Machine Learned Potential for High-Throughput Phonon Calculations of Metal–Organic Frameworks

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1. Introduction

Metal–organic frameworks (MOFs) have garnered significant interest for gas storage and catalysis applications because of their exceptional porosity and chemical versatility. Their performance is heavily dependent on phonon-mediated lattice dynamics, affecting their mechanical and thermal stability. The vast chemical space of MOFs makes experimental screening of such properties impractical, and computational modeling via ab initio methods like Density Functional Theory (DFT) is infeasible due to the large number of atoms in the unit cells and complex anharmonic effects. Therefore, AI-driven models are needed to enable high-throughput phonon calculations with DFT-level accuracy at a fraction of the computational cost.

To address these challenges, we introduce MACE-MP-MOF0, a machine learned potential based on the MACE framework [1], fine-tuned on a curated dataset of 127 diverse and representative MOFs. By leveraging its architecture of equivariant message-passing graph tensor network with many-body information of atomic features encoded in each layer, MACE-MP-MOF0 efficiently predicts phonon density of states and important derived properties like the bulk modulus in agreement with experiments and DFT. Strategic dataset curation to efficiently sample the practically infinite phase-space of MOFs enhances transferability while minimizing computational costs. The novelty of MACE-MP-MOF0 also lies in its ability to perform quasi-harmonic phonon calculations to capture the anharmonic effects of negative thermal expansion comparable to DFT in a high-throughput manner, marking a significant breakthrough in MOF research. This AI-driven model bridges the gap between computational efficiency and predictive accuracy, enabling large-scale phonon calculations and accelerating MOF discovery.

2. Benchmarking against other State-of-the-Art Machine Learning Potentials (MLPs)

The development of MACE-MP-MOF0 brings a significant improvement for MOFs over its foundation model, MACE-MP-0 [2]. While MACE-MP-0 performed well for equilibrium structure predictions of MOFs, it struggled with accurately modeling phonon density of states, often predicting unstable lattice dynamics and spurious imaginary phonon modes even in the most commonly studied MOFs like MOF-5, as shown in Figure 1. This MACE-MP-MOF0 model, fine-tuned on a relatively small DFT dataset of 4768 points, corrects the deficiencies of the foundation model while achieving 50% higher computational efficiency and delivering $10\times$ more accurate optimized geometries, forces, energies, and stress.

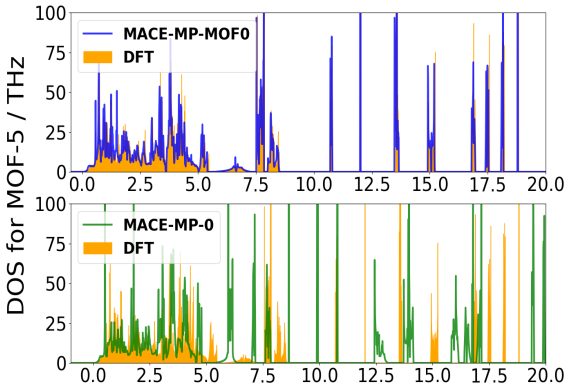

Fig. 1: Comparison of Density of States (DOS) predicted by MACE-MP-MOF0 and the foundation MACE-MP-0 model relative to DFT

2.1 A Scalable and Accurate Alternative to On-the-Fly MLPs

Recently, several neural network-based MLPs such as [3, 4] and on-the-fly MLPs such as kernel-based potentials in the Vienna Ab initio Simulation Package [5, 6, 7, 8] (VASP MLPs) and Moment Tensor Potentials (MTP) [9] reported in [10] have demonstrated sufficient accuracy in obtaining vibrational properties relative to DFT for MOFs.

Hence, we benchmark phonon predictions of MACE-MP-MOF0 against these state-of-the-art VASP MLPs and MTPs reported in [10], using four diverse and representative MOFs spanning a wide range of chemistries and topologies highlighted in Table 1.

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Table 1: Root Mean Square Deviations (RMSDs) in phonon frequencies relative to DFT for the investigated MOFs obtained with MACE-MP-MOF0 and on-the-fly MTP and VASP MLP models

MOF	Space Group	$RMSD_{MACE\text{-}MP\text{-}MOF0}$ (THz)	$RMSD_{MTP}$ (THz)	$RMSD_{VASP\ MLP}$ (THz)
MOF-5 (Zn2+)	Fm-3m	0.033	0.099	0.27
UiO-66 (Zr4+)	F-43m	0.082	0.111	0.312
MOF-74 (Zn2+)	Cc	0.173	0.093	0.126
MIL-53 (Al3+)	R-3	0.138	0.156	0.264

Table 2: The number of reference structures generated for the investigated MOFs in the training sets of the respective MLPs

MOF	MACE-MP-MOF0	On-The-Fly MLPs
MOF-5 (Zn2+)	92	1110
UiO-66 (Zr4+)	58	1373
MOF-74 (Zn2+)	60	2549
MIL-53 (Al3+)	29	3073

As shown in Table 2, these on-the-fly models required 10-100 $\times$ more reference configurations in their training sets per MOF than MACE-MP-MOF0 and need to be retrained for each new MOF, severely limiting their scalability for high-throughput screening. In contrast, MACE-MP-MOF0 is trained as a generalizable model covering 60% of MOF chemistry in its curated training set, eliminating the need for retraining on a case-by-case basis. MACE-MP-MOF0 still achieves an improved or comparable performance in obtaining the phonon spectra for the investigated MOFs, as shown in Table 1. The ability of MACE-MP-MOF0 to generalize across a wide range of MOFs for rapid screening and accurate prediction of phonons, without the prohibitive data and computational costs of on-the-fly training methods, marks a significant advancement in MLPs for MOFs.

3. Experimental Validation of Predicted Physical Properties

Experimental studies focus on tuning the bulk modulus of MOFs to analyze their response to external pressure, guest molecules, and temperature variations for gas storage applications. Modifying metal centers or functional groups allows control over MOF mechanics, but experimental validation is expensive and requires precise synthesis and high-pressure measurements. MACE-MP-MOF0 offers a cost-effective alternative by reproducing experimental bulk moduli for several well-known MOFs in Figure 2. Despite several of them being out-of-sample MOFs, our model accurately captured their mechanical behavior, showing excellent agreement with experimental data and DFT. This validates the model's generalizability and suggests that it can be extended to hypothetical MOFs, accelerating materials discovery by reducing the need for extensive experimentation.

Thus, this work highlights the power of AI-driven models in accelerating MOF discovery by enabling efficient and accurate predictions of lattice dynamics and dependent properties. By bridging the gap between computational speed and experimental accuracy, our work paves the way for high-throughput screening of novel MOFs, unlocking new possibilities for AI-driven materials design and real-world applications.

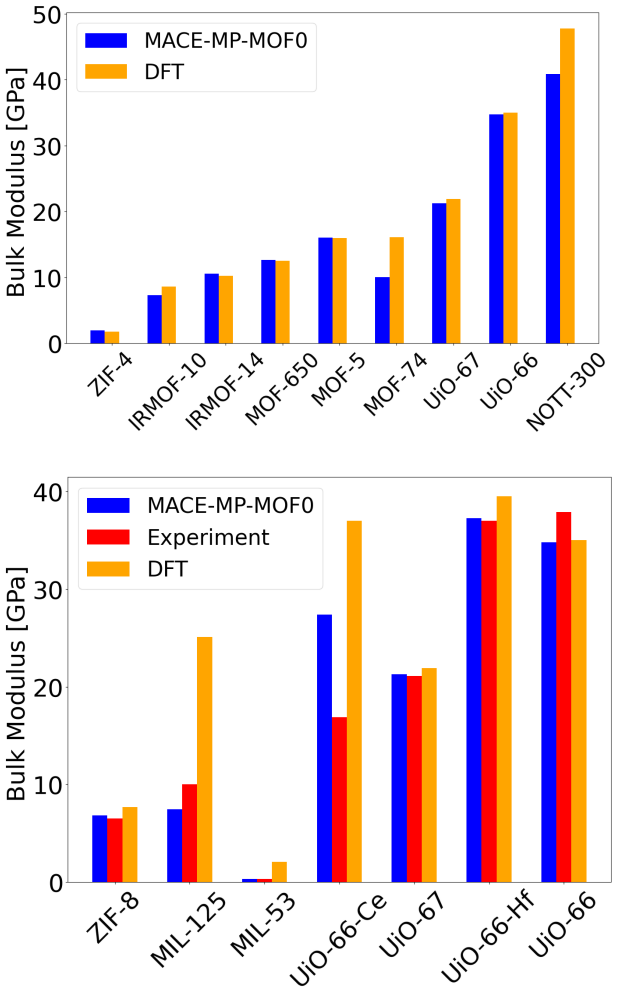

Fig. 2: Bulk modulus predictions of MACE-MP-MOF0 compared to DFT and Experiments. DFT data is self-generated or reported in [11, 12, 13, 14] and experimental data is reported in [15, 16, 17, 18, 19]

Acknowledgments

This research used resources of the National Energy Research Scientific Computing Center (NERSC), a Department of Energy Office of Science User Facility using NERSC award 'GenAI@NERSC'. PDK acknowledges financial support from U.S. National Science Foundation's "The Quantum Sensing Challenges for Transformational Advances in Quantum Systems (QuSeC-TAQS)" program. AME and FZ's work was also supported by Ada Lovelace Centre at STFC (https://adalovelacecentre.ac.uk/), Physical Sciences Databases Infrastructure (https://psdi.ac.uk) under EPSRC grant no. EP/X032663/1 and EPSRC under grant no. EP/V028537/1. ASR acknowledges support via a Miller Research Fellowship from the Miller Institute for Basic Research in Science, University of California, Berkeley. TJI acknowledges support via the Bakar Institute of Digital Materials for the Planet (BIDMaP).

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