Development of High Throughput Computational and Experimental Screening Programs for Carbon Capture Materials

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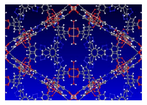
Theoretical Prediction of Material Properties

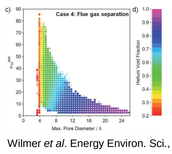
Mature carbon capture technologies currently are projected to increase the price of energy up to 80%. There are an almost infinite number of possible materials that could be explored as alternative carbon capture materials. Given the properties of a carbon capture material (and dependencies on conditions such as gas loadings, temperature and pressure), the CCSI toolset makes possible optimization of the carbon capture process. However, synthesis, characterization and testing of new materials are expensive and time consuming. We are building the capabilities to predict these properties, *via* computational methods (*ab initio* calculations, molecular dynamics and Monte Carlo simulations), not only for existing materials but for hypothetical materials. By linking computational properties prediction to process optimization, not only screening but reverse engineering is possible.

Non-reactive crystalline solid materials: MOFs, ZIFs, COFs, zeolites, etc.

Nu-125 is a promising MOF with properties that have been previously well characterized. It is being used as a test case for our software development.



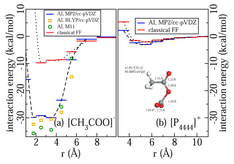
Wilmer *et al.* Energy Environ. Sci., 2013, **6**, 1158

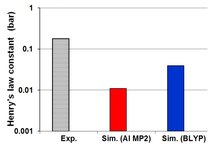


CO_2/N_2 selectivity as a function of max pore diameter derived from simulated gas adsorption in over 130,000 hypothetical MOF structures.

Wilmer *et al.* Energy Environ. Sci., 2012, **5**, 9849

Reactive materials and solvents: amine functionalized MOFs, aqueous amines, strongly-interacting ILs, etc.



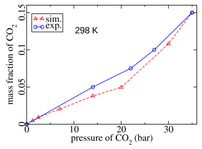


The acetate ion interacts strongly (~12 kcal/mol) with CO_2, making classical force fields inadequate. Here, an interaction potential was created by correcting the classical force field with *ab initio* calculations and using Boltzmann-averaging. The Henry's Law constant is compared to experiment.

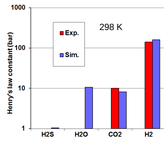
Shi *et al.*, JPCB,2014, **118**, 7383; Steckel, JPCA, 2012, **116**, 11643.

Non-reactive (physical) solvents: Selexol®, Rectisol®, hybrid PDMS, weakly-interacting ILs, etc.

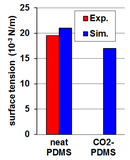
Recent computational work serves both to validate our simulation methods as well as highlight the features of a promising physical solvent. NETL-ORD has created a hybrid polyethylene glycol diethyl ether (PEGDME) polydimethyl siloxane (PDMS) carbon capture solvent that combines the desired carbon capture properties of PEGDME with the hydrophobicity of PDMS.



CO_2 adsorption isotherm for PDMS compared to experiment.

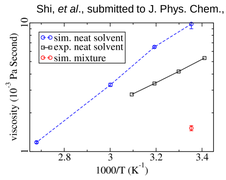


Simulated and measured Henry's law constants for PDMS are in agreement.

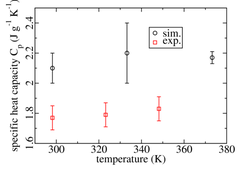


Simulated surface tension compared to experiment for neat PDMS. CO_2 absorption decreases the surface tension due to decreased solvent-solvent interactions and high CO_2 concentration at interface.

Shi, *et al.*, submitted to J. Phys. Chem., 2015



Viscosity-temperature relationship is correctly predicted for hybrid PDMS. CO_2 adsorption in hybrid-PDMS is predicted to drastically reduce viscosity, partly due to volume expansion of the solvent.



Calculated heat capacity of hybrid PDMS compared with experimentally measured values. The differences are within 15%.

Shi, *et al.*, in preparation, 2015.

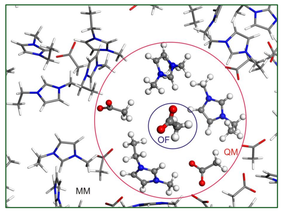
Accuracy of the theoretical prediction for the properties can be further improved by adding more terms or refitting parameters in the classical force field, which could be obtained from *ab initio* calculations

In-house Monte Carlo and molecular dynamics code

Atomistic molecular simulation tools for the calculation of:

- full gas absorption isotherms for both pure and mixed gases
- gas absorption Henry's law constants
- heat of absorption
- excess molar enthalpy, excess molar volume, partial molar volume
- surface tension
- viscosity
- heat capacity
- gas diffusivity
- gas permeability
- thermal conductivity

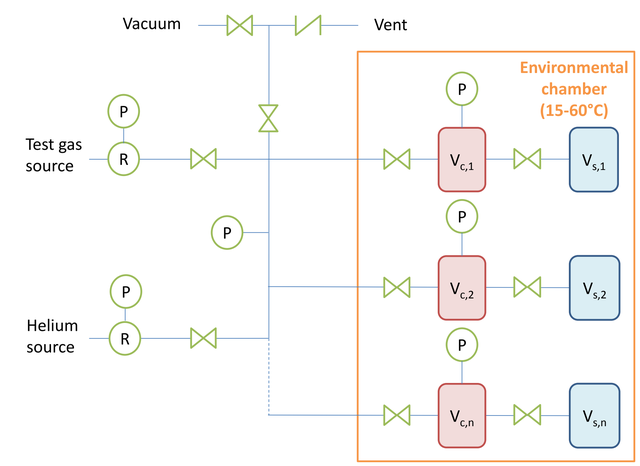
Force matching in the condensed phase



- Force field fitting *via* force matching
- Simulations in the condensed phase
- Objective function minimized *via* an evolutionary strategies algorithm
- Electrostatic fitting in a quantum mechanics / molecular mechanics (QM/MM) scheme
- *Ab initio* calculations in MOLRPO (H.-J. Werner *et al.*, WIREs Comput Mol Sci., 2012, **2**,242.)
- MD portions in TINKER (Y. Shi, *et al.*, JCTC, 2013,**9**, 4046.)
- Non-polarizable / polarizable FF
- Force field fits alternate with MD trajectories to sample configuration space until self-consistency.
- Conditions can be chosen to correspond to the intended use.

Experimental Validation Of Material Performance

- High throughput experimental tools are being conceived and developed as material screening tools and to provide verification of material properties predictions
- For example, high throughput gas sorption analyzer (HTGSA) will measure CO_2 and N_2 sorption into reactive and non-reactive solvents
- Modular, expandable design with automated experiment and data collection *via* LabVIEW, allowing rapid and simple solubility screening of pure or mixed solvents
- A five-cell unit is planned for construction at NETL within the next few months



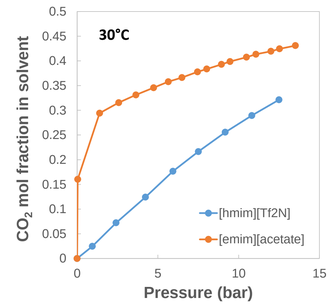
$$n_{s,m} = n_{s,m-1} + \left[\frac{p_{o,m}V_c}{RTZ_{o,m}} + \frac{p_{f,m-1}(V_s - V_l)}{RTZ_{f,m-1}} - \frac{p_{f,m}(V_c + V_s - V_l)}{RTZ_{f,m}}\right]$$

Amount of gas in headspace at charging step

Amount of gas in headspace at equilibration step

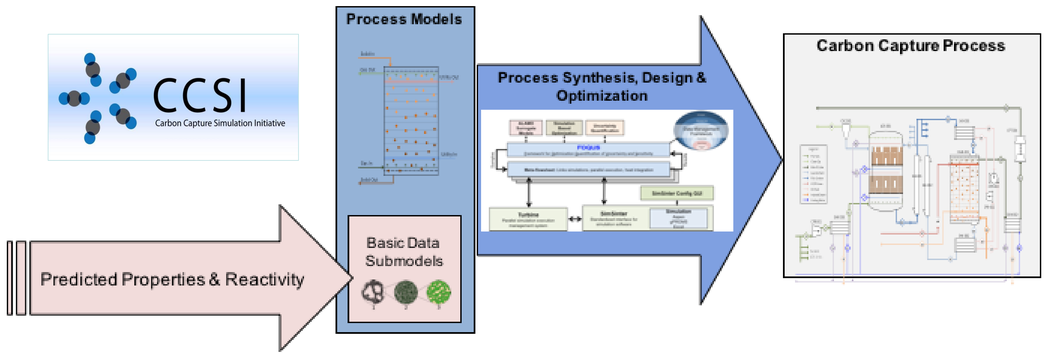
The HTGSA calculates the amount of gas uptake at a particular pressure and temperature based on a well-established dual chamber volume expansion method

Plotting sorption isotherm allows elucidation of sorption behavior, e.g. non-reactive vs. reactive sorption of CO_2



The linkage of high throughput computationally predicted material properties with the CCSI toolset will create an "atoms-to-process" multiscale approach that considers materials performance in the context of a tailored carbon capture process.

The Carbon Capture and Simulation Initiative (CCSI) has developed a suite of computational tools that facilitates the rapid evaluation of new carbon capture materials within the context of a complete process that has been optimized for each material's specific characteristics. By utilizing property data generated by high throughput computational chemistry, the CCSI tools can help identify promising materials for further development and laboratory synthesis.



Goal: Co-Optimization of Carbon Capture Material and Process

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