Supporting Information

Transient mass and thermal transport during methane adsorption into the metal-organic framework HKUST-1

Hasan Babaei,[a,b*] Alan J. H. McGaughey[b] and Christopher E. Wilmer[a]

[a]Department of Chemical & Petroleum Engineering, University of Pittsburgh, 3700 O'Hara St, Pittsburgh, PA, 15261

[b]Department of Mechanical Engineering, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, PA 15213, USA..

Contents

Additional data and information on simulation methodology.

[*] Corresponding author. E-mail address: hasan.babaei@pitt.edu

Table S1 Initial number of gas molecules and gas region length for simulations of different MOF thicknesses.

MOF layer thickness (unit cells)	***Initial number of gas molecules***	***Gas region length (nm)***
4	740	40.4
6	1110	60.6
8	1480	81.1
10	1850	101.1
12	2220	121.3

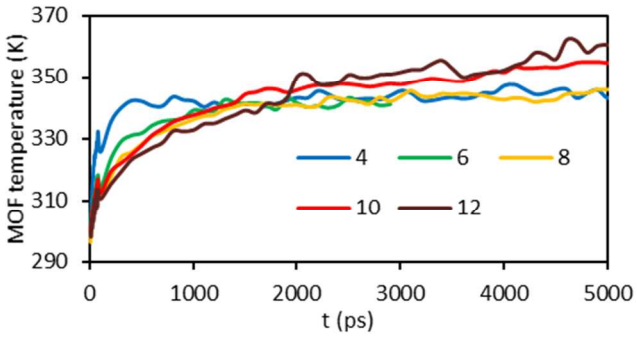

Figure S1 Temperature of HKUST-1 with 4, 6, 8, 10 and 12 unit cell thicknesses as a function of time during gas adsorption.

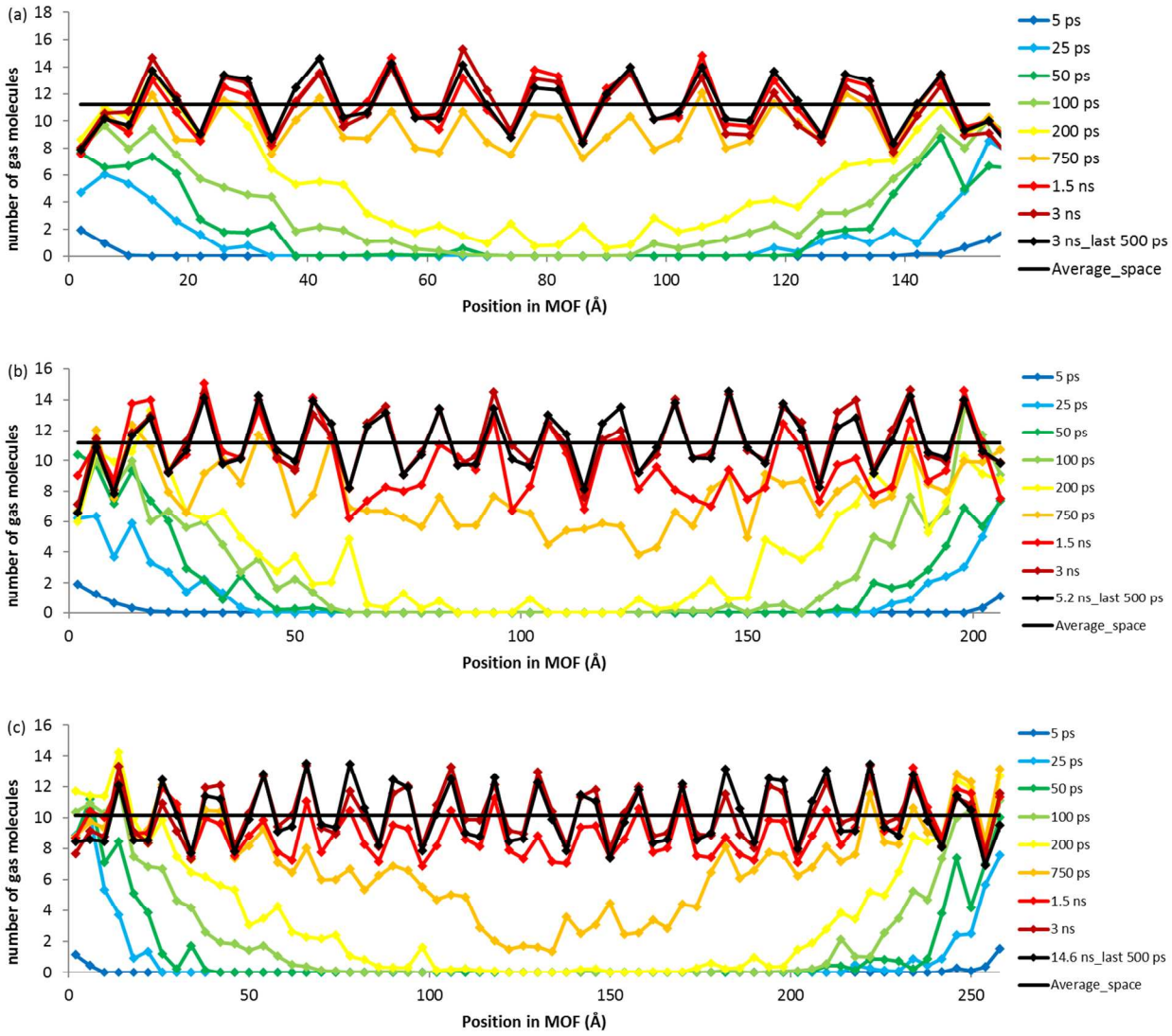

Figure S2 Time evolution of the number of gas molecules in the MOF for thicknesses of (a) 6, (b) 8, and (c) 10 unit cells.

To study the diffusion mechanisms of methane in HKUST-1, four MD simulations with different velocity distributions and gas molecule position were performed for a system containing a single methane molecule inside a 2×2×2 unit cell sample of HKUST-1 with periodic boundary conditions in all directions. The potential energy of the gas molecule as a function of time is plotted in Figure S3. The big and small jumps in potential energy are associated with two hopping mechanisms for diffusion with different time scales: (a) travel from large pores to large pores, and (b) travel between large and small pores.

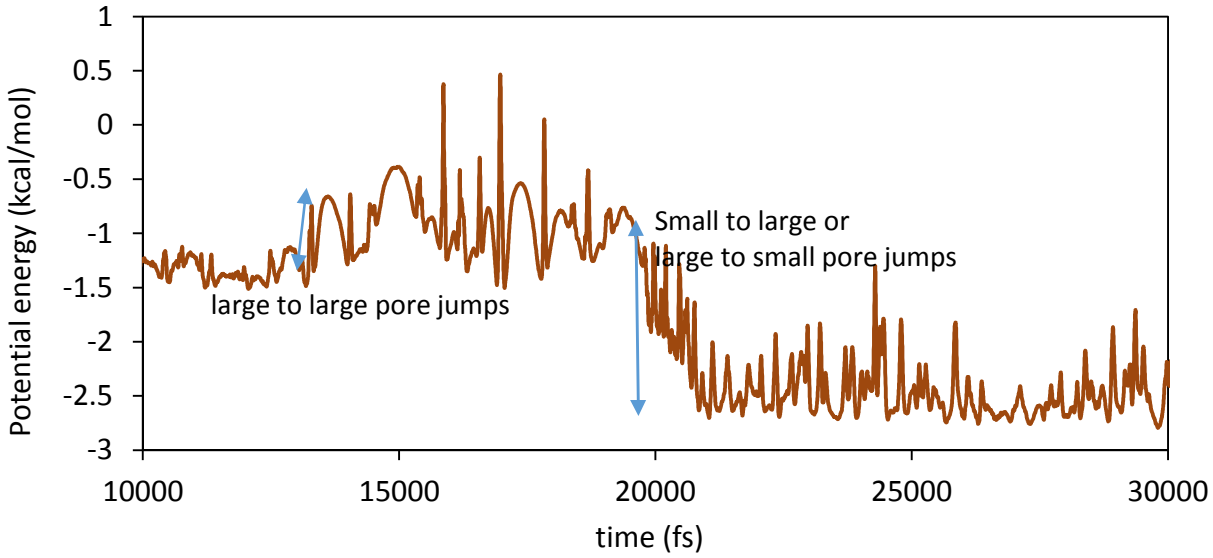

Figure S3 Potential energy of a single molecule in HKUST-1.

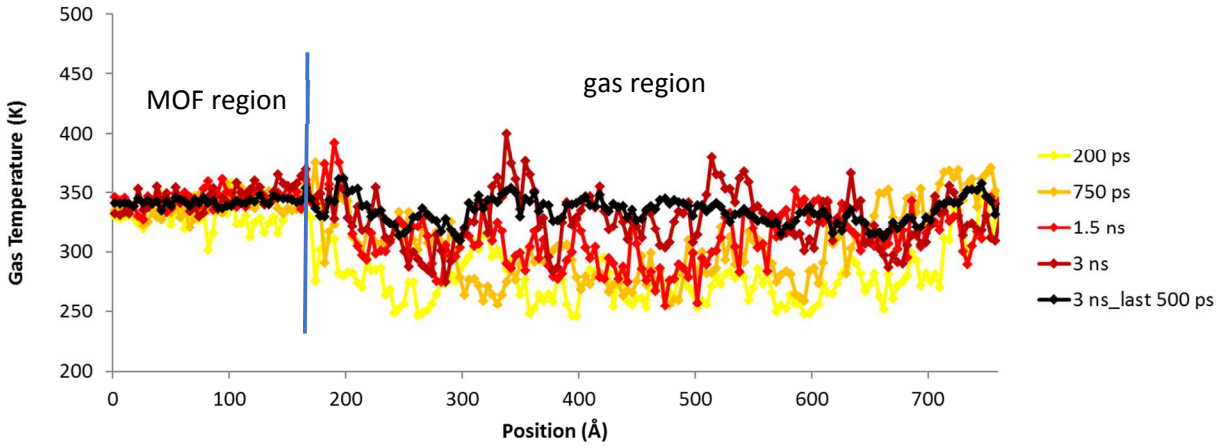

Figure S4 Gas temperature in MOF and gas regions for a thickness of 6 unit cells.

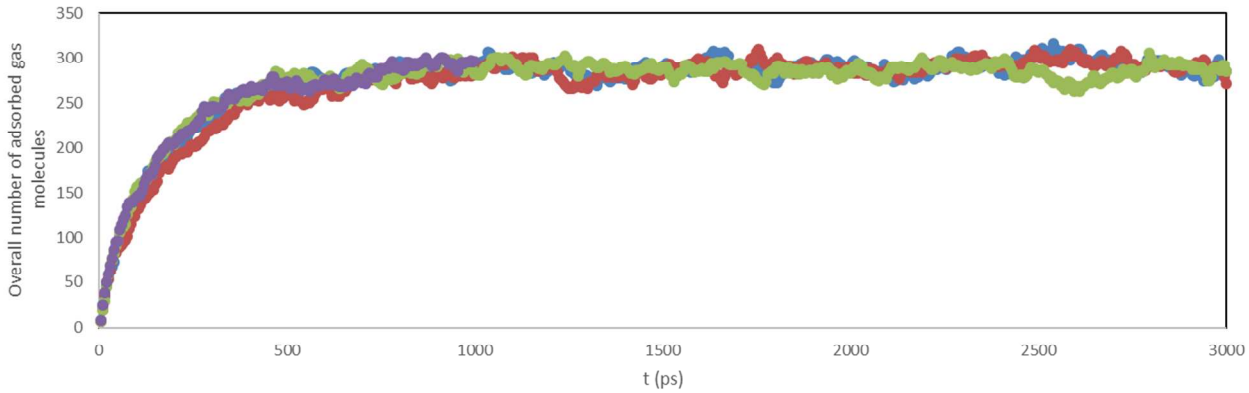

Figure S5 Number of adsorbed gas molecules for the 4 unit cell thick MOF for four simulations with different initial velocity distributions.

The time evolution of the kinetic energy of the whole system for each MOF thickness considered is shown in Figure S6 from the beginning of adsorption (i.e., when the artificial walls are removed) until steady state. In all cases, the kinetic energy increases as gas molecules are adsorbed into the MOF pores. This results indicates that, as expected, methane adsorption is an exothermic process. The heat generated during this exothermic adsorption converts to kinetic energy of both gas molecules and MOF atoms.

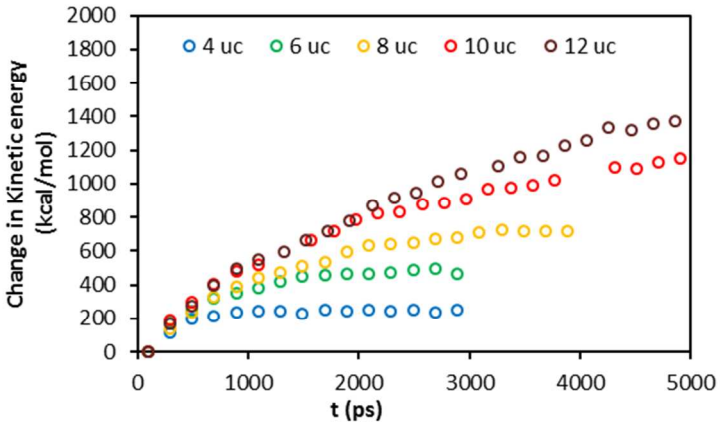

Figure S6 Time evolution of the kinetic energy of the whole system for different MOF thicknesses.

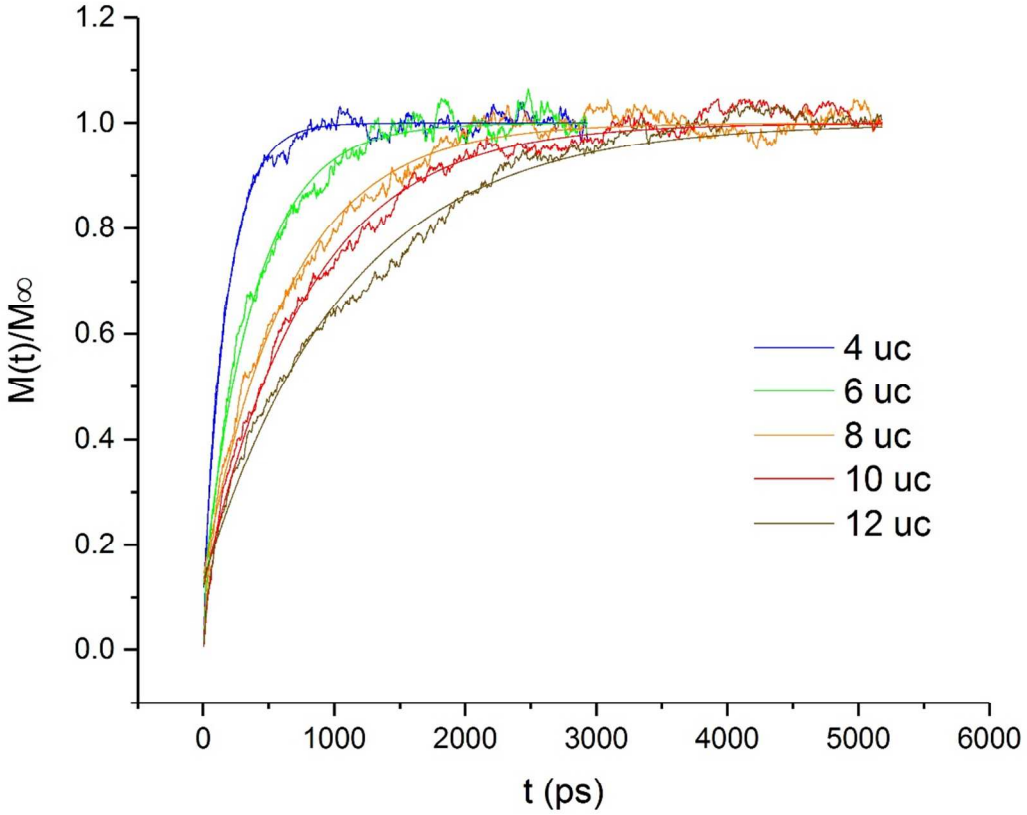

Figure S7 Fitting transient mass curves to the analytical solution given by Eq. (2) to extract the diffusivity and the interface permeability.

Table S2 Predicted diffusivities and permeabilities for different MOF thicknesses.

MOF layer thickness (unit cells)	***Permeability (m/s)***	***Diffusivity (10^{-8} m^2/s)***
4	90.62	8.33
6	87.26	7.98
8	103.21	7.97
10	71.80	11.07
12	78.86	11.05

Green-Kubo calculation of diffusivity

The Green-Kubo relation for diffusivity is[1]:

$$D = \frac{1}{N}\int_0^{\infty} dt \sum_{i=1}^{N}\sum_{j=1}^{N} < v_i(t) v_j(0) >, \quad (1)$$

where N is the number of particles.

The diffusivities as a function of temperature are shown in Figure S8.

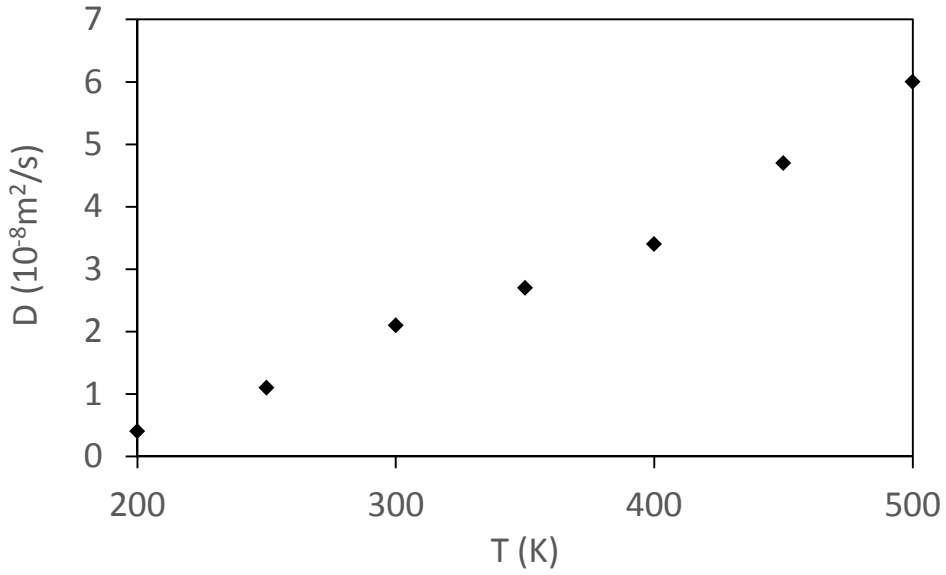

Figure S8 Diffusivity of methane in HKUST-1 as a function of temperature.

References

(1) Maginn, E. J.; Bell, A. T.; Theodorou, D. N. Transport Diffusivity of Methane in Silicalite from Equilibrium and Nonequilibrium Simulations. *J. Phys. Chem.* **1993**, *97* (16), 4173–4181.