ABSTRACT: In this work, MOF bulk properties are evaluated and compared using several force fields on several well-studied MOFs, including IRMOF-1 (MOF-5), IRMOF-10, HKUST-1, and UiO-66. It is found that, surprisingly, UFF and DREIDING provide good values for the bulk modulus and linear thermal expansion coefficients for these materials, excluding those that are not parametrized for. Force fields developed specifically for MOFs including UFF4MOF, BTW-FF, and the DWES force field are also found to provide accurate values for these materials’ properties. While we find that each force field offers a moderately good picture of these properties, noticeable deviations can be observed when looking at properties sensitive to framework vibrational modes. This observation is more pronounced upon the introduction of framework charges.

Because of the nearly limitless range of materials and properties achievable by metal-organic frameworks (MOFs), computational researchers have been invaluable in directing efforts toward materials with optimal properties for various applications. Current computational resources allow the ability to explore materials properties at a fraction of the time and cost compared with experiment, thus making it an instrumental part of a materials design process. Much of the computational work to date has been focused on gas adsorption properties, where the commonly used fixed-framework approximation is exploited to improve computational efficiency. Here it is assumed that any framework movement or vibrations will not contribute significantly to the thermodynamically averaged properties and are simply ignored during calculations. This approximation has been demonstrated to provide relatively accurate results, provided the materials do not deviate significantly from their reported crystallographic representations at the thermodynamic conditions studied.

There are notable cases where freezing the framework atoms in place is inappropriate, however. For example, where gas adsorption results in significant changes in the lattice organization of the MOF framework atoms, as evidenced in several “breathing” structures including MIL-53 and DUT-49, when modeling the fascinating phenomena of negative thermal expansion (NTE) of these materials, or when attempting to accurately model particle diffusion through network pores and small apertures. In these cases, the response of the system to external stimuli with a fully flexible model of the material is necessary. Most of these problems are too large for a density functional theory (DFT) approach, however, so one must resort to modeling properties with empirical force fields, for which there are numerous general-purpose molecular mechanics engines freely available for academic use.

In recognition of the need for accurate models to predict the various interesting properties described by the bonding environment within these materials, a number of force fields have recently been developed specifically for MOFs. The work placed in developing these force fields follows a similar procedure, that is, fit force-field parameters, for instance, bond force constants, and angle-bending terms to accurate data from experiment or ab initio calculations, typically at low temperature. The data can take the form of bulk observable properties, where force fields are fit to very specific and localized properties, or a more general approach involving a system’s first- and second-order energetic derivatives. Alternatively, rule-based force fields can be used to describe MOF properties. Force fields such as the Universal Force Field (UFF) provide parameters for each atomic type and mixing rules for these parameters to dictate the strength of local chemical bonds and angle bends. These force fields have the advantage that they can be adaptable to many chemical environments, however, at the potential cost to simulation accuracy.

It is of importance, therefore, to distinguish if these targeted properties are sensitive to specific force-field parametrizations or if more generalized rule-based force fields can be used. It was shown that good agreement could be obtained between an
approximating the electronic degrees of freedom with a set of long-range potentials. The typical general expression for a force in the large-scale Atomic/Molecular Massively Parallel functional version BTW-FF, however, due to some absent materials simulations. In addition, a comparison is made with a and helpful, albeit sometimes comedic, user forum to aid in unprecedented number of features, active development team, and Snurr (DWES). We have implemented these force studied for various applications and have been the subjects of materials properties commonly used to validate new MOF force fields using "off the shelf" force fields as a measure of comparison. The following will compare the bulk moduli and a brief description of the functions used to describe each force parametrizations. These MOFs are compared using full descriptions of UFF, DREIDING, and the force field by Dubbeldam, Walton, Ellis, and Snurr (DWES). We have implemented these force fields in the large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), which stands out due to its unprecedented number of features, active development team, and helpful, albeit sometimes comedic, user forum to aid in materials simulations. In addition, a comparison is made with a functional version BTW-FF; however, due to some absent energy potentials in LAMMPS, it could not be described in its intended form. The details are discussed further in the article and Supporting Information.

Force fields circumvent expensive ab initio calculations by approximating, yet accurate DFT-based method (DFTB) and UFF, which recently celebrated its 24th birthday, and whose intended application was not solid-state porous materials. The motivation of this work is to critically assess two force fields as a measure of

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Table 1. Description of the Potentials Used in the Force Fields Studied

| Potential               | UFF            | DREIDING       | BTW-FF          | UFF4MOF         | DWES            |
|-------------------------|----------------|----------------|-----------------|-----------------|-----------------|
| bond                    | harmonic       | harmonic/morse | 4th order pol.  | harmonic        | harmonic        |
| angle                   | cosine Fourier | harmonic cosine| 6th order pol.  | cosine Fourier  | harmonic        |
| dihedral                | cosine Fourier | periodic cosine| Fourier         | cosine Fourier  | periodic Cosine |
| improper torsion        | cosine Fourier | harmonic       | 6th order pol.  | cosine Fourier  | periodic Cosine |
| cross terms             | Lennard-Jones  | L/J/Buck       | Buckingham      | Lenard-Jones    | Lennard-Jones   |
| van der Waals           | Ewald          | Ewald          | Ewald           | Ewald           | Ewald           |
| Coulomb                 | Ewald          | Ewald          | Ewald           | Ewald           | Ewald           |

*“DREIDING provides options for functions used in the force field. In this work we have used harmonic and Lennard-Jones for the bond and van der Waals potentials, respectively. LAMMPS does not currently possess sixth-order polynomial functions. A fourth-order polynomial and second-order polynomial were used instead."

Table 2. Bulk Modulus Values Computed from Different Force Fields

| MOF      | BTW-FF (ref 20) | UFF | UFF4MOF | DREIDING | DWES | DFT/exp |
|----------|-----------------|-----|---------|----------|------|---------|
| IRMOF-1  | 13.6 (11.95)    | 14.5| 16.8    | 22.0     | 17.5 | 15.3–18.5 |
| IRMOF-10 | 9.0 (8.25)      | 7.6 | 10.4    | 9.7      | 8.1  | 6.0, 9.09 |
| HKUST-1  | 23.9 (25.05)    | 28.7| 29.4    | 31.1     | 24.5–34.66 |
| UiO-66   | 27.1 (27.15)    | 42.4|         |          |      | 41.0   |

*Units in GPa. *Refs 24, 39, and 41–46. *Refs 47 and 48. *Refs 38 and 39. *Ref 46.

The E_{\text{stretch}} term describing the energy associated with stretching and compressing a bond is described by a spring harmonic term for all of the force fields except for BTW-FF, where a fourth-order polynomial term of the form

\[ E_{\text{stretch}}^{ij} = K_2(R_i^j - R_0^j)^2 + K_3(R_i^j - R_0^j)^3 + K_4(R_i^j - R_0^j)^4 \]

(2)

is used. Here E_{\text{stretch}}^{ij} is the energy of stretching a bond between two bonded atoms i and j, R_i^j represents the distance between the two atoms, and R_0^j is the equilibrium bond distance parameter imposed by the force field for two specific types of atoms. In addition, there are three other empirical values assigned to this bond potential to ensure the correct behavior. Namely the K_2, K_3, and K_4 terms, whose values affect the curvature of the bond potential energy surface.

One should note in Table 1 that, in general, BTW-FF uses functions of higher relative complexity, having bond, angle, and out-of-plane torsion potentials that contain polynomials of order greater than 2. BTW-FF adopted its potential functions from the Molecular Mechanics 3 (MM3) force field, which was developed to reproduce vibrational and thermodynamic properties of hydrocarbons. Because of the extreme precision required to accurately model these values, the MM3 force field also contains a so-called "cross-terms". These terms are included in the form of additional functions between atoms that are two or three bonds apart to accurately model concerted molecular motions (bend–stretch, bend–bend, etc.) at finite temperatures. We note that the authors of the BTW-FF do not provide parameters for these cross-terms, despite their presence in the TINKER implementation of BTW, so we have used the original MM3 values in this work. Table 1 is designed to be a reference to the complexity of each force field, and a more detailed discussion of these potentials is presented in the Supporting Information. We also note that the BTW-FF potentials for the angle bending and improper torsions could not be faithfully reproduced in LAMMPS; however, the energy penalty for these approximations is small, as they only manifest at extreme values for nonequilibrium angles. Further details are provided in Section 5.3.3.6 of the Supporting Information.
In all cases studied, we used the atomic positions from the crystallographic information files provided by the Cambridge Structural Database (CSD). Some of the modern MOF-centric force fields do not encompass the entire set of structures studied here, rendering comparison impossible. For example, the DWES force field contains parameters for IRMOF-1 and IRMOF-10 but not HKUST-1 or UiO-66, and thus properties for these neglected materials cannot be computed.

The computed bulk moduli are presented in Table 2. These values were computed from a procedure where the lattice parameters were isotropically scaled and the atomic positions minimized. With a few exceptions, this gave a smooth energy-volume curve to provide good fits to the Murnaghan equation of state shown in eq 3. This equation was chosen for its relative simplicity, and considering the imposed deviations in volume do not stray far from equilibrium, more complex equations of state were deemed unnecessary.

\[
E = E_0 + \frac{B_0 V}{B'} \left[ \frac{V_0}{V} \right]^{B'} (B' - 1) + 1 \tag{3}
\]

One of the most striking features of Table 2 is that all of the force fields predict the same ranking in increasing order of bulk modulus. Moreover, with the exception of the bulk moduli computed for UiO-66, most values lie within ±5 GPa of DFT or experimentally observed values. This deviation may appear large; however, considering the variability in bulk moduli for HKUST-1 can range from 25 to 35 GPa from DFT calculations. Nevertheless, the bulk moduli computed by these force fields are well within the range of acceptable values.

The first column in Table 2 showing the values reported from the LAMMPS implementation of BTW-FF demonstrates the close agreement with the values reported in the original article by Bristow et al., as all are within 2 GPa of the original values. Discrepancies in these values can be attributed to the subtle differences in the BTW force-field implementations between TINKER and LAMMPS discussed above. It is remarkable that simple force fields such as DREIDING can reproduce the bulk moduli for these MOFs, which uses a single force constant for all bonds of the same order, regardless of the chemical species of its atoms. Likewise UFF, which was not designed for simulations of nanoporous materials, can reproduce the bulk moduli trends and values. We note that the story changes significantly when charges are introduced to each framework and the bulk moduli are recomputed using the UFF, UFF4MOF, and DREIDING force fields. We have presented the bulk moduli using different charge derivation schemes in Section S.6 of the Supporting Information, where the values can deviate up to 18 GPa for the same MOF using methods that obtain partial atomic charges from DFT calculations. While each of these periodic-table-covering force fields does not provide partial charges for its atom types, it seems clear that the introduction of charges yields worse agreement with experimental materials properties.

We note that the parameters for the original Zr and Cu types in UFF are not designed to reproduce the square planar and square antiprismatic geometries in HKUST-1 and UiO-66, respectively. However, an ad hoc adjustment of these values to support the MOF metal coordination geometries yields good agreement with literature values for the bulk moduli, improving upon those values reported for BTW-FF. The adjustment, which fits the original force constants to the existing coordination geometries in each crystal, is discussed in detail in the Supporting Information.

It is instructive to investigate the major contributions to the bulk modulus from each of the energy terms arising from the force-field functions. Figure 1 shows, for each MOF, the second-derivative values arising from the various force field and functional terms, whose magnitudes are directly proportional to their bulk moduli. It is clear that in most cases the bonding function is the primary contributor to the bulk modulus. Notably the nonbonded interactions dominate the bulk modulus contribution for IRMOF-1 with DWES force field. This arises due to the force field’s lack of bonds between Zn(II) ions and the nearby benzene–dicarboxylate ligands, effectively
dislocating the structure from a continuous network of bonding. The replacement of the directionally dependent bonding terms with the isotropic form of the nonbonded functions can be expected to provide similar bulk moduli because the bulk modulus measures the response to uniform hydrostatic pressure imposed on the system. It is likely, therefore, that more significant differences will arise when looking at the individual elements of the stress tensor, where the direction dependence of the potential energy surface will have more of an impact. This is evidenced by the disagreement between elastic constants computed for IRMOF-1, reported in Section S.7 of the Supporting Information.

Interestingly, the BTW-FF predicted bulk modulus for UiO-66 comes from a difference between angle-bending and nonbonded interactions. These contributions arise from the presence of atomic charges in the system and the subsequent distortions that occur from relaxing the atomic positions when the cell shape is changed. We add here that providing charges to the force fields UFF, UFF4MOF, and DREIDING causes erratic bulk modulus values in these materials due to the unpredictable behavior of charge interactions in these materials. The details of charge assignment and observed results are left for the Supporting Information.

Only subtle difference between the force fields are observed in Table 2, which considers uniform stress on MOF systems. A number of recent studies have focused on the fascinating phenomena of negative thermal expansion within MOFs. Here it is understood that certain thermally accessible vibrational modes of these periodic materials will bring about a diminishing volume change as the temperature is increased. This property poses a good test for a force field’s efficacy, as being unable to reproduce this feature will have consequences on the dynamical behavior of these MOFs in a range of associated thermodynamic properties.

Table 3 reports the thermal expansion coefficients for each MOF. Here we see clear differences between the force fields, with the largest deviation coming from the UFF4MOF implementation for IRMOF-1. A direct comparison between UFF and UFF4MOF can be made in this case, as they share both bond topologies and force-field potentials (see Table 1). The 13.2 K⁻¹ difference in IRMOF-1 NTE is attributed to the smaller magnitude of the bonding force constants (40−50 kcal·mol⁻¹·Å⁻²) for the metal ions in UFF4MOF. This translates to a larger NTE observed with UFF4MOF due to the prevalence of higher magnitude vibrations in the cell, as these modes are more thermally accessible due to the smaller bond force constants of the metal–oxygen bonds.

The force fields can yield differences of >100% of the negative thermal expansion coefficients, which is exacerbated when partial atomic charges are included in UFF, UFF4MOF, and DREIDING parametrizations (see Section S.5 of the Supporting Information for details). Here it is clear that this materials property is more sensitive to the force-field parametrization and that each materials’ soft vibrational modes are significantly influenced by both bonded and nonbonded interactions. While UFF4MOF appears to overpredict the negative thermal expansion of IRMOF-1, many of these values agree within ±10 (10⁻⁶ K⁻¹), but without sufficient experimental data, it is difficult to ascertain the accuracy of these calculations.

Recent force-field developments have placed particular focus on ensuring the correct geometries of common sets of inorganic secondary building units (SBUs) such as the copper/zinc paddlewheels and the Zn₆O cluster. It was therefore a matter of curiosity to determine how many potential MOFs in the currently known and computationally ready database (CoRE) of MOFs possess these SBUs. Included in this set are several SBUs shown in Figure 2 corresponding to the square planar Paddlewheel, the octahedral M₆O cluster, the trigonal prismatic M₆O cluster found in the MIL-100 series, a common “rod”-like fragment found in MIL-53, and finally the cuboctahedral 12 connected SBU found in UiO-66 and 67.

The pie chart in Figure 3 demonstrates the few MOFs that possess these SBUs, which can potentially be described by the MOF force fields currently available. The SBUs were found using a 3-D pattern recognition algorithm, whose primary function was to recognize inorganic SBUs in MOFs for unambiguous assignment of correct atom types and bond orders for each force field. The Paddlewheel motif appears to be the most dominant coordination chemistry of those in Figure 2 in the CoRE database, consisting of 7.7% of the total. Of this 7.7%, roughly 34% are Zn paddlewheels and 54% are of the copper variety. Note that there is a significant number of duplicate structures found in the CSD, as was reported recently, and thus 7.7% is a generous measure of the coverage...
of paddlewheels in the CoRE database. This result suggests that further efforts must be directed toward developing a force field that governs a wider variety of periodic lattice materials with differing metal–ligand coordination geometries.

This work has demonstrated that properties based on response to thermal excitation and uniform stress can be reasonably reproduced by all of the force fields used in this study, namely, UFF,28 DREIDING,33 BTW,20 UFF4MOF,21 and the force field by Dubbeldam et al.12 With the exception of UiO-66 modeled with BTW-FF, the reported bulk moduli for IRMOF-1, IRMOF-10, HKUST-1, and UIO-66 were within 5 GPa of experimentally observed or ab initio calculated values for all of the force fields, suggesting that the predominant factor in these calculations is the bonding topology. Likewise, the negative trend of the linear NTE coefficient for each MOF was captured by all of the aforementioned force fields, however, with differences of up to 25 MK. Here subtle interactions between force-field parameters can give rise to different linear thermal expansion coefficients, suggesting that this is a more stringent test for a force-field parametrization. Because the negative expansion of these materials depends on specific vibrational modes of the ligands,49 it is likely that comparing each force field’s vibrational frequencies will yield more pronounced differences. This will certainly affect properties that are more sensitive to vibrational modes, such as the induced breathing observed in the MIL-53 series of MOFs and DUT-49,6,10 as well as the temperature-induced transitions observed in functionalized MOFs.36 It was recently demonstrated that an accurately parametrized force field could qualitatively reproduce this phenomena,59 however, it remains to be seen if more generalized force fields can be developed that cover a larger range of MOF materials.

Each force field studied in this work has been collected into a Python program, which is available at https://github.com/peteboyd/lammps_interface.

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