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Molecular Simulations of Metal-Organic Frameworks

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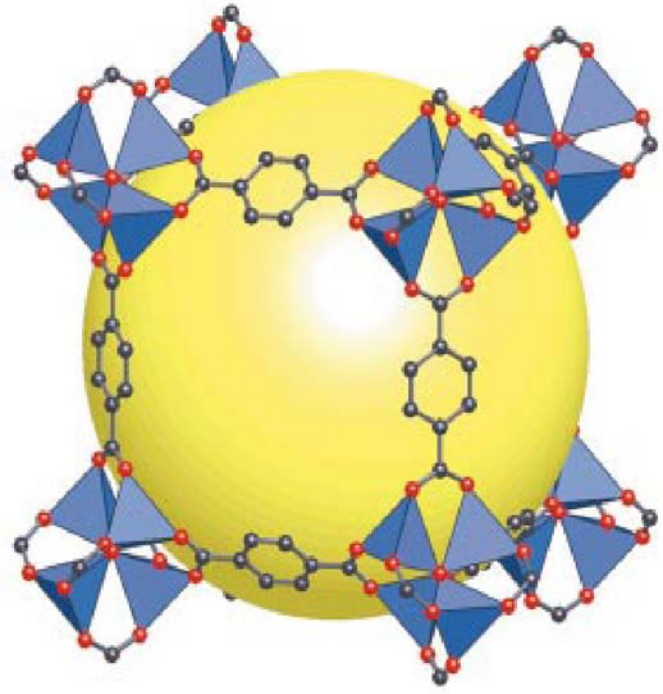
Outline

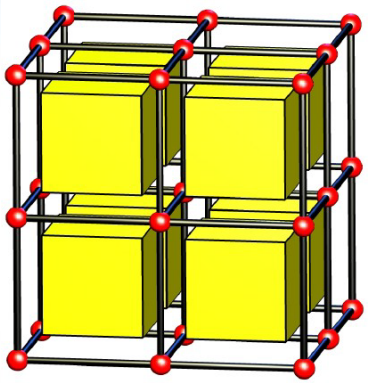
- Metal-organic frameworks (MOFs)
- MD simulation
  - Mechanical properties
  - Vibrational properties
  - Framework stability
- GCMC simulation
  - Code development (Paul Crozier)
  - Adsorption of I_2 by ZIF-8



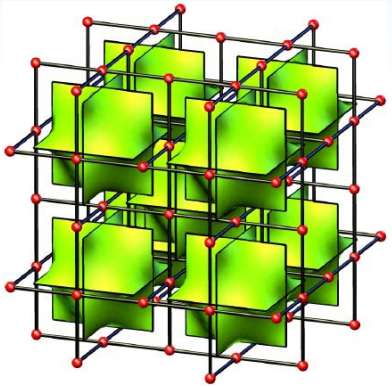
IRMOF-1

Metal-Organic Frameworks (MOFs)

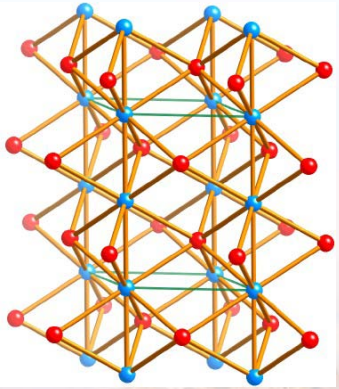
- Crystalline, highly ordered solids
- Metal cations linked by organic linkers
  - ➡ Tunable pore chemistry
- Nanoporous (5-30 Å)
- Huge variety of structures
- Ultrahigh surface areas
  - (as high as 6000 m^2/g)
- Structurally flexible



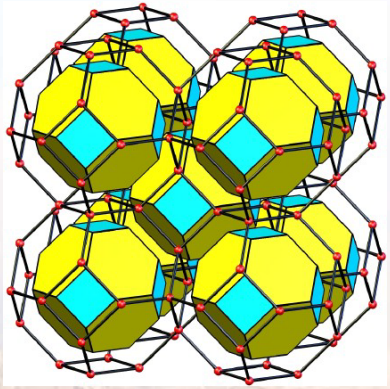
pcu
IRMOF series
Zn_4O cluster



nbo
NOTT-10x, PCN-14
Cu_2 cluster



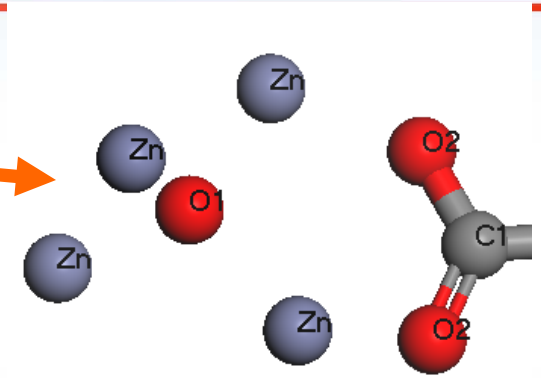
seh
MIL-53(Al)
Al(OH) cluster

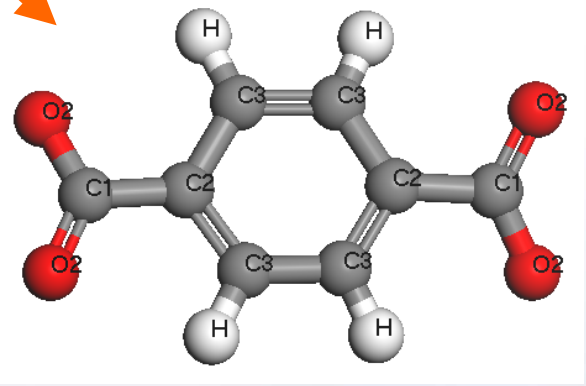


sod
ZIF-8
Zn cluster

MD Simulation

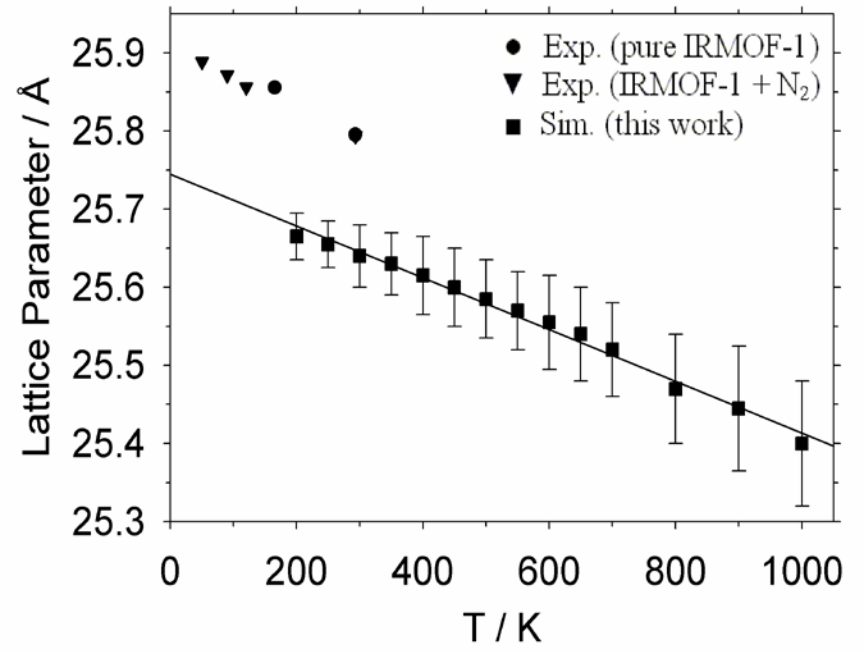
- Potential energy expression:
  - **All atoms:** VDW and electrostatic
  - **Linkers and adsorbates:** CVFF intramolecular parameters (bond, angle, dihedral, out-of-plane
- Constant pressure (NPT) ensemble to calculate volume and lattice parameters (with and without adsorbate).
- Constant volume (NVT) ensemble for elastic and vibrational properties.

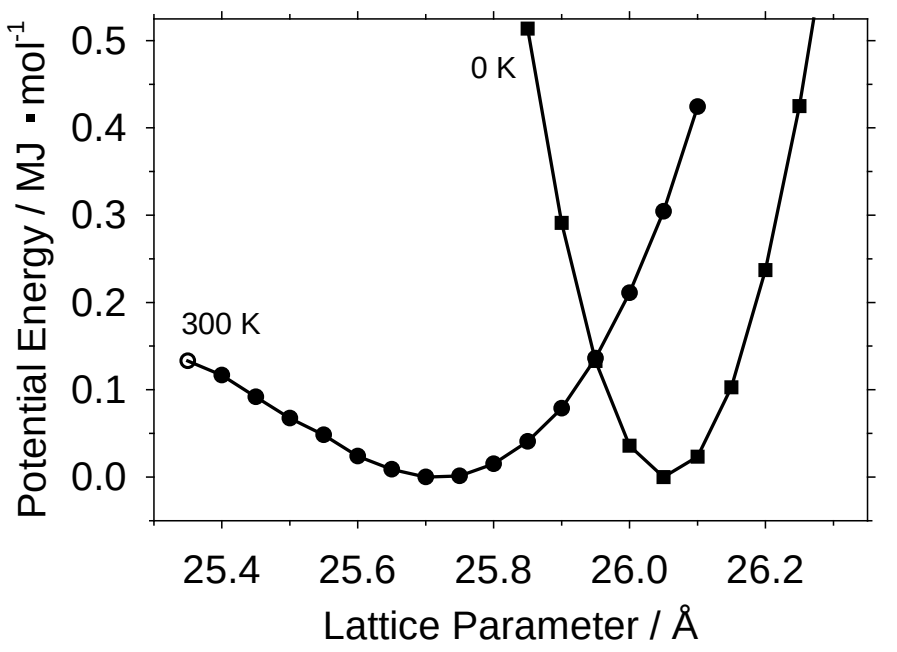




Nonbonded force field approach for IRMOF-1 validated by: T and P effects, elastic properties, vibrational properties, volume changes associated with adsorption (water)

Mechanical Properties of IRMOF-1



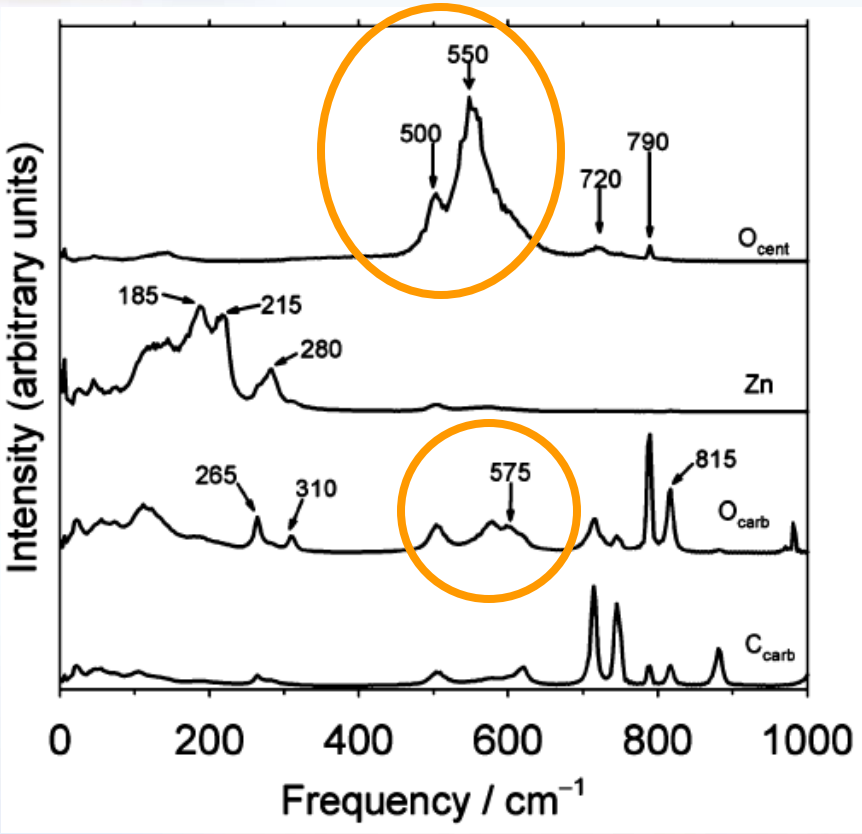


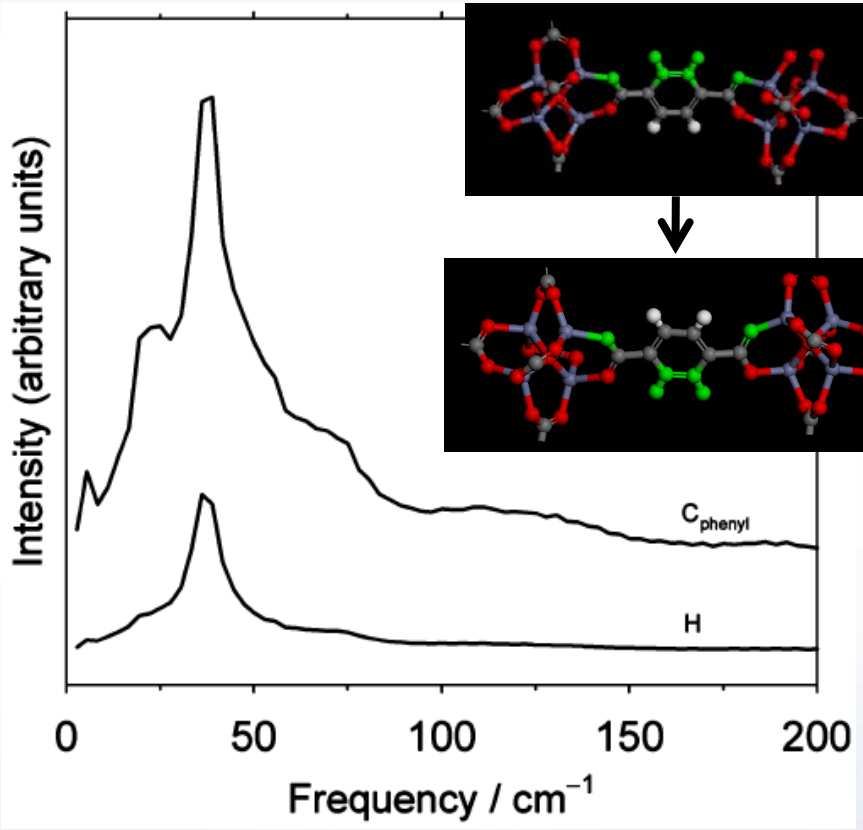
- Trend of negative thermal expansion agrees with experiment.
- 1.0% increase in volume between 30 K – 293 K (0.1 Å in lattice parameter).
- Significant decrease in bulk modulus between 0 K and 300 K

	Energy Min (0 K)		MD Sim (300 K)
	FF	DFT	FF
Bulk Modulus (GPa)	**20.0**	**16.3**	**4.0**

Greathouse and Allendorf, *J. Phys. Chem. C* **2008**.

Vibrational Properties of IRMOF-1





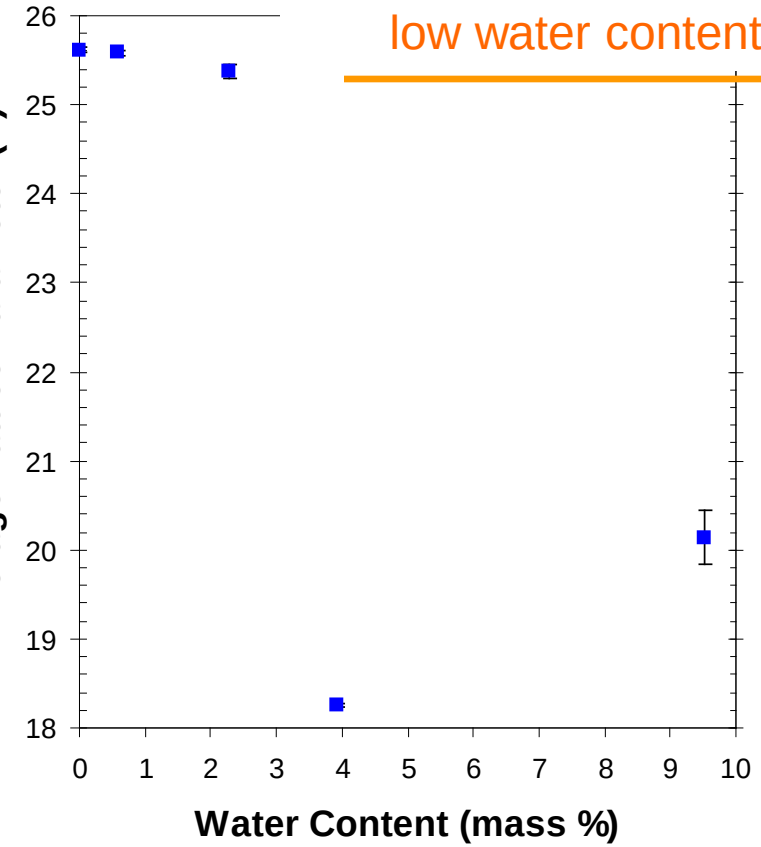
Power spectra for select atom types. Frequencies for ZnO_4 modes are in agreement with experiment.

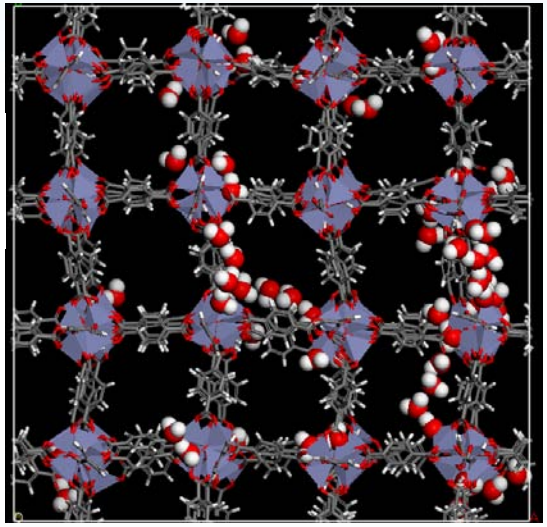
Librational modes due to internal rotation of phenyl groups.

Greathouse and Allendorf, *J. Phys. Chem. C* **2008**.

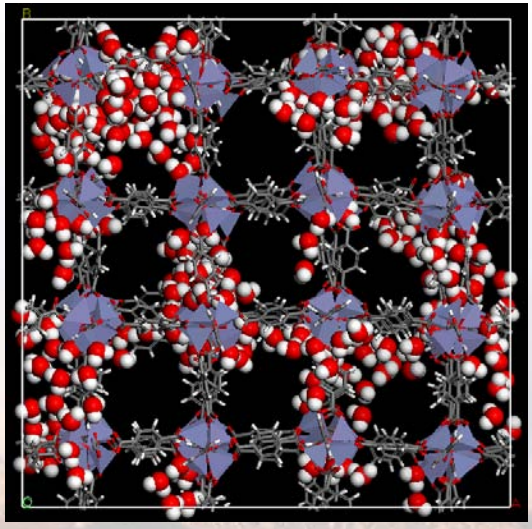
Interaction of IRMOF-1 with Water

Framework distortion at low water content





Framework unstable at higher water content

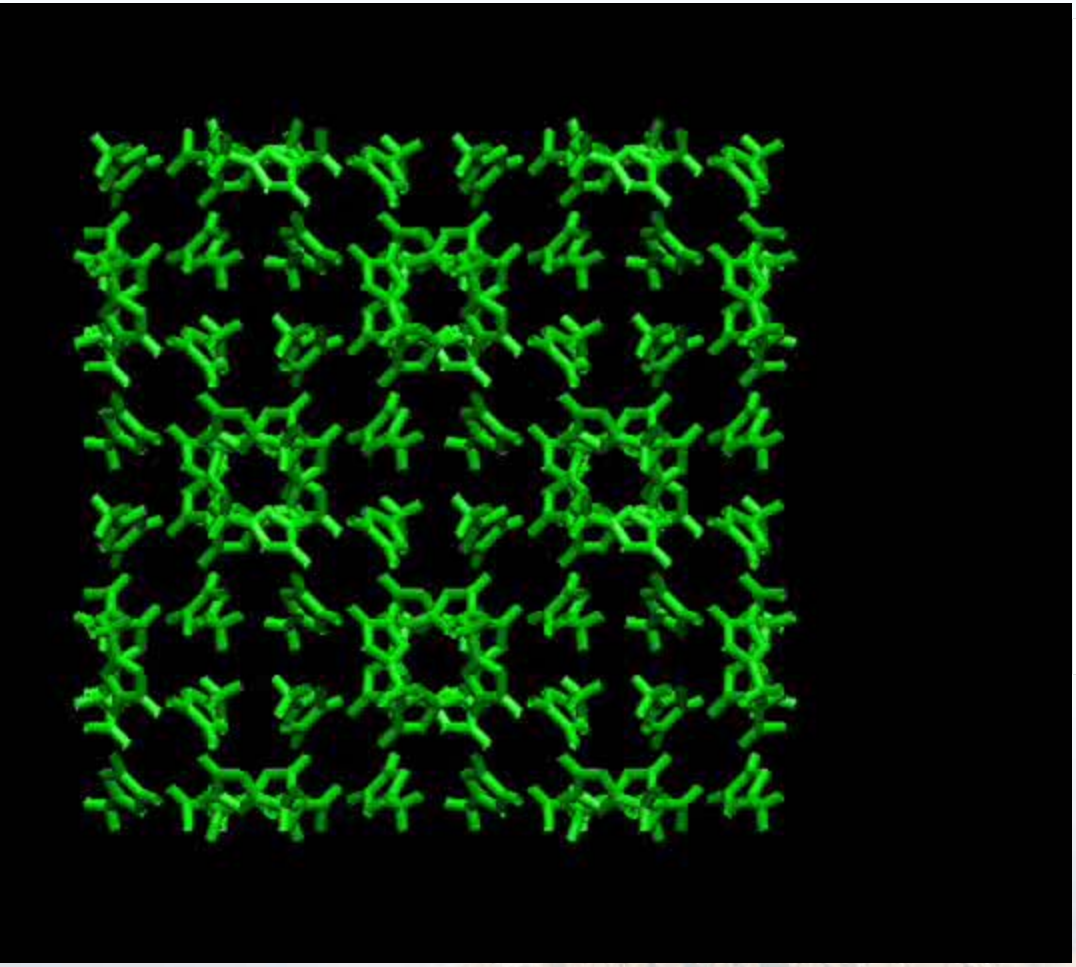


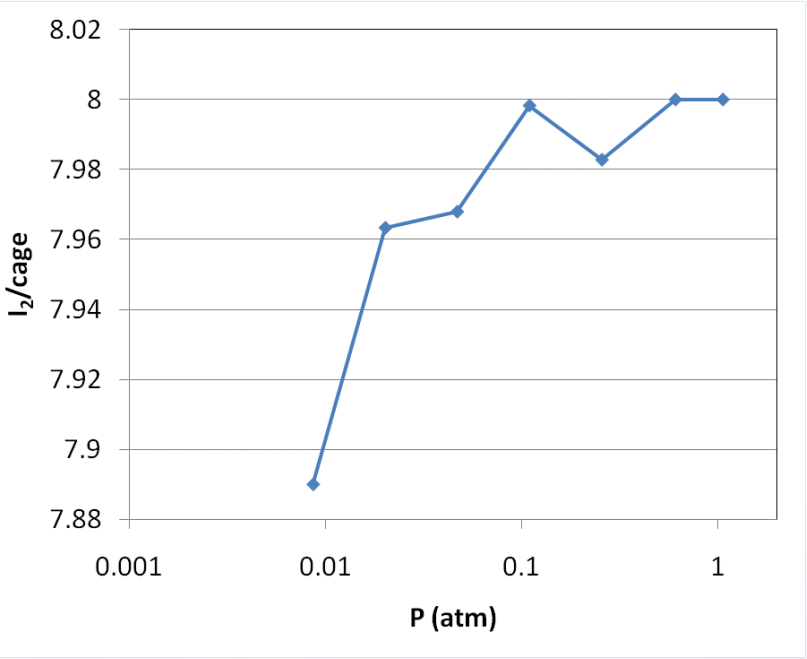
Greathouse and Allendorf, *J. Am. Chem. Soc* **2006**.

Adsorption in LAMMPS: “fix GCMC”

- Grand canonical Monte Carlo (μVT ensemble)
- Standard GCMC features:
  - Particle creation/destruction.
  - Work efficiently, and in parallel on multiple processors.
  - Compatible with other LAMMPS features (MD, ensembles, force fields, computes, etc).
  - Reports relevant statistics.
- Currently limited to monatomic adsorbates and short-range interactions (no electrostatics).

Adsorption of I_2 in ZIF-8





- Spherical model for I_2.
- Predicted I_2 loading in good agreement with x-ray diffraction.

Sava et al, *J. Am. Chem. Soc.* **2011**, in press.

More on “fix GCMC”

Likely to be done soon:

1. More verification testing vs MCCCS Towhee code.
2. Fix code problems identified by beta testers.
3. Improve the documentation in preparation for release.
4. Send updated code & docs out to beta testers and Steve.
5. Release code & docs on main LAMMPS website.

Maybe later if there’s time:

6. Add molecule capability, including MC exchanges, moves, and rotations of molecules.
7. Add ability to measure and report chemical potential.
8. Make it work with long-range electrostatics.
9. Make it scale: better parallel simulation.
10. Add fancier MC moves (configurational bias, etc.).

Acknowledgements

- Sandia National Laboratories
  - Mark Allendorf
  - Paul Crozier
  - Tina Nenoff
  - Dorina Sava