Ab Initio Flexible Force Field for Metal-Organic Frameworks Using Dummy Model Coordination Bonds

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Abstract

We present force fields developed from periodic density functional theory (DFT) calculations that can be used in classical molecular simulations to model M-MOF-74 (M = Co, Fe, Mg, Mn, Ni, Zn) and its extended linker analogs. Our force fields are based on cationic dummy models (CDMs). These dummy models simplify the methodology required to tune the parameters and improve the accuracy of the force fields. We have used our force fields to compare mechanical properties across the M-MOF-74 series, and determine that increasing the size of the linker decreases the framework rigidity. In addition, we have applied our force fields to an extended linker analog of Mg-MOF-74 and characterized the free energy of previously-reported deformation pattern, in which

the one-dimensional hexagonal channels of the framework become irregular. The free energy profiles confirm that the deformation is adsorbate-induced and impossible to access solely by a pressure stimulus. Based on our results, we conclude that the force fields presented here and others that may be developed using our methodology are transferable across metal-organic framework series that share a metal center topology. Finally, we believe that these force fields have the potential to be adapted for the study of complex problems in MOF chemistry, including defects and crystal growth, that have thus far been beyond the scope of classical molecular simulations.

Introduction

Metal-organic frameworks (MOFs) are a class of nanoporous, hybrid organic-inorganic solids that are widely studied for potential applications in a variety of fields, including carbon capture,¹ energy storage,^{2,3} and catalysis.⁴⁻⁶ MOFs can be synthesized using different combinations of constituent metal and organic linker building blocks, a feature which allows them to be tuned for different practical purposes.⁷ The large number of possible building block combinations has resulted in the synthesis of tens of thousands of MOFs,⁸ and the prediction of millions.^{9,10} Because of their porous nature and frequently large internal surface areas, MOFs are promising candidates for adsorption-based applications such as gas separations and storage. The implications for gas adsorption properties of the various crystal structures that result from different building block combinations have therefore been thoroughly investigated.¹¹⁻¹⁴ In particular, for sufficiently rigid materials accurate force fields have been developed to predict the thermodynamic properties of adsorbed gases.^{15,16} However, to predict adsorption in flexible materials and study mechanical properties, one cannot assume that a material is rigid and force fields that allow MOF atoms to move are required.

In principle, *ab initio* methods such as density functional theory (DFT) can be used to study MOF properties influenced by framework flexibility. In practice, the scope of and number of structures included in DFT-based studies is necessarily small (on the order of

hundreds of structures) because of the significant computational expense.^{17–19} By contrast, molecular simulation studies that take advantage of classical force fields have been used to screen the adsorption properties of hundreds of thousands of structures.⁹ It remains difficult, however, to use classical force field-based approaches to capture properties relating to the dynamics and integrity of the framework itself. There is still a practical need for simulations to be able to capture framework flexibility, as recent experimental and theoretical works have demonstrated that both subtle flexible modes and large framework volume changes can influence MOF performance with regards to adsorption-based applications.^{20–23}

There are two approaches to describe flexibility at a MOF’s coordination centers, where metals and atoms on organic linker molecules form coordination bonds.²⁴ Bonded force field terms are the more common approach, using functional forms such as harmonic or Morse potentials to capture the coupled motion of two atoms forming a coordination bond, and similar angle, torsion and dihedral terms to capture three-body and four-body interactions. This is the approach taken by an extension of the Universal Force Field to MOFs (UFF4MOF), the MOF-FF force field, and a number of other force fields made for specific structures.^{25,26} The QuickFF package developed by the Van Speybroeck group, which aims to parameterize force fields on-the-fly from *ab initio* data also uses bonded force field terms.²⁷ A second approach uses only non-bonded potentials to describe interactions between metals and coordinating linker atom. This approach is well suited to describing subtle changes in the framework that preserve coordination geometry. [Non-bonded potentials have been used in structure prediction procedures for inorganic chemistry including,^{28,29} more recently, Zr-based MOFs.³⁰](#) The non-bonded potential approach has been used to demonstrate water-induced dissolution of MOF-5,³¹ [investigate MOF self-assembly^{32–35}](#) and also allowed us in a previous work to computationally establish the occurrence of a novel deformation pattern by an extended linker analog of Mg-MOF-74 upon Argon adsorption.³⁶ The same deformation pattern was experimentally reported as occurring in Co-MOF-74 upon adsorption of *ortho*-xylene.³⁷

In this work, we present a procedure to develop models of metal-coordinating atom inter-

actions using only non-bonded potentials. We focus here on the M-MOF-74 series ($M = \text{Co}, \text{Fe}, \text{Mg}, \text{Mn}, \text{Ni}, \text{Zn}$), but the method can be applied to other frameworks. We demonstrate that the resulting force fields are robust and are transferable to experimentally-synthesized extended linker analogs of M-MOF-74.³⁸ This force field development methodology can help further our understanding of how MOF mechanical properties depend on topology and building block chemistry.³⁹ Our force fields also have the potential to push MOF modeling research into new directions. [Because these force fields allow coordination bonds to break and form, we envision adapting this model to be compatible with reliable parameters for metal-solvent and linker-solvent interactions. A compatible combination of framework-solvent and metal-linker interactions would enable us to study complex problems such as defects, surface properties, formation and dissolution of MOFs, which have thus far been largely inaccessible topics for classical molecular simulations.](#)

Methodology

Overview

We have parameterized classical force fields to be used for molecular simulations of M-MOF-74 analogs by employing cationic dummy models (CDMs),^{40–42} which capture the experimentally-observed octahedral coordination sphere of the metal cations.⁴³ The function of the CDMs is illustrated in Fig. 1. Rather than using a single point charge, the CDMs consist of six point charges arranged in octahedral symmetry around a central bead, which is a center for both a point charge and a Van der Waals interaction. Ligands interact with both the six surrounding point charges and the central bead. Because of the set number and geometrical arrangement of the surrounding point charges, the metals remain bound to the correct number of linker atoms, replicating the effect of octahedrally arranged orbitals.

We present here a method by which we estimate and fit interatomic framework potentials to forces from periodic density functional theory (DFT) calculations. Vanduyfhuys *et*

Figure 1: (a) Cationic Dummy Models (CDMs) in a snapshot of the structure of M-MOF-74 and (b) the distribution of total metal charge q_M on each CDM. Oxygen, carbon, hydrogen, metal atoms and dummy beads are shown in red, grey, white, light green, and dark green, respectively. Charge is delocalized around the central metal atom such that the octahedral coordination environment of the metals is reproduced. Five of the six dummy beads on each CDM form bonds via non-bonded interaction potentials with linker oxygen atoms. One dummy bead forms no bonds with linker oxygens and points towards the center of the pore, reproducing the open-metal site in M-MOF-74.

al. took a related approach when developing their MOF force field development method implemented in the QuickFF package. Their method uses the Hessian matrix (composed of second derivatives of the framework energy with respect to the geometry) of the equilibrium framework structure to develop force field parameters.²⁷ In this work, we take a different approach. Instead of optimizing many force field parameters simultaneously in order to capture the total force acting on each atom, we focus on optimizing one pairwise interaction at a time while fitting each interaction to independent sets of data. We fit potentials that act between the central bead of the metal CDMs and their directly coordinating oxygen atoms. Our fitted potentials are developed by estimating pairwise metal-oxygen forces from total *ab initio* atomic forces.

***Ab Initio* Force Calculations**

For each M-MOF-74 analog, we perform 101 *ab initio* calculations. To fit our force field, we calculate *ab initio* atomic forces on 100 configurations that relate to displacements of a single

metal atom. The procedure for displacing this metal atom is described later. We perform an additional calculation to determine the forces in a structure where the displaced metal atom is far from its original neighbors. The *ab initio* atomic forces from this final calculation are used later to estimate pairwise metal-oxygen forces.

All *ab initio* calculations were performed using DFT with periodic boundary conditions as implemented in the Vienna *Ab initio* Simulation Package.⁴⁴ Calculations were performed with PBE⁴⁵ and projector augmented wave (PAW) pseudopotentials.^{46,47} For all frameworks M-MOF-74 (M = Co, Fe, Mn, Ni), Hubbard U corrections were applied with values optimized specifically for M-MOF-74.⁴⁸ These Hubbard U values were: 5.3, 6.5, 5.5 and 6.7 for Co-, Fe-, Mn- and Ni-MOF-74, respectively. The DFT calculations were spin-polarized for all M-MOF-74 frameworks except Mg-MOF-74 and Zn-MOF-74, with starting magnetic moments that were calculated in a prior work using the optimized Hubbard U values: 2.6, 3.4, 4.3 and 1.7 for Co-, Fe-, Mn- and Ni-MOF-74, respectively.⁴⁸

The DFT calculations of all configurations were based on $3 \times 1 \times 1$ supercells of the geometry-optimized M-MOF-74 structure reported by Lee *et al.*⁴⁹ A supercell was used so that the forces calculated after metal displacements would not be significantly influenced by metals in neighboring periodic unit cells. The cutoff in the plane wave basis set was 800 eV, Γ -point sampling was used and the wave function energy convergence criterion was set to 10^{-7} eV. Performing our displacements on an equilibrium structure affords us consistency between analogs and confidence that the displacement structures as closely as possible reflect physically reasonable configurations.

Generating Configurations

To generate configurations for our DFT calculations, we displace a single metal atom in the framework and calculate forces on its neighbors. By moving only one metal atom at a time and making the assumption that the forces experienced by framework atoms are strictly pairwise, we are able to estimate the pairwise forces between the metal and the neighboring

oxygen atoms.

In prior works, configurations for fitting adsorbate-framework non-bonded potentials were generated by identifying a low-energy pathway in the pore and moving the adsorbate molecule along this pathway.^{16,50} Generating configurations for framework-framework interactions poses a different type of challenge because the framework atoms move less and can explore much less space in the pore than an adsorbate molecule.

We generate 100 configurations per M-MOF-74 analog studied. To make these configurations, we perform a molecular dynamics (MD) simulation of the motion of one metal atom at elevated temperature, using the force field adapted from the work of Duarte *et al.*,⁵¹ which is described under the Classical Molecular Simulations subheading. The MD simulation is run for 1 ps between each stored displacement, freezing all atoms except the dummy beads on all CDMs and the displaced metal atom. At each displacement, the position of all dummy beads in the system are optimized such that the system energy is minimized. The classical system must be at the lowest possible energy for this configuration of atomic centers to be accurately compared to the DFT.

Classical Force Calculation

The functional form used to describe metal-oxygen interactions is a Born-Mayer-Huggins + Coulomb potential to account for dispersion and electrostatic interactions, respectively (Eq. 1 and Eq. 3). The Born-Mayer-Huggins potential was chosen because the exponential term better reproduces *ab initio* repulsive forces compared to the repulsive term in Lennard-Jones potentials.^{16,50} It is common practice to set the parameter σ in the Born-Mayer-Huggins potential to the same value when developing parameters for a series of materials,⁵² and in this work σ is set to 1.5 Å for metal-O_a, -O_b and -O_c interactions. Metal-metal interactions are similarly described using a Lennard-Jones + Coulomb potential to account for dispersion and electrostatic interactions, respectively (Eq. 2 and Eq. 3). Beyond a cutoff distance of 12.0 Å, only electrostatic interactions are accounted for between all pair types.

$$E_{ij} = A_{ij}e^{B_{ij}(\sigma-r_{ij})} - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad \begin{array}{l} r_{ij} \leq 12.0 \text{ \AA}, \\ i = M, j = O_a, O_b \text{ or } O_c \end{array} \quad (1)$$

$$E_{ij} = 4\epsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right) + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad \begin{array}{l} r_{ij} \leq 12.0 \text{ \AA}, \\ i, j = M \end{array} \quad (2)$$

$$E_{ij} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad r_{ij} \geq 12.0 \text{ \AA} \quad (3)$$

For each M-MOF-74 analog studied, we have parameterized the A_{ij} , B_{ij} and C_{ij} terms in Eq. 1 for metal- O_a , metal- O_b and metal- O_c interactions. Similarly, we have parameterized the ϵ_{ij} and σ_{ij} terms in Eq. 2 for metal-metal interactions. Additional force field terms not parameterized in this work are described below.

Force Decomposition

The force decomposition method detailed here is based on the assumption that the forces experienced by framework atoms are strictly pairwise. The procedure for estimating the dispersive pairwise force vector between the displaced metal and its neighbor atoms is as follows:

- 1.** For each configuration structure n_k , a DFT calculation is performed to determine the force on each atom.
- 2.** An additional DFT calculation is performed on structure m , where the displaced metal is moved far from its position in the geometry-optimized structure, effectively removing its interactions with its original neighbor atoms. This procedure will be described in more detail later.
- 3.** For each configuration n_k , the total pairwise force between the displaced metal atom and the neighboring atoms is extracted by assuming that each time a single metal atom is displaced, the force on each atom can be broken down into two parts: interactions with only

the displaced metal and interactions with the rest of the framework. For a given atom j at configuration k , we then write: $F_j(n_k) = F_j(m) + F'_j(n_k)$, where the prime denotes the pairwise force vector and $F_j(m)$ represents the interactions of atom j with the rest of the framework. A visual aid for this step is available in Fig. 2.

4. Having extracted the pairwise forces, we estimate the contributions from electrostatic interactions, as well as the minor contributions resulting from the purely repulsive interactions with dummy beads.⁵¹ The electrostatic forces are calculated using charges determined by Mercado *et al.*¹⁶ The total contributions are subtracted from $F'_j(n_k)$, yielding a final estimate of the dispersive pairwise force vector, $F''_j(n_k)$, between the displaced metal and neighbor atom j .

Figure 2: Example configurations used for DFT calculations of atomic forces. The displaced metal atom is shown in blue, while other metals, oxygen, carbon, and hydrogen are shown in green, red, grey and white, respectively. The force acting on atom j as a result of interactions with only the rest of the framework $F_j(m)$ is calculated in configuration m , while the force including interactions with the displaced metal $F_j(n_k)$ is calculated in configuration n_k . The pairwise force between the displaced metal and atom j $F'_j(n_k)$ can be estimated from these two calculations.

Two possibilities were considered for system m , where the displaced metal atom is not present. In one case, the displaced metal was completely absent from the calculation and the DFT supercell has a net charge, which was accounted for in VASP by adjusting the total number of electrons and using a neutralizing background charge for Ewald summations. In a second case, the displaced metal is moved to the center of the pore and displaced along

the M-MOF-74 c -axis as far as possible from its original position within the DFT supercell. $F_j(n_k)$ and $F'_j(n_k)$ were calculated and extracted in both cases, and the difference between the two sets of estimated forces was negligible. Ultimately, we used the second case of system m , without a net charge in the DFT supercell.

Parameter Optimization

We have parameterized the interactions between metals in M-MOF-74 and the oxygen atoms that coordinate directly to them. There are three distinct types of M-MOF-74 oxygen atoms first described in a prior work⁵⁰ and displayed again in Fig. 3. The carboxylate oxygens, O_a and O_b , are distinguishable by their distance from the phenolic oxygen, O_c .

Figure 3: The linker molecule in M-MOF-74, $\text{dobdc}^{4-} = 2,5\text{-dioxido-1,4-benzenedicarboxylate}$, with atomic labels. Half of the atoms are labeled because the molecule is symmetrical. The interactions between the metal and O_a , O_b and O_c are parameterized in this work.

The A_{ij} , B_{ij} and C_{ij} terms in Eq. 1 are optimized to best fit metal-oxygen forces by minimizing the weighted residual sum of squares (RSS) shown in Eq. 4.

$$\begin{aligned}
RSS = \sum_{j,k} w_k^{gauss} [(F''_{j,x}(n_k) - F_{j,x}^{fit}(n_k))^2 + (F''_{j,y}(n_k) - F_{j,y}^{fit}(n_k))^2 + (F''_{j,z}(n_k) \\
- F_{j,z}^{fit}(n_k))^2] + 3 \frac{N_c}{N_t} \sum_{j,k} w_k^{gauss} (\|F'_j(n_k)\| - (\|F_j^{fit}(n_k) + F_j^{coul}(n_k)\|))^2
\end{aligned} \tag{4}$$

$F''_j(n_k)$, j and k refer to the estimated dispersive pairwise force vector, atoms and configurations from DFT calculations. $F_j^{fit}(n_k)$ is the dispersive pairwise force vector derived from fitted interaction potentials. The x , y and z subscripts on $F''_j(n_k)$ and $F_j^{fit}(n_k)$ indicate the Cartesian components of the force vector. The weighting parameter w_k^{gauss} is dependent on the pairwise distance sampled at n_k , and takes the form of a Gaussian distribution function centered about the distance r_0 , at which the total force is equal to zero, with a standard deviation of 0.5 Å. The $\frac{N_c}{N_t}$ term was included to balance the weighting equally between the component fit and the total force fit, where the total force includes electrostatic contributions. N_c denotes the number of configurations used to fit against components and N_t denotes the number of configurations used to fit against the total force. Further details about the configurations included in the fitting are included in the Supplementary Material.

The ϵ_{ij} and σ_{ij} terms in Eq. 2 are optimized to best fit metal-metal forces by minimizing the weighted RSS shown in Eq. 5.

$$\begin{aligned}
RSS = \sum_{j,k} w_k^{skew} [(F''_{j,x}(n_k) - F_{j,x}^{fit}(n_k))^2 + (F''_{j,y}(n_k) - F_{j,y}^{fit}(n_k))^2 \\
+ (F''_{j,z}(n_k) - F_{j,z}^{fit}(n_k))^2]
\end{aligned} \tag{5}$$

The terms in Eq. 5 are similar to those described above for Eq. 4. The weighting parameter w_k^{skew} is a skewed Gaussian distribution function centered about the same distance r_0 , with a standard deviation of 4.0 Å and a skew factor $\lambda = 4.0$.⁵³ Nelder-Mead optimization as implemented in the SciPy Python library was used for the optimization.

Upon subtracting the electrostatic contributions, we determined that the attractive part of the metal-oxygen pairwise forces was entirely accounted for by electrostatic interactions, due to the large degree of charge separation between the framework metals and their bonded oxygen neighbors. As a result, for many fitted pairs the C_{ij} terms are frequently zero, although in some cases a nonzero C_{ij} improved the quality of the fits without causing the Born-Mayer-Huggins potential to ever be attractive.

Classical Molecular Simulations

MD simulations in the canonical (NVT) ensemble are used to calculate M-MOF-74 radial distribution functions (RDFs) and pressures of M-MOF-74 analogs at various volumes. Simulations to calculate RDFs were 100 ps long, while pressure calculations were 2 ns long. In both cases, the last 50% of the simulation data were analyzed. All MD simulations were run with a timestep of 1 fs using a Nosé-Hoover thermostat (at 298 K for simulations of M-MOF-74 analogs at 87 K for simulations of Mg-MOF-574) in the LAMMPS molecular software package.⁵⁴

Non-bonded interactions between linker atoms are taken from the Dreiding force field.⁵⁵ The bond, angle, dihedral and torsion parameters necessary to describe linker dynamics are also taken from Dreiding. Dreiding Lennard-Jones parameters for carbon and hydrogen are used with geometric mixing rules and the metal-metal interactions determined in this work to compute the non-bonded metal-carbon and metal-hydrogen interactions.

To generate the configurations used for DFT calculations, we rely on a force field based on CDMs parameterized by Duarte *et al.*⁵¹ to model solvated metal cations. This force field will henceforth be referred to as the Duarte *et al.*-adapted force field. The parameters of Duarte *et al.* were used for metal-metal interactions, and geometric mixing rules were used to calculate non-bonded interactions between metals and linker oxygens, carbons and hydrogens with Dreiding Lennard-Jones parameters. This force field also uses Dreiding for bond, angle, dihedral and torsion linker parameters.

Born-Mayer-Huggins, Lennard-Jones and short-range (real space) electrostatic interactions were truncated at 12.0 Å, and Ewald summations were used to calculate long-range electrostatic interactions. For both the fitted and Duarte *et al.*-adapted force fields, M-MOF-74 point charges were taken from the work of Mercado *et al.*¹⁶ The metal point charges were then distributed between the central metal atom and dummy beads as shown in Fig. 1b.

Results and Discussion

Reproducing *Ab Initio* Forces with CDM Models

We optimized metal-metal interactions and metal-oxygen interactions in M-MOF-74 to best fit forces calculated via DFT. Further details about the parameterization, graphs and the fitted force field parameters are available in the Supplementary Material. Because we extract an estimate of the pairwise force between framework atoms, we are able to reduce the risk of overfitting by only parameterizing metal-metal and metal-coordinating atom interactions, and rely upon well-developed organic molecule force fields for the other interactions.⁵⁵ Fig. 4 and Fig. 5 allow us to assess the quality and success of the force field parameterization procedure.

Fig. 4 displays the weighted RSS for metal-metal interactions against the distance between a pair of metal atoms. Each square corresponds to an RSS value calculated at a tested configuration. By displaying the weighted RSS values for both the fitted force field, shown in blue, and the starting point, shown in red, we can demonstrate the improvement in the fit. The peaks in data of each panel of Fig. 4 reflect the correlation of the weighted RSS to the skewed Gaussian weighting function, which is plotted as a black dashed line. In all cases, the fitted force field parameters for metal-metal interactions show markedly better agreement with DFT forces.

The panels of Fig. 5 show the agreement between the *ab initio* metal-O_a forces. The solid lines in Fig. 5 show the parameterized force functions fit to the *ab initio* force data,

Figure 4: The weighted residual sum of squares (RSS) between the force field force vectors and the DFT force vectors resulting from metal-metal interactions in Co-, Fe-, Mg-, Mn-, Ni- and Zn-MOF-74 are shown in panels (a), (b), (c), (d), (e) and (f), respectively. The Duarte *et al.*-adapted RSS values are plotted as red points, while the fitted RSS values are plotted as blue points. Each square point represents an RSS value calculated based on a force vector resulting from a given configuration. The black dashed curve is the skewed Gaussian weighting function with skew factor $\lambda = 4.0$ and standard deviation $4.0 \text{ \AA}$. The energy minima determined from the DFT calculations is plotted as the grey dashed vertical line

Figure 5: Panels (a)-(f) show how the estimated metal- O_a forces from *ab initio* calculations are reproduced by the parameterized Born-Mayer-Huggins + Coulomb potential. Panels (a), (b), (c), (d), (e), and (f) show data for Co-, Fe-, Mg-, Mn-, Ni-, and Zn-MOF-74, respectively. The distance is the distance between a metal- O_a pair. The squares each represent a different system configuration used for a DFT calculation, and the solid lines represent the fitted force functions, while the dashed lines represent the Duarte *et al.*-adapted force functions.

shown as squares, while the dashed lines represent the Duarte *et al.*-adapted force functions. In all cases, the parameterized force functions more accurately reproduce the DFT data, and the Duarte *et al.*-adapted force functions consistently underpredict the minimum energy distance of the metal-oxygen interaction. The minimum energy distance corresponds to the distance at which the force is zero - usually between 1.8 and 1.9 Å. The weighted RSS graphs showing the errors being minimized by the force field parameterization procedure are in the Supplementary Material. The closer the metal-oxygen pair distance sampled by a given configuration is to the minimum energy distance of the metal-oxygen interaction, the higher the weighting of this configuration. Because of this weighting procedure and the fact that the sampled distances have a hard lower bound due to repulsive interactions, the fitted potential reproduces the DFT forces at smaller distances better than at larger distances. As a result, the fitted potential deviates from the DFT forces at large distances, while the small distance data is generally fit accurately.

Validation: Geometric Properties

Fig. 6 shows metal-metal and metal-oxygen radial distribution functions (RDFs) for all M-MOF-74 analogs simulated using both the fitted and Duarte *et al.*-adapted force fields. Both force fields can be compared to the RDF calculated using the DFT optimized structures at 0 K, which is shown as a dashed black line. In many cases, the force field RDF curves at 0 K coincide with the 0 K DFT peaks, meaning that the equilibrium distance in the metal-metal and metal-oxygen interactions as predicted by DFT is also captured by the force field. In other cases, the force field RDF curves are offset from 0 K DFT peaks, meaning that the equilibrium distances as predicted by DFT are either over- or under-predicted by the force field.

The Duarte *et al.* force field was parameterized to model solvated metal cations and was never intended to be used to model MOFs. As a result, the reasonable RDFs that result from many of the Duarte *et al.*-adapted force fields are quite impressive and indicate that

Figure 6: The metal-metal radial distribution functions (RDFs) resulting from the force field-predicted 0 K structures of Co-, Fe-, Mg-, Mn-, Ni- and Zn-MOF-74 are shown in panels (a), (c), (e), (g), (i) and (k), respectively. The metal-oxygen RDFs resulting from force field-predicted 0 K structures of Co-, Fe-, Mg-, Mn-, Ni- and Zn-MOF-74 are shown in panels (b), (d), (f), (h), (j) and (l), respectively. The fitted force field RDFs are plotted in blue, while the Duarte *et al.*-adapted force field RDFs are plotted in red. The RDF calculated from the DFT optimized structure at 0 K is plotted as a black dashed line and is included to facilitate comparisons between the predictions.

the frameworks remain intact when simulated at 298 K, as is shown in the Supplementary Material. The fact that most of the frameworks remain intact is therefore a testament to the adaptability of CDMs. We will later take advantage of this adaptability to model a larger analog of M-MOF-74. A notable exception to the relative success of the Duarte *et al.*-adapted force field is the Ni-MOF-74 analog. When the Ni-MOF-74 analog is annealed using the Duarte *et al.*-adapted force field, the framework falls apart after the metals cluster together unphysically. This feature can be observed in Fig. 9i of the Supplementary Material.

A close examination of the metal-metal RDFs in Fig. 6 shows that the fitted force field captures the DFT-predicted equilibrium distance as well or better than the Duarte *et al.*-adapted force field for all M-MOF-74 analogs except Mn-MOF-74. In the case of Mn-MOF-74, the fitted force field equilibrium distance is incrementally farther off from the DFT distance than that which is predicted by the Duarte *et al.*-adapted force field. Both force fields, however, predict equilibrium distances that are within 0.1 Å of the DFT prediction.

An examination of the metal-oxygen RDFs shows that the fitted force field is able to capture a separation in the first peak that is predicted by DFT for the Mn- and Zn-MOF-74 analogs but missed entirely by the Duarte *et al.*-adapted force field. This is a result of the fact that metal-O_a, -O_b and -O_c interactions are fitted separately, and thus the slightly different equilibrium distances can be captured by the fitted force field parameters. The separation in the first peak becomes less apparent but is still visible for some analogs when the frameworks are simulated at 298 K, as is shown in the Supplementary Material. The equilibrium metal-oxygen distances, accounting for the separation in the first peak by averaging, predicted by the fitted force field are always in better agreement with the DFT predictions than the Duarte *et al.*-adapted force field.

To perform both our fitting procedure and our MD simulations, we assume constant charges on the metals and the linker atoms. [In reality, the charges on the metals and linkers depend on the metal position. When the metals are displaced such that they form longer coordination bonds with linker oxygens, the charge separation between the metals and linker](#)

atoms will increase, and the attractive electrostatic force between metals and oxygens will likewise increase. When the metals are displaced far enough from the linker oxygens that they start to resemble neutral metals, the attractive electrostatic interactions will likely decrease. Thus, we might *a priori* expect our method, which neglects these effects, to fit potentials for metal-oxygen interactions that are too attractive beyond the equilibrium distance but are within the coordination bond range (around 2.5-3.0 Å), and too repulsive at larger distances. We do not see an effect of this limitation on the RDFs shown in Fig. 6, possibly because our Gaussian weights focus our fitting efforts on the vicinity of the equilibrium distance. Because the metal-oxygen distances sampled in MD simulations are generally close to the equilibrium distance.

Validation: Mechanical Properties

We have computed the elastic properties of M-MOF-74 modeled using our fitted force field parameters. These properties are presented in Table 1, and further details about the calculations are available in the Supplementary Material. The bulk moduli B predicted here can be compared to bulk moduli reported for other frameworks. The B that we predict for M-MOF-74 are of a similar range as has been predicted for MOF-5 by force field and DFT-based approaches, as well as has been measured by experiment.⁵⁶ The predicted M-MOF-74 B are, however, lower than the predicted and measured bulk moduli of HKUST-1 and UiO-66.⁵⁶ As all of these frameworks are generally considered to be quite rigid,^{57,58} we find the fitted force field predictions to be in line with our expectations. The shear moduli G predicted here are not exceptionally high, but are well within the range of the experimentally measured values for rigid MOFs.⁵⁷ This is not surprising, as any indication of an easily accessible shear mode for M-MOF-74 without adsorbates would have been unprecedented.

Table 1 also reports the Young’s moduli (Y) predicted by the fitted force field in all M-MOF-74 analogs. In the elastic moduli calculations, the x -axis corresponds to M-MOF-74 crystallographic c -axis, which is well known as the axis in which the one-dimensional rods

Table 1: Bulk (B), shear (G), orientationally-averaged and components of the Young’s (Y) moduli are reported for M-MOF-74 ($M = \text{Co, Fe, Mg, Mn, Ni, Zn}$) in GPa. The unitless measure of ductility (B/G) is also reported.

	Co-MOF-74	Fe-MOF-74	Mg-MOF-74	Mn-MOF-74	Ni-MOF-74	Zn-MOF-74
B	22.78	27.71	12.47	25.46	22.22	29.76
G	3.75	4.38	3.47	3.59	3.84	4.30
B/G	6.07	6.33	3.59	7.09	5.79	6.92
Y	10.66	12.47	9.54	10.28	10.89	12.31
Y_x	33.07	35.18	27.16	26.58	29.49	34.60
Y_y	7.88	14.59	15.30	9.67	8.86	9.72
Y_z	7.82	15.93	13.51	9.86	8.04	10.44

are oriented.⁵⁹ These one-dimensional rods are particularly rigid components. As expected, the x -components of the predicted Y are particularly high, both compared to the predicted y - and z -components as well as the general range of elastic moduli predicted for MOFs. We have established in a prior work that an extended analog of Mg-MOF-74 can deform in a way that changes the crystal symmetry of the framework.³⁶ The deformation is associated with structural changes that take place in the ab -plane, orthogonal to the direction of the one-dimensional rods and hexagonal channels.^{36,59} We might therefore expect the y - and z -components of Y to be relevant to this deformation, as the metal-oxygen distances in the ab -plane must change to accommodate the deformation pattern.³⁶ From the Y reported in Table 1, M-MOF-74 analogs synthesized from Mg do not appear to be more likely to deform than any other analogs, as the Y_y and Y_z values for Mg-MOF-74 are actually the largest of the series. Based on this prediction, M-MOF-74 analogs synthesized from any metal may be susceptible to deformation. This prediction is consistent with the experimental observation of adsorbate-induced Co-MOF-74 deformation.³⁷

Recently, Lee *et al.* computed the elastic moduli of an extended framework analog, M-MOF-274 ($M = \text{Co, Fe, Mg, Mn, Zn}$).⁶⁰ We have applied our M-MOF-74 force fields to the same series, and are thus able to test the transferability of our force field fitting procedure. A comparison of any of the three M-MOF-274 elastic moduli reported in Table 2 to their corresponding values reported in Table 1 leads us to the conclusion that the extended analogs

Table 2: Bulk (B), shear (G) and orientationally-averaged Young’s (Y) moduli are reported for M-MOF-274 (M = Co, Fe, Mg, Mn, Ni, Zn) in GPa, computed both with this force field and by Lee *et al.*⁶⁰ The data for the force field are shown in bold to differentiate from the *ab initio* Lee *et al.* computed moduli, which do not include Ni-MOF-274.

	B	G	Y
Co-MOF-274	5.19	1.62	4.41
Co-MOF-274	8.51	2.55	6.95
Fe-MOF-274	6.00	1.90	5.17
Fe-MOF-274	9.69	3.19	8.63
Mg-MOF-274	5.30	2.40	6.25
Mg-MOF-274	10.05	3.32	8.97
Mn-MOF-274	5.66	1.96	5.27
Mn-MOF-274	11.98	2.28	6.42
Ni-MOF-274	5.70	1.93	5.21
Ni-MOF-274	—	—	—
Zn-MOF-274	7.00	2.26	6.11
Zn-MOF-274	10.28	2.48	6.89

are all less rigid than their smaller-pore counterparts. This result can be rationalized by the fact that the linker in M-MOF-274 has two aromatic rings rather than one, and these rings are connected by a bond which imparts extra flexibility to the structure.

By comparing our elastic moduli to the Lee *et al.* *ab initio* computed moduli, we are also able to assess the accuracy of our predictions. The force field B values are in general a factor of two off from the *ab initio* predictions, with the best and worst agreement corresponding to Co- and Mn-MOF-274. The fact that the classical model consistently underpredicts B may indicate a systematic error, such as insufficiently rigid linker parameters, which were taken from the Dreiding force field and not parameterized in this work. The force field G and Y values also similarly undershoot the *ab initio* predictions, but with even smaller margins of error. Overall, the level of agreement between the force field and *ab initio* predictions are good, especially considering the fact that linker bonded and linker-linker nonbonded interactions were explicitly not parameterized in this work. We therefore conclude that the force field model accurately describes metal-oxygen nodes and that the force field parameterization procedure is transferable to extended M-MOF-74 analogs.

Structural Transitions in M-MOF-74 Series

We have applied our fitted force field for Mg-MOF-74 to the system in which we previously established the M-MOF-74 extended linker series deformation pattern: Mg-MOF-574 with adsorbed Argon. The complex deformation is characterized and can be accessed by a decrease in the equivalent a and b lattice parameters.³⁶ To study the free energy of the deformation, we then performed NVT simulations of this system while recording the instantaneous hydrostatic pressure at different a and b lattice parameters. The same analysis was performed using the Duarte *et al.*-adapted force field, with the results presented in the Supplementary Material. By leaving all other simulation cell parameters unchanged, we have assumed that a hydrostatic external pressure will have no effect on the c lattice parameter or on the triclinic box angles. The Helmholtz free energy at a given volume, which is related to the a and b unit cell parameters, is:⁶¹

$$F(V) - F(V_0) = - \int_{V_0}^V \langle P_i(V') \rangle dV' \quad (6)$$

In Eq. 4, V_0 is set to be the volume of the simulation found to have the lowest free energy, and P_i is the instantaneous hydrostatic pressure. Fig. 7a shows the average hydrostatic pressure as a function of volume, which is implicitly a function of the a and b lattice parameter. Fig. 7b shows the free energy of Mg-MOF-574, calculated using Eq. 6, as a function of volume both with and without adsorbed Argon in the pores. We performed simulations at multiple Argon adsorbate loadings, only one of which, marked with black and cyan circles, induces the structural transition. The cyan-black color spectrum used for the system with 486 Argon per channel represents the extent of deformation observed, which is quantified by the order parameter calculated in Eq. 7.

Figure 7: (a) Average hydrostatic pressures resulting from simulations of Mg-MOF-574 with adsorbed Argon at different volumes modeled using the fitted force field and (b) the free energy profile as a function of volume for the aforementioned system, calculated using the pressures in panel (a) and Eq. 4. Panel (b) also shows the free energy profile for bare Mg-MOF-574 as a function of volume, which is plotted in orange while the data for the systems with adsorbates are plotted in black, magenta and red. The magenta and red curves show data for the framework with slightly more and slightly less adsorbates than the deformed lattice system. Visualizations show snapshots of Mg-MOF-574 with adsorbed Argon simulated at both the system's free energy minimum and the volume corresponding to the free energy minimum of the bare framework. In both panels (a) and (b), the plotted curves are spline functions fitted to the simulation data points, shown as markers, and are included as a guide to the eye. The cyan-black color spectrum for the deformed lattice system shows the extent of deformation quantified by Eq. 7, with cyan indicating more deformation.

$$OP = \frac{1}{N_a} \sum_a \left\langle \frac{1}{|\theta_i - 120^\circ| + 1} \right\rangle \quad (7)$$

In Eq. 7, the sum is performed over all interior angles of the hexagonal channels, where the vertices are determined by calculating the center-of-mass of each one-dimensional metal rod (metal helix). N_a is the number of interior angles, and θ_i is the instantaneous measured value of the interior angle. When the interior angles approach 120° , the hexagons are more regular and the order parameter is closer to 1.0. Similarly, when the hexagon is more deformed and the interior angles deviate from 120° , the order parameter is closer to 0.0. In this study, the order parameter ranged from 0.25 at low volumes to 0.65 at the bare framework stable volume. The plotted colored and black curves are fitted spline functions and are intended to guide the eye.

An examination of the free energy of the system with 486 Argon per channel, plotted in black, and a comparison to its bare counterpart leads us to several conclusions. Most notably, there are two free energy minima in the system with 486 Argon per channel - a global minimum and a local minimum - while the bare system has only one minimum. The global minimum in the Argon system is shifted to a smaller volume. This global minimum corresponds to a framework exhibiting the deformation pattern as previously reported. At the local minimum, which occurs at a volume similar to the empty framework minimum, the framework structure exhibits the standard undeformed hexagonal channels. By contrast, the bare framework has no feature other than a parabolic free energy profile, meaning that the observed deformation pattern is not accessible by pressure alone.

The local minimum in the deformed system occurs at a slightly larger volume. The local minimum volume is therefore evidence of framework swelling upon Argon adsorption. This conclusion is supported by the shift of the free energy minimum volume of the system with 462 Argon per channel, which occurs at a significantly larger volume than the bare system.

In our prior work, we noted that the unit cell parameters measured below the deformation loading changed much more during the simulated Argon adsorption process compared to the experiment.³⁶ It is therefore interesting to note that after the tailored fitting procedure was applied, the framework still appears to be more prone to swelling than was reported in an experimental Argon adsorption study in the Mg-MOF-74 series.⁶²

We can compare the behavior of the systems with slightly more and slightly less adsorbates necessary for the lattice deformation, displayed in Fig. 7b in magenta and red, respectively with the deformed system. This comparison allows us to confirm that our force field captures the expected sensitivity of the deformation. In both our prior work and the experimental adsorption study featuring *ortho*-xylene as an adsorbate, the unit cell parameter associated with the lattice deformation only decreased in a small range surrounding the loading of interest.^{36,62} In the case of Argon, the loading of interest is associated with the pore being close to filled, but not yet saturated. Intra-channel interactions between adsorbates at these conditions favor Argon droplet formation, with the caveat that Argon is adsorbed to the walls of the framework. The complex deformation pattern occurs because it allows the structure to shrink, allowing an Argon droplet to form, and is stabilized by the presence of the adsorbate. At higher loadings, the deformation pattern would compress the adsorbed Argon overmuch such that it is no longer stabilized. Because the magenta and red curves both have only one free energy minima, we see that also in this work we only predict stable deformation in a small range of adsorbate loadings.

Recently, Vanduyfhuys *et al.* described expected experimental responses to stimuli with the shapes of flexible framework free energy profiles as a function of volume.⁶¹ By their descriptions, Mg-MOF-574 loaded with Argon is a triggered disperser, meaning that while the smaller-volume structure is the true free energy minimum, both minima are mechanically stable. This implies that changes in the framework structure will be irreversible, and fluctuations large enough to drive the system over the free energy barrier separating the two minima will result in at least a metastable structure.

Conclusion

We have developed force fields that for the first time allow us to reproduce *ab initio* forces towards modeling framework flexibility in M-MOF-74. Due to the similarity of the metal-oxygen nodes across the M-MOF-74 extended linker series and the fact that our force fields are specifically parameterized to capture the chemistry at these nodes, our force fields are inherently transferable to systems containing octahedrally coordinated M-O secondary building units (SBUs). We have used these force fields to better understand the thermodynamics of structural transitions in an extended linker analog of Mg-MOF-74. We have found that the previously reported deformation pattern in Mg-MOF-574 is truly adsorbate-induced and cannot be accessed purely by external pressure changes. The force field parameterization method presented here is in no way specific to the M-MOF-74 structure and can be easily applied to other MOFs. Importantly, force fields based on CDMs use purely non-bonded potentials to capture coordination chemistry and therefore have the ability to capture bond breakage and formation. We believe our findings provide a strong motivation for further efforts in combining MOF force fields with accurate solvent models such that CDM-based force fields can be used to study complex problems such as defects and crystal growth. Future work should include reconciling the use of framework-specific charges typically present in MOF studies with the full metal ion charges used in the parameterization of accurate metal-solvent force fields.

Acknowledgement

M.W., N.R. and S.J. were supported as part of the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Basic Energy Sciences under Award DE-SC0001015. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the US Depart-

ment of Energy under Contract DE-AC02-05CH11231. S.M.M. acknowledges funding by the Deutsche Forschungsgemeinschaft (DFG, Priority Program SPP 1570). S.J. acknowledges support from an NSF Graduate Research Fellowship.

Supporting Information Available

The Python code performing the parameterization procedure described in this manuscript is available at: https://github.com/sudij/coord_ff. Force field parameters and additional computational details are in the Supplementary Material.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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