Analysis of CO$_2$ Behavior in Zeolites

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Why worry about CO$_2$?

- Increasing CO$_2$ levels in atmosphere.

- Need to reduce production or *sequester*.
  - Sequester is to store away.
  - Realistically impossible to eliminate production.

- Current techniques are expensive or inefficient.
What are Zeolites?

- Crystalline aluminosilicates (fancy rocks)

- All three we are studying (Silicalite, ITQ3, ITQ7) have molecular formula $\text{Si}_{96}\text{O}_{192}$
  - Other zeolites have Al or other metallic imperfections.

- Used as catalysts, ion exchangers, and as molecular sieves.
  - Molecular sieves are materials that contain pores that can adsorb gasses or liquids.
Channels are like tubes. Two kinds: straight and sinusoidal.
Pores are large openings. Windows are narrowings that connect pores.
QuickTime™ and a YUV420 codec decompressor are needed to see this picture.
What is special about zeolites?

- A zeolite can hold more than 3 times as much CO₂ than empty space for a given pressure.

- Neato! So, why does this happen?
How do we answer this question?

- *Computer simulations!*

- Real experiments are very hard to do.

- High pressure and high temperature environments are dangerous to work in.

- Mixtures are particularly hard to produce accurate data for.

- But using computational methods we can get very detailed information!

- Our code was self developed.
Benefits of Computer Simulations

- Can see individual positions of adsorbed atoms and zeolite atoms.

- Can see atomic movement over time.

- Can find total temperature or energy.

- Can find more macroscopic data like amount adsorbed, species selectivity, or specific heat of adsorption.
Modeling the System

- System is made up of zeolite atoms and adsorbent atoms.
- Atoms are modeled as charged points in space.
- Atoms interact with each other in pairs in every possible combination.
- Total potential energy of system is the sum of all potential energies arising from pairwise interactions.
What are these interactions?

L-J potentials model van der Waals attractive forces and Pauli repulsion.

\[ 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \]

Coulombic potential energy models Coulombic interactions.

\[ \frac{q_i q_j}{4 \pi \varepsilon_0 r} \]
Modeling Molecules

- Molecules have fixed bond lengths.
  - \( \text{CO}_2 \) is modeled as a rigid line with three charged L-J centers.
  - \( \text{N}_2 \) is also a rigid line with two negatively charged L-J centers and one positively charged “dummy” atom at its center of mass.
- Charges are very crucial in the modeling process.

\[ 2.32 \text{ Å} \]

\[ 1.1 \text{ Å} \]
Modeling Zeolites

- Fixed lattice of atoms.

- Split into cubic unit cells (smallest repetitive unit).

- Simulations take place in an area of a few unit cells.

- But wouldn’t weird things happen at the edges of cells with just empty space beyond?

![Diagram of Silicalite with UC dimensions: 13.42 Å, 20.07 Å, 19.92 Å]
Simulating the Infinite

- Repeat simulation space in all directions.
- Atoms feel force from “ghost” neighbors.
- Set up periodic boundary conditions where atoms wrap around edges.
Computational Tricks

- "The Grids" are precomputed zeolite-adsorbate interactions.

- Cut off adsorbate-adsorbate interactions after their force becomes "negligible."

- Choose PBC so that all sides are well longer than these cutoffs.
There is still a strong coulombic force even after the cutoff.

Potoff, J. J. et al. AIChE J. 2001, 47, 1676
Comparing Interactions

Coulombic charge is by far the strongest interaction.

LJ is magnified by a factor of 100.

Coulombic charge is by far the strongest interaction.
Calculating Error

- Van der Waals interactions are modeled by Lennard-Jones potentials.
- Coulombic interactions are modeled by coulomb pair potentials.
- We have an infinite system which implies an infinite number of pairwise interactions.
- We truncate the interactions at some cut-off distance, \( r_c \).
- Error can be estimated as

\[
U_{\text{tail}} = \frac{N\rho}{2} \int_{r_c}^{\infty} 4\pi r^2 u(r) dr
\]

- The indefinite integral converges only when \( u(r) \) decays faster than \( 1/r^3 \).
- \( U_{\text{tail}} \) can’t be used to correct coulombic potential energy since it decays as \( 1/r \).
A Solution: *Ewald Method*

- A set of point charges may be considered a set of *screened* charges (a *Gaussian* distribution in our case) minus the smoothly varying screening background.

\[
\begin{align*}
+q & \quad = \quad +q \\
\quad & \quad + \quad \int \quad +q \\
\quad & \quad \sqrt{-q}
\end{align*}
\]

- Contribution of electrostatic potential due to a particle \(i\) is due exclusively to the fraction that is not screened.
- This fraction goes to zero quickly at large distances.
- The electrostatic PE thus becomes “short range!”
- Compensating charge distribution is a *periodic* and *smoothly varying* function which can be represented by a *Fourier* series.
Overview of Ewald

• Point Charges are screened by a smooth distribution of opposite charges so columbic potential energy becomes “short range.”

• “Short range” PE due to charges can now be calculated easily in real space.

• The PE due to the compensating charges can be represented by a Fourier series.

• We can add the two PEs to get the potential energy of the system.
Skipping the Math …☺ or ☹

\[
U_{\text{coul}} = \frac{1}{2V} \sum_{k \neq 0} \frac{4\pi}{k^2} |\rho(k)|^2 e^{\frac{-k^2}{4\alpha}} \\
+ \frac{1}{2} \sum_{i \neq j}^{N} q_i q_j \text{erfc}(\sqrt{\alpha r_{ij}})
\]

\[=-\left(\frac{\alpha}{\pi}\right)^{1/2} \sum_{i=1}^{N} q_i^2 \]

\[=\text{Gaussian Part}\]

\[=\text{Real Charges}\]

\[=\text{Self-correction Term}\]
Simulation Methods

• Two main types.
  • *Molecular Dynamics* (MD)
  • *Grand Canonical Monte Carlo* (GCMC)
Molecular Dynamics

- Uses Newton’s equations of motion to displace molecules over a time step.
- Initial positions are at equilibrium.
What does MD tell us?

- Can calculate diffusion coefficients (area explored by a molecule per unit time).
  - If diffusion is too slow it does not have practical applications.

- Shows realistic movements of molecules.
  - Can see how they explore the zeolite.
  - How adsorbed species interact with each other.
CO$_2$ Diffusion in Silicalite @ 298K
QuickTime™ and a YUV420 codec decompressor are needed to see this picture.
Disadvantages of MD

• It’s *freaking slow.* 2000 ps simulation takes ~2 days.

• We’d be dead before reaching equilibrium using only MD.

• Our code does not simulate adsorption or desorption of molecules.
Grand Canonical Monte Carlo

• For finding equilibrium adsorption data.

• Since MD is slow, we can cheat. Let’s just randomly plop molecules where we they might be.

• *Not* a time dependent simulation.

• “Move” based: insert, remove, rotate, translate, and swap.

• Composition of mixture is input.

• *Random numbers* determine course of simulation.
MC Process

Select Random Molecule’s Position \(d_i\)  

Select Random New Position \(d_{i+1}\)  

Calculate PEs \(U(d_i)\) and \(U(d_{i+1})\)  

Boltzman Distribution

\[ e^{-\frac{(U(d_{i+1}) - U(d_i))}{k_B T}} \]

\(U(d_{i+1}) < U(d_i)\)

- No
  - Random
  - Yes
    - Accept
    - Yes
    - Reject

- Yes
Step 1

1. Randomly Select Move Type

2. Select Random Molecule’s Position \( (d_i) \)

3. Select Random New Position \( (d_{i+1}) \)

4. Calculate PEs \( U(d_i) \) and \( U(d_{i+1}) \)

5. If \( U(d_{i+1}) < U(d_i) \) then Accept

Diagram:
- Randomly Select Move Type
- Translation
- Select Random Molecule’s Position \( (d_i) \)
- Select Random New Position \( (d_{i+1}) \)
- Calculate PEs \( U(d_i) \) and \( U(d_{i+1}) \)
- If \( U(d_{i+1}) < U(d_i) \) then Accept
Step 2

1. Randomly Select Move Type
2. Select Random Molecule’s Position ($d_i$)
3. Select Random New Position ($d_{i+1}$)
4. Calculate PEs $U(d_i)$ and $U(d_{i+1})$
5. If $U(d_{i+1}) < U(d_i)$, calculate $\frac{e^{-\frac{(U(d_{i+1}) - U(d_i))}{k_B T}}}{e} > \text{Random}$.
   - If true, accept; if false, reject.
   - If false, reject without comparison.
Why use GCMC?

- More efficient use of computer (depending on what you want).
- Can get adsorption data: *isotherms*, specific heat of adsorption, selectivity.

Disadvantages:
- Says nothing about how molecules got there.
- Molecules could be in impossible to reach cavities.
CO₂ is strongly adsorbed by silicalite.
$\text{N}_2$ is not as strongly adsorbed.
CO$_2$ replaces N$_2$ inside of silicalite in mixtures.
Our simulations agree with reality.
Atmospheric Adsorption in Silicalite @ 298K

Even at very low concentrations, Silicalite prefers CO₂.
Selectivity is very high consistently.
What about other zeolites?

Void space is not the indicator of absorption ability.

More Selectivity

All three favor CO₂ strongly.

Importance of Coulombic Forces

Comparison of .5 CO$_2$ / .5 N$_2$ Mixture In Silicalite @ 298K

Coulombic forces are key to understanding adsorption.
Very good agreement between cutoff and Ewald data.
Is Ewald worth it?

- Ewald involves more computational (simulation) time.

- We don’t know yet!!!

- Graphs of preliminary results indicate that there is not much difference between adsorption of both CO$_2$ and N$_2$ in the various materials with cutoff and Ewald.
Felix’s Future Plans

- Study in detail the difference between using Ewald and cutoff and to determine when it is worth using Ewald.
David’s Future Plans

• Investigate mixtures more thoroughly.

• Check diffusion in mixtures.

• Visualize grids.
Red is repulsive force. Blue is attractive.
C in CO$_2$ Silicalite Columbic Grid

Red is repulsive force. Blue is attractive.
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