THE UNIVERSITY of TENNESSEE

Multiscale Materials Modeling At the University of Tennessee

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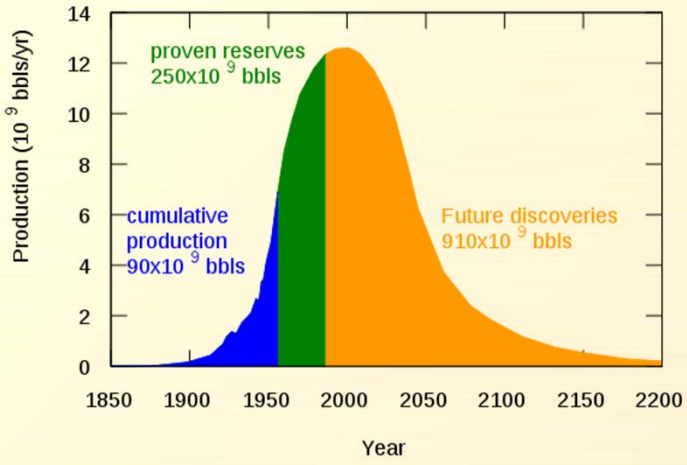
MSE 101
University of Tennessee, Knoxville
April 9, 2014

Multiscale Materials Modeler

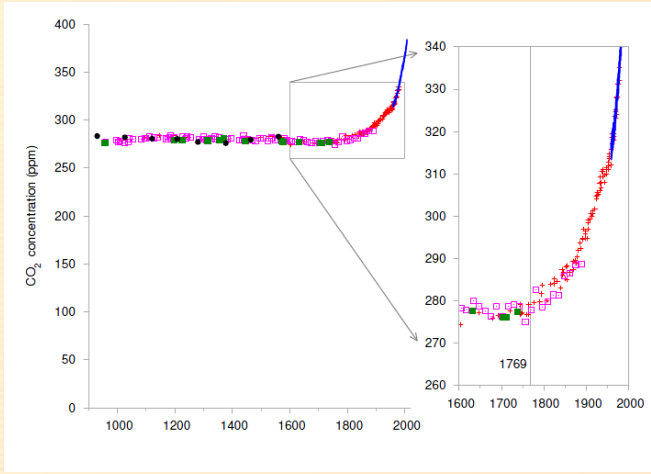
Renewable Energy: The Defining Challenge of Your Generation



Peak Oil

Fossil fuels are a finite resource

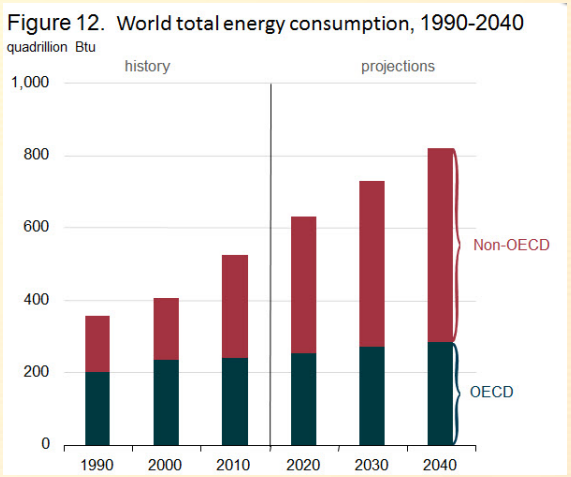
http://en.wikipedia.org/wiki/Peak_oil



Climate Change

Atmospheric CO_2 over the past 1100 years

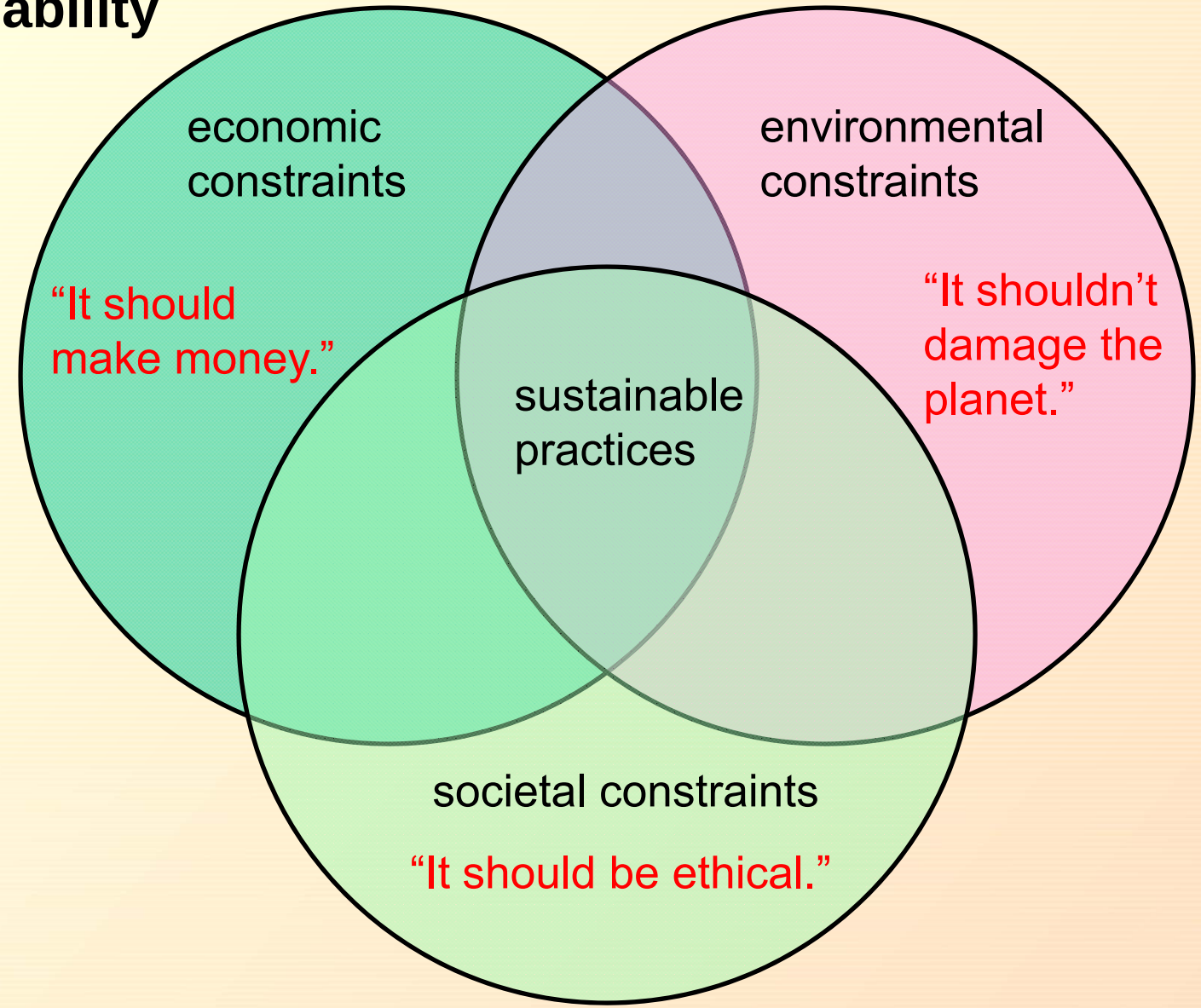
Sustainability without the Hot Air, MacKay



Global Energy Demand is Rising

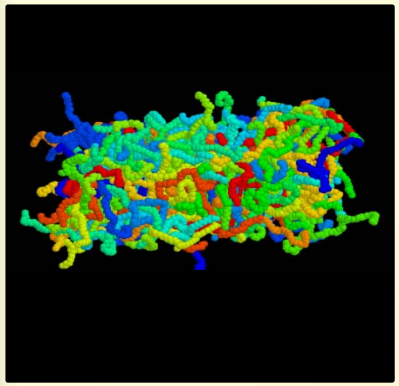
http://www.eia.gov/forecasts/ieo/world.cfm

Sustainability



Interdisciplinary problem: Materials Scientists play critical role.

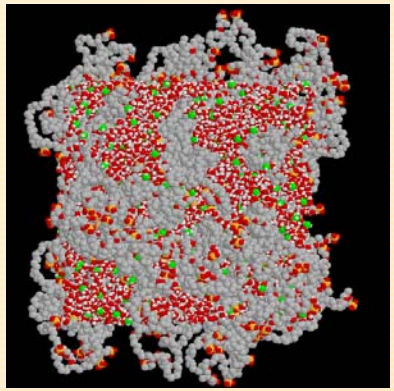
Apply simulation tools to develop structure/property relationships

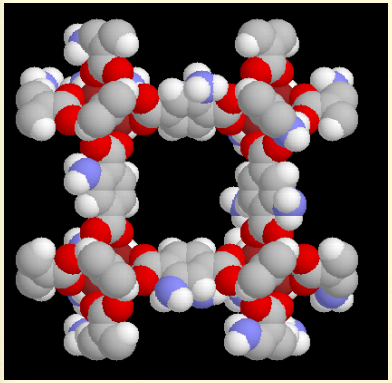


polymeric materials

polymers at equilibrium and under flow (PE, PET)

polymer electrolyte membranes (PEMs) in fuel cells

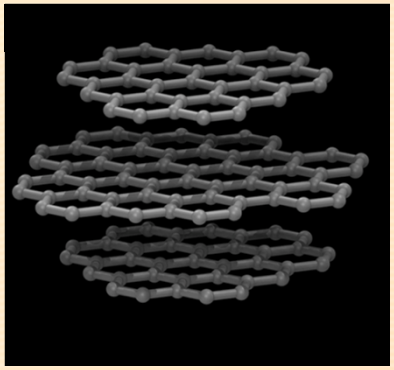


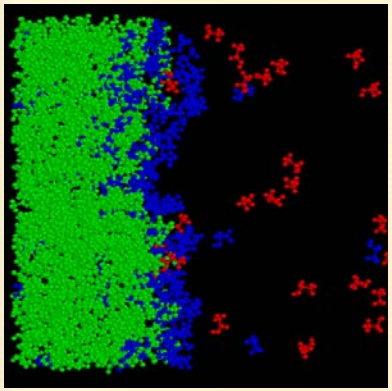


nanoporous materials

hydrogen sorption in metal organic frameworks (MOFs)

bio-derived, nanostructured battery anodes

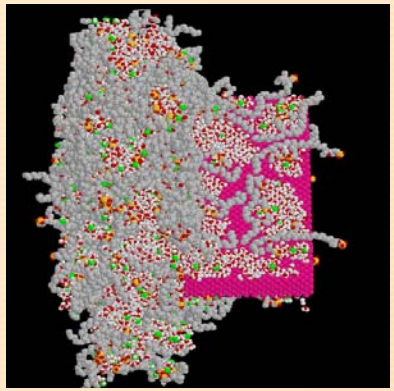




interfacial systems

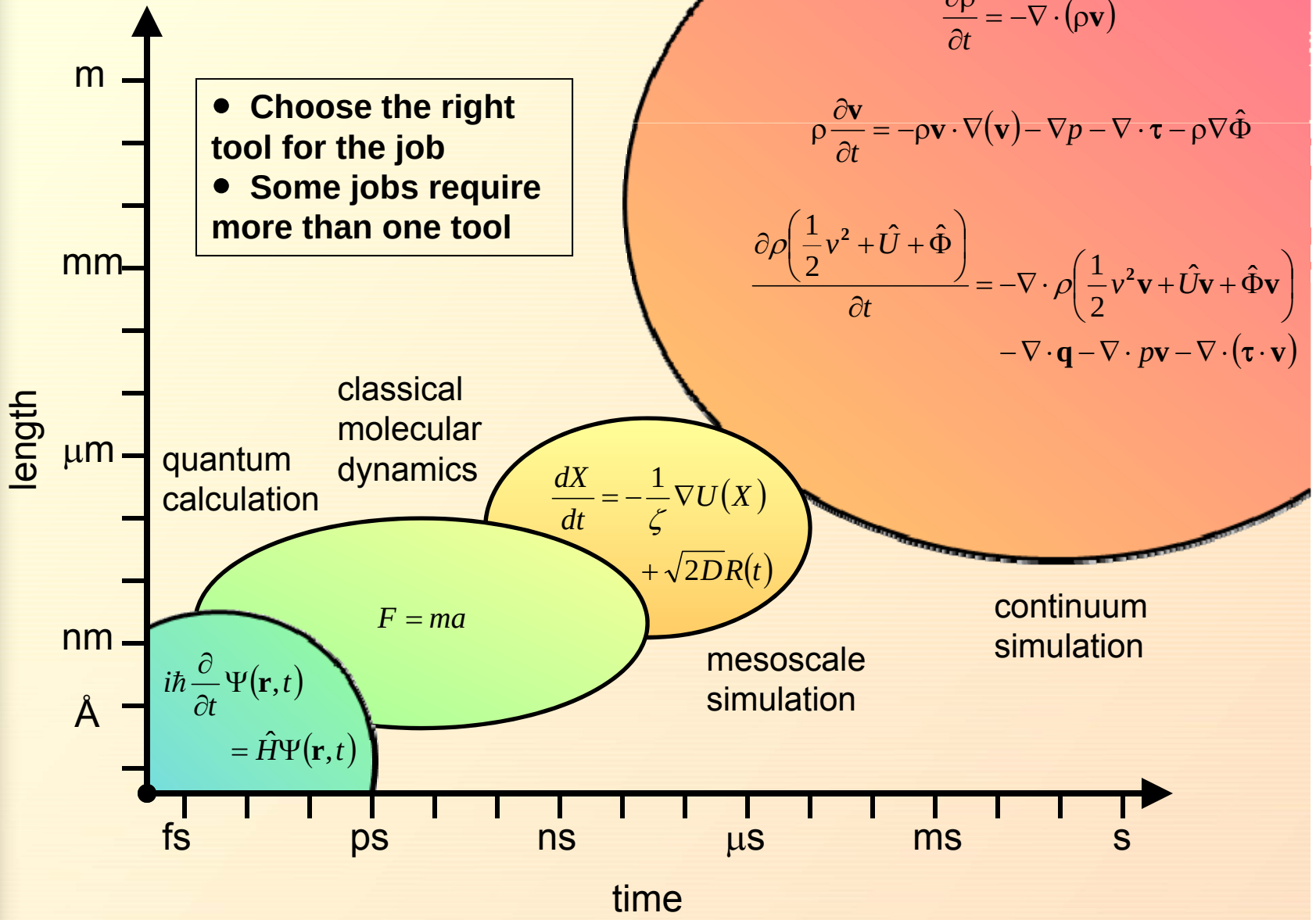
near critical vapor-liquid interface structure

fuel cell electrode/ electrolyte interfaces



Time and Length Scales

- **Choose the right tool for the job**
- **Some jobs require more than one tool**



Collaboration with Oak Ridge National Laboratory

OAK RIDGE NATIONAL LABORATORY
Managed by UT-Battelle for the Department of Energy

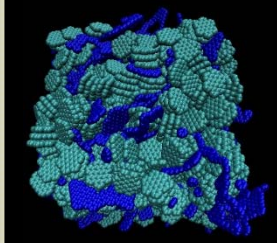
National Center for Computational Science

Today the computing resources of the NCCS are among the fastest in the world, able to perform more than 119 trillion calculations per second.

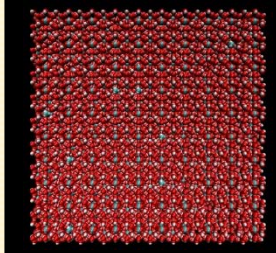
To solve systems of ODEs (largest system thus far is several million), we use the massively parallel supercomputers at ORNL.

These resources are available to researchers at UT through discretionary accounts of the program directors.

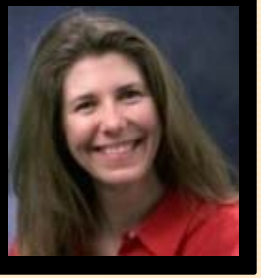
A Complementary Tool: Experimental Collaborators (2013)

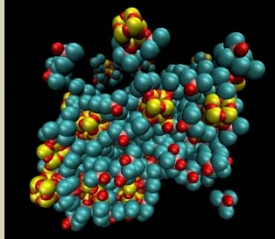


Orlando Rios
(ORNL)
nanostructured
battery
electrodes

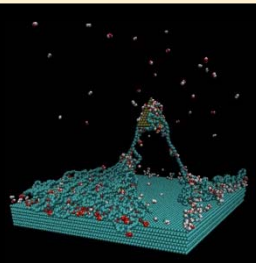


Claudia Rawn
(UT MSE)
methane &
carbon dioxide
hydrates



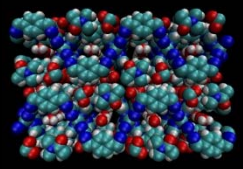


Craig Barnes
(UT Chem)
nanostructured
single-site
catalysts

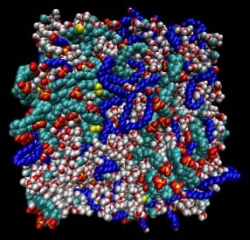


David Joy
(UT MSE/ORNL)

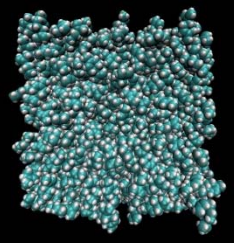
PEM fuel cell
catalyst layer



David Jenkins
(UT Chem)
breathable
metal-organic
nanotubes

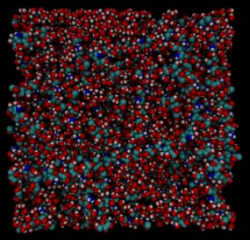


Jimmy Mays
(UT Chem/ORNL)
fuel cell
proton exchange
membranes



Bob Compton
(UT Phys)

racemic
mixtures



Kevin Kit
(UT MSE)
renewable
polymer
films

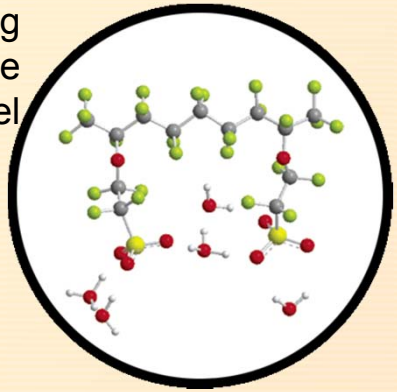
Moving toward fuel cell-powered vehicles

H_2-powered autos become a reality

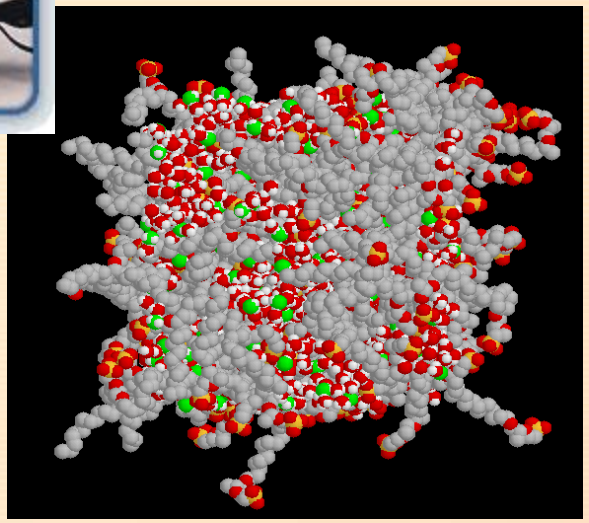
impacts fuel cell performance

improved nanoscale design of membrane/electrode assembly

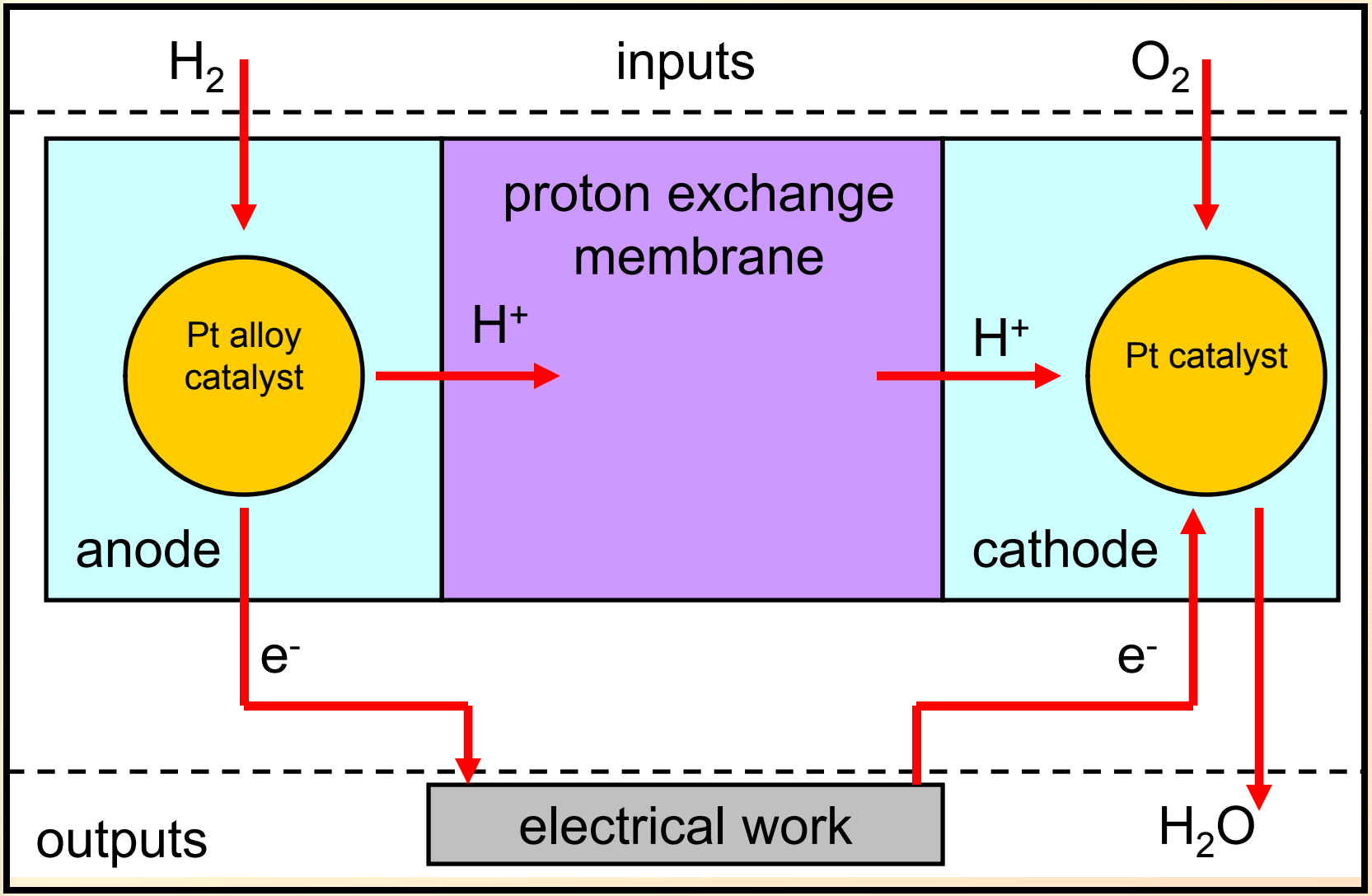
understanding starts at the quantum level



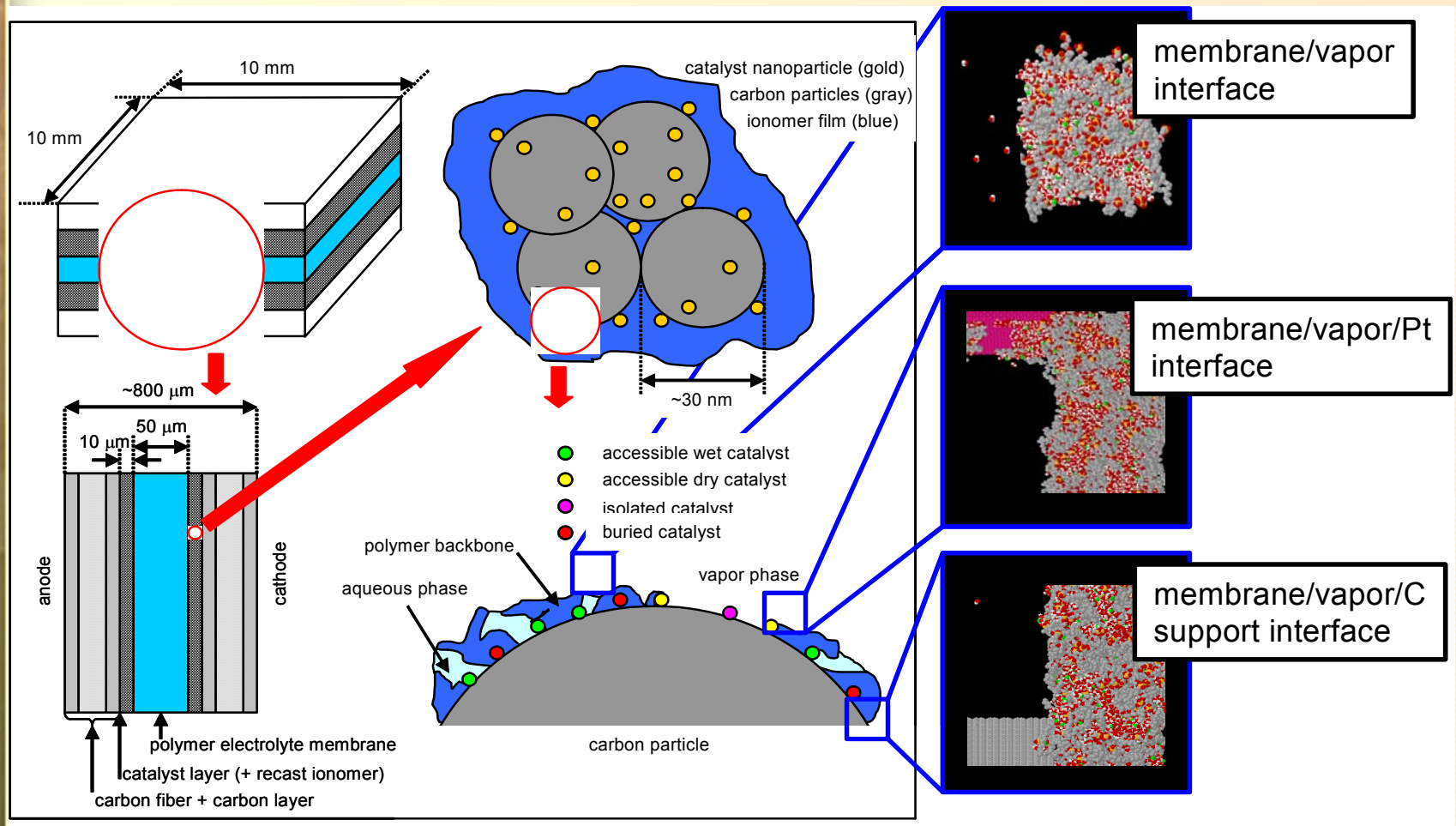
leads to high-fidelity coarse-grained models



how fuel cells work: conceptual level



Fuel Cells are composed of a number of nanostructured materials:
carbon fibers, catalyst nanoparticles, polymeric electrolyte membranes.

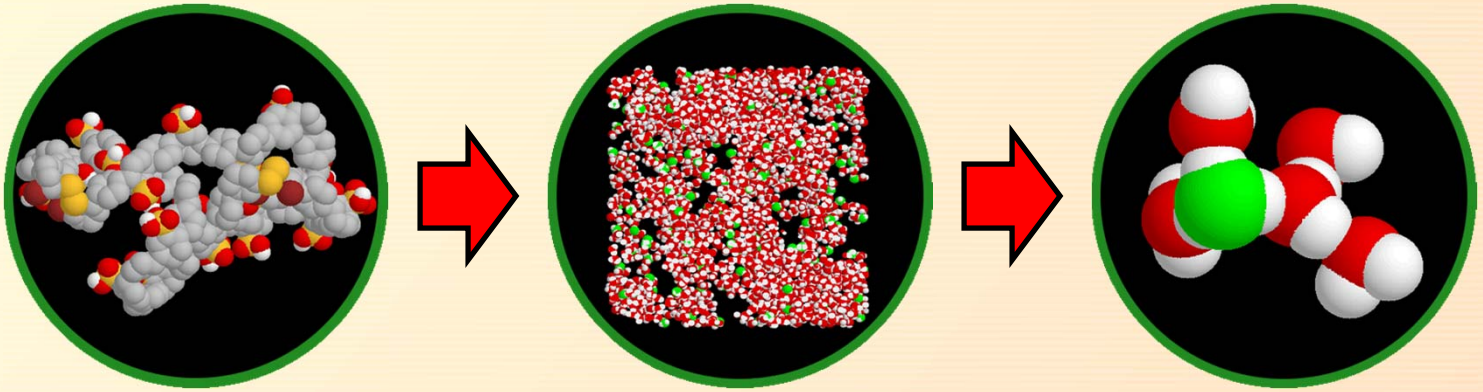


A membrane electrode assembly from the macroscale to the molecular scale.

Research Questions

1. **What is the relationship between polymer chemistry and the morphology of the hydrated membrane?**

2. **What is the relationship between the morphology of the hydrated membrane and the membrane transport properties?**



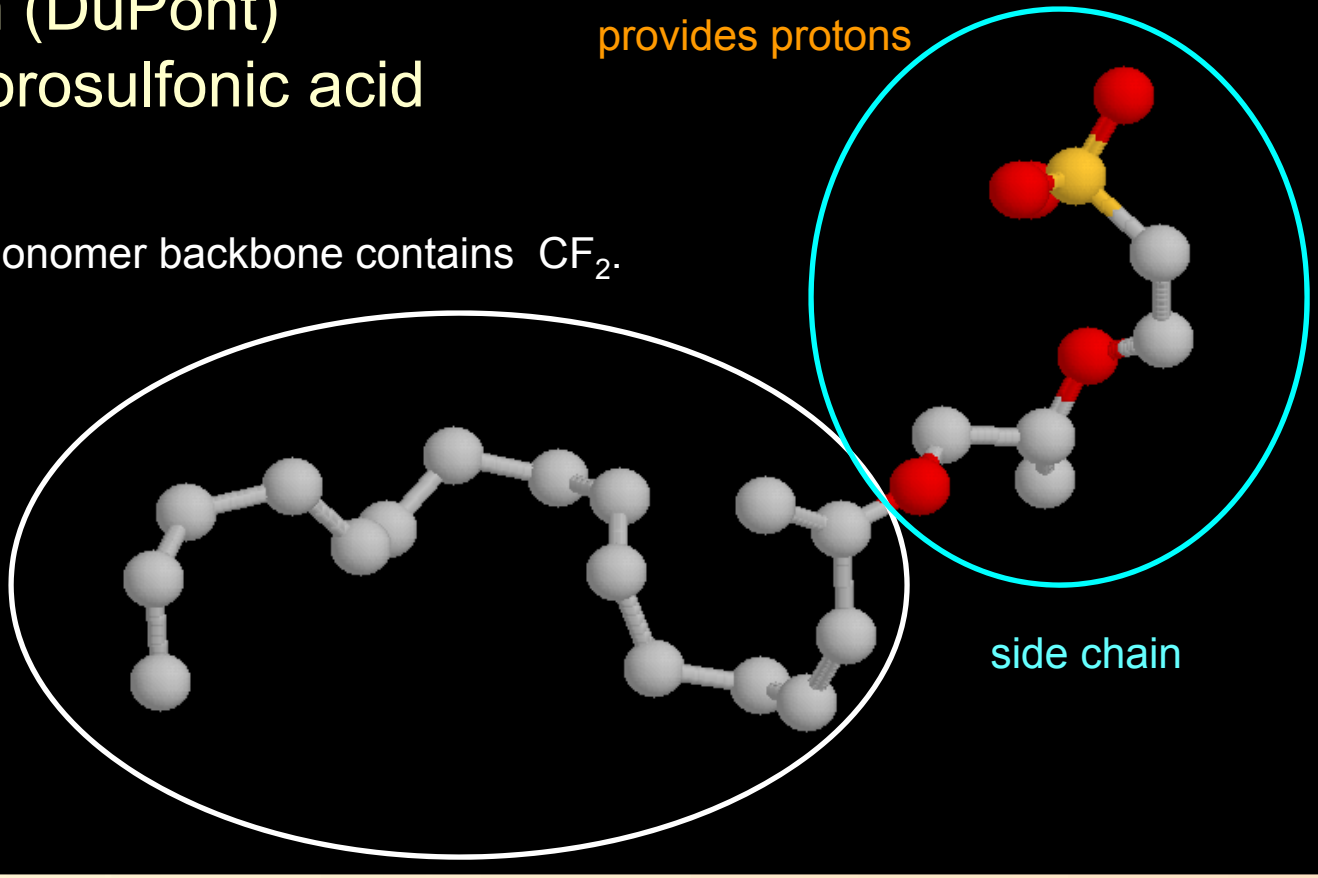
polymer chemistry **membrane morphology** **proton transport**

proton exchange membranes are polymer electrolytes

industry standard:
Nafion (DuPont)
perfluorosulfonic acid

sulfonic acid at
end of side chain
provides protons

monomer backbone contains CF_2.



side chain

CF_2 = gray, O = red, S = orange, cation not shown.

Motivation for new proton exchange membranes

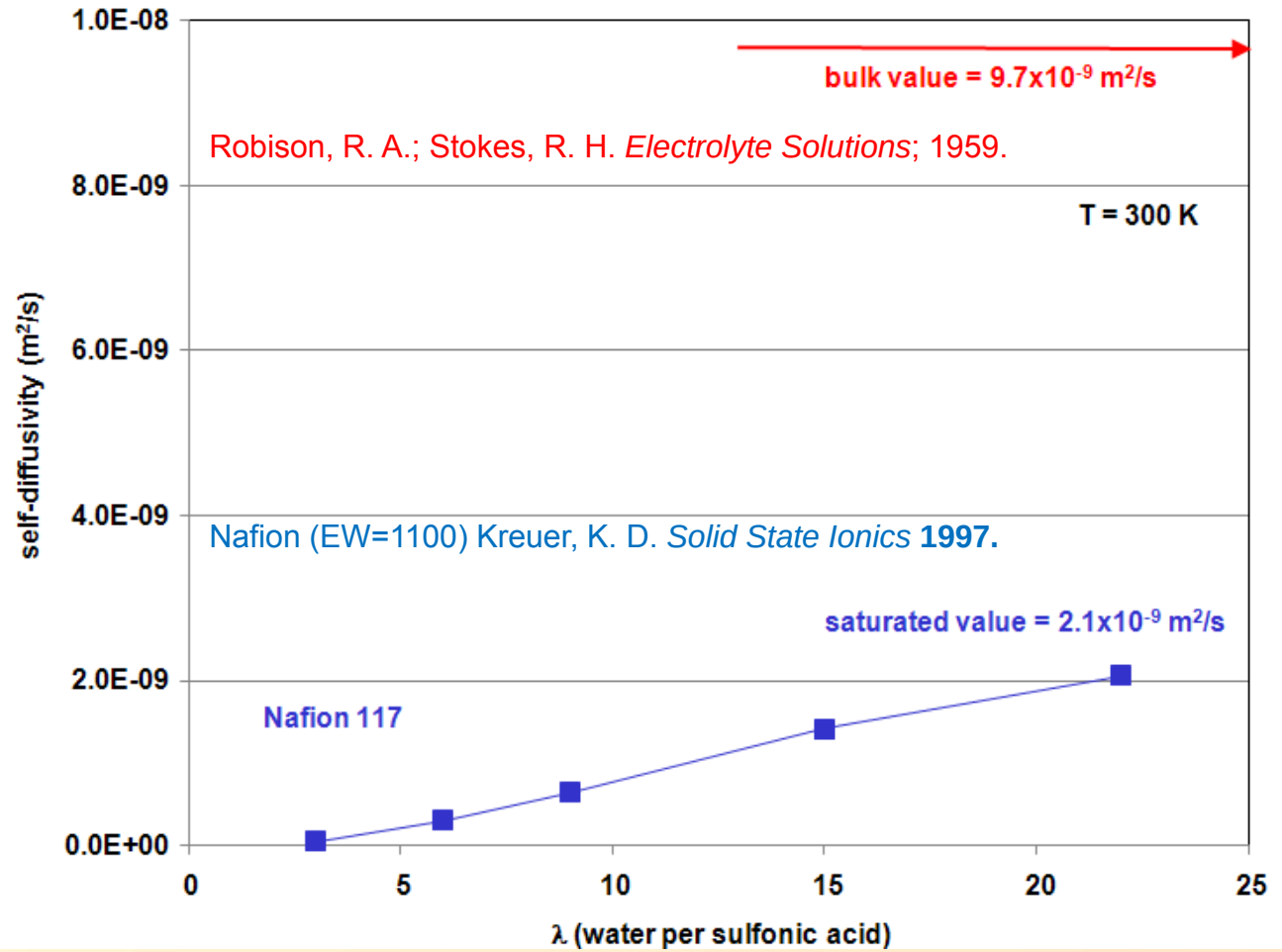
- Lower Cost
  reduce noble metal (Pt or Pt alloy) catalyst content

- Higher Operating Temperature
  - catalyst
    - ► higher activity
    - ► less susceptible to poisoning due to fuel impurities (CO)

  - membrane
    - ► dries out
    - ► conductivity drops

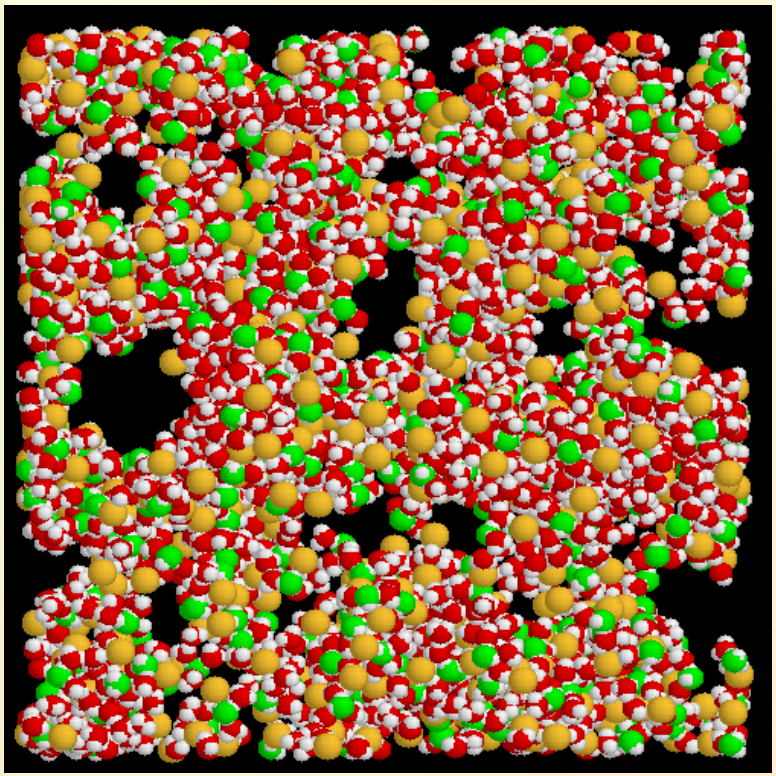
- High Temperature (120 °C) proton exchange membranes
  - retain moisture at higher temperatures
  - maintain high conductivity at lower water content

Proton Transport in Bulk Water and PEM Experimental Measurements

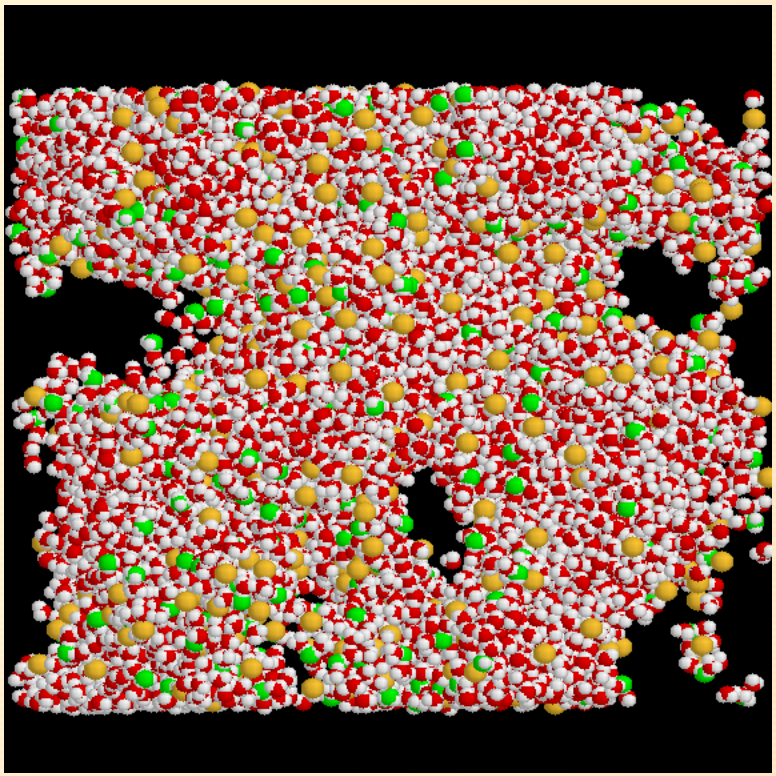


Even at saturation, the self-diffusivity of charge in Nafion is 22% of that in bulk water.

PEM morphology is a function of water content



Nafion (EW = 1144) λ = 6 H_2O/HSO_3
small aqueous channels



Nafion (EW = 1144) λ = 22 H_2O/HSO_3
much larger aqueous channels

As the membrane becomes better hydrated, the channels in the aqueous domain become larger and better connected, resulting in higher conductivity.
(The challenge to finding high-temperature membranes is to find one that can retain moisture at elevated temperatures.)

Determination of Diffusivities from MD Simulation

Einstein Relation – long time slope of mean square displacement to observation time

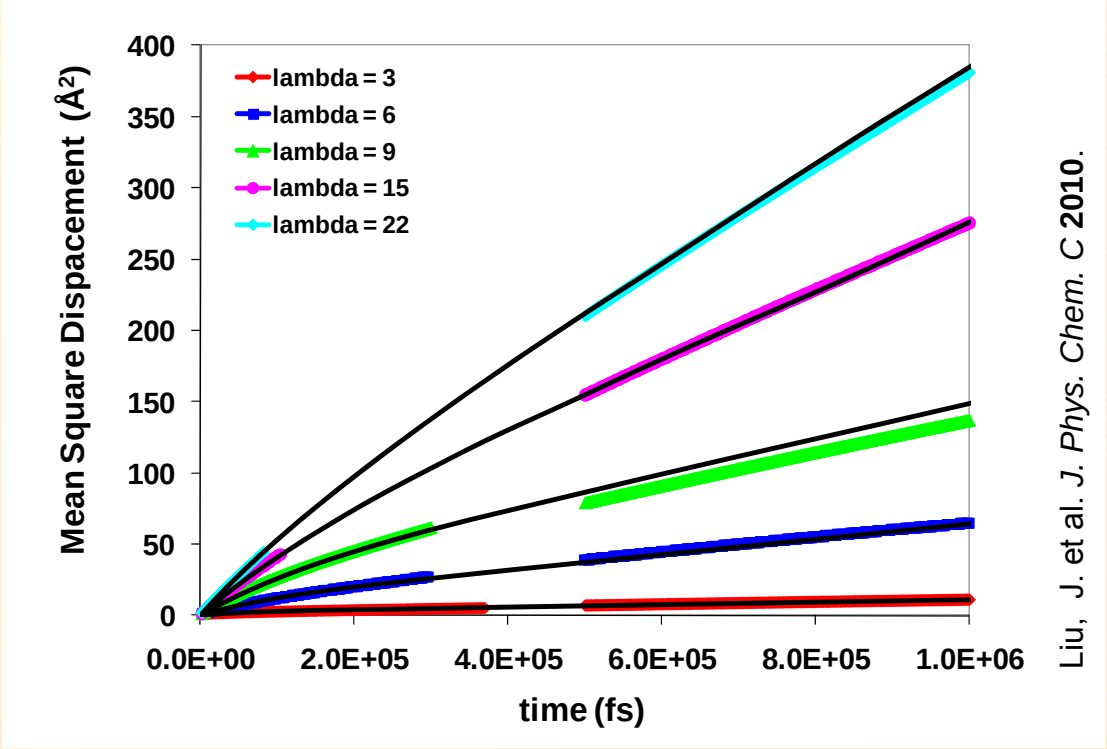
$$D = \lim_{\tau\to\infty} \frac{MSD}{2d\tau} = \lim_{\tau\to\infty} \frac{\left\langle \left[r_i(t+\tau) - r_i(t) \right]^2 \right\rangle}{2d\tau}$$

$r_i(t)$: position of particle *i* at time *t*

Einstein Relation works well for bulk systems.

But for simulation in PEMs, we can't reach the long-time limit required by Einstein relation.

MD simulations alone are not long enough.

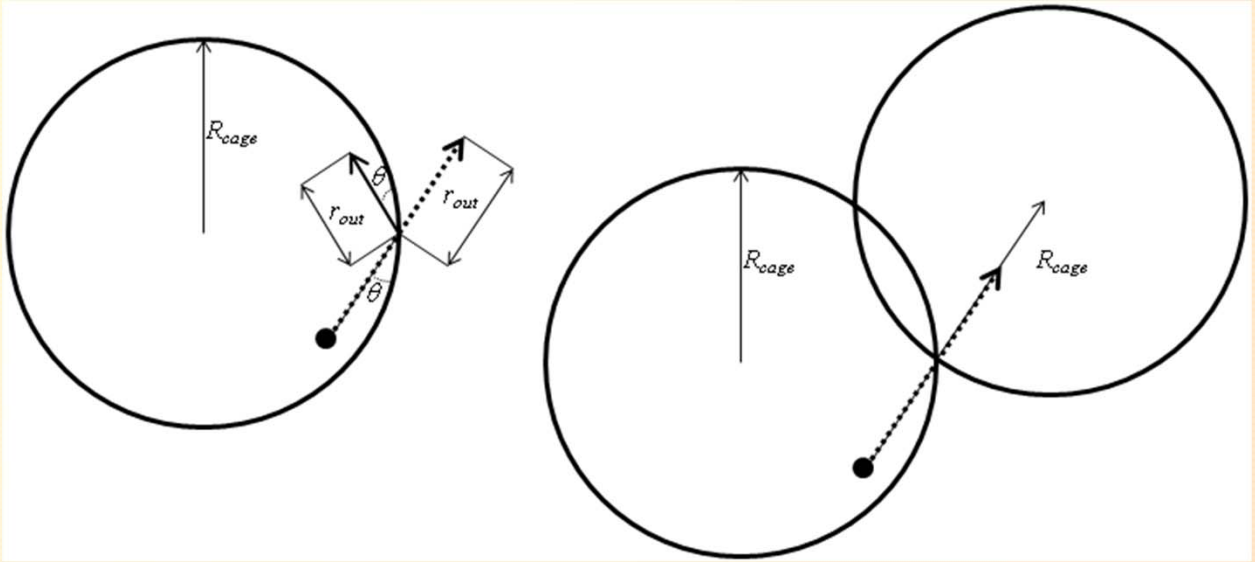


MSDs don't reach the long-time (linear) regime.

Confined Random Walk Simulation

Mesoscale Model

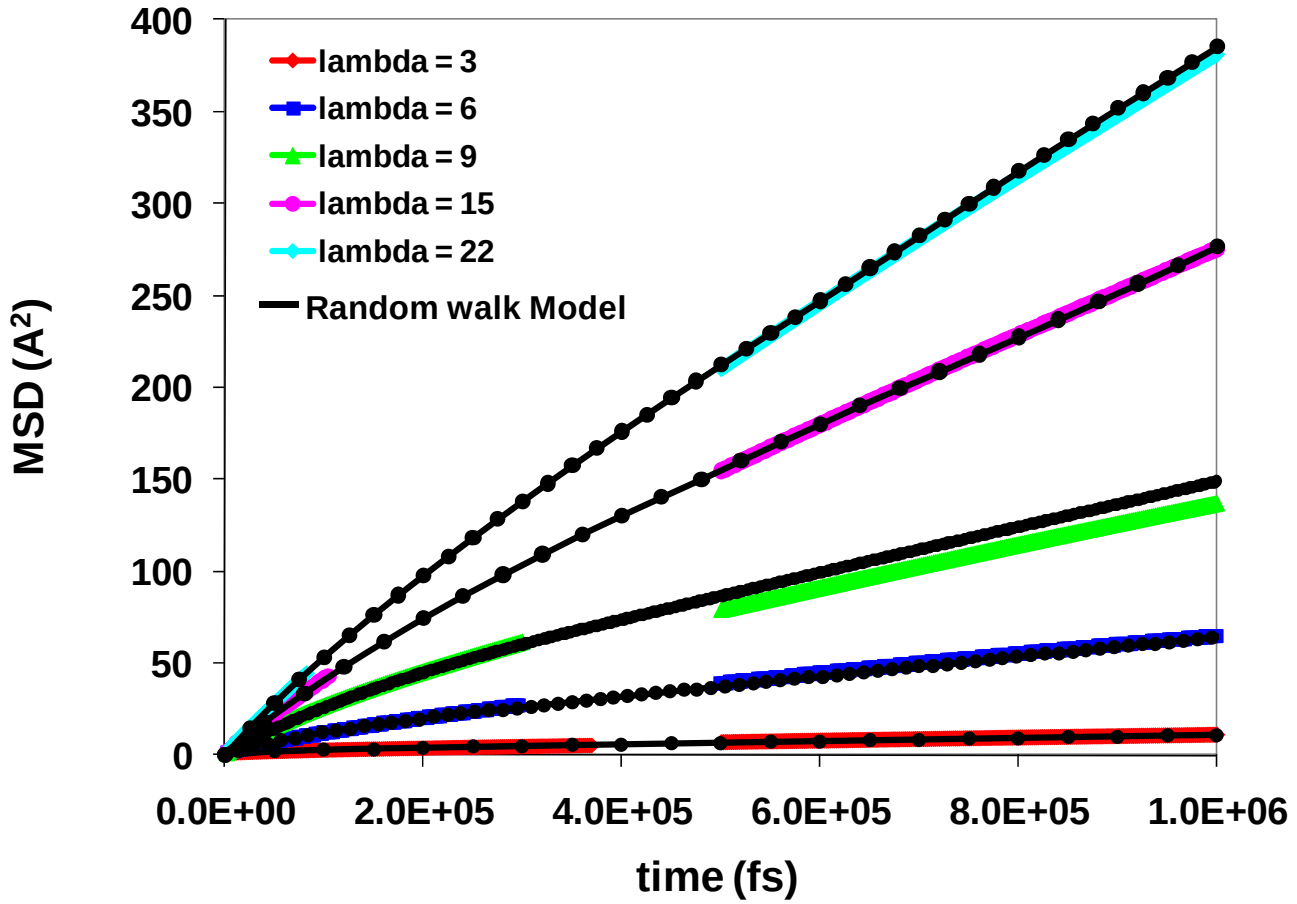
- non-interacting point particles (no energies, no forces)
- sample velocities from a Maxwell-Boltzmann distribution
- two parameters
  - cage size
  - cage-to-cage hopping probability
- parameters fit to MSD from Molecular Dynamics Simulation
- runs on a laptop in a few minutes



unsuccessful move successful move

Calvo-Muñoz, E.M., Esai Selvan, M., Xiong, R., Ojha, M., Keffer, D.J., Nicholson, D.M., Egami, T", *Phys. Rev. E*, **83**(1) 2011 article # 011120.

Couple MD with Confined Random Walk (CRW) Theory

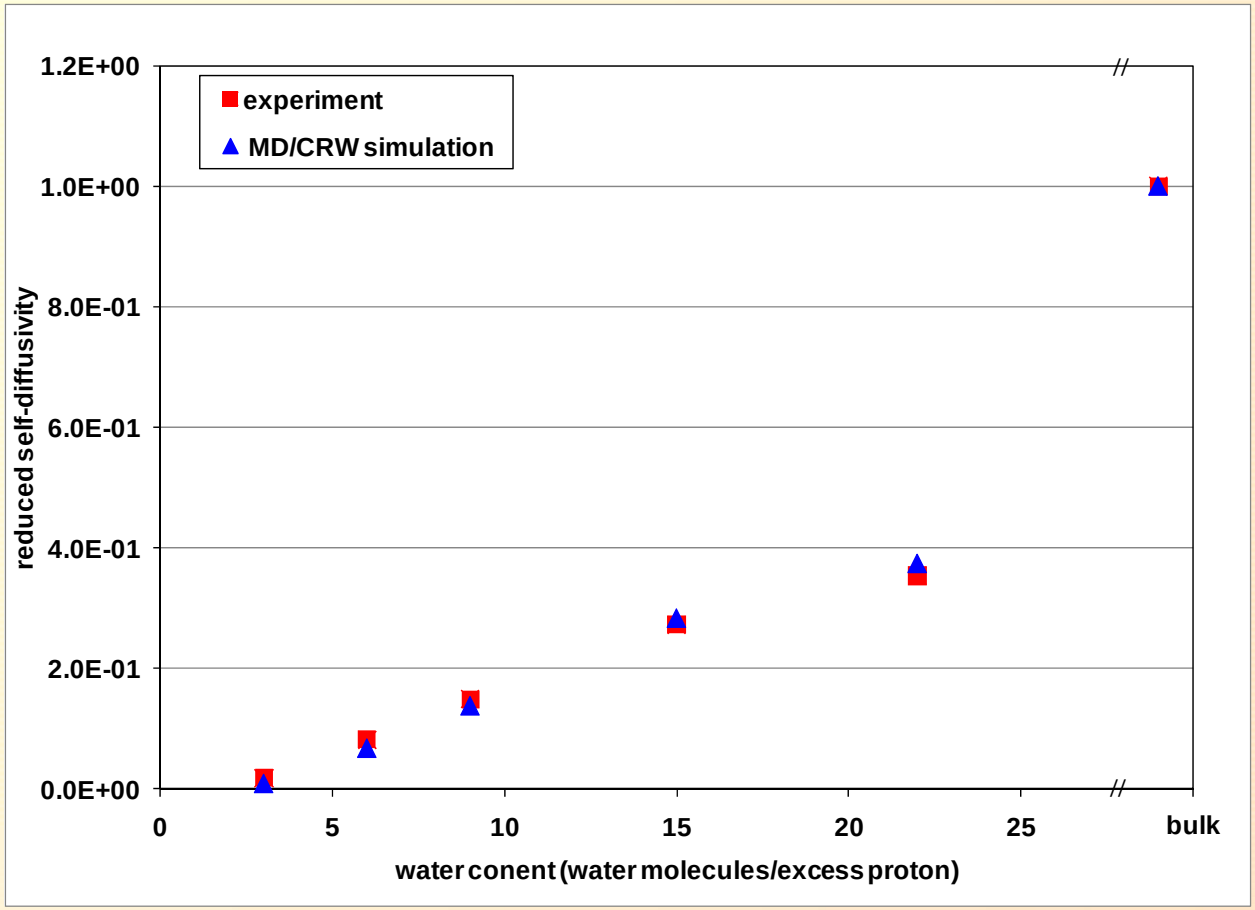


Calvo-Muñoz, E.M., Esai Selvan, M., Xiong, R., Ojha, M., Keffer, D.J., Nicholson, D.M., Egami, T", *Phys. Rev. E*, **83**(1) 2011 article # 011120.

- Fit MD results (1 ns) to Confined Random Walk (CRW) Theory.
- Extend Mean Square Displacement to long-time limit (100 ns).
- Extract water diffusivity.

Comparison of MD/CRW Simulation with Experiment

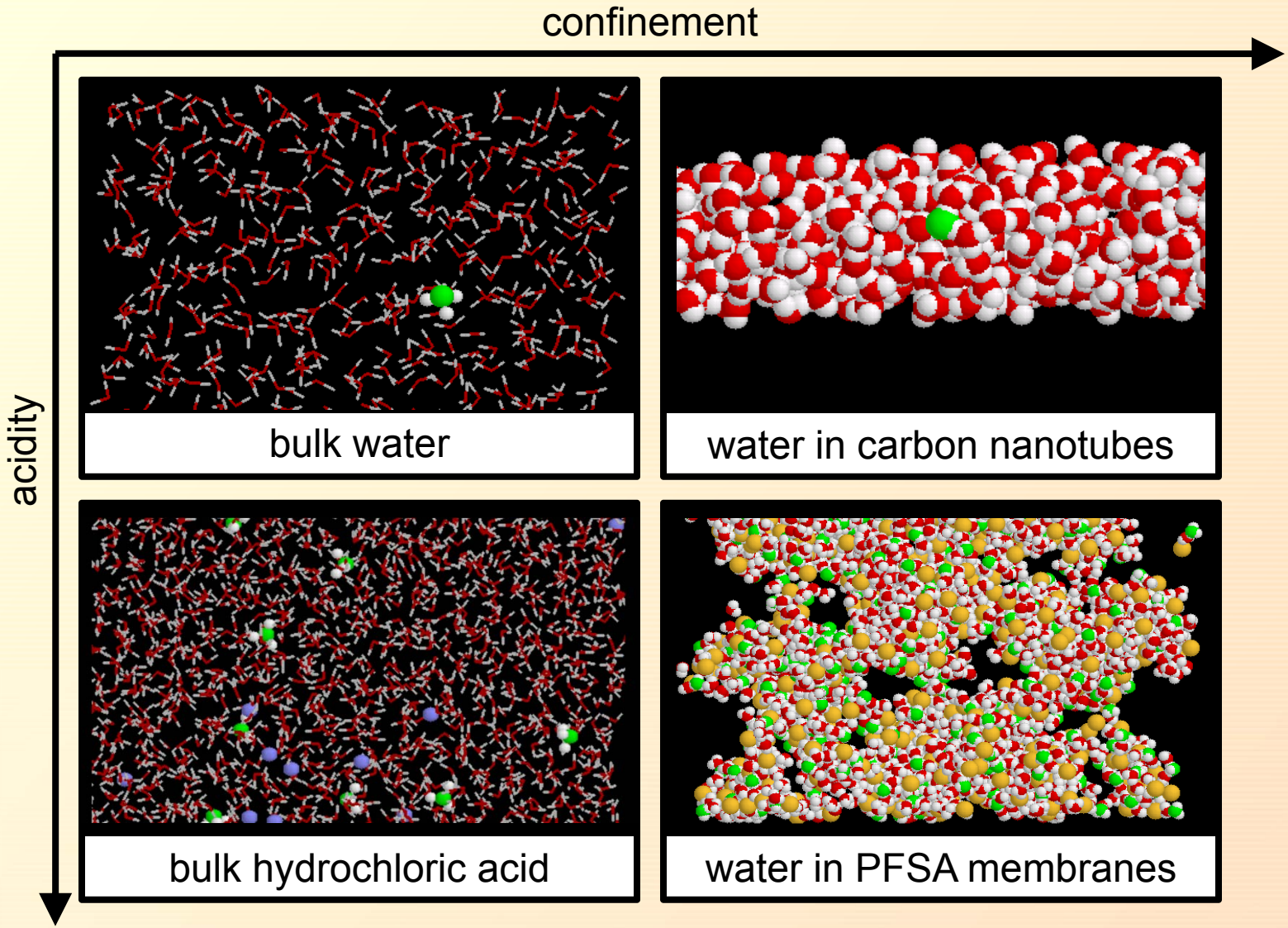
self-diffusivity of water



Robison, R. A.; Stokes, R. H. *Electrolyte Solutions*; 1959.
Nafion (EW=1100,) Kreuer, K. D. *Solid State Ionics* **1997.**
Esai Selvan, M., Calvo-Muñoz, E.M., Keffer, D.J., *J. Phys. Chem. B*, dx.doi.org/10.1021/jp1115004 , 2011.

- Excellent agreement between simulation and experiment for water diffusivity as a function of water content
- Can we predict the self-diffusivity of water without computationally expensive simulations?

Acidity and Confinement Effects on Proton Mobility

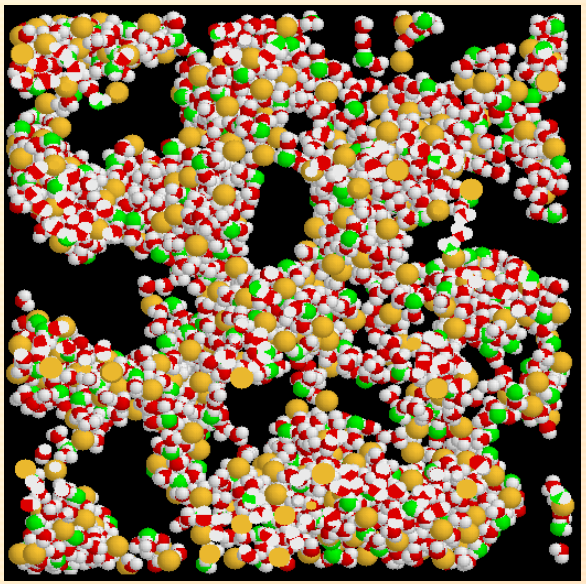


Water Mobility in Bulk Systems – Effect of Connectivity

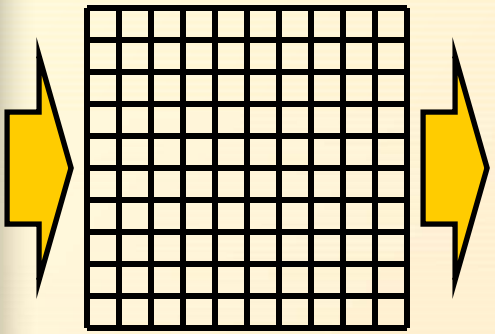
Invoke Percolation Theory to account for connectivity of aqueous domain within PEM and obtain effective diffusivity.

$$\int_0^{\infty} \frac{D_{eff} - D}{\left(\frac{z}{2} - 1\right) D_{eff} + D} g(D) dD = 0$$

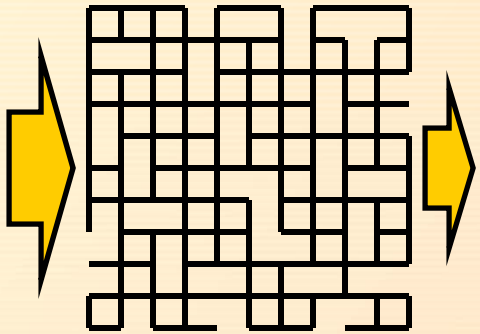
$$g(D) = p_{EMA}\delta(D - D_b) + (1 - p_{EMA})\delta(D - D_o)$$



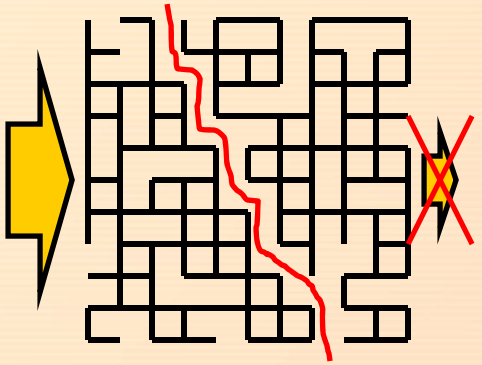
Percolation theory relates the effective diffusivity to the fraction of bonds that are blocked to diffusion.



no blocked bonds
$D = D_{open}$



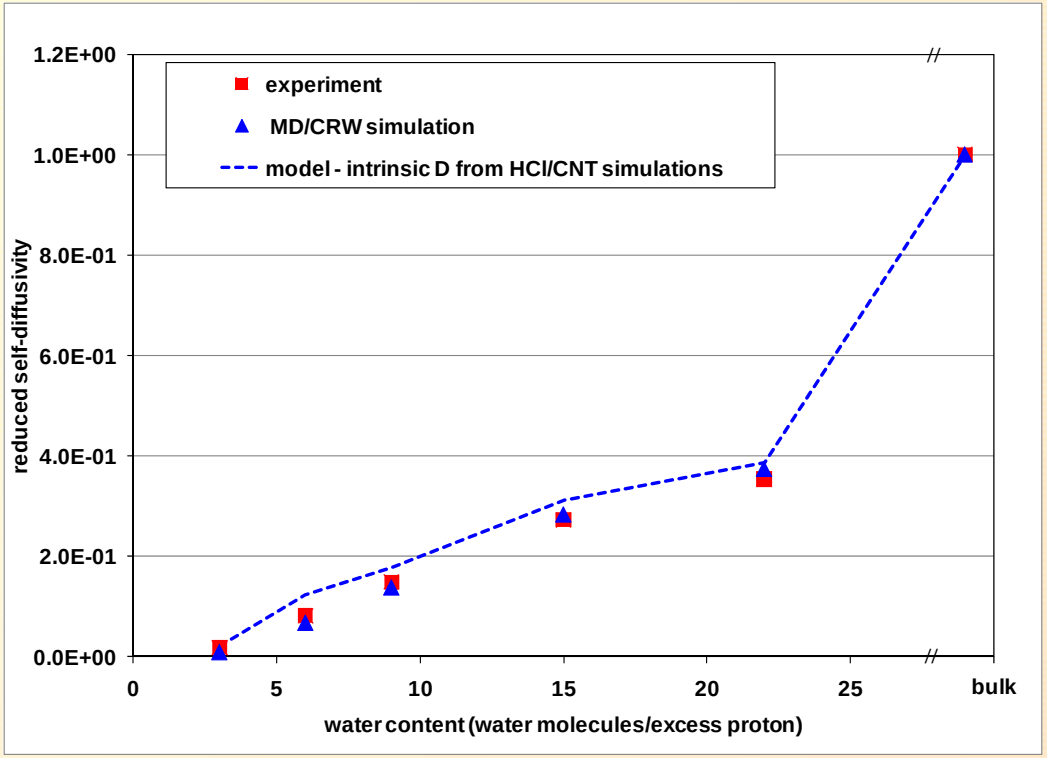
some blocked bonds
$0 < D < D_{open}$



beyond threshold
$D = 0$

Structure-Based Analytical Prediction of Self-diffusivity

- Acidity – characterized by concentration of H_3O^+ in aqueous domain
  (exponential fit of HCl data)
- Confinement – characterized by interfacial surface area
  (exponential fit of carbon nanotube data)
- Connectivity – characterized by percolation theory
  (fit theory to MD/CRW water diffusivity in PEMs)



Excellent agreement of theory with both simulation and experiment.

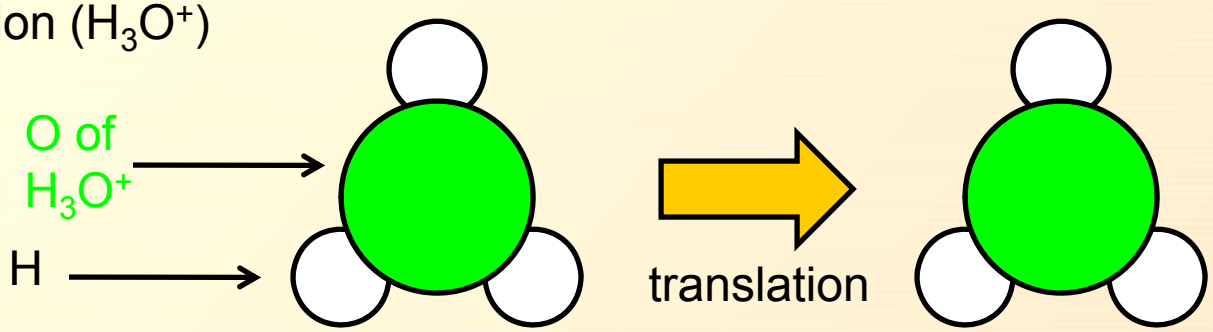
Theory uses only structural information to predict transport property.

Water is solved!
What about charge transport?

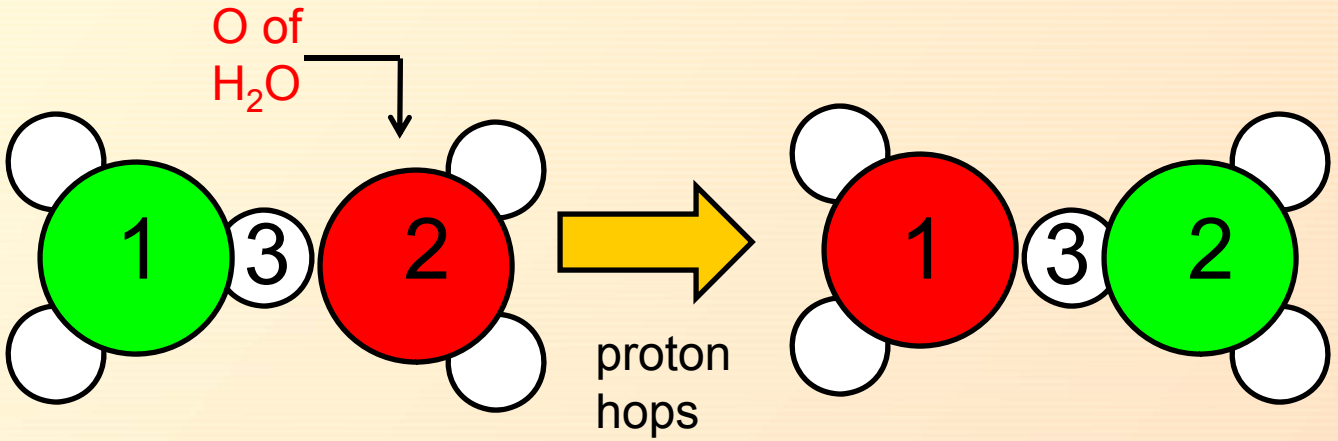
Esai Selvan, M., Calvo-Muñoz, E.M., Keffer, D.J., *J. Phys. Chem. B* **115**(12) 2011 pp 3052–3061.

Proton Transport – Two Mechanisms

Vehicular diffusion: change in position of center of mass of hydronium ion (H_3O^+)



Structural diffusion (proton shuttling): passing of protons from water molecule to the next (a chemical reaction involving the breaking of a covalent bond)

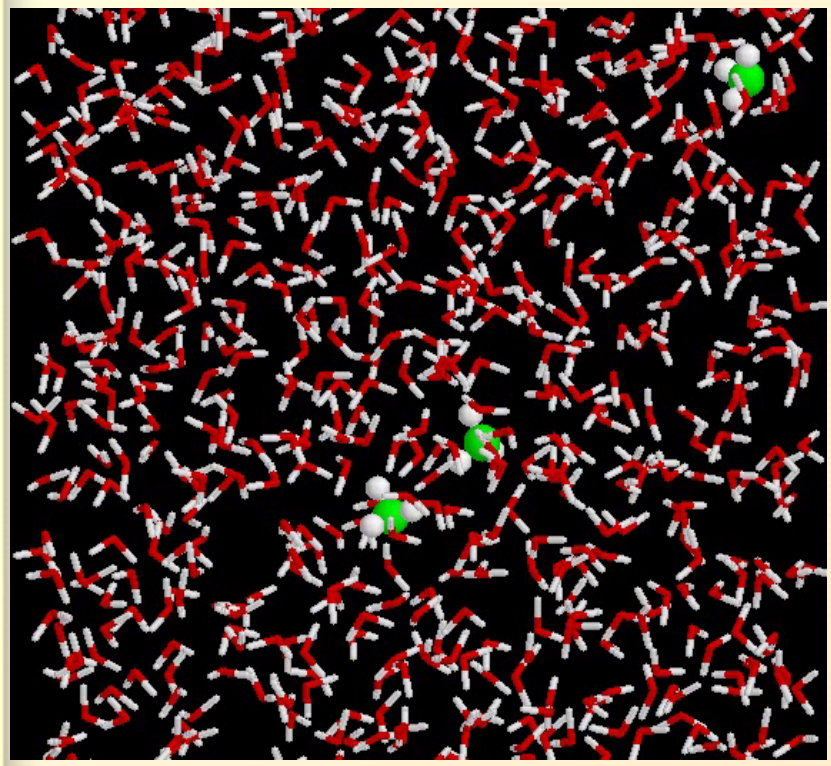


In bulk water, structural diffusivity is about 70% of total diffusivity.

RMD In Water

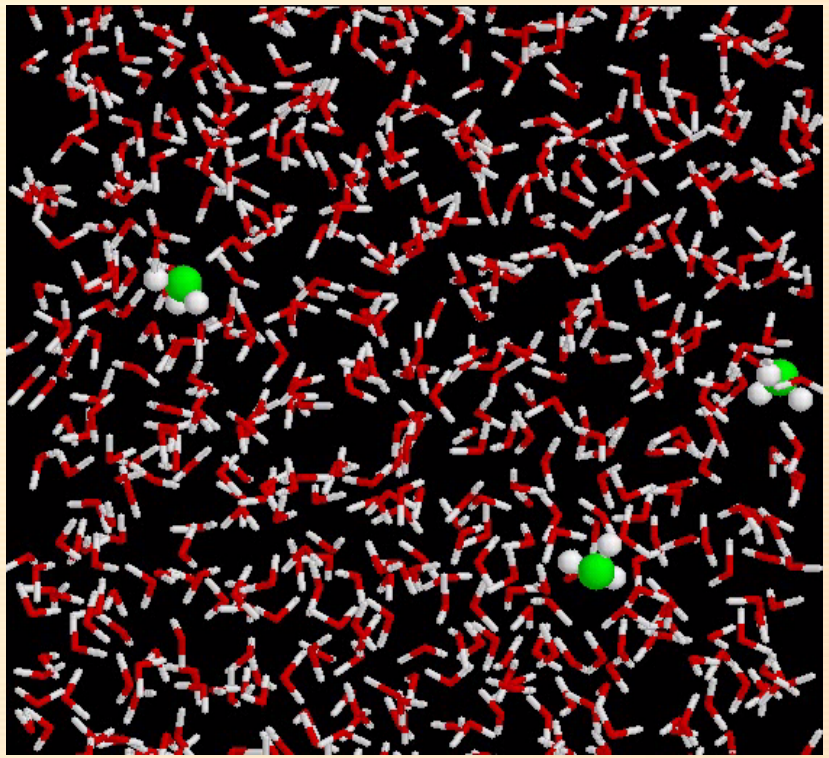
Proton Diffusion in Bulk Water

Non - Reactive System



Vehicular Diffusion

Reactive System



Structural and Vehicular Diffusion

Structure-Based Analytical Prediction of Self-diffusivity

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  (exponential fit of HCl data)
- Confinement – characterized by interfacial surface area
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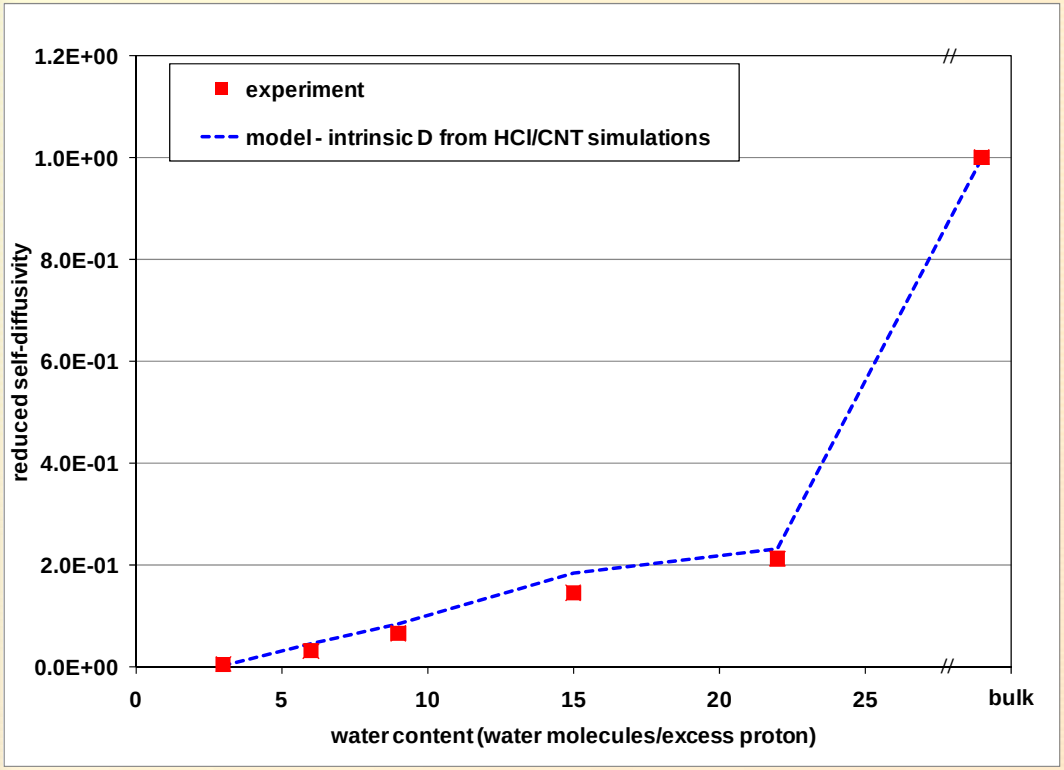
- Connectivity – characterized by percolation theory
  (fit theory to MD/CRW water diffusivity in PEMs)



Good agreement of theory with experiment.

Theory uses only structural information to predict transport property.

Proton transport is well-described by this simple model.

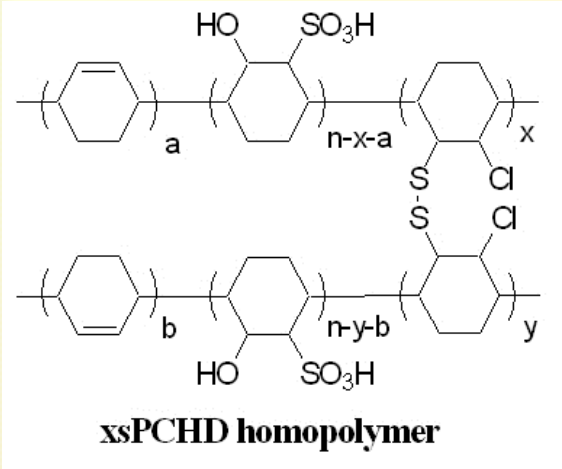
Esai Selvan, M., Calvo-Muñoz, E.M., Keffer, D.J., *J. Phys. Chem. B*, dx.doi.org/10.1021/jp1115004 , 2011.

Generalizability of the Analytical Approach

Determine the extent to which a small set of structural descriptors can be used to describe transport in nanostructured materials

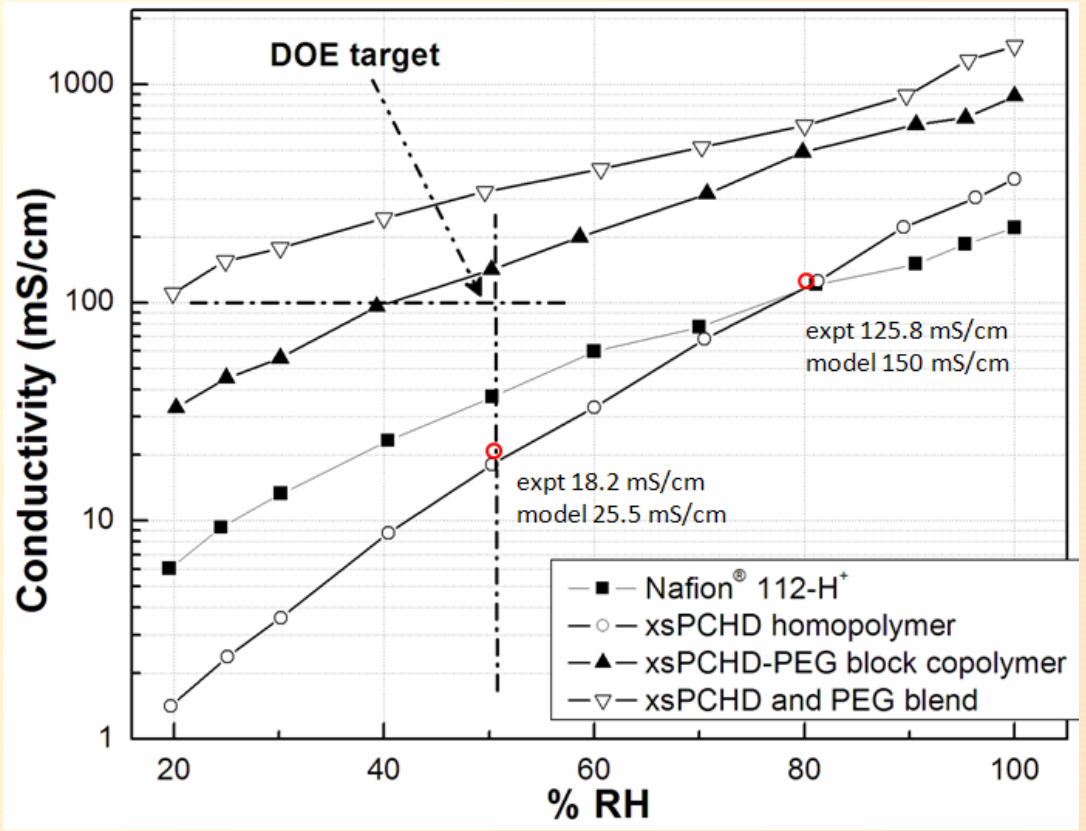
- other proton exchange membranes composed of homopolymers
- other proton exchange membranes with additives or blends
- Li+ ion transport in nanostructured electrodes

cross-linked and sulfonated Poly(1,3-cyclohexadiene)

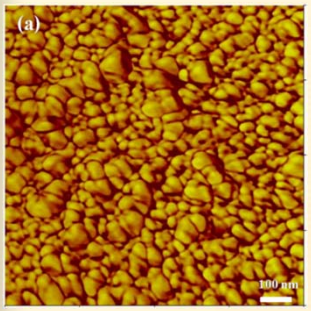


xsPCHD homopolymer

Percolation theory approach works for xsPCHD membrane as well.

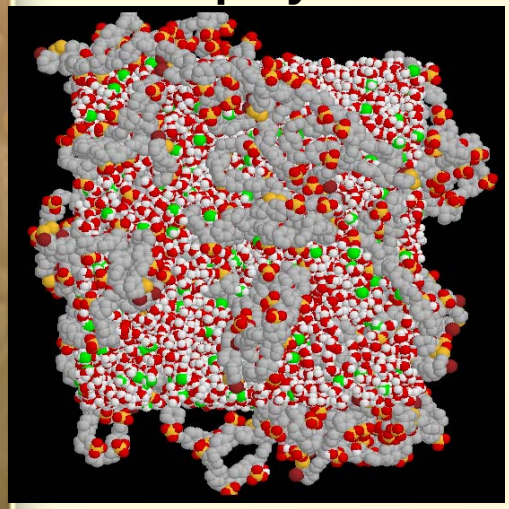
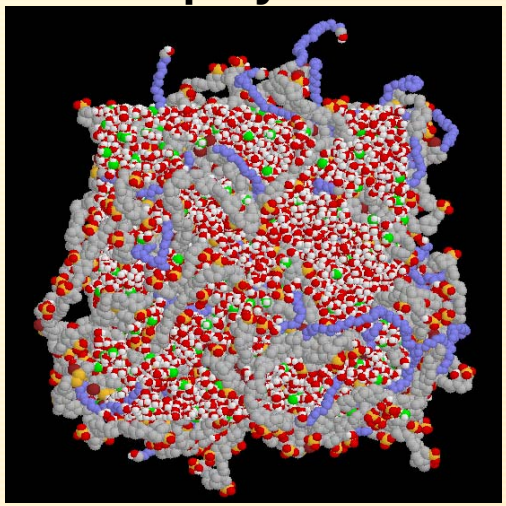
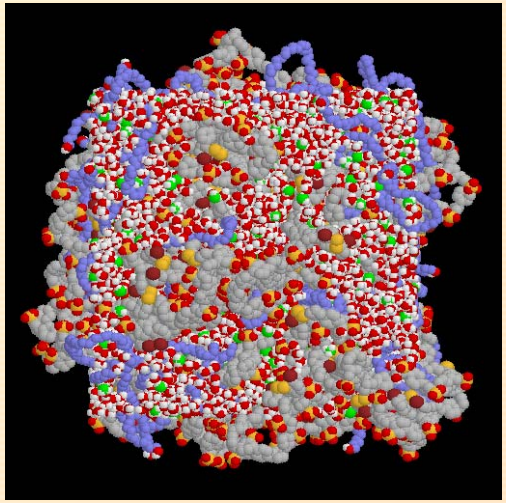
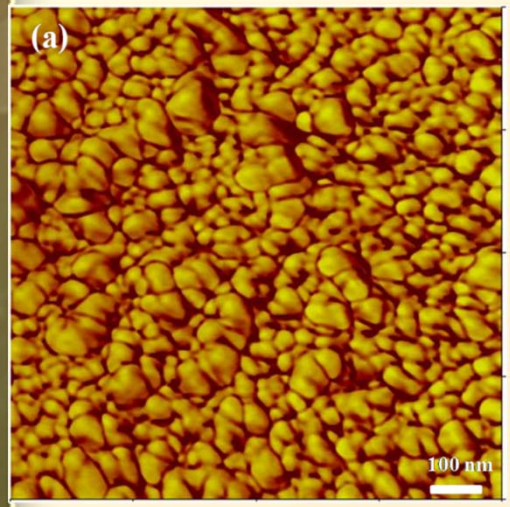
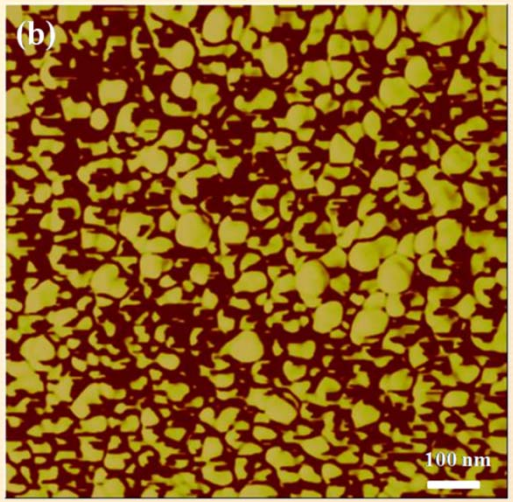
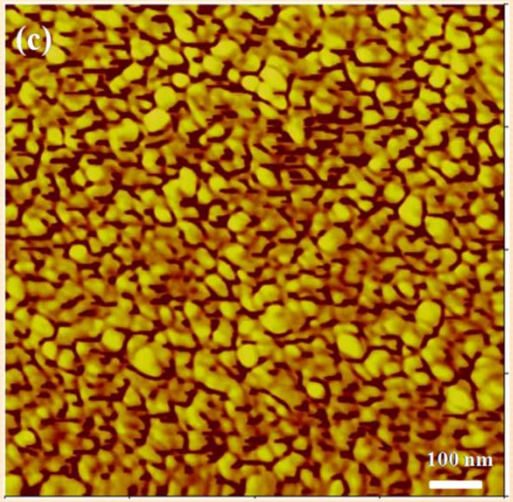


Wang, Q., Suraweera, N.S., Keffer, D.J., Deng, S., Mays, J.W., *Macromolecules*, DOI: 10.1021/ma300383z 2012.



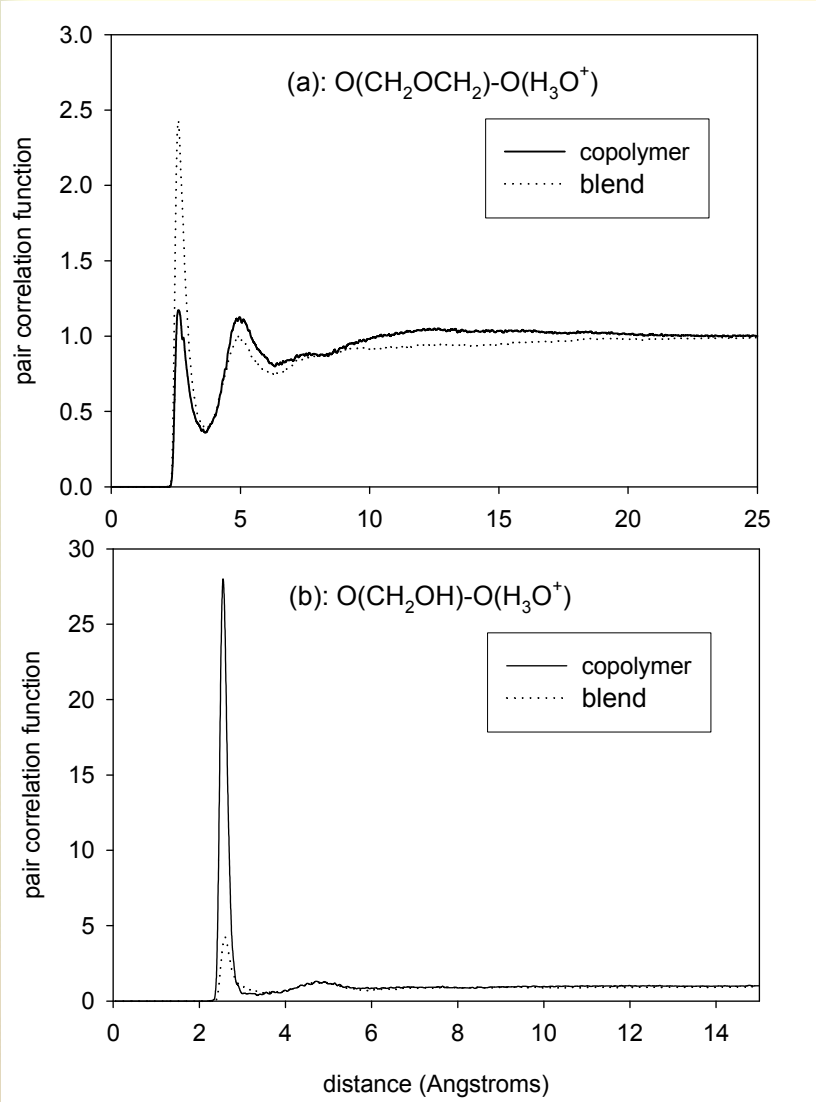
"Polymer Electrolyte Membranes with Enhanced Proton Conductivities at Low Relative Humidity based on Polymer Blends and Block Copolymers of Poly(1,3-cyclohexadiene) and Polyethylene Glycol
By *Suxiang Deng*, *Amol Nalawade*, *Mohammad K. Hassan*, *Kenneth A. Mauritz*, and *Jimmy W. Mays**
Advanced Materials, 2012, under review.

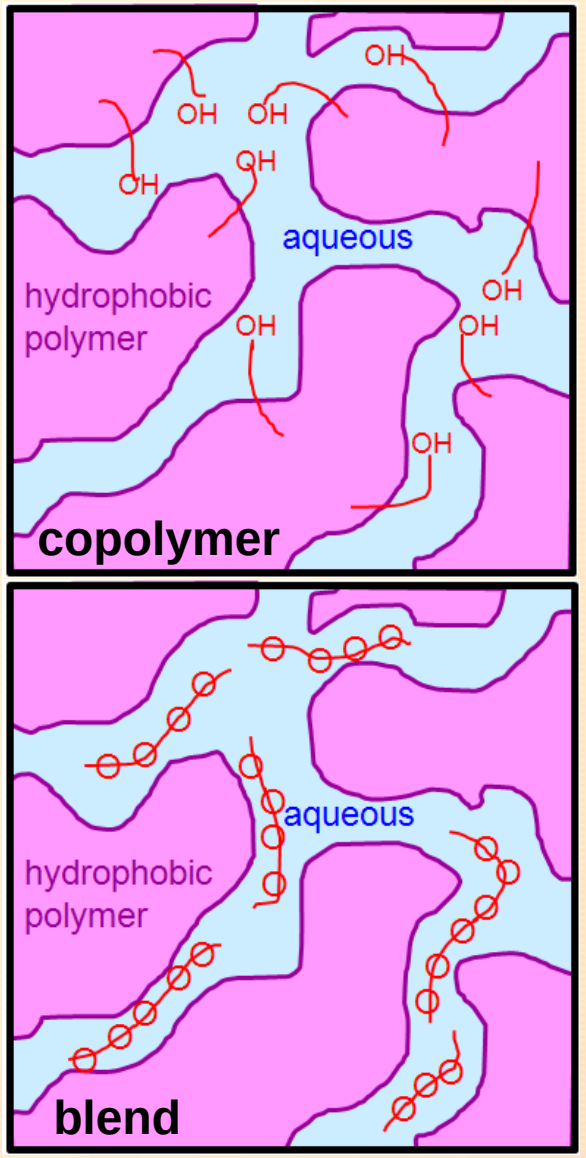
cross-linked and sulfonated Poly(1,3-cyclohexadiene)

	xs-PCHD homopolymer	xs-PCHD/PEG copolymer	xs-PCHD/PEG blend
simulation			
AFM			

xs-PCHD/PEG blend shows best performance.

xsPCHD/PEG copolymer and blend: structure





PEG: H-[OCC]$_n$-OH

Distribution of PEG in membrane is very different for copolymer and blend.

Acknowledgments

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OAK RIDGE NATIONAL LABORATORY
Managed by UT Battelle for the Department of Energy

Access to the massively parallel machines at Oak Ridge National Laboratory through the UT Computational Science Initiative.

All xsPCHD experimental data from Suxiang Deng & Prof. Jimmy Mays, UTK Chemistry.

Qifei Wang,
PhD 2011,
xsPCHD

Myvizhi Esai Selvan
PhD, 2010
Reactive MD

Junwu Liu,
PhD, 2009
MD in Nafion

Nethika Suraweera
PhD, 2012
Vol & Area Analysis

Elisa Calvo-Munoz
undergraduate
Random Walks

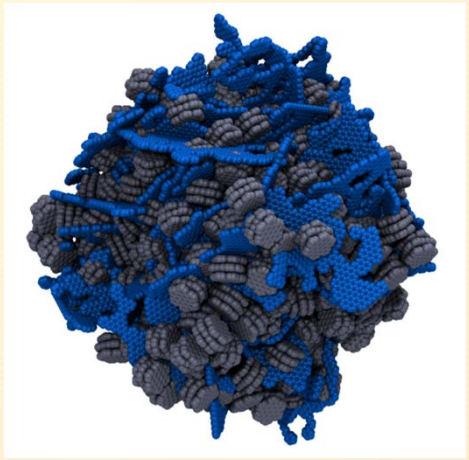
THE UNIVERSITY of TENNESSEE

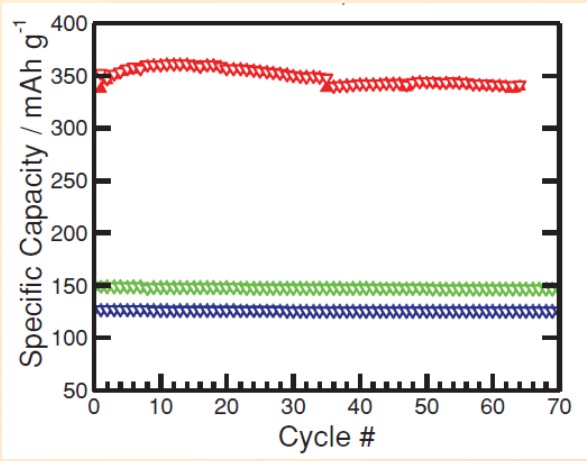
Multiscale Modeling of Carbon Composite Electrodes From Renewable Materials

David J. Keffer[1], Nicholas W. McNutt, Khorgolkhuu Odbadrakh & Orlando Rios[2]
[1]University of Tennessee & [2]Oak Ridge National Laboratory

dkeffer@utk.edu

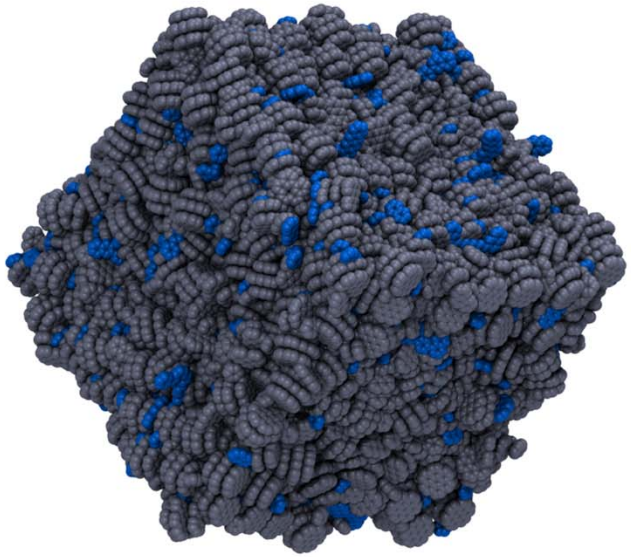
Objective: The objective of this work is to understand the molecular-level mechanisms responsible for the exceptionally high ion storage and fast charging and discharging rates observed in the novel lignin-based carbon composite electrodes synthesized by Rios at ORNL. This knowledge can be used to further guide development of improved materials for battery electrode applications.





Molecular Models of Experimentally Synthesized Composites

Pyrolysis temperature controls nanostructure.



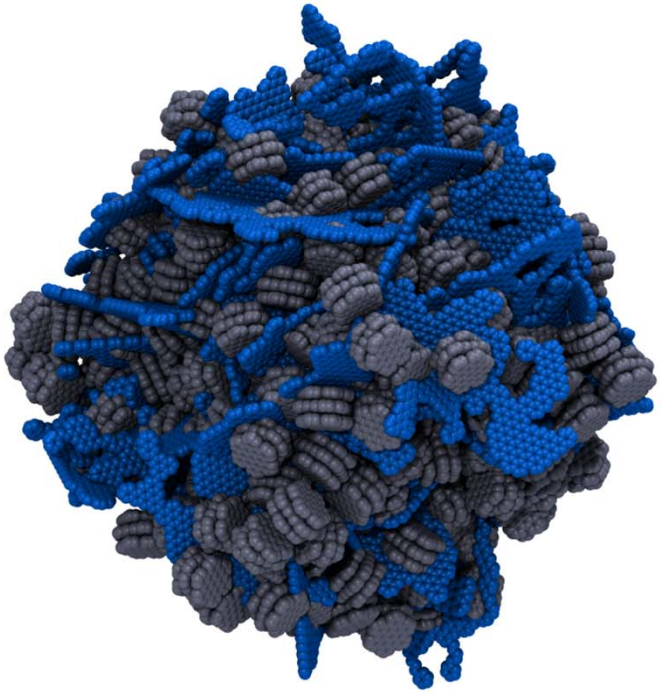
1000 K

r_c = 5 Å

Φ_c = 0.9

ρ = 1.94 g/cm^3

The composite materials are composed of graphitic nanocrystallites (gray) and amorphous carbon (blue).



1500 K

r_c = 7 Å

Φ_c = 0.5

ρ = 1.51 g/cm^3

2000 K

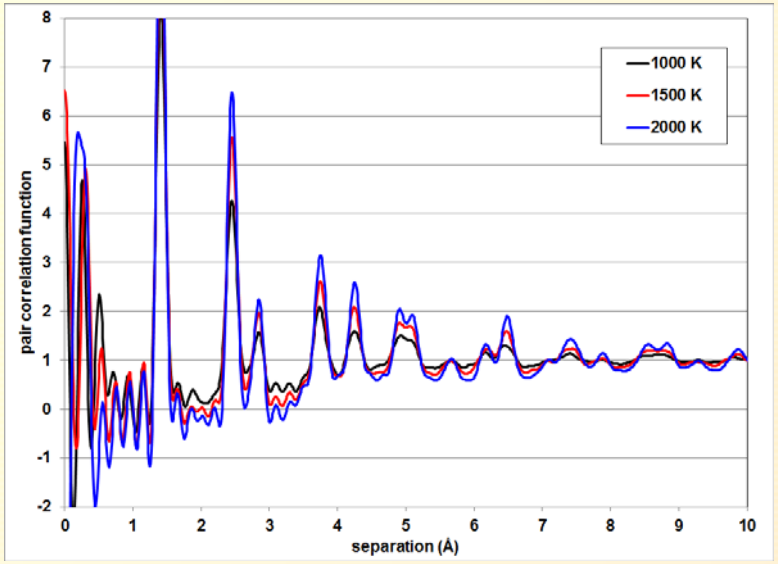
r_c = 17 Å

Φ_c = 0.1

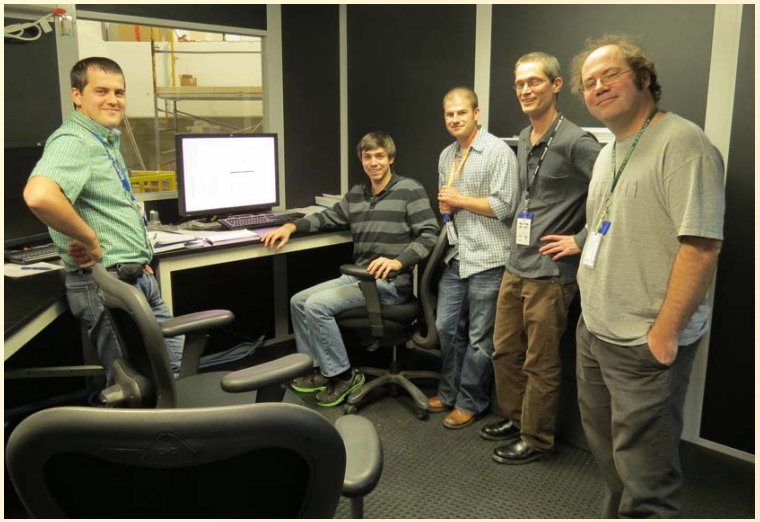
ρ = 1.38 g/cm^3

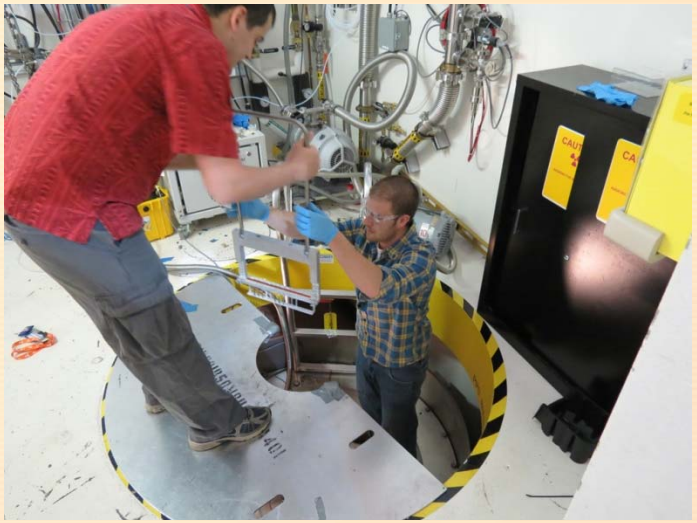
These models capture experimental crystallite size, crystalline volume fraction and total density.

Neutron Diffraction from NOMAD

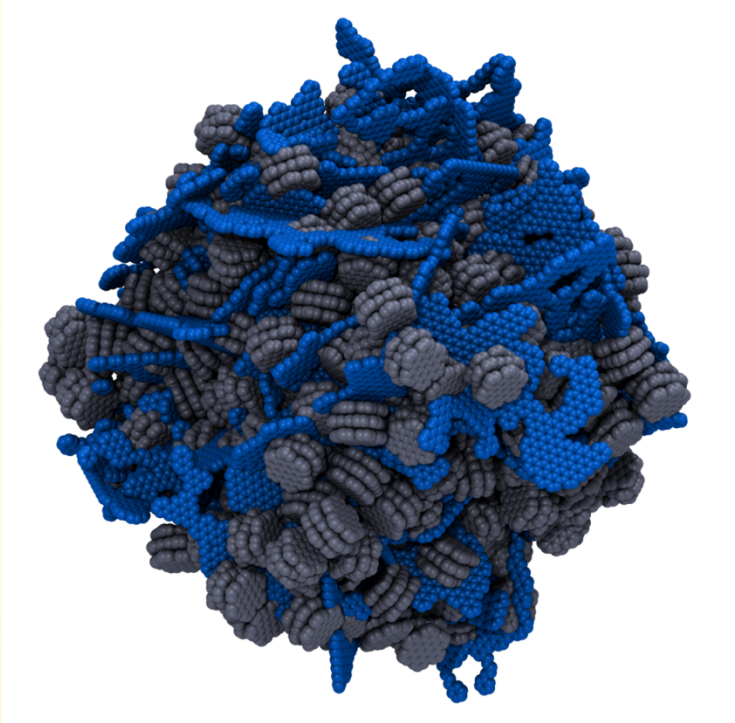


NOMAD is a high-flux, medium-resolution diffractometer that uses a large bandwidth of neutron energies and extensive detector coverage to carry out structural determinations of local order in crystalline and amorphous materials.





Interpretation of Nomad Data



1500 K	
r_c	= 7 Å
Φ_c	= 0.5
ρ	= 1.51 g/cm^3

Process

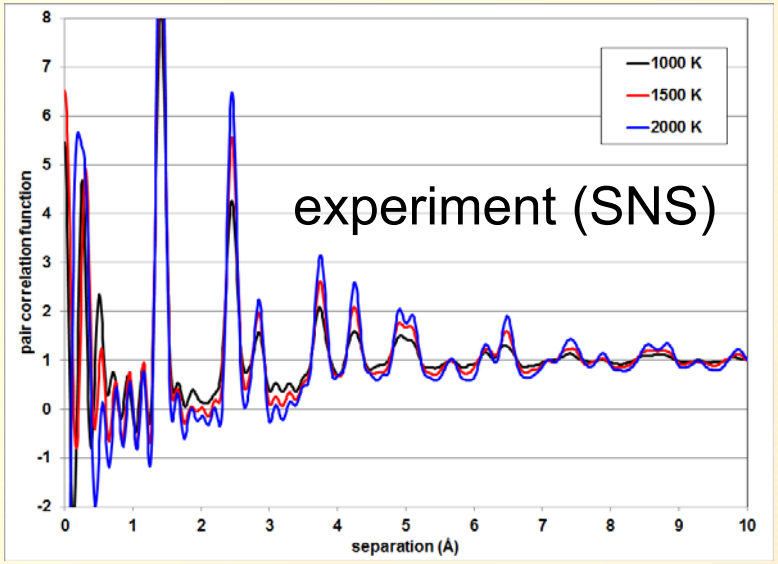
Modelers use their knowledge and imagination to hypothesize structures.

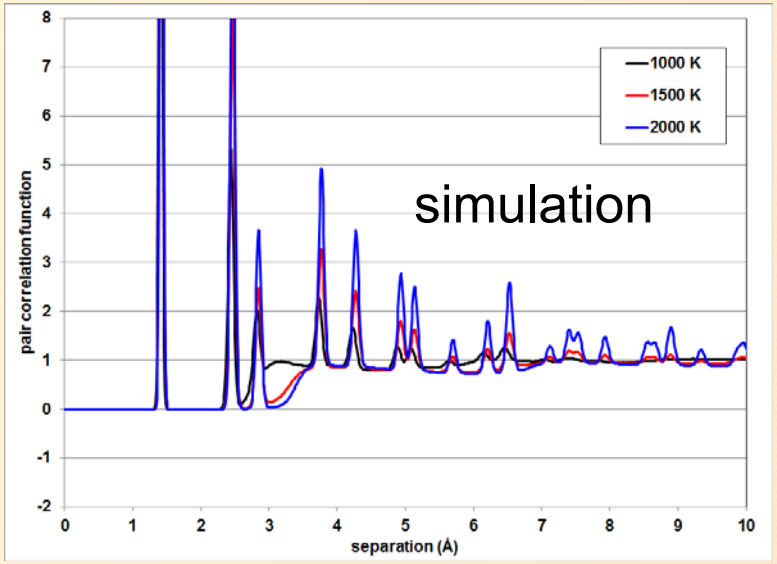
Perform MD simulations.

Generate pair correlation functions (PCFs).

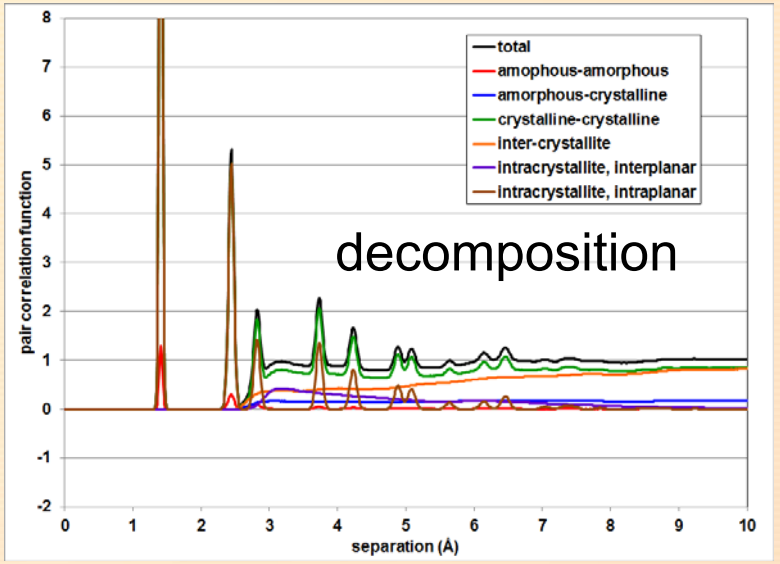
Compare simulated and experimental PCFs.

Composite Models Provide Interpretation of Neutron Data

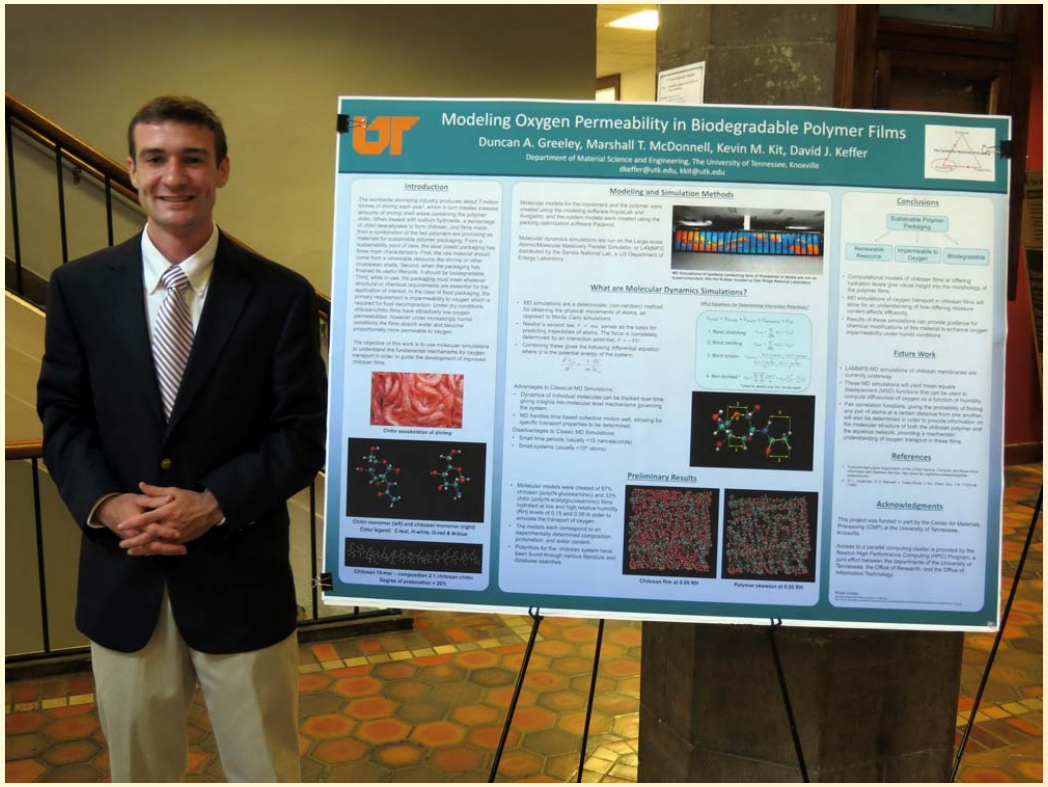


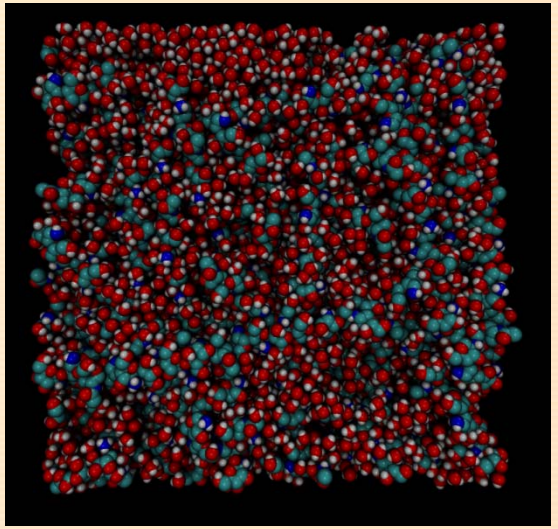


Neutron diffraction data from the SNS (top left) are difficult to interpret for even partially amorphous materials. However, clear trends are seen with respect to pyrolysis temperature. Pair correlation functions (PCFs) for the corresponding models (top right) provide clean, unambiguous data. Moreover, the simulated PCFs can be completely decomposed (right) to reveal the structural origins of all features in the spectra, providing clear understanding of the experimental data from the SNS.



Undergraduates Perform Research in MSE at UT





Duncan Greeley performs MD simulations of oxygen transport in chitosan films to provide insight into biodegradable plastics made from renewable resources. (2013)

Conclusions

- The search for renewable energy sources and systems is the defining challenge of your generation.
- Materials Scientists & Engineers play a critical role in this search for sustainability.
- Students in the Materials Science & Engineering Department at the University of Tennessee are performing state-of-the-art research using the world's best supercomputers and neutron sources to develop new materials for alternative energy systems.
- Multiscale Materials Modeling is a complementary tool to experiment, providing unique insight.
- Experimental/Computational collaborations are fruitful and fun!

Questions?