Theoretical Chemistry and Computational Modelling



Statistical Mechanics and Applications on Simulations



Practical session 3

Calculation of a gas/solid absorbent adsorption isotherm from Monte Carlo simulations

Ramón Sayós and Hèctor Prats

1

Grand canonical Monte Carlo (GCMC) method



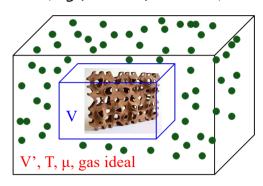
• In a grand canonical ensemble (μVT) volume (V), temperature(T) and chemical potential of each species (μ_i) in the different phases are fixed.

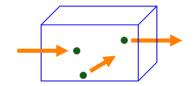
$$dG = VdP - SdT + \sum_{i} \mu_{i} dn_{i}, \quad \mu_{i} = \left(\frac{\partial G}{\partial n_{i}}\right)_{P,T,n_{j} \neq n_{i}}$$

- This ensemble allows the study of systems with material equilibrium (i.e., chemical and/or phase equilibria). For instance, this can be used for adsorption studies (e.g., gas/solid absorbent).
- In this ensemble:
 - The system exchanges <u>heat and particles</u> with a reservoir at T and V fixed (open system). Hence, N is a fluctuating quantity.
 - o The chemical potential of an <u>ideal gas</u> of density ρ (reservoir) will be equal to its value inside the <u>system with interactions</u> (real) of density ρ '.

• For instance adsorption/absorption of a gas into a porous material (e.g., zeolite, silicalite):







 $\mu_{gas(reservoir)} = \mu_{gas-ad/solid}$ (with equilibrium)

- Acceptable trial moves will be:
 - o Insertion or removal of particles in the system of volume V (i.e., pores of material); random position or a randomly selected particle.
 - Displacement of a particle (e.g., translation or rotation if it is a rigid molecule); molecule, direction and distance at random.
- The gas pressure (reservoir) and the chemical potential are related:

$$\mu = \mu^o + RT \ln \frac{P}{P^o} \quad \textit{(ideal gas)}, \quad \mu = \mu^o + RT \ln \frac{f}{f^o} \quad \textit{(real gas, f} \equiv \textit{fugacity)}$$

3

Metropolis algorithm (i→f trial change/move):



If
$$U_f < U_i \rightarrow Prob = 1$$
, $i \rightarrow f$ accepted
If $U_f > U_i \rightarrow Prob \propto e^{-\beta \left[U_f - U_i\right]} < 1$, $i \rightarrow f$ accepted if $\xi \leq Prob$
(random number $0 < \xi < 1$)

1. Displacement: translation or rotation (50%/50%), Δ_{max} =0.5 \pm Å)

$$Prob_{(s \to s')} = min \left(1, e^{-\beta \left[U_{f(s)} - U_{i(s')} \right]} \right)$$

2. Insertion or removal (50%/50%):

$$\begin{split} &\operatorname{Prob}_{(N \to N+1)} = \min \left(1, \ \frac{V}{\Lambda^3 (N+1)} e^{\beta \mu} e^{-\beta \left(U_{f(N+1)} - U_{i(N)} \right)} \right) \\ &\operatorname{Prob}_{(N \to N-1)} = \min \left(1, \ \frac{\Lambda^3 N}{V} e^{-\beta \mu} e^{-\beta \left(U_{f(N-1)} - U_{i(N)} \right)} \right) \\ &\Lambda = \sqrt{\frac{h^2}{2\pi \ m \ k_h T}} \ \ \text{(thermal de Broglie wavelength)}, \ \beta = \frac{1}{k_h T} \end{split}$$



Study of CO_2 adsorption/absorption into a porous material based on SiO_4 tetrahedra units (silicalite). It is a polymorph of silicon dioxide:

$n(SiO_2)$

- Monte Carlo simulations with a grand canonical ensemble (µVT)
- Silicalite and CO₂: rigid structures
- Use of an empirical force field (L–J and Coulomb) for silicalite/CO₂ interactions. Two kind of interaccions allowed:
 - 1. gas-gas
 - 2. gas-silicalite

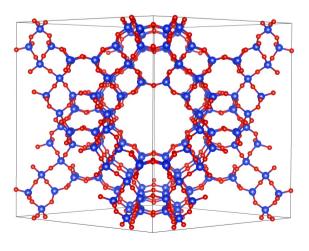
(silicalite/silicalite atom interactions are constant)

$$U_{total} = \sum_{i=1}^{N} \sum_{j>i}^{N} U_{ij}, \qquad U_{ij} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{1}{4\pi\epsilon_{o}} \frac{q_{i}q_{j}}{r_{ij}}$$

Supercage

5

- Use of dummy atoms to block sodalite cages
- Calculation of adsorption isotherms at several T
- Unit cell: a=b=c= 24.2576 Å
- Use of LAMMPS code



Si in blue O in red

Unit cell of silicalite: Si₁₉₂O₃₈₄



Type III

Type I

Type II



-Inputs:

run.in: read all simulation parameters (i.e., L_x , L_y , L_z , T, P, steps,...).

CO2.in: contains the structure of a single CO_2 molecule (read by run.in).

silicalite.in contains the structure of silicalite (read by run.in).

-Outputs:

lammps.out: shows the simulation parameters and the different calculated properties at several timesteps.

lammps.ave: gives the average number of adsorbed molecules.

(log.lammps, err.lammps, out.lammps)

7

Input: run.in



```
# -----Init Section
units
               real
                                             (type of units: Å, kcal/mol, atm,...)
boundary
                                             (3D periodic conditions)
               ppp
atom style
               full
pair style
               lj/cut/coul/long 12.0
                                             (force field type: Coulomb + Lennard-Jones)
kspace_style ewald 1.0e-5
# -----Atom Definition Section
read data
               silicalite.in
                                             (read silicalite structure from silicalite.in file)
               faujasite type 1 2 3 (assign an ID for each type of atom: O_{EAU} = 1, Si_{EAU} = 2, X=3)
group
molecule
               CO2 CO2.in offset 3 1 0 0 0
               CO2 type 4 5
group
                                 # O(solid) (atom group definition for charges)
               O type 1
group
               sodalite type 3
                                 # dummy atoms
group
               group O charge -0.39299
                                             (atomic charges definition)
set
               group Si charge 0.78598
set
set
               group sodalite charge 0.00000
```

```
Input: run.in (cont.)
                                                                                           iqtc
            àtoms ID ε
                            σ
                * * 0.0 0.0
                                  # Si(FAU) - O(FAU) no interaction
pair coeff
pair coeff
               2 4 0.0 0.0
                                  # Si(FAU) - C(CO2) no vdW interaction
pair coeff
               2 5 0.0 0.0
                                  # Si(FAU) - O(CO2) no vdW interaction
               1 4 0.07471 3.511 # O(FAU) - C(CO2) vdW
pair coeff
pair coeff
               1 5 0.15695 3.237 # O(FAU) - O(CO2) vdW
               440.059602.745 \# C(CO2) - C(CO2) vdW (CO<sub>2</sub> – silicalite interactions: L-J)
pair coeff
               4 5 0.10063 2.880 # C(CO2) - O(CO2) vdW
pair coeff
pair coeff
               5 5 0.17024 3.017 # O(CO2) - O(CO2) vdW
               3 4 0.00100 3.000 # sodalite - C(CO2) repulsive
pair coeff
pair coeff
               3 5 0.00100 3.000 # sodalite - O(CO2) repulsive
# ------ Settings Section ------
compute modify
                   thermo temp dynamic yes
neighbor
               2 bin
neigh modify every 1 delay 0 check no one 100000 page 5000000
neigh modify exclude group faujasite faujasite (not calculation of silicalite-silicalite interactions)
variable
               CO2ad equal (atoms-584)/3 (calculation of CO<sub>2</sub> adsorbed molecules:
                                                        192 \, Si + 384 \, O + 8 \, dummy \, atoms = 584)
     ------ Run Section ------
            1 faujasite rigid single force 1 off off torque 1 off off off (rigid faujasite)
fix
            averages all ave/time 50 51 5000 v CO2ad file lammps.ave
fix
                      (calculation of average number of adsorbed molecules (file lammps.ave))
            fxgc CO2 gcmc 1 1 1 0 123456789 303.15 -0.5 0.5 mol CO2 pressure 1 full_energy
fix
                                                 (parameters. T = 303.15 K, P = 1 atm)
thermo 50
                                                                  \sim (\mu, NOT USED)
thermo style
                 custom step v CO2ad pe density temp (output variables every step)
run 5000 (number of steps; check the optimal value)
```

9

10011101C 10101011C 111qtc0 010111101 010000010 Institut de Química Teórica 1 Computacional

Input: silicalite.in

```
584 atoms (number of atoms)
696 bonds (number of bonds)

5 atom types (number of types of atoms)
2 bond types (number of types of bonds)

0.0000 24.2576 xlo xhi (simulation cell)
0.0000 24.2576 ylo yhi
0.0000 24.2576 zlo zhi

Masses (masses of all atoms)

1 15.999400 # O FAU
2 28.085501 # Si FAU
3 0.000001 # dummy (sodalite)
4 12.001100 # C CO2
5 15.999400 # O CO2
```

```
Atoms (cartesian coordinates)

1 1 2 0.000000 22.949631 3.039478 0.870605 # Si
2 1 2 0.000000 1.307970 21.218124 23.386995 # Si
3 1 2 0.000000 19.501171 3.024923 12.999405 # Si
.....
583 1 3 0.000000 3.03220 3.03220 3.03948 # O
584 1 3 0.000000 21.22540 21.22540 21.21812 # O

Bonds (data of bond types)

1 1 1 209
2 1 1 550
....
695 1 192 487
696 1 192 383
```

Input: CO2.in



3 atoms *(number of atoms)* 2 bonds *((number of bonds)*

Coords (cartesian coordinates)

1 0.0000 0.0000 0.0000 2 -1.1490 0.0000 0.0000 3 1.1490 0.0000 0.0000

Types (types of atoms)

Charges (atomic charges)

1 0.6512 2 -0.3256 3 -0.3256 Bonds (bond definitions)

1 1 1 2 2 1 1 3

Special Bond Counts

Special Bonds

11

output: lammps.out



N_{step}	N _{CO2_aa}	Total potent	tial Density	Temperature
Step	CO2a	d PotEng	Density	Temp
0	0	-7912.2666	1.3420473	0
50	4	-7923.7189	1.3625219	141.34237
100	3	-7921.1317	1.3574033	76.852569
150	3	-7922.6295	1.3574033	70.046754
200	4	-7927.3528	1.3625219	75.411294
250	6	-7932.7825	1.3727593	61.873455
300	7	-7936.2548	1.377878	102.70847
350	8	-7935.1519	1.3829966	122.41205
400	6	-7933.6742	1.3727593	89.413866
450	5	-7929.3982	1.3676406	109.69059
500	2	-7918.4085	1.3522846	53.404244
550	7	-7933.3350	1.377878	85.772262
4900	4	-7923.3738	1.3625219	227.28958
4950	5	-7924.9860	1.3676406	168.38861
5000	4	-7925.8321	1.3625219	99.215715



- Execution:
 - A) Using QUBUNTU OS (LAMMPS_2017):
 - open a terminal
 - create directory /PS3
 - cd to directory /PS3
 - download the files from UAM (Moodle) or from cerqt2.qt.ub.es:
 e.g., scp your_user@cerqt2.qt.ub.edu:/work/MEAS/PS3/*.
 - lammps < run.in > lammps.out & (execute in background)

13



- B) Using an external cluster (IQTCUB), LAMMPS_2015:
- Connect to the cluster (ssh):
 ssh -I -X your_user_cerqt2.qt.ub.edu (or ssh -Y)
- Make a directory in your home: mkdir PS3
- Copy input files and scripts from /work/MEAS/PS3 into your directory:

cd PS3
cp /work/MEAS/PS3/* .

Send your calculation with LAMMPS to a batch queue:
 qsub -N name lammps_sub (put a name for the calculation)
 qstat (show the status of your job)

Tasks to do:



- 1. T = 303 K, $P_{CO2} = 1 \text{ atm}$, 5.000 steps (CPU time $\approx 8-10 \text{ min}$)
 - See the file lammps.out: steps, N_{CO2} ad, potential energy, density
 - See the file lammps.ave: <N_{CO2} ad>
 - Remove text lines and keep only columns with variables:

 cat lammps.out | head -n166 | tail -n101 > lammps.data

 (or using vi or gedit editors)
 - Plot N_{CO2} ad vs. t and check if N_{steps} is appropriate:
 - gnuplot
 - plot "lammps.data" u 1:2 w lp
- 2. Change the temperature, for instance:

 $T = 350 \text{ K}, P_{CO2} = 1 \text{ atm}, 5.000 \text{ steps}$ Which is the temperature effect?

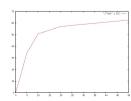
15



- 3. Determine the isotherm at T = 303 K.
 - Calculations at P = 0.1, 0.5, 1, 5, 10, 50, 100 and 200 atm
 - 5000 20000 steps (check the optimal number of steps)
 - Calculate the uptake (in mols CO₂/kg silicalite):

$$\begin{array}{c} \text{uptake (mols CO}_2\text{/kg FAU}) = \frac{\left< N_{\text{CO2_ad}} \right> \text{ molec.CO}_2 \text{ ad}}{1 \text{ unit cell FAU}} \times \frac{1 \text{ mol CO}_2}{6.023 \cdot 10^{23} \text{ molec.CO}_2} \times \frac{1 \text{ unit cell FAU}}{1.916 \cdot 10^{-23} \text{ kg FAU}} \\ \\ \text{(unit cell:Si}_{192}\text{O}_{384} \rightarrow 11535.94 \text{ amu}) \end{array}$$

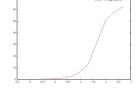
- Create a file (uptake) with the calculated pressure values and uptakes:
- Plot the isotherm (uptake vs. P at fixed T):
 - gnuplot
 - plot "uptake" u 1:2 w lp

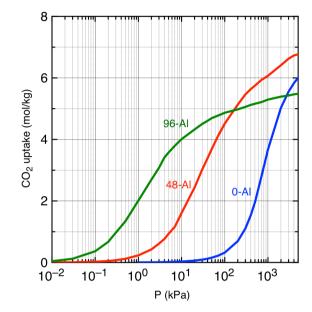






- gnuplot
- plot "uptake" (log10(\$1)):2 w lp





Si₁₉₂O₃₈₄
Na₄₈Al₄₈Si₁₄₄O₃₈₄
Na₉₆Al₉₆Si₉₆O₃₈₄

 CO_2 with some faujasites and silicalite at T = 313

(H. Prats et al. Journal of CO2 Utilization 19 (2017) 100-111)

17



- Additional tasks and questions:
- Is it possible to estimate the time to achieve the gas/solid adsorption equilibrium?
- Do you know alternative methods to GCMC for this kind of studies?
- Check the quality of your averages:

 In file run.in we put:

fix averages all ave/time 50 51 5000 v_CO2ad f ile lammps.ave (Nevery = 50, Nrepeat = 51, Nfreq = 5000)

Change: Nevery, Nrepeat, Nfreq to see the effect in your calculations



- -Why we do not select values from all 5000 steps?
- -Check the temperature average. Is that different from the selected value? Why?
- -Print out the CO_2 velocities (v_x, v_y, v_z) ($^A/fs$) at the end and compare the mean velocity modulus (v) for the step with the maximum N_{CO2_ad} number with the expected Maxwell-Boltzmann value at T=303 K (use a large P).
 - add a line in run.in file: dump velocities CO2 custom 100 lammps.vel id type vx vy vz and send a new calculation

19



- Check if the calculated isotherm follows a Langmuir type or another one.

$$\theta_{A} = \frac{u_{A}}{u_{A(max)}} = \frac{K \cdot P_{A}}{1 + K \cdot P_{A}} \Rightarrow u_{A} = \frac{u_{A(max)} \cdot K \cdot P_{A}}{1 + K \cdot P_{A}} \quad \text{(Langmuir isotherm)}$$

$$\frac{1}{u_{A}} = \frac{1}{u_{A(max)}} + \frac{1}{K \cdot u_{A(max)}} \frac{1}{P_{A}} \quad \text{(1/u}_{A} \text{ vs. 1/P}_{A} \text{ linear)}$$

$$(u \equiv uptake)$$

