High Throughput Computational Screening of Mixed Matrix Membranes
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Outline

• Brief Mention of Other Computational Work in CO$_2$ Capture at NETL
  – Catalysts: Collaboration With CAER/University of Kentucky
  – Computational Modeling of CO$_2$ in Physical Solvents: Bulk, Interface, Reverse Micelle
  – Computational Designing and Screening of Solid CO$_2$ Capture Materials

• High-Throughput Computational Screening of Mixed Matrix Membranes
  – Goals and Project Design
  – Hypothetical MOF Generator
  – Simulations
  – Maxwell Equation
  – Predictions of H-H-MMMs
A series of metal-organic catalysts have been developed by UKy, which increase the CO₂ absorption rate by ~30% in aq. MEA.

Molecular dynamics simulation of the interface region

15800 water + 2000 MEA + 10 catalysts

Catalysts concentrate at the surface. This is important in understanding foaming.

Interface properties are difficult to determine from experiment. Our goal is to use simulations to predict the extent of foaming based on solution properties: interface surface tension, density, viscosity, elasticity.
Molecular Modeling of UKy Catalysts: First Principles Calculations

- DFT calculations on a series of catalysts (collaboration with UKy)
- What is the stable structure in amine solution?
- Estimates of reaction enthalpy with respect to the reference state in kcal/mol
Effects of CO$_2$ Physical Absorption on Solvent Properties

Upon CO$_2$ loading:
- solvent volume increases by 24%,
- solvent viscosity decreases by 500%,
- diffusivity increases by 500%,
- solvent surface tension decreases by 20%
Modelling CO₂ at Interfaces and Reverse Micelles

• CO₂ absorption in suspension and the interface between solvent & nano-porous material [1]
  – Interface region exhibits CO₂ loading, diffusivity and permeability significantly different from the bulk solvent

• Significantly (10 times) improved CO₂ mass transport in ionic liquid reverse micelle: a multiscale modeling study [2]

• Surfactant-like catalyst behavior in aqueous amine solution for CO₂ absorption [3]

Solid materials are potential candidates for CO$_2$ sorbents. By combining database mining with *ab initio* thermodynamic calculations, we implemented a novel theoretical methodology to screen solid sorbents from known materials databank and to synthesize new materials with improved CO$_2$ capture capabilities for further experimental validation.

The strength of our method is to screen complex sorbent materials for which thermodynamic properties are not available.

Hundreds of solid materials have been investigated.

Now, we are working on screening of multi-components, substituted, doped, and mixed materials to search for good CO$_2$ sorbents.

Yuhua Duan
In this project, we have used atomistic simulations in order to predict the properties of a database of hypothetical metal organic frameworks. These properties have been combined with the experimentally measured properties for polymers in order to make predictions, using the Maxwell Equation, about hypothetical mixed matrix membranes. The overall goal is to discover novel mixed matrix membranes that could be useful for CO$_2$ capture processes.

NETL’s Joule Supercomputer https://hpc.netl.doe.gov/
Mixed Matrix Membranes

Why do we want to predict properties of MMMs?

• MOFs: good selectivity – but expensive, difficult to implement.
• Polymeric membranes – better price, implementation, trade-off.
• In mixed matrix membranes, a small amount of an inorganic filler is introduced into the polymer in order to improve selectivity without sacrificing permeability.

Polymer Matrix
Inorganic Filler (MOF)
Screening Strategy

We are at this stage currently

~137,000 hypothetical MOFs:
- Geometrical analysis
- Brief atomistic simulations
- MOF atoms held at fixed positions

Top 5%:
- Higher accuracy atomistic simulations

“The 1%”:
- Flexible Force Field generation
- Density Functional Theory
- Molecular modeling of polymer
- Model for the interface region
Sketch of the Project

DB of ~137,000 Hypothetical MOFs

Simulations

MEEP
PIM 1
PIM 7
PTMSP
....

Expt. Props of ~10 Polymers

Maxwell Eq.

DB of ~1,370,000 Hypothetical-Hypothetical-MMMs
Creation of the Hypothetical MOF Database

DB of ~137,000 Hypothetical MOFs
Creation of the Hypothetical MOF Database

Existing MOFs deconstructed into a library of building blocks (metal centers and organic ligands). The building blocks are re-assembled to create hypothetical MOFs.

The hypothetical MOF generation program starts by selecting building blocks of three types from its library:

1: Metal Center

2: Organic Linkers

3: Functional Groups

The building blocks are combined using simple geometrical rules in order to create the periodic, 3D structure of a hypothetical MOF.
Building Blocks Combined to Create “Jeff”, a Hypothetical MOF
Simulations of Properties of Hypothetical MOFs

- Geometrical Characterization
  - Largest cavity diameter (LCD)
  - Pore limiting diameter (PLD)
  - Surface area

- MC Calculations
  - Gas Adsorption
    - MOF atomic positions held fixed
    - Atomic charges calculated via EqEq Method
    - UFF force field for MOF atoms
    - TraPPE force field for gases

- MD Simulations
  - Diffusivity
    - Force field parameters as in MC Calculations
    - Velocity autocorrelation function used to calculate diffusivity

Samir Budhathoki
Simulations of Properties of Hypothetical MOFs

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Maxwell Equation: Predicting Properties of MMMs

MEEP
PIM 1
PIM 7
PTMSP

Expt. Props of ~10 Polymers

Maxwell Eq.

DB of ~1,370,000 Hypothetical-Hypothetical-MMMs
Maxwell Equation: Predicting Properties of MMMs

- Incorporation of a filler material into a membrane will change the behavior of gas permeation through the composite membrane.
- The behavior of gas permeation through the composite may be predicted by application of the Maxwell equation.
- (The theory was developed for predicting the dielectric behavior of composite materials.)

Maxwell Equation

\[ P_{\text{eff}} = P_c \left[ \frac{P_d + 2P_c - 2\varphi_d (P_c - P_d)}{P_d + 2P_c + \varphi_d (P_c - P_d)} \right] \]

- \( P_{\text{eff}} \) – the effective permeability of the MMM
- \( P_c \) – the permeability of the continuous phase
- \( P_d \) – the permeability of the dispersed phase
- \( \varphi_d \) – the volume fraction of the dispersed phase


Car, A.; Stropnik, C.; Peinemann, V. K. *Desal.* 200, 2006, 424-426 (PDMS + CUBTC)

Molecular Organic Frameworks

![Graph showing the relationship between CO₂ permeability and permeability selectivity for various materials.](image-url)
Questions?