

Modelling Gas Adsorption in Metal-Organic Frameworks using a Grand-Canonical Monte Carlo Simulation

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Introduction

Gasoline is extremely potent as a fuel source due to its high energy density, but its greenhouse gas emissions are cause for concern [1]. Natural gas is a prime alternative for gasoline in vehicle use during the transition to renewable energy sources because of lower emissions, large supply, and the ease with which existing infrastructure can be adapted to transport and use it [2]. However, storage of natural gas is difficult because it requires extreme conditions to be stored as either liquefied natural gas (around 162°C) or compressed natural gas (around 200 bar) [3]. To make natural gas vehicles viable, there needs to be a more efficient method for storing it for use in vehicles. Metal-organic frameworks are of interest here because they have been shown to increase storage of usable fuel at a much lower pressure of 65 bar [4].

Metal-organic frameworks (MOFs) are promising novel materials for gas separation and storage that are modular by design [5]. They are comprised of metal nodes and organic linkers that self-assemble into organized crystal structures with nano-pores when the component parts are combined in solution. The high internal surface areas formed by these nano-pores provide ideal adsorption sites for a variety of gaseous atoms and molecules. They can be used to improve gas storage without requiring extreme temperature and pressures, a useful tool for implementing in natural gas vehicles [4]. The linkers and nodes can be selected to create the MOF for higher selectivity of a gas molecule, increasing the storage or separation capabilities of the MOF. This modularity means that there are thousands of potential MOFs that can be synthesized and tested, so traditional synthesis and evaluation is not viable for testing each MOF.

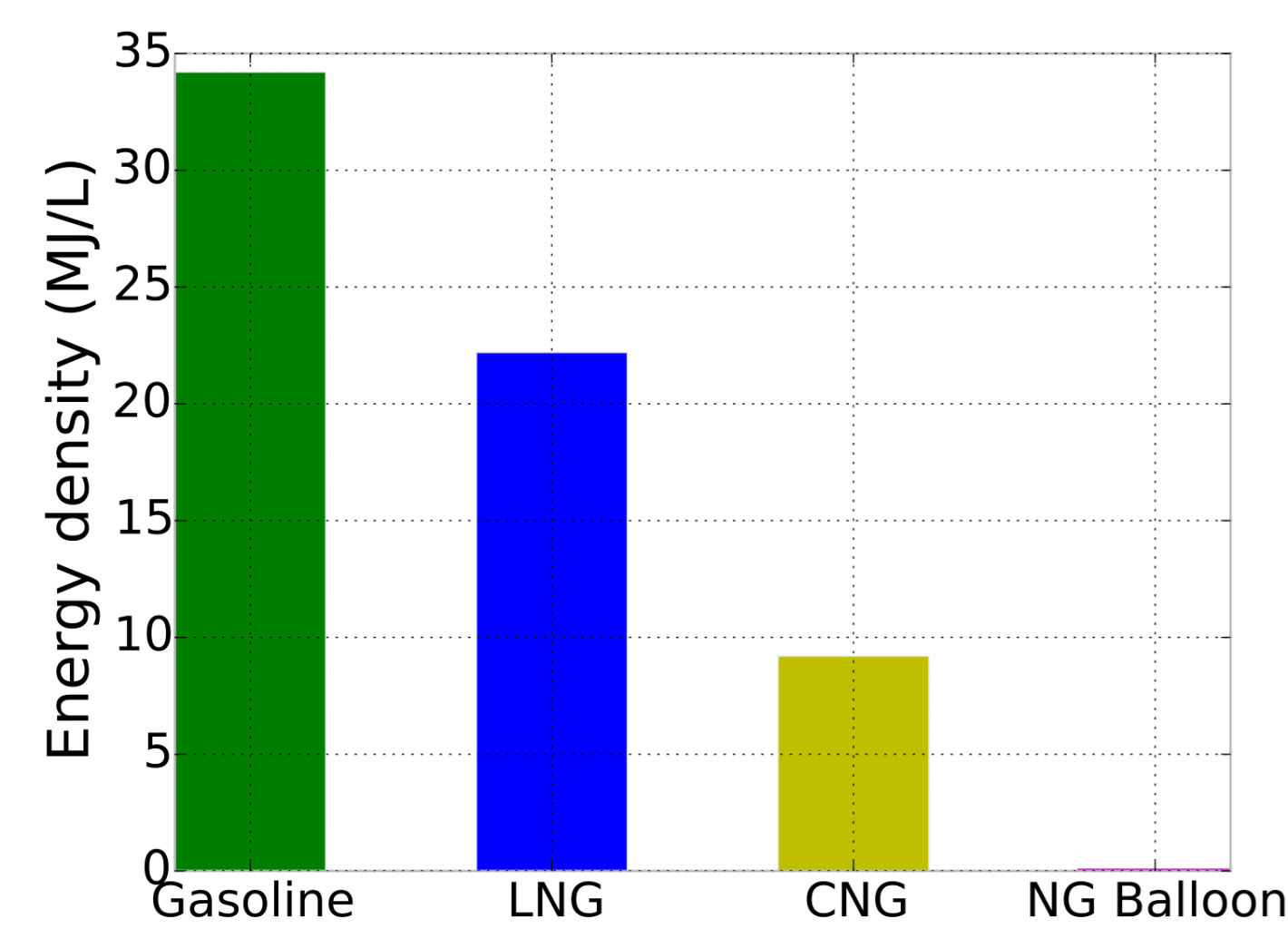


Figure 1: This graph shows the volume energy density of fuels. It compares gasoline to methane being stored in various ways.

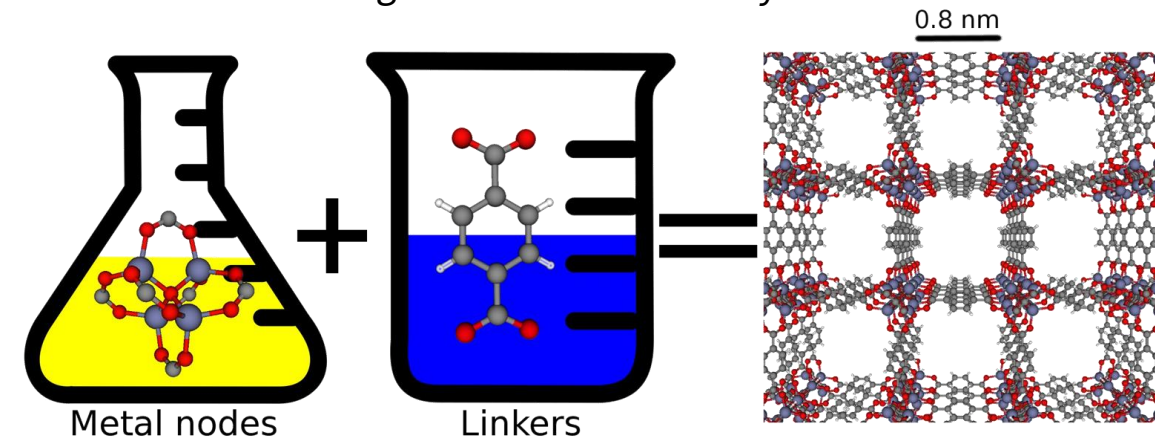


Figure 2: This figure shows how MOFs are created. Solutions of metal nodes and linkers are combined, and they organize into a repeating crystal structure.

PorousMaterials.jl

PorousMaterials.jl is a free and open-source software package written for Julia that can model adsorption within nano-porous materials such as metal-organic frameworks. Its main functionality is the grand-canonical (μVT) Monte Carlo simulation that estimates the total adsorption of gas within a metal-organic framework. It can also track and output adsorbate positions to understand where molecules are adsorbing to the structure. To better understand the structure itself, PorousMaterials.jl is capable of inferring and storing bond information so as to analyze the topology itself. This has uses ranging from identifying solvents and interpenetrated metal-organic frameworks to modifying linkers while still retaining a bonded structure.

Grand-Canonical (μVT) Monte Carlo Simulation

The grand-canonical (μVT) Monte Carlo simulation estimates the adsorption properties of a metal-organic framework by exploring its statespace through insertions, deletions, and translations of molecules. The statespace of a metal-organic framework is not uniformly distributed, so instead of sampling the statespace it will be explored using a Metropolis-Hastings algorithm. This exploration is accomplished by proposing to insert, delete, or translate one adsorbate at a time. Then these moves are accepted or rejected with a probability calculated from the acceptance rule for that proposal (shown to the right). These acceptance rules are derived from the Metropolis Hastings algorithm and the partition function in the μVT ensemble of equations.

The acceptance rules are set up such that the system only explores probable states and then information from the visited states can be used to estimate what the "average" state might look like. With these rules, the system will always accept proposals to more energetically favorable states. It will also reject proposals to energetically impossible states, such as ones where atoms are overlapping. The simulation will randomly accept proposals that result in a slight increase in energy as a means for escaping local minima. This ensures that the model can explore the statespace in its entirety.

Statespace of Adsorbates in MOF

$$R := \{N, \{\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N\}\}$$

Simulation Cycle

$$\text{Current State: } R_k = \{N, x^N\}$$

$$\text{Proposed State: } R_{k+1} = \{M, x^M\}$$

$$\text{if } \text{acc}(R_{k+1}, R_k) > \text{random number } [0, 1]:$$

$$\text{change to state } R_{k+1}$$

else:

$$\text{remain in state } R_k$$

Acceptance Rules

$$\text{acc}(ins) = \min\left(\frac{VP}{k_B T(N+1)} e^{-\beta \Delta E}, 1\right)$$

$$\text{acc}(del) = \min\left(\frac{k_B T N}{VP} e^{-\beta \Delta E}, 1\right)$$

$$\text{acc}(trn) = \min(e^{-\beta \Delta E}, 1)$$



Verifying the Simulation

To verify that the model is working correctly, the results from the simulation can be compared with experimental data. The graphs below depict adsorption isotherms for methane inside IRMOF-1 and Co(bdp).

IRMOF-1 is a rigid structure that PorousMaterials.jl is able to model with a high degree of accuracy. The simulation and experimental data match up almost exactly, with the simulation only overestimating by a small amount. This is promising for modelling metal-organic frameworks with similar atomic makeups because it shows that the simulation and the atomic interaction variables can produce accurate results.

Co(bdp) is of interest because it is a flexible metal-organic framework, meaning it has a higher amount of usable fuel that can be recovered from storage. It has a closed position at low pressures and an open position at high pressures. There is a transition point where the metal-organic framework will "pop" open and function as normal. When the pressure decreases past this point, the metal-organic framework will rapidly close and expel all gas remaining. PorousMaterials.jl does a good job of modelling the closed and open forms as rigid structures, so at the very low and very high pressure ranges it yields accurate data. However, because the model is built on the μVT ensemble of equations, it is unable to model the change in volume.

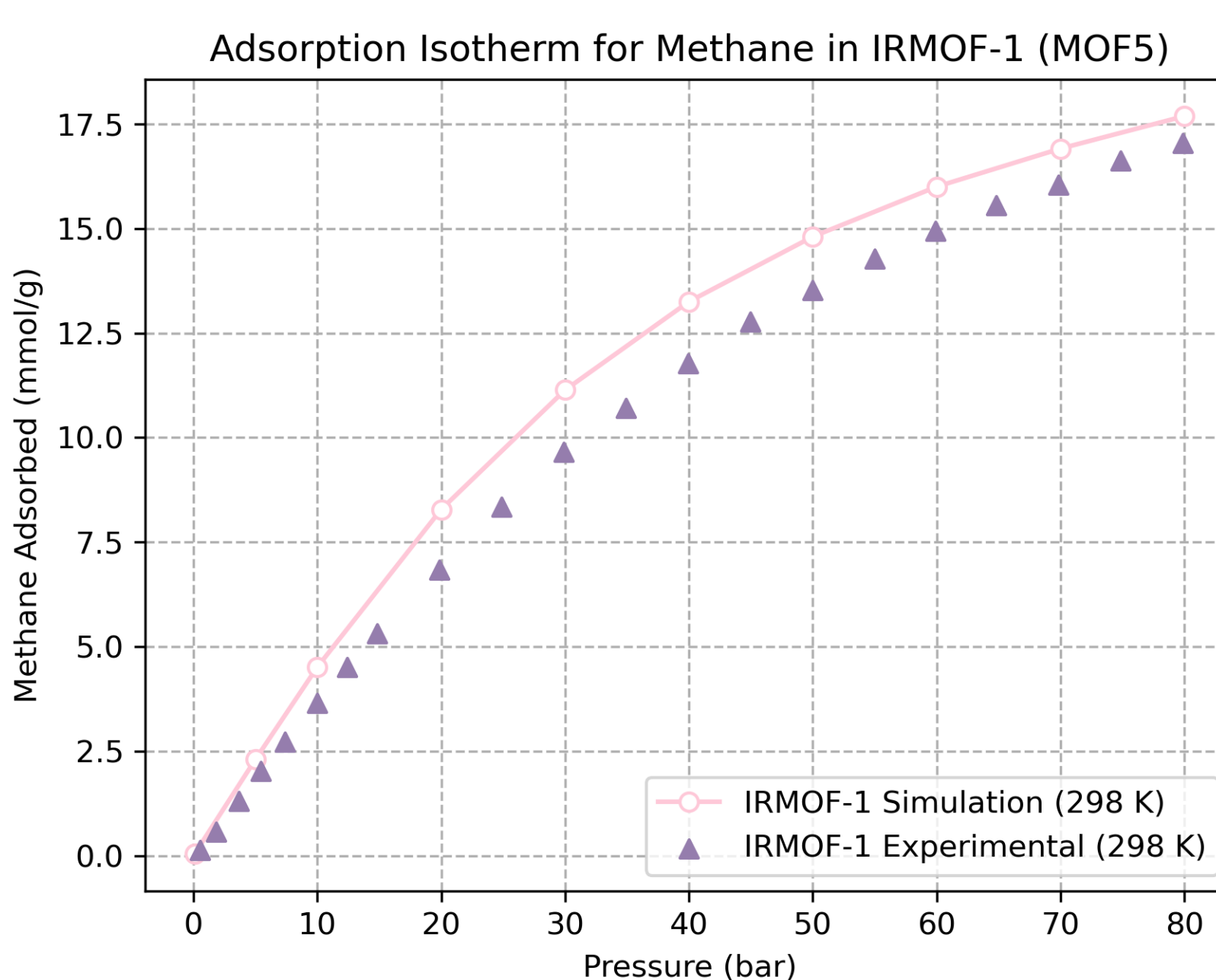


Figure 3: Simulated and experimental adsorption isotherms for IRMOF-1. The simulation was run at 298.0K using a Dreiding forcefield for the atomic parameters [6]. It was compared to experimental data collected by Mason, et. al. [7].

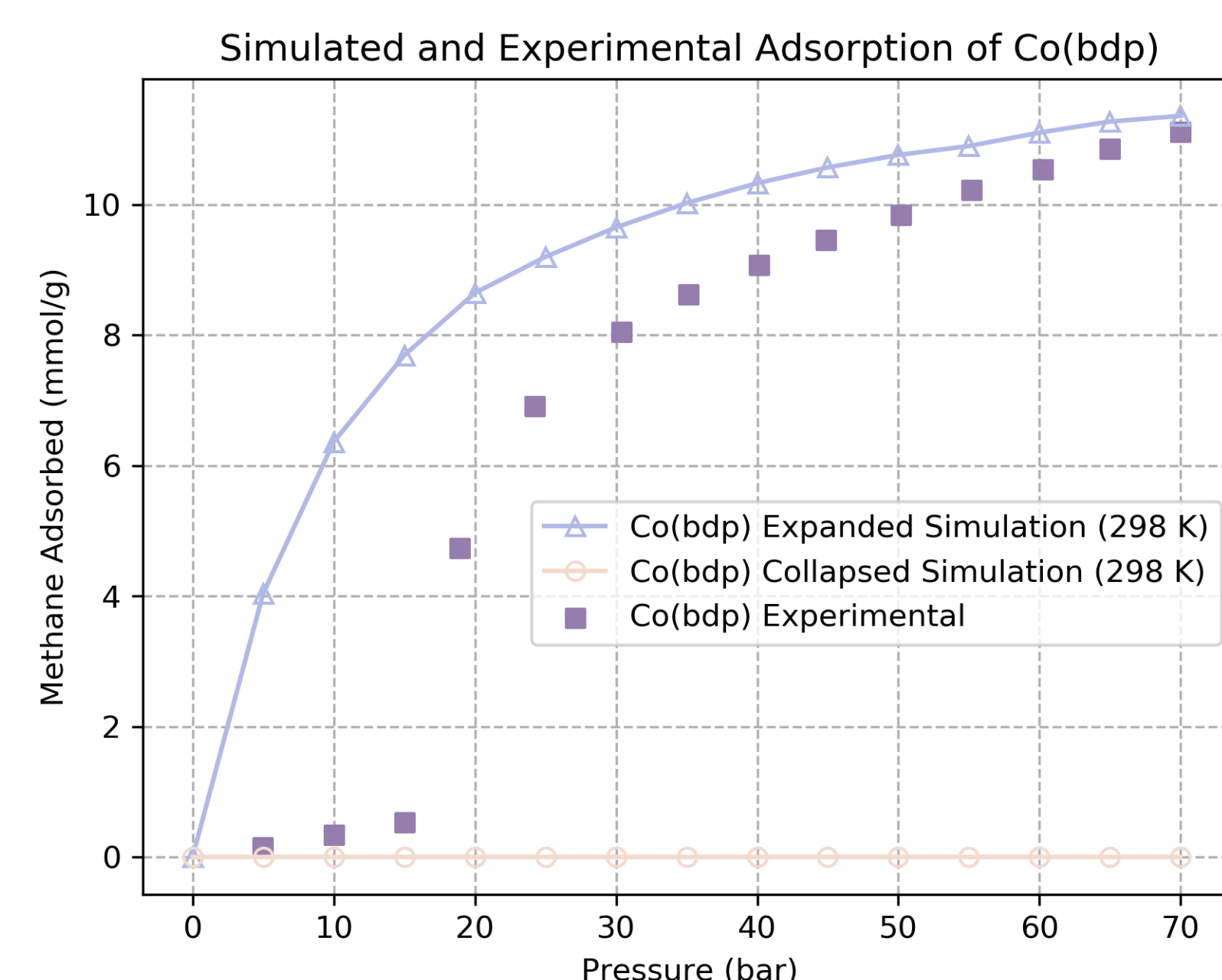


Figure 4: Simulated and experimental adsorption isotherms for Co(bdp) in its expanded and collapsed forms. The simulation was run at 298.0K using a Dreiding forcefield for the atomic parameters [6]. It was compared to experimental data collected by Mason, et. al. [4].

Snapshots

When studying gas adsorption in nano-porous materials, it is important to know where the molecules are located in relation to the structure. It can be difficult to get this information through experimentation, but the functionality of PorousMaterials.jl can easily be extended to provide insight. Because the simulation has to store the positions of all adsorbates already, their positions simply need to be aggregated and output to the user in a meaningful way. To show where likely adsorption sites are located, a 3D grid is superimposed over the simulation box such that each element of the grid corresponds to a uniformly sized voxel in the simulation box. When PorousMaterials.jl periodically takes "snapshots" it will convert the position of the adsorbate to an index in the grid. Then that element will be incremented to show an adsorbate was present.

This density grid can be visualized as a cloud plot laid over the structure. This showcases where the adsorbates are most likely to be found and can inform decisions to alter the structure to increase adsorption or selectivity. Below we can see the results from collecting 10,000 snapshots of methane adsorbing inside IRMOF-1. The dark blue sections of the cloud show locations with a high probability of observing methane while the light blue and white sections are areas with little to no chance of having a methane adsorb. It is important to note that this is showing where the center of the methane will likely be located, but it does not portray the physical space a methane molecule would occupy.

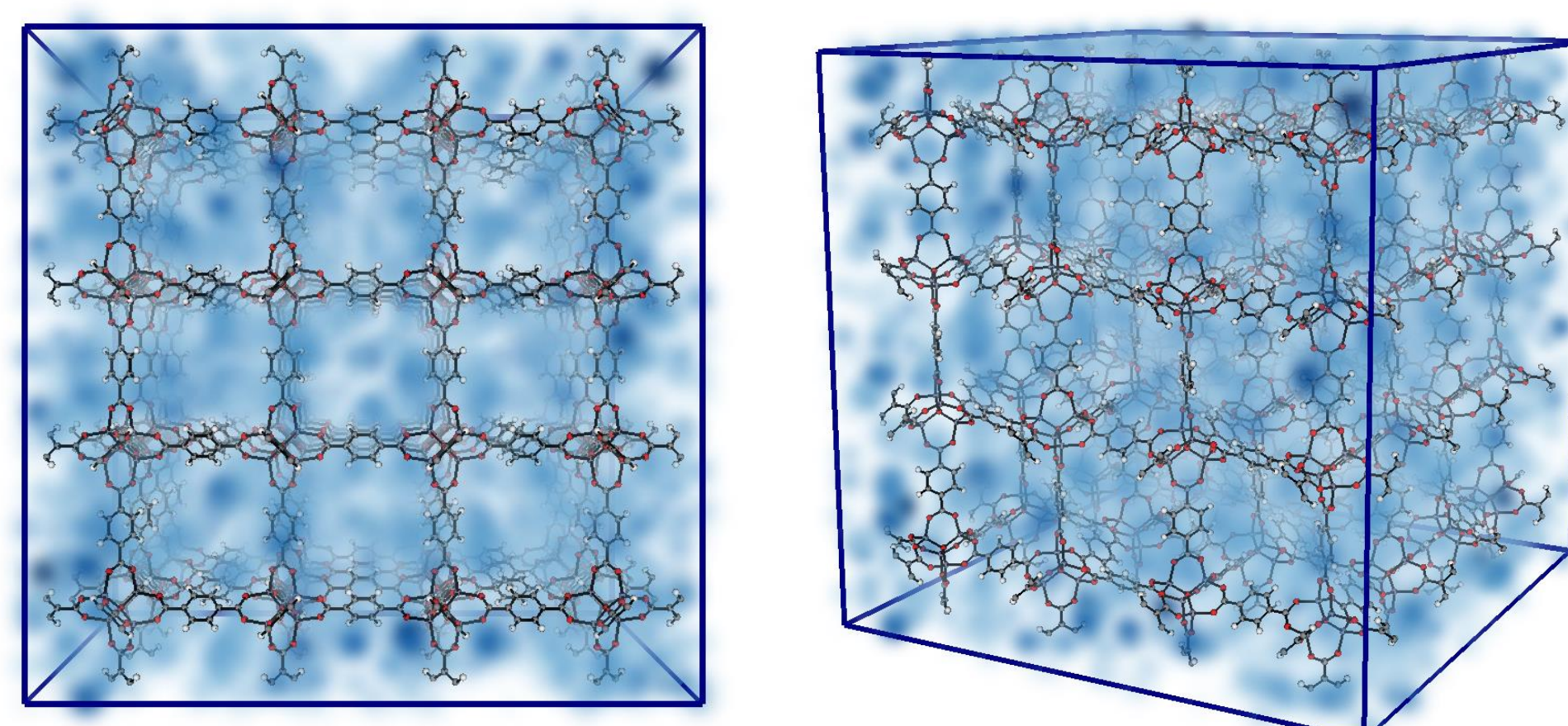


Figure 5: cloud density plots showing the likely adsorption sites for methane in IRMOF-1. This was run at 298.0K and 50.0 taking 10,000 snapshots. It used the Dreiding forcefield to define atomic interactions [6]. The image on the left shows how materials are likely to be found in the center of the pores.

Bond Information

PorousMaterials.jl also supports inferring and storing bond information present in metal-organic frameworks. This was initially inspired by a need to control the topology of a metal-organic framework when using molecular dynamics software. It has proven to be useful in a variety of other contexts as well. Bonds are stored using a graph within PorousMaterials.jl such that each node in the graph corresponds to an atom in the structure, and each edge between nodes in the graph represents a bond between two atoms. To infer bonds, the user first defines a set of bonding rules with minimum and maximum distances defined for pairs of elements. Then, PorousMaterials.jl can be used to iterate through every pair of atoms and determine if they are bonded under that set of rules. It will add an edge to graph if they are.

This bonding information is useful when stored as a graph because there is a well defined set of functions for traversing and analyzing them. One example of this is identifying connected components. This amounts to finding disjoint sets of bonded atoms in the crystal structure.

These connected components can be used to identify interpenetrated metal-organic frameworks. These are metal-organic frameworks that are made up of separate layers woven together. They are not always labeled on online repositories for crystal structure files, so this can be used to determine if downloaded crystals are interpenetrated. The user simply needs to infer bonds over the structure, find the connected components in the bond graph and then isolate atoms based on these components. The number of components tells how many distinct structures are present. Figure 6 shows the interpenetrated metal-organic framework NiPyC2 with the distinct structures colored red and blue.

Another use for the connected components is to find solvents present in crystal files. Crystallographic information files may still contain solvents from the original metal-organic framework construction, and these interfere with results of the simulations. They occupy the adsorption sites in the pores of the material, so they need to be removed before use. Using the bonding information about the material, these solvents can be isolated from the structure and removed to automate the "cleaning" process. The connected components are powerful here because each component represents a separate bonded set of atoms, so the metal-organic framework will appear separate from each of the solvents. The largest component should be the structure, and the remaining components are simply solvents. Figure 7 shows the full contents of the CaSDB crystal structure file with the solvents colored in red and CaSDB in blue. This visualization shows that the solvents can successfully be separated based on the bonding information.

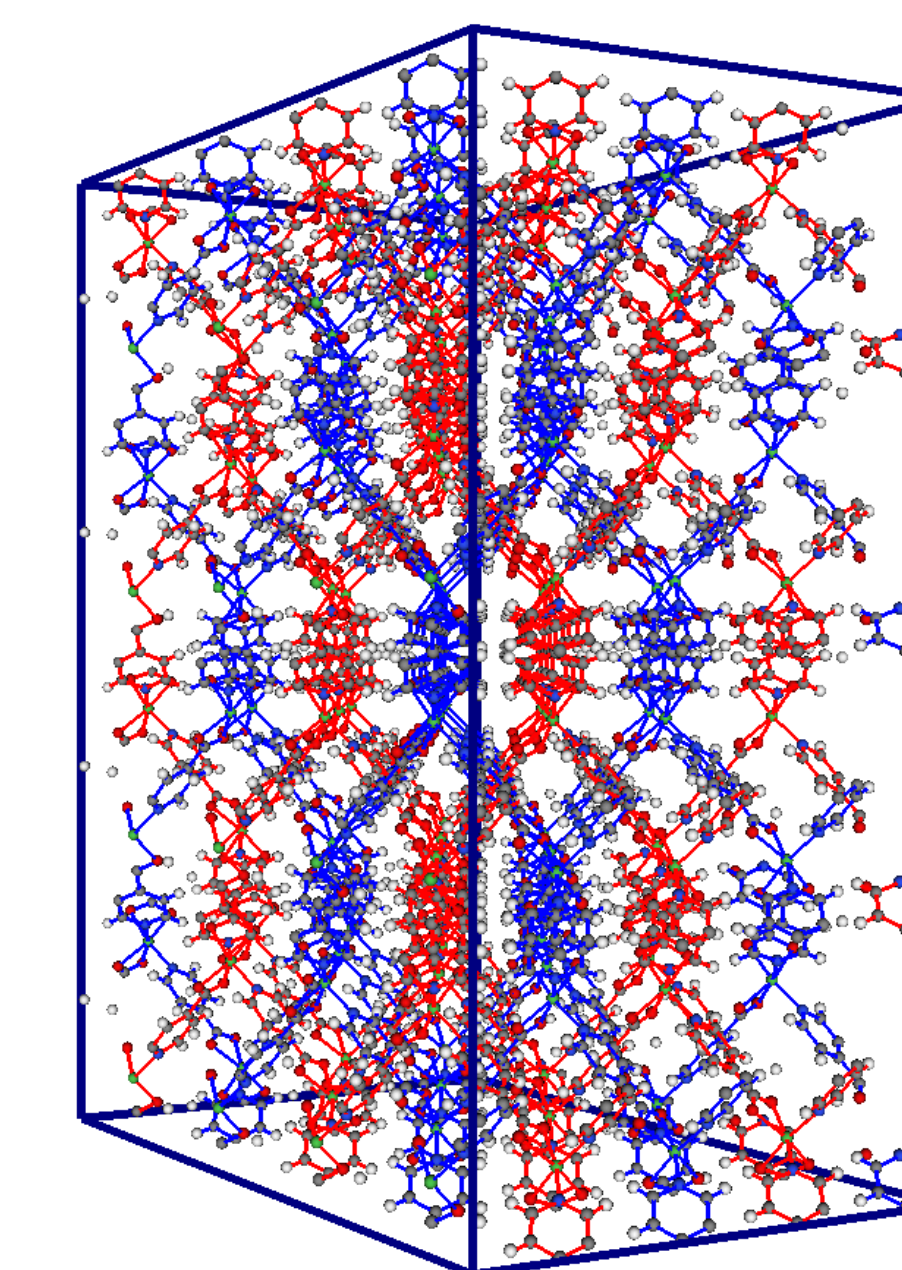


Figure 6: NiPyC2 colored to indicate the distinct structures present. The unit cell was replicated to $2 \times 2 \times 2$ for the layers to reveal themselves

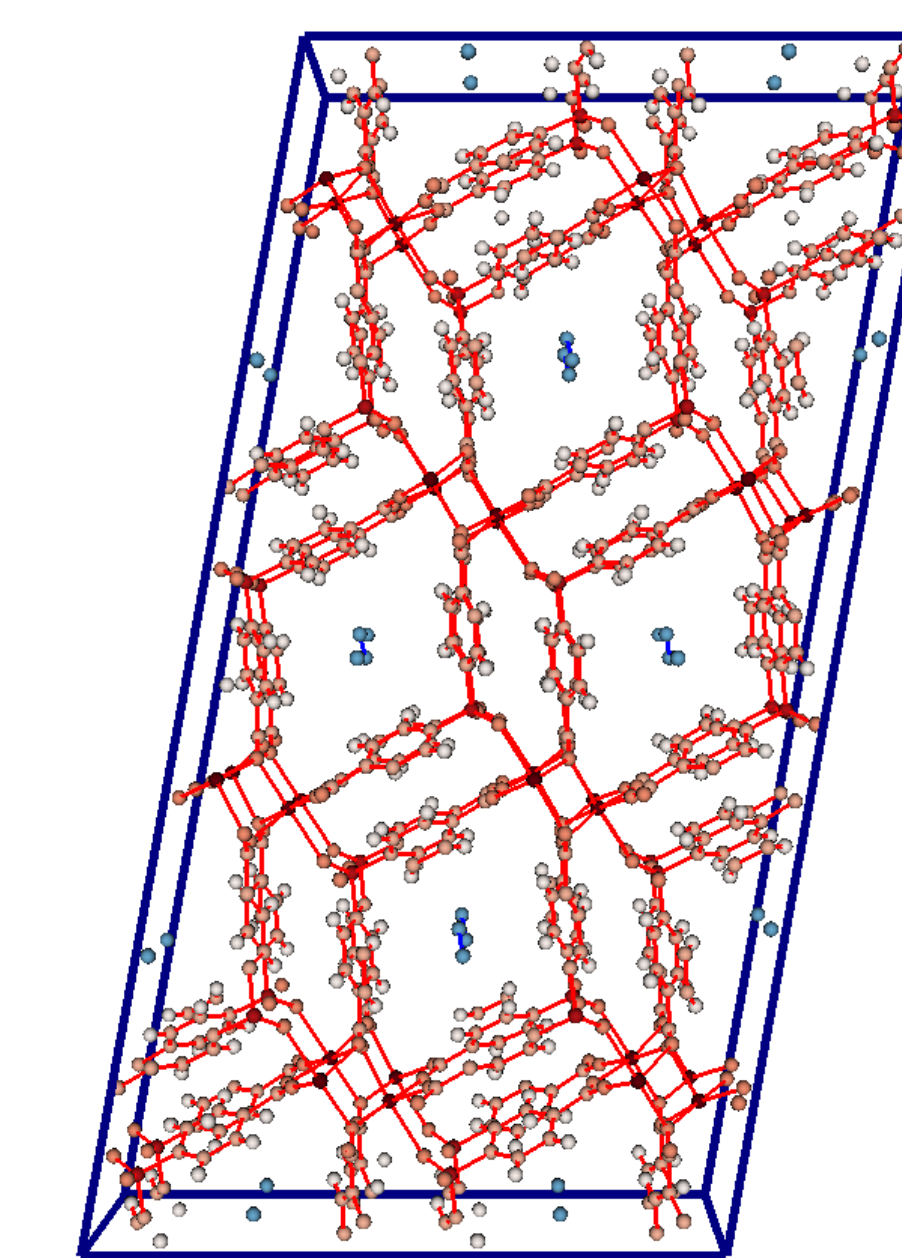


Figure 7: The crystal structure file for CaSDB has solvents present (shown in blue) that need to be removed before the file can be used for simulation. The largest connected component of the bond graph signifies the structure (red) and can be separated from the solvents to clean it.

Conclusion

PorousMaterials.jl is a powerful software package that provides tools for examining metal-organic frameworks through computation. The original functionality of generating adsorption isotherm data has been extended to give a varied analysis and offer insights into many aspects of these structures. PorousMaterials.jl can now locate likely adsorption sites in the materials it simulates through the snapshot functionality in the μVT simulation. It is also possible to analyze and modify the topology of these frameworks because of the graphical representation of bonds within the code. PorousMaterials.jl can provide great insight into metal-organic frameworks that current experimentation cannot (such as finding adsorption sites) or is impractical (like high throughput computation). This makes it very useful for guiding current research and gaining a better understanding of how gasses interact with these promising materials.

References

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