Supporting Information: Coarse-Graining of Force Fields for Metal-Organic Frameworks

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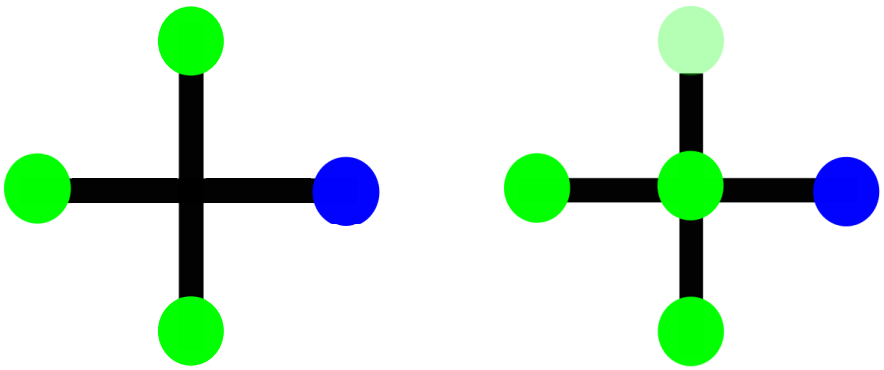
1 MOF-FF-CG and MOF-FF-CGNB Parameter

1.1 Out-of-plane Bending Environment

In the absence of non-bonding interactions, the difference between in-plane and out-of-plane bending can not be captured properly, since out-of-plane bending terms are only considered for trigonal centers. Note that in case of the atomistic MOF-FF explicit 1,3-vdW interactions are included for such square planar transition metal fragments, which helps to resolve this problem. As a consequence we developed a special out-of-plane bending term for four coordinated square planar systems. Because of the ambiguity in the definition of the reference plane the special out-of-plane bending term consists of a set of two different types of out-of-plane bending terms, relying on the Wilson-Decius definition of the out-of-plane angle θ_o and using a simple harmonic potential. The first set (see Fig. 1a) uses the three other outer beads to define the plane for bending the forth, ignoring the central atom. In the other set (see Fig. 1b) the reference plane is defined by two outer beads and the central one. For symmetry reasons every type has to occur four times per square planar site, leading to a total of eight out-of-plane terms added up.



(a) (b)

Fig. S1: Schematic visualization of the two different types of out-of-plane bending terms. The green beads define the plane and the blue one is bended. All symmetry-related permutations of the bended bead have to be included.

1.2 Bonded Parameters

In the following, the bonded parameters used in both MOF-FF-CG and MOF-FF-CGNB are listed in the key-file format as read by *pydlpoly*. For the linker and the SBU bead, the numerical atom types 101 and 102 are used, respectively. The atom type 100 corresponds to the bead representing CH_3 in the indentation calculations. Note that the parameters belonging to atom type 100 are not explicitly fitted to atomistic reference information. Force constants k are given in mdynÅ^{-1}, reference bond distances r_0 in Å, angle and out-of-plane force constants k in mdynÅrad^{-2}, reference angles θ_0 in degrees, and torsional and Fourier angle barriers in kcal mol^{-1}.

```
atom      102 SBU
atom      101 LINKER
atom      100 CH3
          #atomkey          #k       #r0
bond      101 102           1.195200 5.428460
bond      100 102           1.19     4.2
                            #V       #phi0      #multiplicity
anglef    101 102 101       0.066100 180.000000 4
anglef    100 102 100       0.066100 180.000000 4
                            #k       #phi0
angle     102 101 102       0.7749   120.0
                            #barriers
torsion   101 102 101 102   0.0 -1.741 0.0 0.0
torsion   102 101 102 100   0.0 -1.741 0.0 0.0
                            #k
opbend    101 101 101 101   0.000560
opbend    102 101 101 101   0.127544
opbend    101 102 102 102   0.026152
opbend    100 101 101 101   0.000560
opbend    101 100 101 101   0.000560
opbend    102 100 101 101   0.127544
```

- The `anglef` keyword defines the Fourier angle bending potential (in plane) for the square planar unit.
- In the `torsion` keyword the four barriers refer to multiplicities of $n = 1 - 4$.
- The first two `opbend` entries refer to the out-of-plane bending of the SBU bead as represented in the main paper in Fig. 4a and 4b, respectively. The last entry contains the parameter for the out-of-plane bending of the trigonal linker bead.

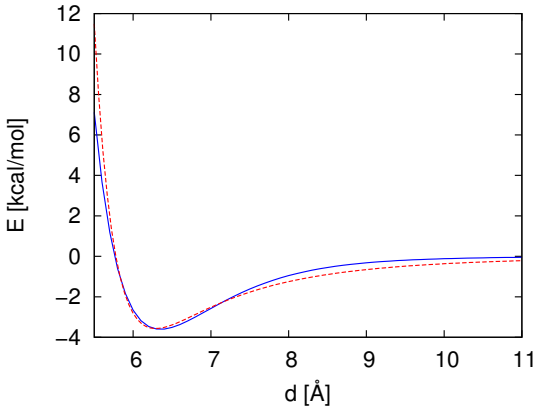
1.3 Non-bonded Parameter

Potential energy curves have been determined by using the atomistic SBU model, and benzene as a model for the aromatic linker, in their fixed optimized configuration with the C_3 and/or C_4 symmetry axis aligned, changing the distance along this axis. The following shifted Buckingham potential was fitted to these curves by a least squares procedure.

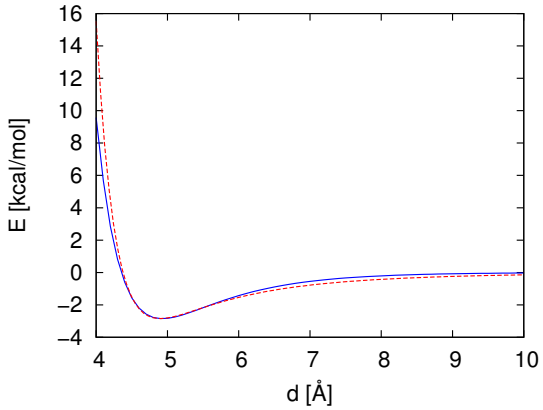
$$E_{ij}^{vdW+C} = Ae^{-B(d_{ij}-d_{ij}^0)} - \frac{C}{(d_{ij}-d_{ij}^0)^6}. \tag{1}$$

Table S1: Parameters for the modified Buckingham potential (see Eq. 1) applied for the long range interactions in MOF-FF-CGNB obtained by fits to the potential energy scans shown in Fig. S2.

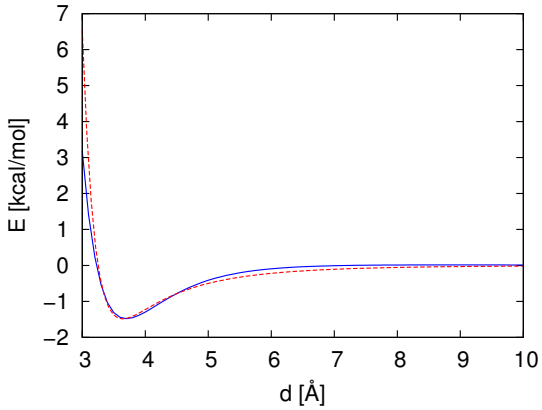
	SBU-SBU	SBU-Benz	Benz-Benz
A[kcal mol^{-1}]	$6.14 \cdot 10^{11}$	$3.50 \cdot 10^{11}$	$4.40 \cdot 10^{11}$
B[Å^{-1}]	3.82866	3.74453	5.06901
C[kcal/molÅ^{-6}]	580127	490335	50503.1
D[Å]	-0.796787	-2.25307	-1.82394



(a) SBU-SBU



(b) SBU-Benz



(c) Benz-Benz

Fig. S2: Potential energy scans for the non-bonded interactions. Blue: potential obtained by atomistic MOF-FF; dashed red: least squares fit to Eq. 1.

Table S2: Parameters for the modified Buckingham potential (see Eq. 1) applied for the long range interactions in MOF-FF-CGNB for the tip slab interactions and the CH_3 interactions. These parameters are not fitted to any potential energy scans.

	tip-SBU	tip-Benz	tip-CH_3	SBU-CH_3	Benz-CH_3	CH_3-CH_3
A[kcal mol^{-1}]	184000	184000	184000	$3.50 \cdot 10^{11}$	$3.50 \cdot 10^{11}$	$3.50 \cdot 10^{11}$
B[Å^{-1}]	3.8	2.7	5.0	3.74453	3.74453	3.74453
C[kcal/molÅ^{-6}]	0.0	0.0	0.0	490335	490335	490335
D[Å]	0.0	0.0	0.0	-2.9	-2.9	-2.9

2 Total Energies

Table S3: Absolute energies per formula unit S_3T_4 for the **tbo** and **pto** phase of HKUST-1 calculated with the atomistic MOF-FF and both CG FFs. All energies are given in kcal mol^{-1}.

	tbo			**pto**		
	MOF-FF	MOF-FF-CG	MOF-FF-CGNB	MOF-FF	MOF-FF-CG	MOF-FF-CGNB
total	-1443.35	-79.39	-81.58	-1430.84	-55.71	-65.40
vdW	15.77	0.00	-2.19	0.36	0.00	-9.71
Coulomb	-1501.54	0.00	0.00	-1497.31	0.00	0
stretch	5.47	0.00	0.00	4.50	0.00	0.02
bend	35.14	3.03	3.17	35.76	0.00	0
oop bend	0.90	0.52	0.46	0.0	0.00	0
torsion	0.92	-82.93	-83.01	25.85	-55.71	-55.71

3 Indentation Curves

The tip consists of 310 tungsten atoms cut from a primitive cubic packing with a cell constant of 3.16 Å. It has a lateral size of 18.99 Å and a height of 15.82 Å. In total the tip consists of 11 stacked layers of tungsten atoms in z-direction, where the lower 6 layers consist of 1 (1×1) to 36 atoms (6×6) and the upper 5 layers consist of alternating layers of 49 (7×7) and 36 (6×6) atoms.

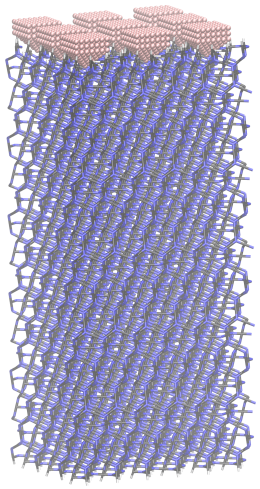


Fig. S3: $1 \times 1 \times 6$ supercell of coarse grained HKUST-1 in the [111] orientation with the tip at the maximal penetration position with periodic boundary conditions applied in the lateral x and y-dimensions. The figure illustrates the artifact of periodic boundary conditions arising from the small unit cell in this case. Instead of one isolated tip penetrating into the material, multiple close by tips are compressing the material in an uniaxial fashion (color scheme: black: SBU bead; blue: linker bead; white: CH_3-bead; brown: Tungsten).

Table S4: Results for the fit of the curves in Fig. 7 in the interval between $s = 10$ and $s = 22.5\,\text{Å}$ to a parabola of the form $E(s) = \frac{1}{2}k(s - s^0)^2$.

	$1 \times 1 \times 6$	$2 \times 2 \times 6$	$3 \times 3 \times 6$	$4 \times 4 \times 6$	$5 \times 5 \times 6$
k[kcal/molÅ^{-2}]	9.70	16.90	18.32	18.42	18.46
s^0[Å]	7.7982	8.10593	7.9501	7.83134	7.7714