Supporting Information for "Rapid Diffusion of CH_4/H_2 Mixtures in Single-walled Carbon Nanotubes"

Haibin Chen and David S. Sholl

This supporting information describes some details of our equilibrium molecular dynamics (EMD) simulations. Adsorbed molecules were modeled as spherical particles with all interactions modeled via the Lennard-Jones potential. The Lennard-Jones interaction parameters are listed in Table S1.

Pair interaction	σ(Å)	ε(K)
CH_4 - C	3.565	64.363
H_2 - C	3.18	30.95
CH_4 – CH_4	3.73	147.9
H_2 – H_2	2.96	34.2
CH_4 – H_2	3.07	71.133

Table S1: Lennard-Jones interactions parameters for adsorbate-nanotube and adsorbate-adsorbate interactions. C denotes an atom in a nanotube.

Simulations were performed with a simulation volume that contained a single carbon nanotube with minimum axial length 200 Å. EMD trajectories were computed using a time step of 1.0 fs. Each adsorbate configuration was equilibrated with 10^4 canonical Monte Carlo (MC) steps, and 150000 MD steps were then applied before data on particle trajectories was collected. Data was collected for 15 ns for each MD trajectory. In analyzing the mean square displacements that give rise to the computed Onsager coefficients, the first 6 ns of each trajectory was discarded in order to avoid the long ballistic region that exists for these materials with extremely rapid diffusion.

In computing the matrix of Fickian diffusivities, it is necessary to have an expression for the binary adsorption isotherm. We performed binary Grand Canonical Monte Carlo simulations over a broad range of bulk pressures and compositions. The resulting binary adsorption data was fitted to

$$c_1 = \frac{a_1 P_1}{a_2 P_1 + a_3 P_2 + a_4} + \frac{a_5 P_1}{a_6 P_1 + a_7 P_2 + a_8}, \quad \text{(S1)}$$

$$c_2 = \frac{b_1 P_2}{b_2 P_1 + b_3 P_2 + b_4} + \frac{b_5 P_2}{b_6 P_1 + b_7 P_2 + b_8}. \quad \text{(S2)}$$

Here, as elsewhere, species subscripts 1 (2) refer to CH_4 (H_2). The fitting parameters for Eqs. (S1) and (S2) are summarized in Table S2. Parameter a_1, a_5, b_1, b_5 have units of molecules per unit cell. Parameters a_4, a_8, b_4, and b_8 have the units of pressure (bar). The rest of the parameters are dimensionless.

Parameter	Value	Parameter	Value
a_1	6.643	b_1	0.1010
a_2	4.150	b_2	0.02164
a_3	0.06566	b_3	0.03655
a_4	7.648	b_4	14.36
a_5	0.1478	b_5	0.4409
a_6	0.02842	b_6	13.96
a_7	0.02842	b_7	0.3061
a_8	5.533	b_8	9.210

Table S2: Parameters used in Eqs. (S1) and (S2). a_1, a_5, b_1, b_5 have units of molecules per unit cell, where one unit cell of the nanotube has axial length 4.919 Å. Parameters a_4, a_8, b_4, and b_8 have units of bar. The remaining parameters are dimensionless.