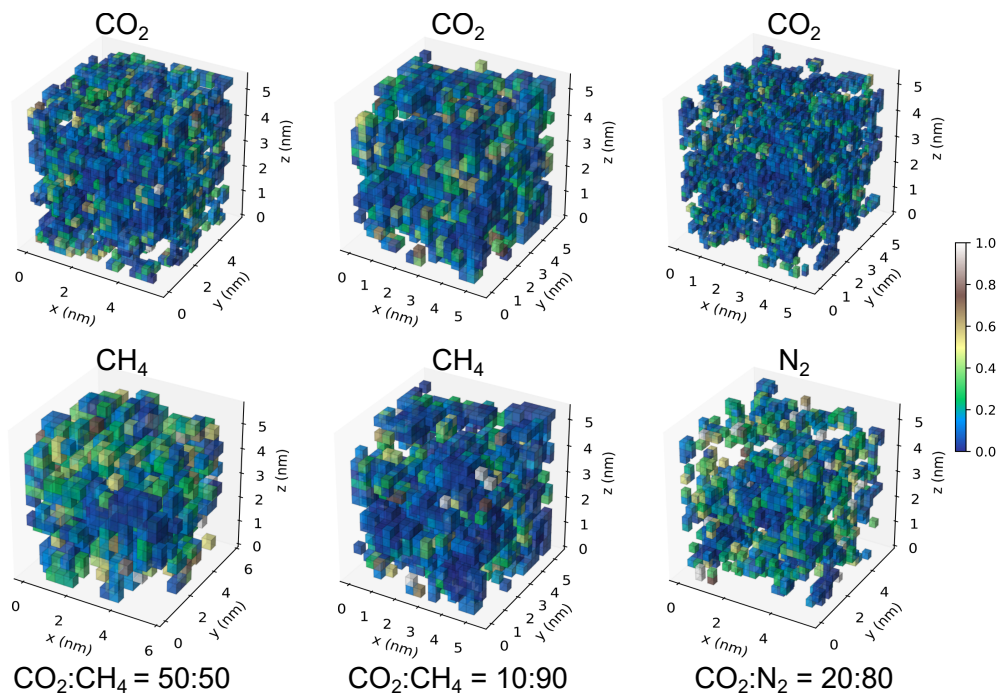
CO₂:CH₄ = 50:50   CO₂:CH₄ = 10:90   CO₂:N₂ = 20:80

Figure S2: Probability of survival in a voxel for different binary gas mixture systems at 20 bar pressure.
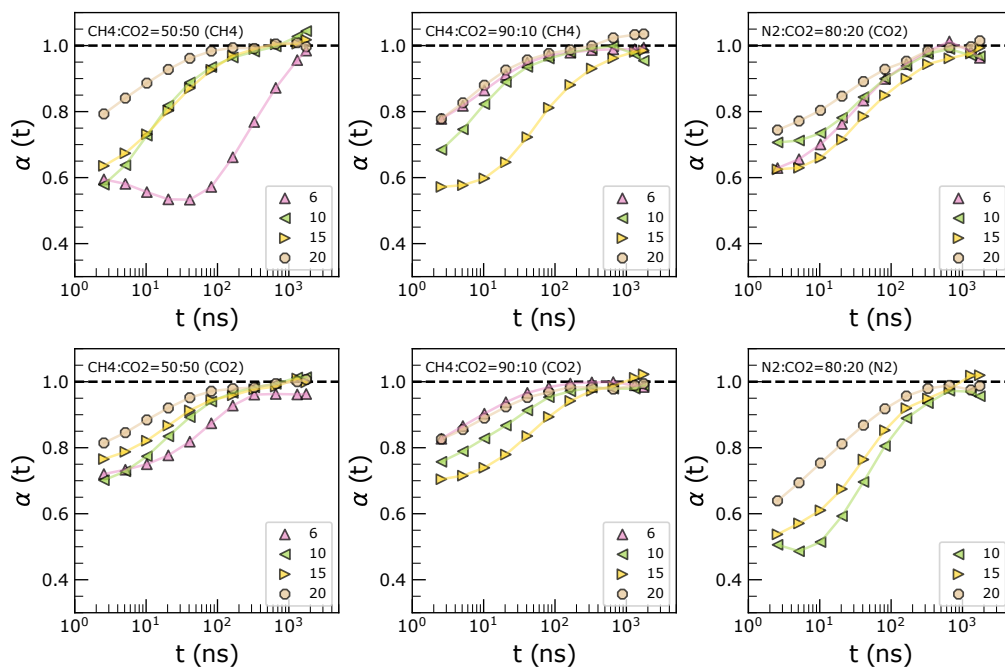

Figure S3: Time series of MSD exponent (α) for the different binary mixture systems studied. The legend shows different pressure, P (bars).

mixture diffusion coefficients of the different gases. We find the diffusivities are significantly different in the mixture compared with the pure gases shown in the main accompanying text. The diffusivity of CO_2 is comparable to CH_4 or N_2 only for low pressures. The diffusivity is also affected by the molar ratio of the mixtures.

References

(1) Potoff, J. J.; Siepmann, J. I. Vapor–Liquid Equilibria of Mixtures Containing Alkanes, Carbon Dioxide, and Nitrogen. *Aiche J.* **2001**, *47*, 1676–1682.

(2) Roy, P. K.; Kumar, K.; Thakkar, f. M.; Pathak, A. D.; Ayappa, K. G.; Maiti, P. K. Investigations On 6fda/Bpda-Dam Polymer Melt Properties and CO2 Adsorption Using Molecular Dynamics Simulations. *Journal of Membrane Science* **2020**, *613*, 118377.

(3) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. Dreiding: A Generic force Field for Molecular Simulations. *Journal of Physical Chemistry* **1990**, *94*, 8897–8909.

(4) Berendsen, H.; Grigera, J.; Straatsma, T. The Missing Term in Effective Pair Potentials. *Journal of Physical Chemistry* **1987**, *91*, 6269–6271.

(5) Schneider, T.; Stoll, E. Molecular-Dynamics Study of A Three-Dimensional One-Component Model for Distortive Phase Transitions. *Physical Review B* **1978**, *17*, 1302.

(6) NosÉ, S. A Unified formulation of the Constant Temperature Molecular Dynamics Methods. *The Journal of Chemical Physics* **1984**, *81*, 511–519.

(7) Hoover, W. G. Canonical Dynamics: Equilibrium Phase-Space Distributions. *Physical Review A* **1985**, *31*, 1695.

(8) Ryckaert, J.-P.; Ciccotti, G.; Berendsen, H. J. Numerical Integration of the Cartesian Equations of Motion of A System With Constraints: Molecular Dynamics of N-Alkanes. *Journal of Computational Physics* **1977**, *23*, 327–341.

(9) Hockney, R. W.; Eastwood, J. W. *Computer Simulation Using Particles*; Crc Press, 2021.

(10) Mark, P.; Nilsson, L. Structure and Dynamics of the Tip3p, Spc, and Spc/E Water Models At 298 K. *The Journal of Physical Chemistry A* **2001**, *105*, 9954–9960.

(11) Tsimpanogiannis, I. N.; Moultos, O. A.; Franco, L. F. M.; de M. Spera, M. B.; Erdos, M.; Economou, I. G. Self-diffusion coefficient of bulk and confined water: a critical review of classical molecular simulation studies. *Molecular Simulation* **2019**, *45*, 425–453.

(12) Dasgupta, S.; M., R.; Roy, P. K.; foram M. Thakkar; Pathak, A. D.; Ayappa, K. G.; Maiti, P. K. Influence of Chain Length On Structural Properties of Carbon Molecular Sieving Membranes and Their Effects On CO2, CH4 and N2 Adsorption: A Molecular Simulation Study. *Journal of Membrane Science* **2022**, *664*, 121044.

(13) Mills, R. Self-Diffusion in Normal and Heavy Water in the Range 1-45. Deg. *The Journal of Physical Chemistry* **1973**, *77*, 685–688.

(14) Price, W. S.; Ide, H.; Arata, Y. Self-Diffusion of Supercooled Water To 238 K Using Pgse Nmr Diffusion Measurements. *The Journal of Physical Chemistry A* **1999**, *103*, 448–450.