Continuous Fractional Component Monte Carlo Simulations of High-Density Adsorption in Metal-Organic Frameworks

Benjamin J. Sikora, Yamil J. Colón, and Randall Q. Snurr*

*Department of Chemical and Biological Engineering, Northwestern University
Evanston IL, 60208, USA*

E-mail: snurr@northwestern.edu

*To whom correspondence should be addressed

Lennard-Jones Parameters

Lennard-Jones parameters between atoms of different types were calculated using the Lorentz-Berthelot mixing rules (i.e., geometric average of well depths and arithmetic average of diameters).

Table S1: Lennard-Jones parameters for argon and silicalite.

Atom	ϵ/k_b (K)	σ (Å)
Ar	124.0	3.418
O	89.6	2.806

Table S2: Lennard-Jones parameters for krypton, xenon, and HKUST-1.

Atom	ϵ/k_b (K)	σ (Å)
Kr	166.4	3.636
Xe	221.0	4.10
Cu	2.518	3.114
O	48.19	3.03
N	38.98	3.26
C	47.89	3.47
H	7.65	2.85

Table S3: Lennard-Jones parameters for DMA, DMB, and Cd-BINOL.

	Atom	ϵ/k_b (K)	σ (Å)
DMA	CH ₃	72.0	3.92
	C	33.2	3.50
	H	15.1	2.50
DMB	CH ₃	98.1	3.77
	CH ₂	47.0	3.93
	CH	12.0	4.10
Cd-BINOL	Cl	114.2	3.95
	C	52.8	3.85
	H	22.1	2.89
	O	30.2	3.50
	N	34.7	3.66
	Cd	114.7	2.85

Kr and Xe Single Component Isotherms

Figure S1: Adsorption of Kr (a) and Xe (b) in HKUST-1 at 273 K. Results from Ryan et al.,¹ traditional CB GCMC, and CFC CB GCMC are compared.

Table S4: Results from traditional CBMC and CFC CBMC for single component Kr and Xe adsorption in HKUST-1 at 273 K and comparison with literature results.¹

Method	Pressure (MPa)	Kr [atoms/uc]	Xe [atoms/uc]
Ryan et al.	0.1	14.3 ± 0.04	48.8 ± 0.30
CBMC	0.1	14.4 ± 0.31	48.6 ± 0.94
CFC CBMC	0.1	14.3 ± 0.33	49.0 ± 1.4
Ryan et al.	1.0	73.3 ± 0.10	98.5 ± 0.41
CBMC	1.0	73.0 ± 0.94	98.7 ± 0.43
CFC CBMC	1.0	74.0 ± 0.90	98.2 ± 0.91
Ryan et al.	3.0	118.4 ± 0.34	110.1 ± 0.24
CBMC	3.0	118.7 ± 0.71	109.9 ± 0.67
CFC CBMC	3.0	117.9 ± 0.58	110.1 ± 2.3

¹Ryan, P., Farha, O. K., Broadbelt, L. J., and Snurr, R. Q. *AIChE J.*, 57(7), 1759–1766 (2011).

Table S5: Binary adsorption of (R,S)-DMA in Cd-BINOL at 300 K. Results from traditional CB GCMC, CFC CB GCMC using one fractional molecule with identity change (IC), and CFC CB GCMC using two fractional molecules are compared.

Method	Fugacity (Pa)	R-DMA [molecules/uc]	S-DMA[molecules/uc]
CBMC	50	15 ± 3.6	8.0 ± 0.54
CFC CBMC (IC)	50	13 ± 1.9	7.5 ± 0.36
CFC CBMC	50	15 ± 1.5	7.7 ± 0.61
CBMC	150	34 ± 3.9	23 ± 1.1
CFC CBMC (IC)	150	33 ± 3.3	23.2 ± 0.98
CFC CBMC	150	35 ± 1.2	23.2 ± 0.98
CBMC	300	58 ± 2.5	43 ± 1.7
CFC CBMC (IC)	300	56 ± 1.4	42.6 ± 0.74
CFC CBMC	300	57 ± 2.1	42 ± 2.2
CBMC	500	73 ± 1.9	56 ± 2.1
CFC CBMC (IC)	500	69 ± 2.2	55.1 ± 0.64
CFC CBMC	500	72 ± 3.2	55 ± 1.9
CBMC	1000	86.5 ± 0.96	67 ± 1.4
CFC CBMC (IC)	1000	82 ± 2.5	67 ± 2.7
CFC CBMC	1000	84 ± 2.6	66 ± 1.8
CBMC	2000	94 ± 2.6	74 ± 1.9
CFC CBMC (IC)	2000	90 ± 1.6	73.6 ± 0.87
CFC CBMC	2000	92 ± 1.9	73 ± 1.3
CBMC	4000	98 ± 2.1	79 ± 2.9
CFC CBMC (IC)	4000	95 ± 3.8	79 ± 1.3
CFC CBMC	4000	99 ± 2.2	77 ± 2.3

Table S6: Adsorption of (R,S)-DMA in Cd-BINOL at high density ($P = 2$ MPa, $T=300$ K). Results from traditional CB GCMC and CFC CB GCMC, using two fractional molecules, are compared at varying mole fractions of R-DMA in the bulk phase.

Method	Mole Fraction R-DMA	R-DMA [molecules/uc]	S-DMA [molecules/uc]
CBMC	0	0	203 ± 1.4
CFC CBMC	0	0	204 ± 3.8
CBMC	0.25	65 ± 2.2	141 ± 4.0
CFC CBMC	0.25	64 ± 4.5	139 ± 4.8
CBMC	0.50	113 ± 1.1	92 ± 2.2
CFC CBMC	0.50	112 ± 4.3	93 ± 4.9
CBMC	0.75	159 ± 2.5	45 ± 1.3
CFC CBMC	0.75	159 ± 1.6	44.8 ± 0.87
CBMC	1.0	203 ± 2.3	0
CFC CBMC	1.0	204 ± 2.8	0