



## Practical session 3

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

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### *Grand canonical Monte Carlo (GCMC) method*

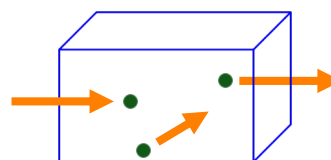
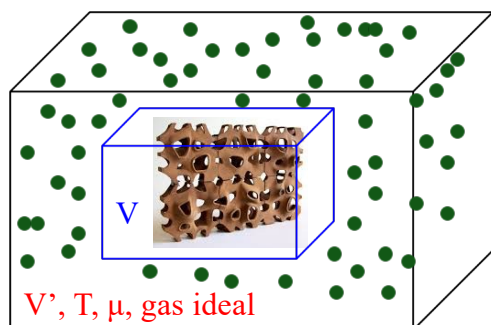
- In a *grand canonical ensemble* ( $\mu VT$ ) volume ( $V$ ), temperature ( $T$ ) and chemical potential of each species ( $\mu_i$ ) in the different phases are fixed.

$$dG = VdP - SdT + \sum_i \mu_i dn_i, \quad \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{P, T, n_j \neq n_i}$$

- 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 heat and particles with a reservoir at  $T$  and  $V$  fixed (*open system*). Hence,  $N$  is a fluctuating quantity.
  - The chemical potential of an ideal gas of density  $\rho$  (reservoir) will be equal to its value inside the system with interactions (real) of density  $\rho'$ .

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



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

- Acceptable trial moves will be:
  - 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:

$$\mu = \mu^0 + RT \ln \frac{P}{P^0} \quad (\text{ideal gas}), \quad \mu = \mu^0 + RT \ln \frac{f}{f^0} \quad (\text{real gas, } f \equiv \text{fugacity})$$

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- Metropolis algorithm** ( $i \rightarrow f$  trial change/move):

If  $U_f < U_i \rightarrow \text{Prob} = 1, \quad i \rightarrow f \text{ accepted}$

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

- Displacement: translation or rotation (50%/50%),  $\Delta_{\text{max}} = 0.5 \pm \text{\AA}$

$$\text{Prob}_{(s \rightarrow s')} = \min \left( 1, e^{-\beta[U_{f(s)} - U_{i(s')}] } \right)$$

- Insertion or removal (50%/50%):

$$\text{Prob}_{(N \rightarrow N+1)} = \min \left( 1, \frac{V}{\Lambda^3(N+1)} e^{\beta\mu} e^{-\beta(U_{f(N+1)} - U_{i(N)})} \right)$$

$$\text{Prob}_{(N \rightarrow N-1)} = \min \left( 1, \frac{\Lambda^3 N}{V} e^{-\beta\mu} e^{-\beta(U_{f(N-1)} - U_{i(N)})} \right)$$

$$\Lambda = \sqrt{\frac{h^2}{2\pi m k_b T}} \quad (\text{thermal de Broglie wavelength}), \quad \beta = \frac{1}{k_b T}$$

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**Unit cell of silicalite:  $Si_{192}O_{384}$**



atoms ID  $\varepsilon$   $\sigma$ 
$$192 \text{ Si} + 384 \text{ O} + 8 \text{ dummy atoms} = 584$$

*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)*

1 1  
2 2  
3 2

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

1 2 0 0  
2 1 1 0  
3 1 1 0

Special Bonds

1 2 3  
2 1 3  
3 1 2

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output: *lammps.out*

<i>N<sub>step</sub></i>	<i>N<sub>CO2_ad</sub></i>	<i>Total potential energy</i>	<i>Density</i>	<i>Temperature</i>
.....				
Step	CO2ad	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

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– *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/\* .*
- *lammips < run.in > lammips.out & (execute in background)*

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*B) Using an external cluster (IQTCUB), LAMMPS\_2015:*

- *Connect to the cluster (ssh):  
ssh -l -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 lammips\_sub (put a name for the calculation)  
qstat (show the status of your job)*







- 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<sub>2</sub> velocities ( $v_x$ ,  $v_y$ ,  $v_z$ ) (Å/fs) at the end and compare the mean velocity modulus ( $v$ ) for the step with the maximum  $N_{\text{CO}_2_{ad}}$  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

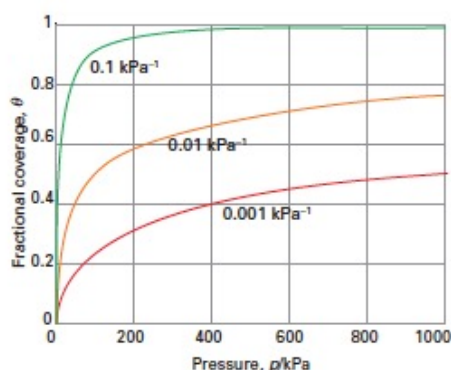
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- Check if the calculated isotherm follows a *Langmuir type* or another one.

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

$$\frac{1}{u_A} = \frac{1}{u_{A(\max)}} + \frac{1}{K \cdot u_{A(\max)}} \frac{1}{P_A} \quad (1/u_A \text{ vs. } 1/P_A \text{ linear})$$

( $u \equiv \text{uptake}$ )



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