RASPA Workshop/School Exercises Day 1

2 September 2024

Note: Always examine all the input- and output files in detail. Options are explained in the provided manual.

Exercise 1: Monte Carlo of methane in a box

To get started and learn the basics, we are going to do a Monte Carlo run of 30 methane molecules in a $30 \times 30 \times 30$ Å box. After 1000 cycles of initialization the production run is started. A movie is written and every 10th configuration is appended to the movie. The movie is stored in `movies`.

The input file for this simulation is:

```
{
  "SimulationType" : "MonteCarlo",
  "NumberOfCycles" : 1000,
  "NumberOfInitializationCycles" : 1000,
  "PrintEvery" : 100,

  "Systems" :
  [
    {
      "Type" : "Box",
      "BoxLengths" : [30.0, 30.0, 30.0],
      "ExternalTemperature" : 300.0,
      "ChargeMethod" : "None",
      "OutputPDBMovie" : true,
      "SampleMovieEvery" : 10
    }
  ],

  "Components" :
  [
    {
      "Name" : "methane",
      "TranslationProbability" : 1.0,
      "CreateNumberOfMolecules" : 30
    }
  ]
}
```

In RASPA, the cycle is define as max(20,N) steps, where N is the number of molecules in the system. In every cycle, each of the molecules has on average been used for a Monte Carlo move (accepted or rejected). There is a minimum of 20 steps to avoid that systems with a

small amount of molecules are not sampled well. The definition of a cycle is less dependent on the system size. The number of Monte Carlo steps is roughly the number of cycles times the average number of molecules.

Run this very short simulation to view the change of the particles in the system. Use `iRASPA` or `vmd` to view the movie `movie.s0.pdb` found in directory `movies`.

Questions:

1. Examine the methane molecule file `methane.json`. How is the methane molecule modeled?
2. Examine the force field file `force_field.json`. What are the defined interactions in the system?
3. The default cutoff is 12 Å. The system box is set to $30 \times 30 \times 30$ Å. What is the smallest choice possible for the box size?
4. What are the benefits and downsides of using smaller/larger box sizes?
5. How should you determine the appropriate box size?
6. Why is the box cubic?

Question:

7. The simulation writes output to a file. Examine the output file found in `output/output_300_0.s0.data`. How do you know the Monte Carlo move energies were properly book-kept? (Hint: look for the `drift`)

Question:

8. Change methane to CO_2, what should be changed in the `simulation.json`? (the CO_2 definition file is already present in the working directory)
9. How is the CO_2 molecule modeled?
10. Complete the `force_field.json` file with the following properties for the carbon of CO_2: mass 12.0 a.u., charge +0.6512 e, $\epsilon/k_B = 29.933$ K, $\sigma = 2.745$ Å, and for the oxygen of CO_2: mass 15.9994 a.u, charge -0.3256 e, $\epsilon/k_B = 85.671$ K and $\sigma = 3.017$ Å.
11. How is the cross-interaction (the interaction LJ parameters for `C` and `O`) computed?

Exercise 2: Investigation of the structure of frameworks

Next, we are going to change from a fluid to a simulation with a framework present, for example a zeolite. We are going to use two example zeolites:

- ITQ-29 (all-silica LTA, Linde Type A): a cubic zeolite with edge-length 11.8671 Å.
- MFI (Mobile Five): an orthorhombic structure with edge-lengths $a = 20.022$ Å, $b = 19.899$ Å, and $c = 13.383$ AA.

To get an idea of what these structures look like, and how different they are, we are going to visualize them using iRASPA.

1. What are the structural features of ITQ-29?
2. Can you spot a potential problem for Monte Carlo simulations? Propose a fix to the problem.

3. What is the topology (i.e. connectivity of the pores) and general shape and size of the channels of MFI?

Exercise 3: CO_2 in ITQ-29

Next, we are going to look at the behavior of a single CO_2 molecule in a ITQ-29 zeolite.

The input file for this simulation is:

```
"SimulationType" : "MonteCarlo",
"NumberOfCycles" : 1000,
"NumberOfInitializationCycles" : 1000,
"PrintEvery" : 100,

"Systems" : [

    "Type" : "Framework",
    "Name" : "ITQ-29",
    "NumberOfUnitCells" : [2, 2, 2],
    "ChargeMethod" : "Ewald",
    "CutOff": 11.8,
    "ExternalTemperature" : 300.0,

    "OutputPDBMovie" : true,
    "SampleMovieEvery" : 1

],

"Components" : [

    "Name" : "CO2",
    "TranslationProbability" : 0.5,
    "RotationProbability" : 0.5,
    "blockingPockets" : [
        [0.0,       0.0,        0.0,       4.0],
        [0.5,       0.0,        0.0,       0.5],
        [0.0,       0.5,        0.0,       0.5],
        [0.0,       0.0,        0.5,       0.5]
      ],
    "CreateNumberOfMolecules" : 1

]
```

Go to `exercise_3_co2_in_itq-29` and run the program.

1. View the movie-files in `iRASPA`. What do you expect to see and what do you actually see?

2. What could be the problem and how are you going to fix this? Using this fix, run the code again, and review the movie. What has changed?

Exercise 4: Energy Distributions of CO_2 in ITQ-29 and MFI

Next, we are going to investigate the energy histograms of adsorbates as they move around inside the framework. Let's start with CO_2 in MFI.

The input file for this simulation is:

```
"SimulationType" : "MonteCarlo",
"NumberOfCycles" : 100000,
"NumberOfInitializationCycles" : 1000,
"PrintEvery" : 5000,

"Systems" : [

    "Type" : "Framework",
    "Name" : "MFI_SI",
    "NumberOfUnitCells" : [2, 2, 2],
    "ChargeMethod" : "Ewald",
    "CutOff": 12.0,
    "ExternalTemperature" : 300.0,

    "OutputPDBMovie" : false,
    "SampleMovieEvery" : 1,

     "ComputeEnergyHistogram": true,
     "NumberOfBinsEnergyHistogram" : 400,
     "MininumRangeEnergyHistogram" : -5000.0,
     "MaximumRangeEnergyHistogram" : 1000.0,
     "SampleEnergyHistogramEvery" : 1,
     "WriteEnergyHistogramEvery" : 5000

],

"Components" : [

    "Name" : "CO2",
    "TranslationProbability" : 0.5,
    "RotationProbability" : 0.5,
    "ReinsertionProbability" : 1.0,
    "CreateNumberOfMolecules" : 1

]
```

1. Why are $2 \times 2 \times 2$ unit cells needed for MFI?

Run the program and leave it running. Go to the directory `exercise_4_co2_energy_histogram_zeolites/300K/mfi` and use `gnuplot` to plot the energy histograms (you can use the `plot` file using the command: `gnuplot plot_mfi`). Do the same for 600K and compare the histograms. Next, compute the histograms of CO_2 in ITQ-29, both at 300K and 600K.

2. Why is the energy negative?
3. Is a positive energy possible?
4. What happens with the higher temperature curve? why?
5. What would you expect in the limit of zero temperature? What is this type of simulation called? Can you think of problems you might encounter trying to obtain a zero temperature result?

Run the program and leave it running. Go to the directory `exercise_4_co2_energy_histogram_zeolites/300K/itq-29` and use `gnuplot` to plot the energy histograms (you can use the `plot` file using the command: `gnuplot plot_itq-29`). Do the same for 600K and compare the histograms.

6. What is the most striking difference between the 300K and 600K graphs?
7. Do you have an hypothesis why this happens? How can you prove this hypothesis?
8. How does the histogram at 300K look like without blocking?

The enthalpy of adsorption ΔH at infinite dilution is given by

$$\Delta H = \Delta U_{hg}^{\text{total}} - \Delta U_{h}^{\text{total}} - \Delta U_{g}^{\text{total}} - RT \tag{1}$$

where $\Delta U_{hg}^{\text{total}}$ is the average energy of the adsorbate with the host, $\Delta U_{h}^{\text{total}}$ is the average total energy of the framework (zero for a rigid framework), and $\Delta U_{g}^{\text{total}}$ is the average total energy of the adsorbate molecule (zero for a rigid molecule).

9. What are the enthalpies of adsorption of CO_2 in ITQ-29 and MFI? Hint: use the average total energies from the output-files.

Exercise 5: Where is CO_2 in ITQ-29 located?

Lastly, we are going to elucidate the behavior of the energy histogram of CO_2 in ITQ-29. On Day 3, we will also see the effect this has on the adsorption-isotherm of CO_2. To find out where the adsorbates are on average we are going to make a three-dimensions histogram of the positions of the CO_2 atoms.

We add to the `simulation.input` of the previous exercise (to the `Systems` section):

```
"SimulationType" : "MonteCarlo",
"NumberOfCycles" : 100000,
"NumberOfInitializationCycles" : 1000,
"PrintEvery" : 5000,

"Systems" : [

    "Type" : "Framework",
    "Name" : "ITQ-29",
    "NumberOfUnitCells" : [2, 2, 2],
    "ChargeMethod" : "Ewald",
    "CutOff": 11.8,
    "ExternalTemperature" : 300.0,
    "ComputeDensityGrid" : true,
    "SampleDensityGridEvery" : 10,
    "DensityGridSize" : [128, 128, 128]

],

"Components" : [

    "Name" : "CO2",
    "TranslationProbability" : 0.5,
    "RotationProbability" : 0.5,
    "ReinsertionProbability" : 1.0,
    "blockingPockets" : [
         [0.0,       0.0,        0.0,       4.0],
         [0.5,       0.0,        0.0,       0.5],
```

```
        [0.0,       0.5,        0.0,       0.5],
        [0.0,       0.0,        0.5,       0.5]
      ],
    "CreateNumberOfMolecules" : 1

]
```

1. Run the CO_2 in ITQ-29 case at 300K and 600K. Leave it running and visualize the `density_grids/grid_ITQ-29_component_CO2.s0.cube` files using iRASPA. Where is the CO_2 located at low loading?