

NE451

Simulation Methods

GCMC simulation of CO₂ adsorption in IRMOF-1 using RASPA3

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Theoretical Background

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GCMC: Grand Canonical Monte Carlo Simulation

- ▶ Statistical mechanics method for simulating adsorption in porous materials.
- ▶ Operates under the μ VT ensemble (chemical potential, volume, temperature).
- ▶ Enables insertion and deletion of molecules to simulate equilibrium adsorption/desorption.
- ▶ Particularly suited for studying gas adsorption in porous materials like MOFs.

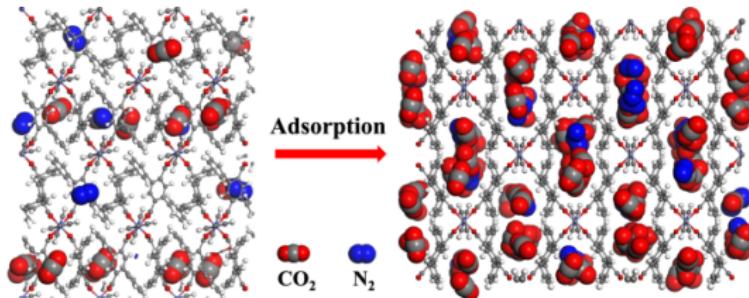


Figure: Gas adsorption in porous material



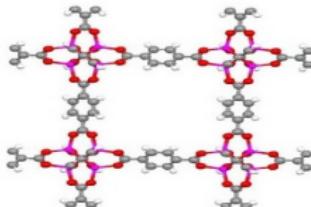
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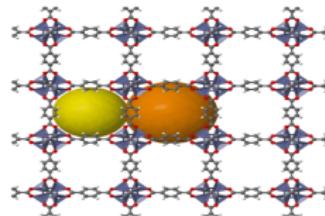
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IRMOF-1 or MOF-5 : A Prototype Metal–Organic Framework

- ▶ IRMOF = Isoreticular Metal–Organic Framework.
- ▶ Composed of Zn_4O clusters connected by benzene dicarboxylate (BDC) linkers.
- ▶ Features high porosity, thermal stability, and large surface area.
- ▶ Widely studied model system for gas storage and separation.
- ▶ Used in this tutorial for simulating CO_2 adsorption.



(a) One Unit Cell of IRMOF-1



(b) Multi Unit Cells of IRMOF-1



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RASPA3: Molecular Simulation Software for Porous Materials

- ▶ Open-source simulation package tailored for adsorption, diffusion, and thermodynamics.
- ▶ Supports GCMC, Molecular Dynamics (MD), and hybrid MC/MD methods.
- ▶ JSON-based input files for flexible system and simulation definitions.
- ▶ Supports complex frameworks (e.g., MOFs, zeolites) and various force fields.
- ▶ Ideal for simulating gas uptake, mixture separations, and diffusion mechanisms.



Required Input Files for RASPA3

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RASPA3 expects JSON-formatted input files and .cif file as structure file.

- ▶ *simulation.json* – main control file
- ▶ *force_field.json* – contains atomic and interaction parameters and defines pseudo atoms
- ▶ CIF file – defines framework structure
- ▶ *component.json* – define gas molecules



How to write JSON file

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JSON (JavaScript Object Notation) is a lightweight data format used to store structured information — widely used in RASPA3 for defining frameworks, components, and simulations.

Basic Rules for Writing JSON

- ▶ **Key-Value Pairs:** Data is stored as "key": value
- ▶ **Data Types:**
 - ▶ Strings in double quotes → "name": "CO2"
 - ▶ Numbers without quotes → "mass": 44.01
 - ▶ Boolean values → true or false
 - ▶ Arrays → [1, 2, 3] or ["O", "C"]
 - ▶ Objects → nested dictionaries { "key": value }

```
{  
  "name": "CO2",  
  "mass": 44.01,  
  "rigid": true,  
  "atoms": [  
    ["O", [0.0, 0.0, 1.149]],  
    ["C", [0.0, 0.0, 0.0]],  
    ["O", [0.0, 0.0, -1.149]]  
  ]  
}
```



simulation.json

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simulation.json usually contains 3 sections:

- ▶ General options
 - ▶ simulation types, steps, and prints
- ▶ System options
 - ▶ system info, temperature, pressure, charge, outputs
- ▶ Component options
 - ▶ molecules info (e.g., CO₂, N₂, H₂, etc.)



simulation.json

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Example of *simulation.json* file

```
{  
    "SimulationType" : "MolecularDynamics",  
    "NumberOfCycles" : 100000,  
    "NumberOfInitializationCycles" : 1000,  
    "NumberOfEquilibrationCycles" : 10000,  
    "PrintEvery" : 1000,  
}  
} — General options.  
  
{  
    "Systems" : [  
        {  
            "Type" : "Framework",  
            "Name" : "Cu-BTC",  
            "NumberOfUnitCells" : [1, 1, 1],  
            "ChargeMethod" : "Ewald",  
            "ExternalTemperature" : 323.0,  
            "ExternalPressure" : 1.0e4,  
            "OutputPDBMovie" : false,  
            "SampleMovieEvery" : 10  
        }  
    ],  
}  
} — System options.  
  
{  
    "Components" : [  
        {  
            "Name" : "CO2",  
            "FugacityCoefficient" : 1.0,  
            "TranslationProbability" : 0.5,  
            "RotationProbability" : 0.5,  
            "ReinsertionProbability" : 0.5,  
            "SwapProbability" : 0.0,  
            "WidomProbability" : 0.0,  
            "CreateNumberOfMolecules" : 20  
        }  
    ]  
}  
} — Component options.
```



force_field.json

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```
{  
    "PseudoAtoms" :  
    [  
        {  
            "name" : "Zn1",  
            "framework" : true,  
            "print_to_output" : true,  
            "element" : "Zn",  
            "print_as" : "Zn",  
            "mass" : 65.37,  
            "charge" : 1.275  
        }  
    ],  
    "SelfInteractions" :  
    [  
        {  
            "name" : "Zn1",  
            "type" : "lennard-jones",  
            "parameters" : [0.42, 2.7],  
            "source" : "literature or database (optional)"  
        }  
    ],  
    "MixingRule" : "Lorentz-Berthelot",  
    "TruncationMethod" : "shifted",  
    "TailCorrections" : false  
}
```

PseudoAtoms Block

SelfInteractions Block

GlobalSettings Block



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```
{  
    "PseudoAtoms" :  
    [  
        {  
            "name" : "Zn1",  
            "framework" : true,  
            "print_to_output" : true,  
            "element" : "Zn",  
            "print_as" : "Zn",  
            "mass" : 65.37,  
            "charge" : 1.275  
        },  
        "SelfInteractions" :  
        [  
            {  
                "name" : "Zn1",  
                "type" : "lennard-jones",  
                "parameters" : [0.42, 2.7],  
                "source" : "literature or database (optional)"  
            },  
            {"MixingRule" : "Lorentz-Berthelot",  
             "TruncationMethod" : "shifted",  
             "TailCorrections" : false  
        ]  
    ]  
}
```

PseudoAtoms Block

"name": Atom type identifier used in the structure.

"framework": Set true if atom belongs to MOF.

"print_to_output": If true, includes atom info in output files.

"element": Chemical element (for output/visualization).

"print_as": label for atom in trajectory/output files.

"mass" and **"charge"**: Atomic mass (amu) and partial charge (e).



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```
{  
    "PseudoAtoms" :  
    [  
        {  
            "name" : "Zn1",  
            "framework" : true,  
            "print_to_output" : true,  
            "element" : "Zn",  
            "print_as" : "Zn",  
            "mass" : 65.37,  
            "charge" : 1.275  
        }  
    ],  
    "SelfInteractions" :  
    [  
        {  
            "name" : "Zn1",  
            "type" : "lennard-jones",  
            "parameters" : [0.42, 2.7],  
            "source" : "literature or database (optional)"  
        }  
    ],  
    "MixingRule" : "Lorentz-Berthelot",  
    "TruncationMethod" : "shifted",  
    "TailCorrections" : false  
}
```

SelfInteractions Block

“name”: Atom name from CIF file

“type”: “type” must be “lennard-jones” in RASPA3.

“parameters”:

- Format: ϵ (K), σ (\AA)
- ϵ (epsilon): Depth of the LJ potential well (interaction strength).
- σ (sigma): Distance where the potential = 0 (size of atom).
- ϵ (K), σ (\AA) values are usually obtained from ForceFields (i.e., UFF, DRIEDING, TraPPE, etc.) literatures.

“source” (optional): literature or database ref.



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```
{  
    "PseudoAtoms" :  
    [  
        {  
            "name" : "Zn1",  
            "framework" : true,  
            "print_to_output" : true,  
            "element" : "Zn",  
            "print_as" : "Zn",  
            "mass" : 65.37,  
            "charge" : 1.275  
        }  
    ],  
    "SelfInteractions" :  
    [  
        {  
            "name" : "Zn1",  
            "type" : "lennard-jones",  
            "parameters" : [0.42, 2.7],  
            "source" : "literature or database (optional)"  
        }  
    ],  
    "MixingRule" : "Lorentz-Berthelot",  
    "TruncationMethod" : "shifted",  
    "TailCorrections" : false  
}
```

GlobalSettings Block

- **"MixingRule"**: How cross interactions (e.g., Zn–O, Zn–CO₂) are calculated.
 - **Lorentz-Berthelot** (default):
 - $\sigma_{ij} = (\sigma_i + \sigma_j) / 2$
 - $\varepsilon_{ij} = \sqrt{(\varepsilon_i * \varepsilon_j)}$
- **"TruncationMethod"**: "shifted" smoothly decays potential at cutoff.
- **"TailCorrections"**: If false, long-range LJ corrections are ignored.



Framework CIF File

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The .cif (Crystallographic Information File) defines the atomic coordinates, unit cell, and symmetry of the MOF framework used in simulations.

- ▶ **Cambridge Structural Database (CSD)**
 - ▶ Website: <https://www.ccdc.cam.ac.uk/>
- ▶ **CoRE MOF Database (Computation-Ready Experimental MOFs)**
 - ▶ Website: <https://doi.org/10.5281/zenodo.3228673>
 - ▶ Website: <https://doi.org/10.5281/zenodo.7691378>
- ▶ **Materials Cloud / MOF Database (MOFDB)**
 - ▶ Website: <https://www.materialscloud.org/discover/menu>
- ▶ **Crystallography Open Database**
 - ▶ Website: <http://www.crystallography.net/>
- ▶ **Published Literature**

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How to create *component.json* file

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Example: *CO2.json*

```
{  
    "CriticalTemperature": 304.1282,  
    "CriticalPressure": 7377300.0,  
    "AcentricFactor": 0.22394,  
    "Type": "rigid",  
    "pseudoAtoms": [  
        ["O_co2", [0.0, 0.0, 1.149]],  
        ["C_co2", [0.0, 0.0, 0.0]],  
        ["O_co2", [0.0, 0.0, -1.149]]  
    ]  
}
```

- ▶ "CriticalTemperature": T_c in Kelvin (e.g., 304.1282 K for CO₂)
- ▶ "CriticalPressure": P_c in Pascals (e.g., 7377300.0 Pa)
- ▶ "AcentricFactor": Non-sphericity factor (e.g., 0.22394)
- ▶ "Type": Molecule behavior: "rigid" (fixed geometry)
- ▶ "pseudoAtoms": Atom positions (in Å) in molecule's local frame Format: `["AtomType", [x, y, z]]`

Where to Get These Values

- ▶ Literature: Force field papers (e.g., TraPPE, DREIDING, EMP2).



How to perform GCMC simulation using RASPA3

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In this tutorial, we will conduct a GCMC simulation for CO₂ adsorption in IRMOF-1 using the RASPA3 program.

Steps for GCMC:

- ▶ **Helium Void Fraction:**
 - ▶ Estimates accessible pore volume for adsorbate molecules.
 - ▶ Simulates helium (non-interacting, small) to find void volume inside MOF.
 - ▶ Normalizing adsorption uptake (e.g., cm³/g STP).
- ▶ **Charge Equilibration:**
 - ▶ Assigns partial charges to framework atoms based on charge equilibration methods.
 - ▶ Improved realism in adsorbate–framework interactions.
- ▶ **GCMC Simulation:**
 - ▶ Simulates real gas adsorption isotherms at given pressure and temperature.
 - ▶ Random insertions/deletions/moves of gas molecules using GCMC algorithm.
 - ▶ Outputs: adsorption loading (mol/kg), isotherms, heat of adsorption, and density profiles.



How to run calculations on C1 cluster

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Assignment

- ▶ Open terminal and login to C1 cluster:

```
$ ssh username@c1.sci.uwaterloo.ca
```

- ▶ Switch HEAD node to compute node.

```
$ srun --pty bash
```

- ▶ Create, browse, print new directory.

```
$ mkdir dir_name  
$ cd dir_name  
$ pwd (result: /scic/home/username/dir_name)
```

- ▶ To check available module.

```
$ module avail
```

- ▶ To load a module

```
$ module load raspa3/3.0.5
```



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- ▶ To submit a job using bash script, prepare a bash script such as job.sh.

job.sh

```
#!/bin/bash
#SBATCH --time=1-00:30      # Max time (DD-HH:MM)
#SBATCH --cpus-per-task=6   # Number of CPUs
#SBATCH --mem=6G            # Memory per node

module load raspa3/3.0.5

raspa3 simulation.json
```

- ▶ Submit the bash script

```
$ sbatch job.sh
```



File Transfer using SCP

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Assignment

SCP File transfer: from local computer to c1 cluster

- ▶ Open terminal and browse to current working directory
- ▶ To transfer a single file from local to c1

```
$ scp filename.extension  
username@c1.sci.uwaterloo.ca:  
/scic/home/username/dir_name
```

- ▶ To transfer all files from local to c1

```
$ scp * username@c1.sci.uwaterloo.ca:  
/scic/home/username/dir_name
```

- ▶ To transfer entire directory from local to c1

```
$ scp -r local_dir_name  
username@c1.sci.uwaterloo.ca:  
/scic/home/username/dir_name
```



File Transfer using SCP

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Assignment

SCP File transfer: from c1 cluster to local computer

- ▶ Open terminal and browse to local current working directory
- ▶ To transfer a single file from c1 cluster directory to local working directory

```
$ scp username@c1.sci.uwaterloo.ca:  
/scic/home/username/dir_name  
/filename.extension .
```

- ▶ To transfer a single file from c1 cluster directory to local working directory

```
$ scp "username@c1.sci.uwaterloo.ca:  
/scic/home/username/dir_name/*" .
```

- ▶ To transfer entire directory from c1 to local

```
$ scp -r username@c1.sci.uwaterloo.ca:  
/scic/home/username/dir_name .
```



Calculate Helium Void Fraction

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Assignment

- ▶ Helium void fraction calculations require the following files:
 - ▶ *force_field.json*
 - ▶ *helium.json*
 - ▶ *IRMOF-1.cif*
 - ▶ *simulation.json*
 - ▶ *job.sh*
- ▶ Download GCMC tutorial contents from GitHub to your local directory.

```
$ wget https://github.com/Feugmo-Group/NE451/archive/refs/heads/main.zip  
$ unzip main.zip  
$ cd NE451-main  
$ ls  
$ cd gcmc_tutorial
```



Calculate Helium Void Fraction

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Assignment

- ▶ Open the "gcmc_tutorial/1_HeliumVoidFraction" folder containing the above listed files to run the helium void fraction calculation.
- ▶ All calculations will be running on the c1 cluster. Open a terminal, log in to the c1 cluster, and switch to compute node.
- ▶ Create a directory named "gcmc_tutorial" and browse to it. Under the "gcmc_tutorial" directory, create a new directory named "1_HeliumVoidFraction" and browse to it.
- ▶ Transfer all the above listed files from your local machine to the "1_HeliumVoidFraction" directory on the c1 cluster.
- ▶ Finally, submit the job by typing "sbatch job.sh"



Calculate Helium Void Fraction

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Assignment

- Once the calculations are complete, download or transfer all the files to your local directory.
- Open the “output/output_300_0.s0.txt” file in any text editor and locate the “Average Rosenbluth weight”.

```
Monte-Carlo moves statistics
=====
Component 0 [helium]
    Widom           all:        20000
    Widom          total:      20000
    Widom   constructed: 20000
    Widom      accepted:     0
    Widom      fraction:    0.000000
    Widom   max-change:   0.000000

    Widom insertion Rosenbluth weight statistics:
=====
    Block[ 0] 8.165113e-01
    Block[ 1] 8.151528e-01
    Block[ 2] 8.142274e-01
    Block[ 3] 8.174460e-01
    Block[ 4] 8.127074e-01

    Average Rosenbluth weight:  8.152090e-01 +/- 2.316333e-03 [-]
```

- The “Average Rosenbluth weight” is the Helium Void Fraction, which is represented as “8.152090e-01” or “0.815”. This value will be used in subsequent calculations.



Perform Charge Equilibration

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Assignment

- ▶ Charge Equilibration calculations require the following files:
 - ▶ *force_field.json*
 - ▶ *IRMOF-1.cif*
 - ▶ *simulation.json*
 - ▶ *job.sh*
- ▶ To perform charge equilibration, you need to access the “simulation.json” file. The “HeliumVoidFraction,” “UseChargeFrom,” and “ChargeMethod” sections are essential for this process.
- ▶ Create a new directory named “2_ChargeEquilibration” within the “gcmc_tutorial” directory on the c1 cluster.
- ▶ Upload all the files listed above to the “2_ChargeEquilibration” directory on the c1 cluster.
- ▶ Finally, submit the job using the “sbatch job.sh” command.

```
{  
    "SimulationType" : "MonteCarlo",  
    "NumberOfCycles" : 0,  
    "NumberOfInitializationCycles" : 0,  
    "NumberOfEquilibrationCycles" : 0,  
    "PrintEvery" : 100,  
  
    "Systems" : [  
        {  
            "Type" : "Framework",  
            "Name" : "IRMOF-1",  
            "NumberOfUnitCells" : [1, 1, 1],  
            "HeliumVoidFraction" : 0.815,  
            "UseChargesFrom" : "ChargeEquilibration",  
            "ChargeMethod" : "Ewald",  
            "ExternalTemperature" : 300.0,  
            "ExternalPressure" : 0.0,  
            "CutOff" : 12.0  
        }  
    ]  
}
```



Assign Charges to the CIF file

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Assignment

- Once charge equilibration is complete, we need to assign charges to the structure CIF file (e.g., IRMOF-1.cif).
- Download all the contents of the “2_ChargeEquilibration” directory to your local directory.

Component definitions

Framework 0 [IRMOF-1]

```
Box:    25.83200  0.00000  0.00000
        0.00000  25.83200  0.00000
        0.00000  0.00000  25.83200
Lengths: 25.83200  25.83200  25.83200
Angles: 90.00000  90.00000  90.00000
Perpendicular widths: 25.83200  25.83200  25.83200
```

```
number Of Atoms:                                424 [-]
mass:                                         6158.59424 [amu]
  0: Zn1   position  0.29340  0.20660  0.20660, charge  1.21151
  1: O1    position  0.25000  0.25000  0.25000, charge -0.96731
  2: O2    position  0.28190  0.21810  0.13400, charge -0.48285
  3: C1    position  0.25000  0.25000  0.11130, charge  0.32116
  4: C2    position  0.25000  0.25000  0.05380, charge -0.06436
  5: C3    position  0.28290  0.21710  0.02690, charge -0.02336
  6: H1    position  0.30490  0.19510  0.04480, charge  0.05378
use charge from: charge-equilibration method
net charge:                                     0.00000 [e]
smallest charge:                               -0.96731 [e]
largest charge:                                 1.21151 [e]
number of bonds:  0
```

- Open the “2_Charge_Equilibration_2/output/output_300_0.s0.txt” file and locate the “Component definition” section.
- These calculated charges must be assigned to the IRMOF-1.cif file.



Assign Charges to the CIF file

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Assignment

(a) Before assigning charge

```
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Zn1    Zn2+    0.2934    0.2066    0.2066
O1      0        0.25      0.25      0.25
O2      0        0.2819    0.2181    0.134
C1      C        0.25      0.25      0.1113
C2      C        0.25      0.25      0.0538
C3      C        0.2829    0.2171    0.0269
H1      H        0.3049    0.1951    0.0448
```

(b) After assigning charge

```
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_charge
Zn1    Zn      0.2935    0.2065    0.2065    1.21151
O1      0        0.25      0.25      0.25    -0.96731
O2      0        0.2818    0.2182    0.1339    -0.48205
C1      C        0.25      0.25      0.1105    0.32116
C2      C        0.25      0.25      0.0538    -0.06436
C3      C        0.2831    0.2169    0.0263    -0.02336
H1      H        0.3049    0.1951    0.0448    0.05378
```

- Add the line “`_atom_site_charge`” to the “`loop_`” section in the IRMOF-1.cif file. Assign all the atoms’ charges to the last column. If the “`_atom_site_charge`” line is the last line under “`loop_`”, the charge column must be the last column.



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Assignment

- ▶ Once charges are assigned to the CIF file, we need to run a test to check if the system's total charge is neutral. The system must be charge neutral for GCMC simulation.
- ▶ GCMC simulation requires the following input files:
 - ▶ *force_field.json*
 - ▶ *CO2.json*
 - ▶ *IRMOF-1.cif* (charge assigned)
 - ▶ *simulation.json*
 - ▶ *job.sh*
- ▶ In this simulation, we will perform CO₂ gas adsorption in the IRMOF-1 framework. Therefore, the “CO2.json” file must be present in the current directory.

```
{  
    "CriticalTemperature": 304.1282,  
    "CriticalPressure": 7377300.0,  
    "AcentricFactor": 0.22394,  
    "Type": "rigid",  
    "pseudoAtoms": [  
        ["O_co2", [0.0, 0.0, 1.149]],  
        ["C_co2", [0.0, 0.0, 0.0]],  
        ["O_co2", [0.0, 0.0, -1.149]]  
    ]  
}
```



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Assignment

As we are running a test, we would like to create a very short simulation to check if the system's net charge is zero.

- ▶ In the “simulation.json” file, we’ll use very small cycles for this test.
- ▶ Make sure to use “UseChargeFrom”: “CIF_File” under the “system” block since we’re using a charge-assigned CIF file.
- ▶ We’re running a GCMC simulation at 300K external temperature and 1e6 Pa (10 atm) external pressure.
- ▶ Once input file preparations are complete, upload all the files to a new directory called “gcmc_test-1” within the “gcmc_tutorial” directory on the c1 cluster.
- ▶ Finally, submit the job.

```
{  
    "SimulationType" : "MonteCarlo",  
    "NumberOfCycles" : 500,  
    "NumberOfInitializationCycles" : 100,  
    "PrintEvery" : 10,  
  
    "Systems" : [  
        {  
            "Type" : "Framework",  
            "Name" : "IRMOF-1",  
            "NumberOfUnitCells" : [1, 1, 1],  
            "HeliumVoidFraction" : 0.81,  
            "UseChargesFrom" : "CIF_File",  
            "ChargeMethod" : "Ewald",  
            "CUTOFF" : 12.0,  
            "ExternalTemperature" : 300.0,  
            "ExternalPressure" : 1e6  
        },  
  
        "Components" : [  
            {  
                "Name" : "CO2",  
                "MolFraction" : 0.5,  
                "FugacityCoefficient" : 1.0,  
                "TranslationProbability" : 0.5,  
                "RotationProbability" : 0.5,  
                "ReinsertionProbability" : 0.5,  
                "SwapProbability" : 1.0,  
                "CreateNumberOfMolecules" : 0  
            }  
        ]  
    ]  
}
```



Re-assign charges

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- Once the "gcmc_test-1" is complete, open the "gcmc_test-1/output/output_300_1e+06.s0.txt" file and locate the "Component definition" section. Check if the net charge is zero.
- If you see "net charge: 0.00," you're good to go for the final GCMC run. However, if you see something like "net charge: -0.00024," you need to reassign the charges. This step can be a bit tricky.
- Your system's net charge is now "-0.00024." To make it neutral, you need to add a charge of "+0.00024" to your system. Then, you need to equally distribute this charge to all the framework atoms in your system.

Component definitions

Framework 0 [IRMOF-1]

```
Box:      25.66900  0.00000  0.00000
          0.00000  25.66900  0.00000
          0.00000  0.00000  25.66900
Lengths:  25.66900  25.66900  25.66900
Angles:   90.00000  90.00000  90.00000
Perpendicular widths:  25.66900  25.66900  25.66900
```

```
number Of Atoms:           424 [-]
mass:                      6158.59424 [amu]
0: Zn1    position  0.29350  0.20650  0.20650, charge  1.21151
1: O1     position  0.25000  0.25000  0.25000, charge -0.96731
2: O2     position  0.28180  0.21820  0.13390, charge -0.48205
3: C1     position  0.25000  0.25000  0.11050, charge  0.32116
4: C2     position  0.25000  0.25000  0.05380, charge -0.06436
5: C3     position  0.28310  0.21690  0.02630, charge -0.02336
6: H1     position  0.30490  0.19510  0.04480, charge  0.05378
```

use charge from: CIF-file

net charge: -0.00024 [e]

smallest charge: -0.96731 [e]

largest charge: 1.21151 [e]

number of bonds: 0



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- ▶ To determine the number of framework atoms in your system, first check the “NumberOfUnitCells” value in the “simulation.json” file. In this example, we used “NumberOfUnitCells”: [1, 1, 1], indicating that we need to count the framework atoms in the one-unit cell of IRMOF-1.
- ▶ Next, visualize the IRMOF-1.cif file using VESTA and identify the atoms within the unit cells. Save the structure as IRMOF-1.pdb.
- ▶ Then, visualize the IRMOF-1.pdb file with ChimeraX and remove all the atoms that are outside the unit cells.
- ▶ Finally, count the total number of atoms. In this case, the total number of atoms of IRMOF-1 inside one unit cell are 424.

```
{
  "SimulationType" : "MonteCarlo",
  "NumberOfCycles" : 500,
  "NumberOfInitializationCycles" : 100,
  "PrintEvery" : 10,

  "Systems" : [
    {
      "Type" : "Framework",
      "Name" : "IRMOF-1",
      "NumberOfUnitCells" : [1, 1, 1],
      "HeliumVoidFraction" : 0.81,
      "UseChargesFrom" : "CIF_File",
      "ChargeMethod" : "Ewald",
      "CutOff" : 12.0,
      "ExternalTemperature" : 300.0,
      "ExternalPressure" : 1e6
    },
    {
      "Components" : [
        {
          "Name" : "CO2",
          "MolFraction" : 0.5,
          "FugacityCoefficient" : 1.0,
          "TranslationProbability" : 0.5,
          "RotationProbability" : 0.5,
          "ReinsertionProbability" : 0.5,
          "SwapProbability" : 1.0,
          "CreateNumberOfMolecules" : 0
        }
      ]
    }
  ]
}
```



Re-assign charges

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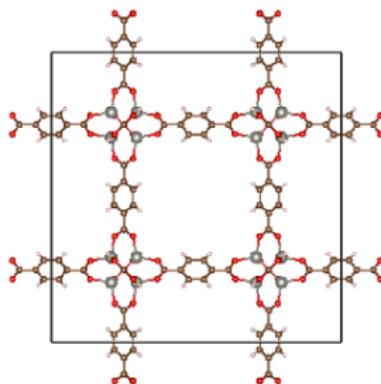
29

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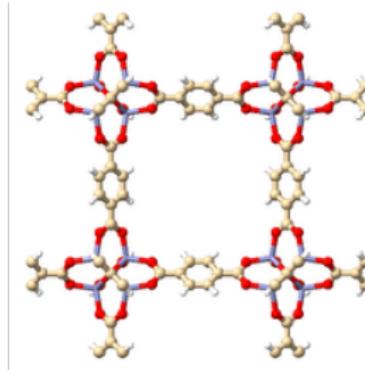
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- ▶ Finally, count the total number of atoms. In this case, the total number of atoms of IRMOF-1 inside one unit cell are 424.



(a) All inside and outside atoms (616 atoms) of one-unit cell of IRMOF-1



(b) Only inside atoms (424 atoms) of one-unit cell of IRMOF-1



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- ▶ From the first GCMC test run, we received the net charge of “-0.00024”.
- ▶ The structure of the CIF file contains 424 atoms in a single unit cell.
- ▶ To account for this charge, we need to add +0.00024 to our system. Therefore, we need to add $0.00024/424 = 0.00000056603774$ charge to every atom in the CIF file. For example, the charge of the Zn1 atom was 1.21151. After adding 0.00000056603774, its charge becomes 1.21151056603774.
- ▶ Now, we need to update the charges of all atoms in the IRMOF-1.cif file.
- ▶ It is important to keep charge values up to 14 decimal point. Otherwise, system charge may not be neutral. You can use as many decimal point as you want to make system net charge zero.



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loop_					
_atom_site_label					
_atom_site_type_symbol					
_atom_site_fract_x					
_atom_site_fract_y					
_atom_site_fract_z					
_atom_site_charge					
Zn1	Zn	0.2935	0.2065	0.2065	1.21151
O1	O	0.25	0.25	0.25	-0.96731
O2	O	0.2818	0.2182	0.1339	-0.48205
C1	C	0.25	0.25	0.1105	0.32116
C2	C	0.25	0.25	0.0538	-0.06436
C3	C	0.2831	0.2169	0.0263	-0.02336
H1	H	0.3049	0.1951	0.0448	0.05378

Figure: Before re-assign charges

loop_					
_atom_site_label					
_atom_site_type_symbol					
_atom_site_fract_x					
_atom_site_fract_y					
_atom_site_fract_z					
_atom_site_charge					
Zn1	Zn	0.2935	0.2065	0.2065	1.21151056603774
O1	O	0.25	0.25	0.25	-0.96730943396226
O2	O	0.2818	0.2182	0.1339	-0.48204943396226
C1	C	0.25	0.25	0.1105	0.32116056603774
C2	C	0.25	0.25	0.0538	-0.06435943396226
C3	C	0.2831	0.2169	0.0263	-0.02335943396226
H1	H	0.3049	0.1951	0.0448	0.05378056603774

Figure: After re-assign charges



Second GCMC test run

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Assignment

- ▶ Once charges are reassigned, we need to run a second GCMC test run to verify that the system net charge is zero.
- ▶ GCMC simulation required the following files:
 - ▶ *force_field.json*
 - ▶ *CO2.json*
 - ▶ *IRMOF-1.cif* (charge re-assigned)
 - ▶ *simulation.json*
 - ▶ *job.sh*
- ▶ Once input file preparations are complete, upload all files to a new directory named “*gcmc_test-2*” within the “*gcmc_tutorial*” directory on the *c1* cluster.
- ▶ Next, submit the job.
- ▶ Once the job is finished, open the output file located at “*/gcmc_test-2/output/output_300_1e+06.s0.txt*” and verify that the system net charge is zero.
- ▶ If the system net charge is zero, proceed to the final GCMC simulation.



Final GCMC Simulation

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- ▶ GCMC simulation required the following files:
 - ▶ *force_field.json*
 - ▶ *CO2.json*
 - ▶ *IRMOF-1.cif* (charge re-assigned)
 - ▶ *simulation.json*
 - ▶ *job.sh*
- ▶ In the final GCMC simulation, we will increase the number of cycles to at least 50,000 in the *simulation.json* file.
- ▶ Once the input files are prepared, upload all the above-listed files to a new directory called “3_GCMC_Final” within the “gcmc-tutorial” directory on the c1 cluster.
- ▶ Finally, submit the job.

```
{
  "SimulationType" : "MonteCarlo",
  "NumberOfCycles" : 50000,
  "NumberOfInitializationCycles" : 25000,
  "PrintEvery" : 5000,

  "Systems" : [
    {
      "Type" : "Framework",
      "Name" : "IRMOF-1",
      "NumberOfUnitCells" : [1, 1, 1],
      "HeliumVoidFraction" : 0.81,
      "UseChargesFrom" : "CIF_File",
      "ChargeMethod" : "Ewald",
      "CutOff" : 12.0,
      "ExternalTemperature" : 300.0,
      "ExternalPressure" : 1e6
    },
    "Components" : [
      {
        "Name" : "CO2",
        "MolFraction" : 0.5,
        "FugacityCoefficient" : 1.0,
        "TranslationProbability" : 0.5,
        "RotationProbability" : 0.5,
        "ReinsertionProbability" : 0.5,
        "SwapProbability" : 1.0,
        "CreateNumberOfMolecules" : 0
      }
    ]
}
```



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- ▶ Once GCMC simulation is complete. Open the output file and locate "Abs. loading average" and "Excess loading average" under "Component 0 (CO₂)" section.
- ▶ Absolute (Abs.) loading: The total number of gas molecules present in the porous material at equilibrium — regardless of whether they are in pores or in free space inside the simulation box.
- ▶ Excess loading: The number of adsorbed molecules beyond what would be in the free gas phase (i.e., over and above what would be there just due to bulk gas at the same pressure/temperature if the pores were empty). This matches experimental gravimetric adsorption measurements, especially from volumetric or gravimetric isotherm setups.
- ▶ Therefore, we basically looking for Excess loading average for CO₂ adsorption



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► Example of GCMC output:

Component 0 (CO₂)

```
Block[ 0] 8.577000e+01
Block[ 1] 9.311000e+01
Block[ 2] 9.137000e+01
Block[ 3] 9.558000e+01
Block[ 4] 8.892000e+01
```

```
Abs. loading average 9.095000e+01 +/- 4.695963e+00 [molecules/cell]
Abs. loading average 9.095000e+01 +/- 4.695963e+00 [molecules/uc]
Abs. loading average 1.476798e+01 +/- 7.625057e-01 [mol/kg-framework]
Abs. loading average 6.497734e+02 +/- 3.354934e+01 [mg/g-framework]
```

```
Block[ 0] 8.226949e+01
Block[ 1] 8.960949e+01
Block[ 2] 8.786949e+01
Block[ 3] 9.207949e+01
Block[ 4] 8.541949e+01
```

```
Excess loading average 8.744949e+01 +/- 4.695963e+00 [molecules/cell]
Excess loading average 8.744949e+01 +/- 4.695963e+00 [molecules/uc]
Excess loading average 1.419959e+01 +/- 7.625057e-01 [mol/kg-framework]
Excess loading average 6.247648e+02 +/- 3.354934e+01 [mg/g-framework]
```



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- ▶ To perform an adsorption isotherm, you need to run a series of GCMC simulations at different temperatures and different pressures.
- ▶ Then, generate the adsorption isotherm graph.

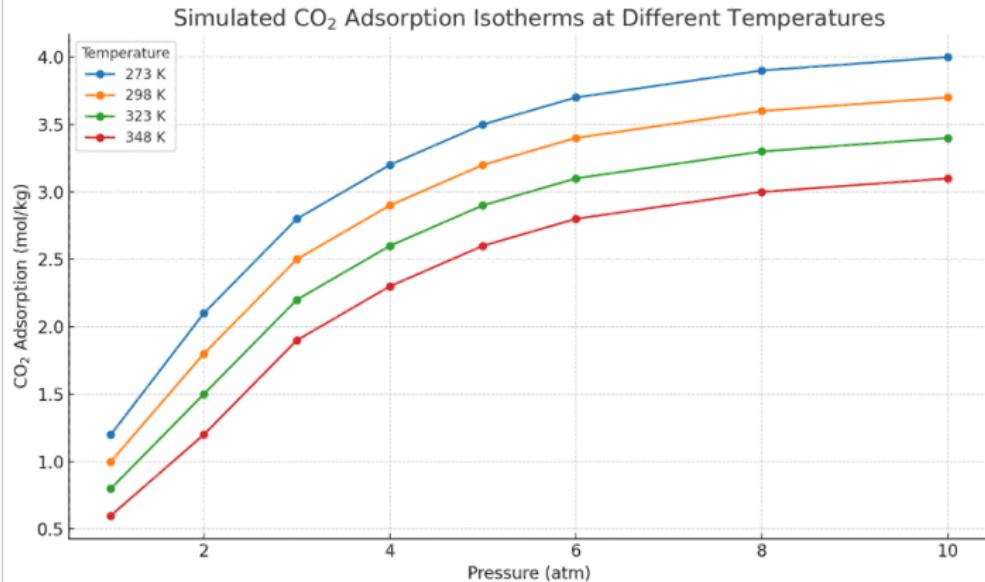


Figure: Example Gas adsorption isotherm.



Assignment

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Calculate the CO₂ adsorption isotherm in IRMOF-1 using GCMC simulation in RASPA3.

Instructions:

- ▶ Use all input files from the “3_GCMC_Final” steps.
- ▶ Run a series of GCMC simulations at different temperatures and pressures.
- ▶ Use the following temperatures: 273K, 300K, and 325K.
- ▶ Use the following pressures: 2.0e5, 4.0e5, 6.0e5, and 8.0e5 Pa, which are equivalent to 2, 4, 6, and 8 atm, respectively.
- ▶ Run GCMC at one temperature and one pressure at a time, so you need to run 12 GCMC simulations.
- ▶ Once all simulations are done, collect the “Excess loading average” data ([molecules/uc]) from all simulations.
- ▶ Generate a CO₂ adsorption isotherm graph “CO₂ Adsorption [molecules/uc] vs Pressure (atm)” at the specified temperatures.