Computational Screening of Novel Carbon Capture Materials

Jihan Kim
(LBNL)

GTC 05/17/12
Outline

- Introduction
- High-Throughput Characterizations of Porous Materials
  - Low pressure range: Henry coefficient calculations
  - High pressure range: Grand canonical Monte Carlo (GCMC)
- Simulation Results
Carbon capture and storage (CCS): separate CO$_2$ from other gases and store them.

- Current technology (amine scrubbing): regeneration cycles can be energy intensive

- Search for alternative materials to reduce the cost of CO$_2$ capture
Porous Materials

- Porous materials: contain void spaces that can be used to capture guest gas molecules via adsorption.

- Difficulties: Many properties of guest gas molecules (e.g. CO\textsubscript{2} and N\textsubscript{2}) are similar.

<table>
<thead>
<tr>
<th>Application</th>
<th>Gases separated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas</td>
<td>CO\textsubscript{2}/N\textsubscript{2}</td>
</tr>
<tr>
<td>Syngas</td>
<td>CO\textsubscript{2}/H\textsubscript{2}</td>
</tr>
<tr>
<td>Natural gas</td>
<td>CO\textsubscript{2}/CH\textsubscript{4}</td>
</tr>
</tbody>
</table>
Many Candidates, Not Enough Time

Metal-organic frameworks

Hypothetical zeolite structures (2.7million+)

Can we explore a very large database of zeolites efficiently?

~190 zeolites in IZA

*Deng et al. Science, 327, 2009


http://www.iza-structure.org/databases/
Can We Characterize a Large Database of Materials Using GPUs?

- Adsorption Isotherm
  - Amount of adsorbate on adsorbent as a function of pressure
  - Grand canonical Monte Carlo
  - Long simulation time (hours)!

- Henry Coefficient \((K_H)\)
  - Slope of the isotherm at zero pressure

\[
K_H = \beta \langle \exp(-\beta U_{ins}) \rangle
\]

- Much shorter simulation time (minutes)!!!
GPU Code Algorithm*

1. Generate high-resolution energy grids
   Utilize the energy grid to obtain local adsorption property information inside the porous materials

2. Identify and block inaccessible pockets
   Diffusively inaccessible regions within the material must be blocked to obtain accurate adsorption properties

3. Compute material adsorption properties
   Utilize MC sampling to compute (a) the Henry coefficients (low pressure), and (b) adsorption isotherms (high pressure)

1. GPU Energy Grid Construction

- 3D energy grids: pair-wise potential between guest molecule and host framework atoms*
  - Lennard Jones Potential
    \[ U_{\text{LJ}}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]
  - Coulomb Potential (Ewald Summation)
    \[ U_{\text{coul}}(r) = \frac{q_i q_j}{4\pi\varepsilon_0 r} \]
- Store framework atoms in constant memory (typical size, N = 500-1000)

GPU Rotation Routine

- CO₂: three-atoms with bond length = 1.16 Angstroms
- Need to get “average” CO₂ energy per grid point
  - Fix central ‘C’ atom per grid point
  - Conduct N = 100 random test rotations (two ‘O’ atoms) and sample energy
    - CURAND Library
    - Interpolating functions
  - Obtain Boltzmann weighted average energy per grid point
2. CPU Blocking Algorithm

- Block low energy regions that have diffusion limitations and thus inaccessible!
  - Energy above $15k_B T$: considered inaccessible (experimental timescale)
  - Construct binary grid based on accessibility
  - Flood fill algorithm: check for connection to channels
  - Blocked regions: mark as high energy
  - Not enough parallelism to map into GPU hardware

LTA (unit cell), CO$_2$ Energy Profile

Need to block these regions
3(a) GPU Henry Coefficient Calculations

- Monte Carlo Widom insertion moves to obtain averaged adsorption property of the material
  \[ K_H = \beta \langle \exp(-\beta U_{\text{ins}}) \rangle \]
  - CUDA threads, independent insertion moves (sum at the end)
  - Test insert gas molecule and read interpolated energy values from grid
  - CUDA CURAND Library
187 IZA zeolites
0.1 Angstrom energy grid space
100 test rotation for CO₂
~ 10 million Widom test particle insertion moves
Single Precision
NERSC Dirac Cluster (Fermi, Tesla C2050)
  1.74 seconds for CH₄ K_H
  10.72 seconds per CO₂ K_H
  Roughly 50x faster than single core CPU (“Nehalem” 2.67 GHz processors)
Screening Results for 130,000+ Zeolites

3(b) Adsorption Isotherm Calculations

- Adsorption isotherm
  - Full characterization of adsorption materials via GCMC simulations
  - Expensive compared to Henry coefficient calculations
  - Typically calculation for a complete isotherm can take hours of CPU wall time

Problem size seems too small ($N_{CO2} < 200$) for efficient parallelization

Mapping CUDA threads
- Each CUDA block -> 14 different pressure values
- 8 CUDA blocks -> same pressure value (get more MC statistical data at production cycles)
- 32 threads within CUDA block -> parallelize MC energy calculations
GCMC: Optimization Technique 2

- Utilize energy grids (gas-host, gas-gas) as lookup table during MC moves
- MC Bottleneck Routine: pair-wise interaction for Ewald Fourier term

\[ U_{ij}^k(r) = \frac{1}{2L^3} \sum_{k \in K^3, k \neq 0} \frac{4\pi}{k^2} \exp\left(-k^2/4\alpha^2\right)q_i q_j \exp(-i\vec{k} \cdot \vec{r}_{ij}) \]

<table>
<thead>
<tr>
<th>Method</th>
<th>Limiting Factor</th>
<th>Number of Operations per Pair Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>No grid</td>
<td>Compute bound</td>
<td>9k_x k_y k_z summations</td>
</tr>
<tr>
<td>Gas-gas grid</td>
<td>Memory bound</td>
<td>72 array reads</td>
</tr>
</tbody>
</table>
Evaluation of gas-gas Ewald term: still expensive, $O(n)$

Can we get away with neglecting this term?

- **Case 1**: include gas-gas direct/reciprocal Coulomb terms
- **Case 2**: neglect gas-gas reciprocal Coulomb until end of equilibration cycles
- **Case 3**: no gas-gas reciprocal Coulomb interactions
- **Case 4**: no gas-gas direct/reciprocal Coulomb interactions
50-80% of the zeolite simulation box have very high \((E_O + 300k_B T)\) gas-host energy values.

Biased sampling
- **Red**: no bias
- **Green**: bias (< \(E_O + 300k_B T\), 100% equilibration cycles)
- **Blue**: bias (< \(E_O + 3k_B T\), 1% of equilibration cycles)
GCMC: Optimization and Performance Summary

1. Map CUDA threads to GCMC simulations at different pressure values

2. Utilize gas-host (direct and reciprocal space) and gas-gas (reciprocal space component) energy grids -> 15 to 45x speedup

3. Selectively include gas-gas reciprocal component (does not impact adsorption properties greatly) -> 2.5 to 3x speedup

4. Density-biased sampling into low energy regions for MC insertion moves -> 3-4x speedup
Cations Change Zeolite’s Properties

1. Replace N Si with N Al atoms
2. Construct cation (i.e. Na\(^+\)) energy grid
3. Insert cation at min. energy grid point
4. Compute gas adsorption properties (similar to before)

Optimize Each Zeolites with Cations

Summary

- High-throughput GPU molecular molecular simulation code developed from scratch to characterize adsorption properties of a large database of carbon capture materials
  - Henry coefficients: few seconds
  - Full adsorption isotherm curves: few minutes

- Extension of code to obtain diffusion coefficients from the energy grid (ongoing research)
Acknowledgements

- Berend Smit (UC Berkeley, LBNL)
- MolSim Group (UC Berkeley)
- Alice Koniges (LBNL)
- Maciej Harancyzk (LBNL)
- Richard Martin (LBNL)
- Oliver Ruebel (LBNL)
- EFRC