Sustainable Technology through Advanced Interdisciplinary Research

Multiscale Materials Modeling via Petascale Computing

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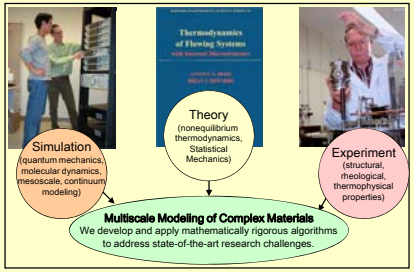
Abstract

The Computational Materials Research Group at the University of Tennessee (UT CMRG; http://clausius.engr.utk.edu/cmrg/index.html) synergistically integrates a broad repertoire of materials modeling tools to develop structure/property relationships for complex, nanostructured materials. These tools include quantum mechanical modeling, classical equilibrium and non-equilibrium molecular dynamics, Monte Carlo methods, reactive molecular dynamics, mesoscale models and continuum models. This suite of tools is applied to develop a molecular-level understanding of the fundamental mechanisms underlying the structure/property relationship of interest. Examples include (i) proton transport in PEM fuel cells, (ii) chain dynamics in flowing polymers, and (iii) nanoporous materials tailored for sensing of explosive materials.

Computational Materials Research Group



Personnel Development

Sustainable Technology through Advanced Interdisciplinary Research

NSF

STAIR: An NSF-sponsored IGERT training grant

- **Develops a new, interdisciplinary curriculum at UT in sustainable energy.**
- **Supports 16 US citizen PhD students for 5 years**
- **Includes significant computational component.**
- **Involves over 20 faculty and staff at UT and ORNL**

Acknowledgments

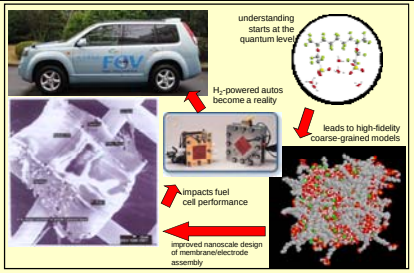
Proton Transport in Fuel Cells
UT: Junwu Liu, Myvizhi Esai Selvan, Stephen Paddison, Shengting Cui, Brian Edwards, + Bill Steele (ORNL)
Funding: DOE BES, NSF

Polymer Physics
UT: Chunggi Baig, Tudor Ionescu, Jun Mo Kim, Brian Edwards, Bamin Khomami + Tony Habenschuss (ORNL), Martin Kroger (ETH, Zurich), Vagelis Harmandaris (MPI, Mainz), Vlasis Mavrantzas (Patras, Greece); Funding NSF, AFOSR & UT Science Alliance

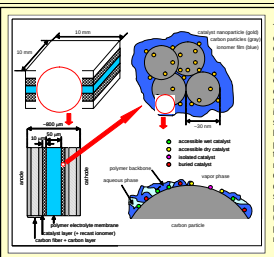
Explosive Sensors
UT: Jared Fern, Ruichang Xiong + Miguel Fuentes-Cabrera (ORNL), Don Nicholson (ORNL)
Funding: NSF & UT Science Alliance

STAIR: Sustainable Technology through Advanced Interdisciplinary Research Training Program
20 faculty and staff at UT and ORNL
Funding: NSF

proton transport in fuel cells

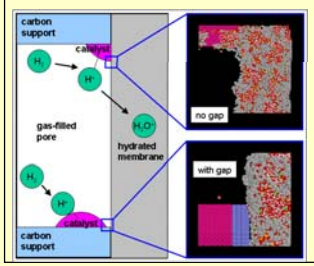


Proton Transport at the Electrode/Electrolyte Interface



The interface between the electrode and the polymer electrolyte membrane in the membrane electrode assembly (MEA) of a PEM fuel cell is an extremely complex system consisting of many bulk phases thin films, each with many interfaces. Understanding the structure/property relationship between interface structure and proton conductivity is a problem that requires multiscale modeling involving structural diffusion of protons (at the quantum scale), nanophase segregation of the hydrated polymer electrolyte membrane (at the molecular level) and polymer morphology at the mesoscale.

Can protons cross gaps?



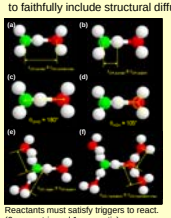
The continuity of a path for proton transport from the catalyst nanoparticle (CNP) to the polymer electrolyte membrane (PEM) is crucial.

Our simulations have shown that a gap as small as 1.4 nm in this path is sufficient to completely disrupt proton transport and render the catalyst useless.

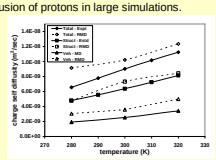
Legend: hydrated Nafion membrane-gray, water-red, graphite-blue, platinum-pink.

Reactive Molecular Dynamics of Proton Transport

We have developed a coarse-grained reactive molecular dynamics scheme based on mapping of quantum results to classical simulations that allows us to faithfully include structural diffusion of protons in large simulations.



Reactants must satisfy triggers to react. (6 geometric and 1 energetic)



Comparison of experimental and simulated self diffusivity of charge in bulk water. The decomposition of the experimental number into structural and vehicular components is based on the analysis of Agmon.

Polymer Physics

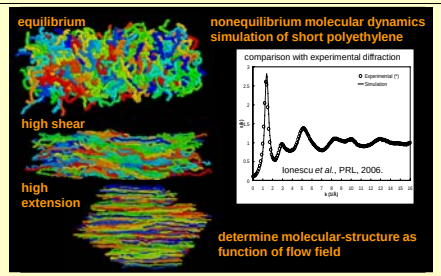
Goal: Understand the relationship between flow history and material properties by using nonequilibrium molecular dynamics to provide the missing structural information.

flow history → molecular structure → material properties

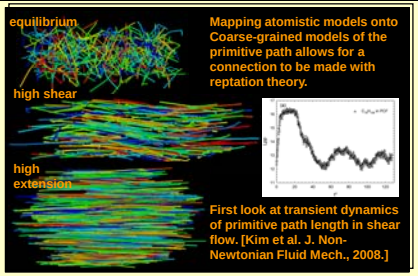
computational approach: use molecular structure as the link.

Computational Challenges: Entangled polymers can have relaxation times on the order of seconds, but NEMD simulations last perhaps 100 ns. Need not only multiscale algorithms with coarse-grained models but also highly efficient implementation on petascale machines.

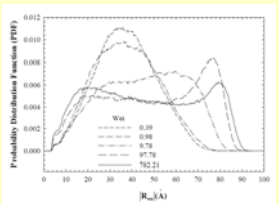
Polymer Rheology



Polymer Physics



Polymer Physics



NEMD simulation shows that the distribution of chain end-to-end distances changes with flow field. Existing reptation theories that assume a Gaussian distribution will only work well near equilibrium. This insight will lead to new mesoscale models that better predict experiment.

MOFs for Explosive Sensing

Addressing the new level of threats, and dynamical environment with the help of new computational tools and technologies

New Generation Smart Nanoporous Explosive Preconcentrators:

Recent experimental work

Preconcentrator based on MOF adsorbents fitting in a 0.5 microliter (uL) groove. Source: Zheng (Richard) Ni, UIUC

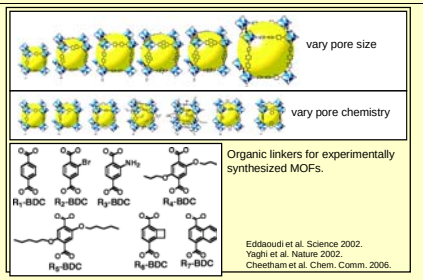
New cost effective, high yield, high quality, fast synthesis technique;

New potential design simplifications thanks to the small amount of high capacity selective preconcentrator MOFs;

MOFs can be tailored to absorb a specific target molecule, leading to the Smart Preconcentrator;

This device needs SNPs!

Functionalization of MOFs

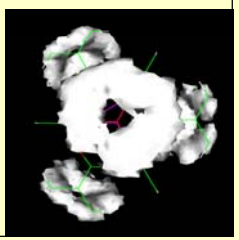


Organic linkers for experimentally synthesized MOFs.

Eddaoudi et al. Science 2002.
Yaghi et al. Nature 2002.
Cheetham et al. Chem. Comm. 2006.

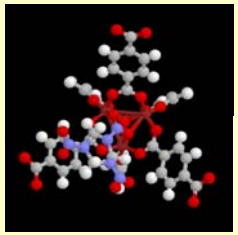
RDX in IRMOF-1

RDX density distribution contours



Above: RDX resides almost exclusively near the vertices of the big cages in IRMOF-1. Right: The adsorption sites at the vertex have a 3-fold symmetry with facile movement between sites at the same vertex in the same cage.

RDX in IRMOF-1



Analysis: The adsorption of RDX in IRMOF-1 is dominated by the interaction of one nitro group in RDX with one octahedral Zn carboxylate complex. The other two nitro groups in RDX are not strongly bound.

New Design: The synthesis of new MOFs with polar groups in the vicinity of these unbound nitro groups may enhance the selectivity of the MOF for RDX. This investigation is underway.

One RDX at one IRMOF-1 vertex: Legend: C-gray, H-white, O-red, N-blue, Zn-maroon