Computational Study of MOFs for Direct Air Capture Using Flexible Force Fields

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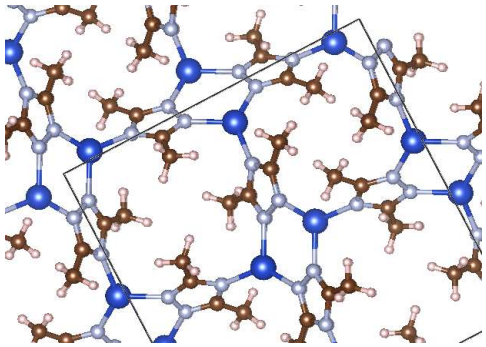
Industry need

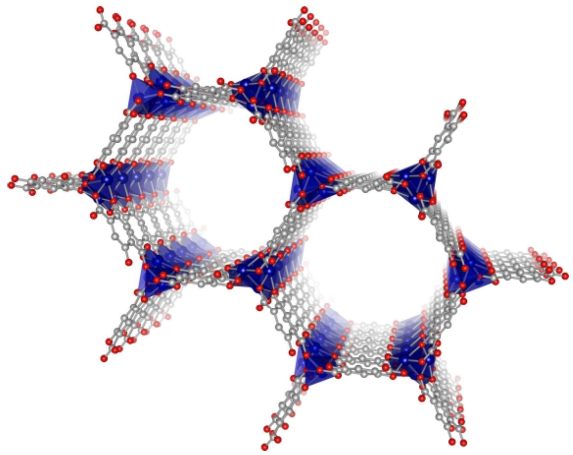
- An estimated 35 billion tons of CO_2 are released into the atmosphere annually (Schoedel et al. Nat. Energy 2016)
- Point source carbon capture can help slow the rate at which humans are emitting CO_2 into the atmosphere, but current estimates indicate that this won't be enough to avert the worst effects of climate change.
- Direct air capture (DAC) methods will be needed to **reduce** the global atmospheric CO_2 concentration.
- Metal-organic framework materials show potential for Direct Air Capture due to promising gas sorption properties

Approach

Metal Organic Frameworks

- MOFs are “are highly porous crystalline materials created via the self-assembly of inorganic metal or metal oxide subunits with organic linkers” (Budhathoki et al., EES, 2019)
- Beneficial Qualities of MOFs
  - Potential for high CO_2 adsorption
  - High surface area
  - Quick, low temperature regeneration of DAC sorbent material
  - Low energy penalty carbon capture

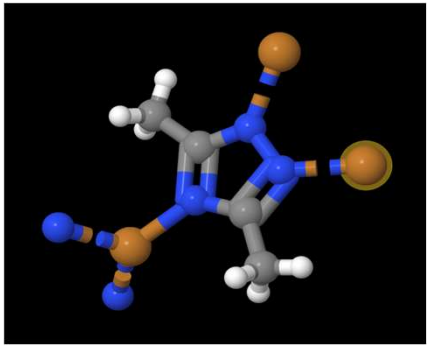




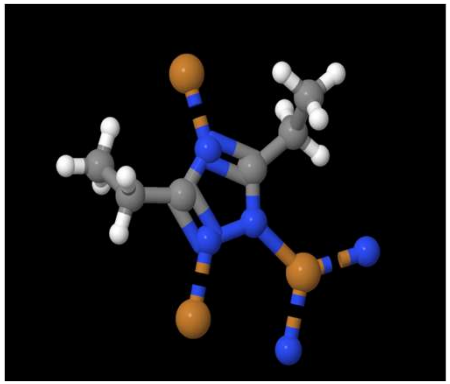
Vervoots et al., ACS Appl. Mater. Interfaces, 2020

Metal Organic Frameworks

- NETL is carrying out a screening study where gas sorption behavior will be calculated for thousands of MOFs using a general flexible force field made with the help of machine learning
- The MOFs studied in the summer project are referred to as ASUQIO and MAF-2
- Both are copper MOFs containing triazole rings
  - ASUQIO has methyl substituents, MAF-2 has ethyl groups



ASUQIO



MAF-2 (BOGXIF)

Objective

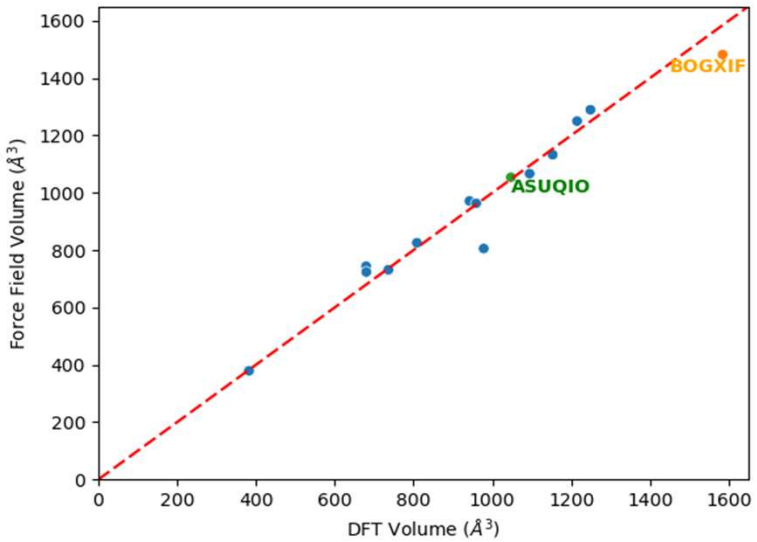
- Determine accuracy of MOF calculations using rigid vs. flexible force fields
- Flexible force fields provide faster, cheaper alternative to ab initio force field methods and could provide increased accuracy relative to fixed-atom force fields (Heinen and Dubbeldam, Wiley Interdiscp. Rev. Comput. Mol. Sci., 2018)
- Force fields were generated in this project using the software QuickFF

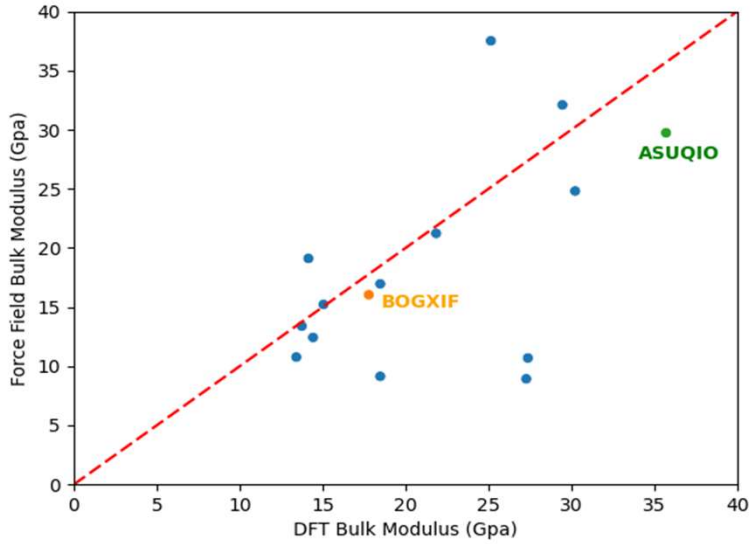
QuickFF

- Input data used was from Density Functional Theory (DFT) calculations; DFT is our “reference”.
- MOF structures were minimized using molecular dynamics simulations
- QuickFF was used to generate flexible force fields
- Force field accuracy verified by calculating equilibrium volume and bulk modulus

Comparison Between DFT (reference) and Flexible Force Field Results for Volume and Bulk Modulus

- QuickFF flexible force field reproduces the DFT bulk moduli and equilibrium volume with acceptable accuracy for a screening study





Hybrid Monte Carlo- Molecular Dynamics Simulations

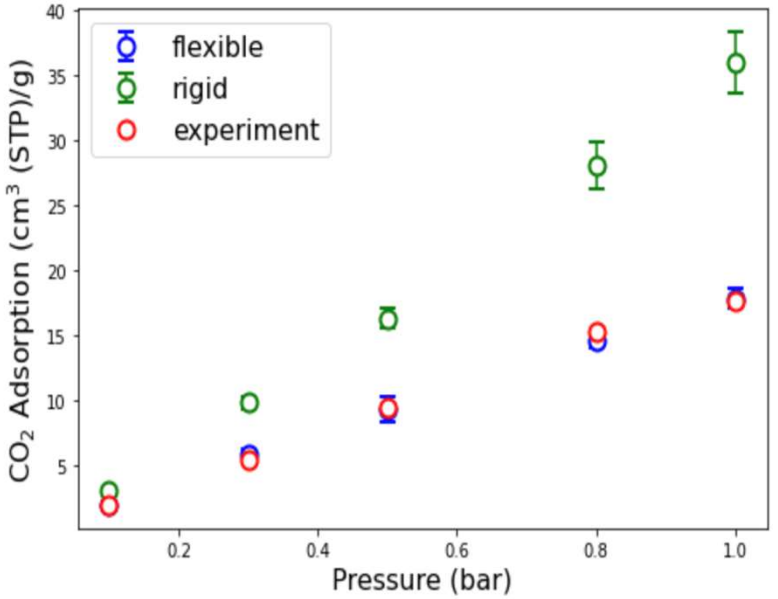
- Hybrid Grand Canonical Monte Carlo (GCMC) + molecular dynamics (MD) simulations were used to determine gas adsorption properties in the MOFs
- In GCMC simulations, temperature, volume, and chemical potential of the system are fixed. Atoms or molecules are exchanged (inserted or deleted) with an imaginary ideal gas reservoir via Monte Carlo moves such as translation and molecular rotation within the simulation cell (Frenkel and Smit, Academic Press, 2002)
- In the hybrid approach, GCMC was used for insertion and deletion of gas molecules and all the atoms were moved using molecular dynamics

CO_2 Sorption Calculations

- Performed four independent simulations at five pressures, at 298K using LAMMPS software: .1, .3, .5, .8, and 1 bar
  - CO_2 molecules parameterized with TraPPE force field
- No adsorption was observed for ASUQIO, further calculations performed only using MAF-2

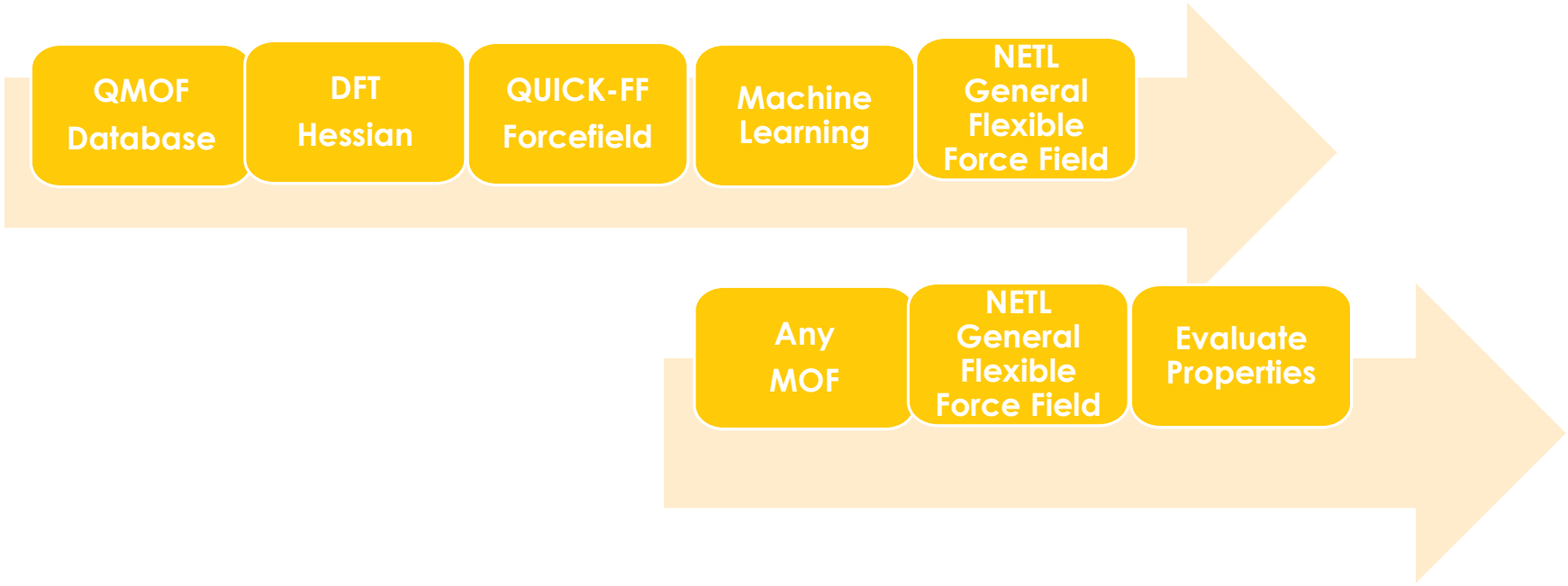
Results

- The flexible QuickFF force field predicted the CO_2 adsorption properties of MAF-2 with much greater accuracy than the fixed atom force field



NETL Team Machine Learning Project

- My NETL team is using machine learning to generate a **general flexible force field** for MOFs.
- The reference data for the machine learning is a collection of Quick-FF forcefields for MOFs.
- The impact of the general flexible force field will be that **properties may be evaluated for any MOF** without performing computationally expensive DFT calculations.



Rosen et. al., Matter, 4, 1–20, May 5, 2021

Student accomplishments

- My results allowed my NETL team to make a comparison between calculated and measured CO_2 adsorption for MAF-2. This MOF is a good example to use because there is a published experimental gas adsorption study on it.
- My results showed that the Quick-FF flexible force field gave a **significant improvement in accuracy** compared to the rigid forcefield. The team is using Quick-FF force fields as reference data for their machine learned NETL General Flexible Force Field for MOFs.
- I learned:
  - Skills specific to my project (Quick-FF, setting up and running Monte Carlo simulations).
  - Various coding skills such as python and bash scripting.
  - Fundamentals of molecular simulations, some principles of machine learning
  - How computational projects can accelerate the development of materials for cost effective carbon capture technologies.

Benefits

What are the benefits of your results?

- Computational screening/design of a high-performance material with tailored properties for direct air capture can enable cost-effective direct air capture.
- In addition to point source capture, direct air capture is urgently needed to prevent the worst effects of climate change.
- My team is using force fields like this in their machine learning project, so my work was helpful to my team in benchmarking the accuracy of their database.
- I am working with my NETL team to develop my results into a manuscript to be submitted to a peer-reviewed journal this fall.

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