THE UNIVERSITY of TENNESSEE

STAIR
Sustainable Technology through Advanced Interdisciplinary Research

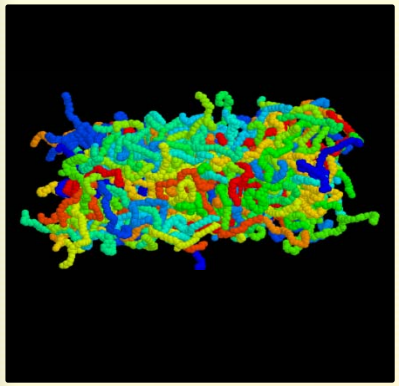
Multiscale Modeling of Materials

David Keffer
Dept. of Materials Science & Engineering
The University of Tennessee
Knoxville, TN 37996-2100
dkeffer@utk.edu
http://clausius.engr.utk.edu/

ASM Summer Materials Camp
University of Tennessee, Knoxville
June 18, 2014

multiscale materials modeler

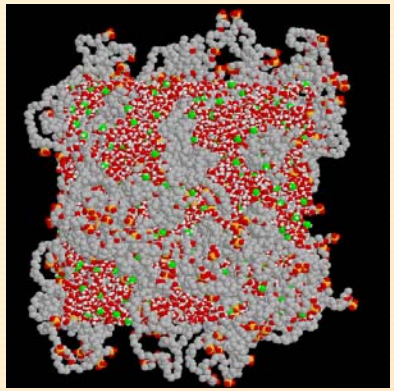
Apply molecular simulation to develop structure/property relationships

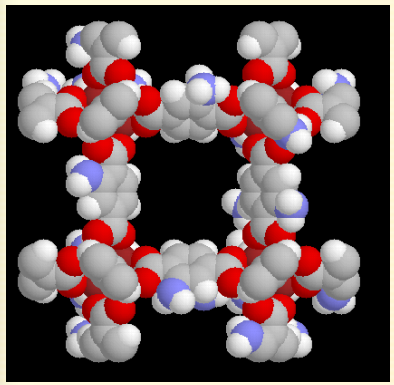


polymeric materials

polymers at equilibrium and under flow (PE, PET)

polymer electrolyte membranes (PEMs) in fuel cells

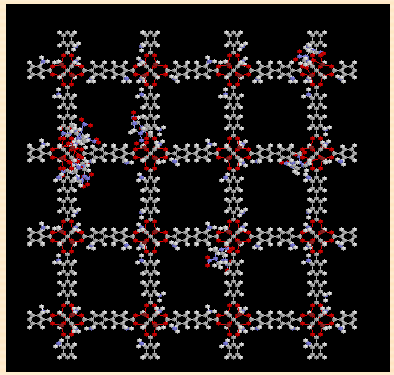


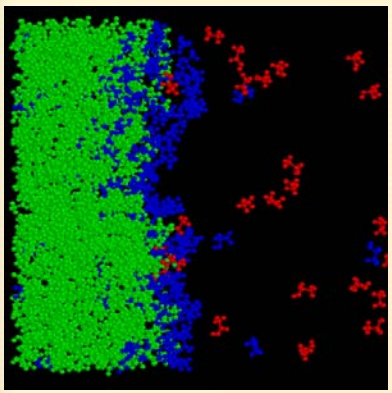


nanoporous materials

hydrogen sorption in metal organic frameworks (MOFs)

Sensing of RDX, TATP and other explosives in MOFs

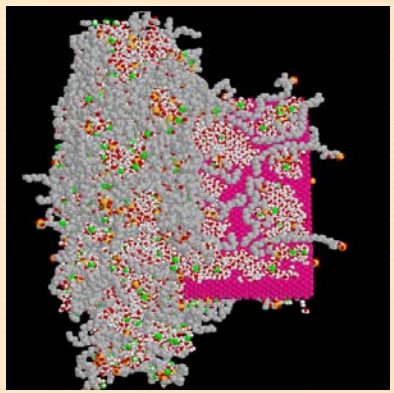




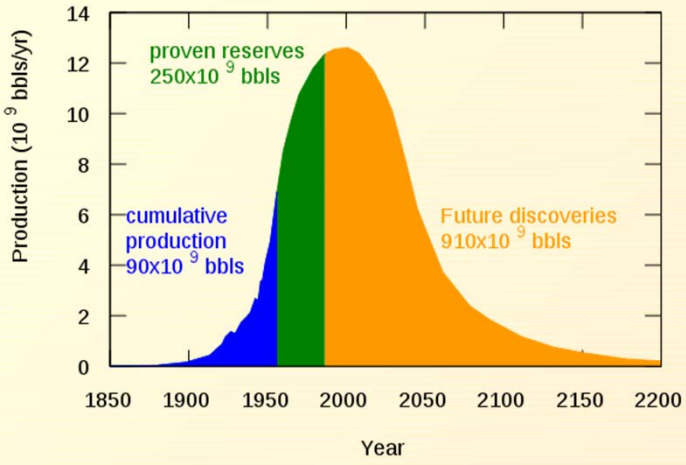
interfacial systems

near critical vapor-liquid interface structure

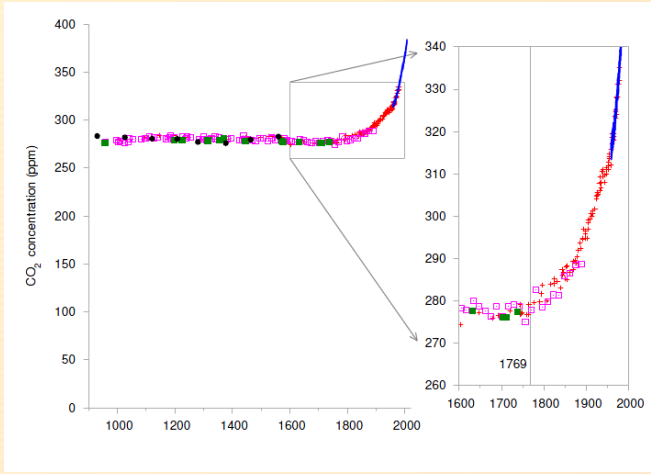
fuel cell electrode/ electrolyte interfaces



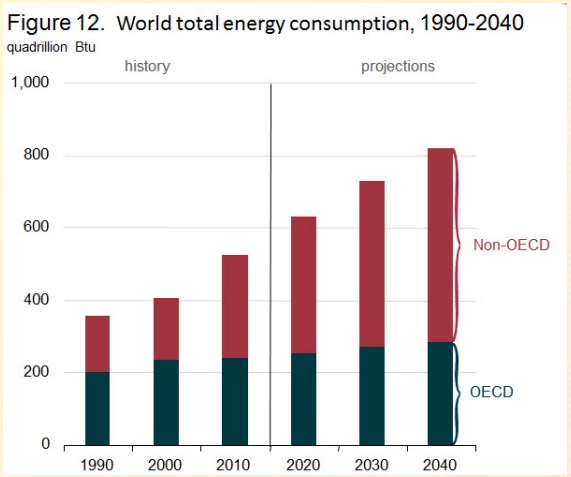
Renewable Energy: The Defining Challenge of Your Generation



Peak Oil
Fossil fuels are a finite resource
http://en.wikipedia.org/wiki/Peak_oil

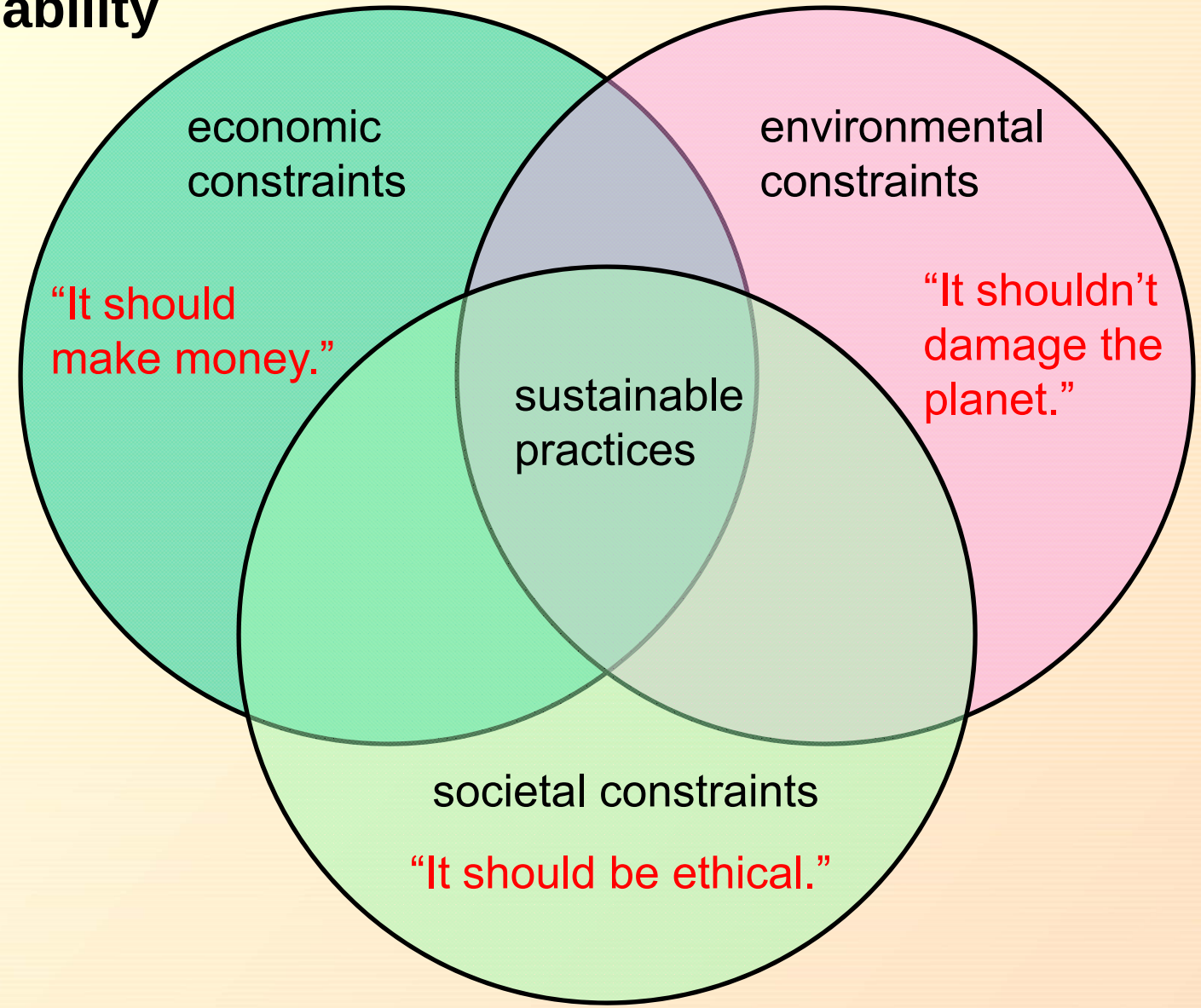


Climate Change
Atmospheric CO_2 over the past 1100 years
Sustainability without the Hot Air, MacKay



Global Energy Demand is Rising
http://www.eia.gov/forecasts/ieo/world.cfm

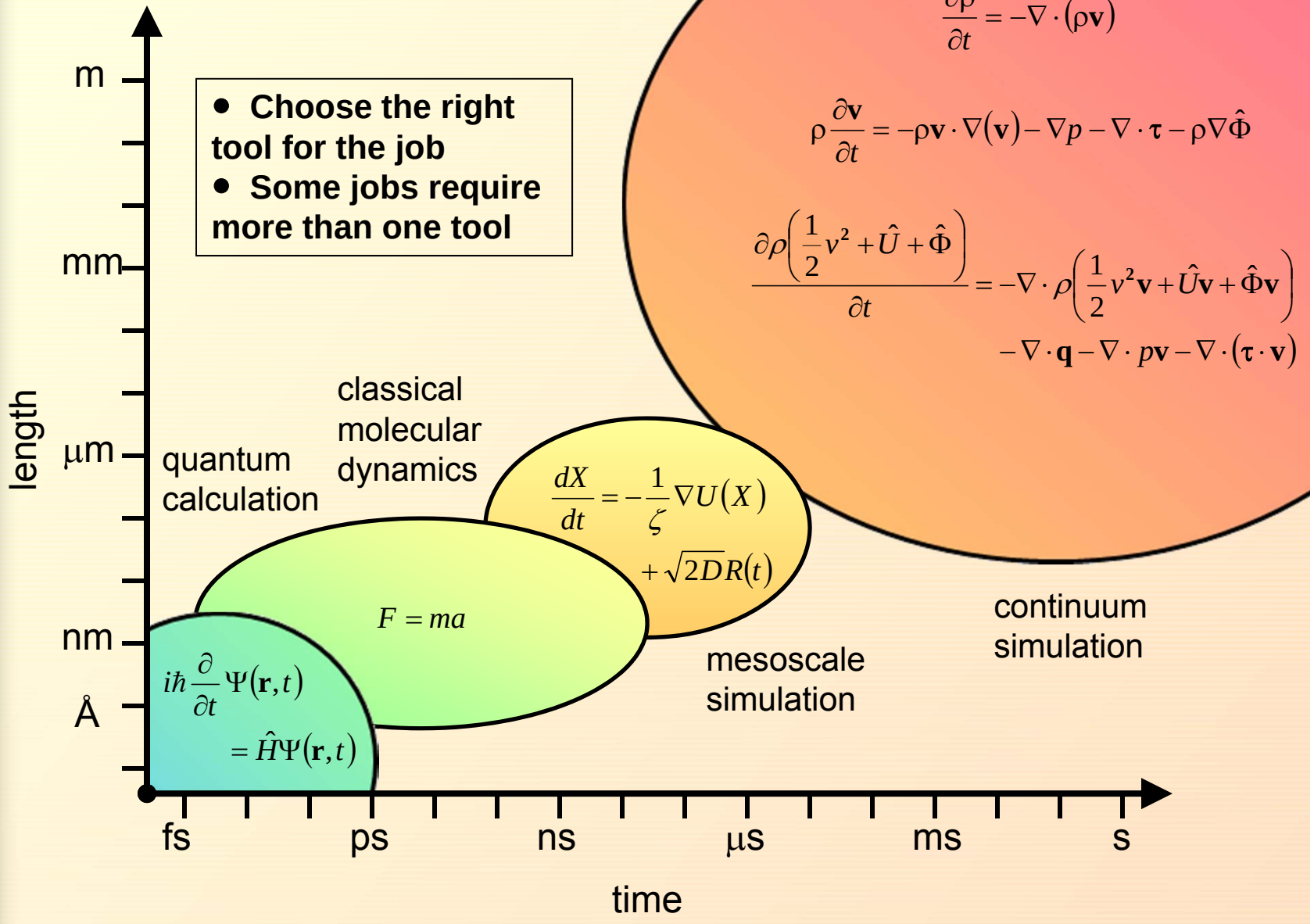
Sustainability



Interdisciplinary problem: Materials Scientists play critical role.

Time and Length Scales

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



Molecular Dynamics (MD) Simulation

Newton

MD is a deterministic method.
To simulate N atoms in 3-D, you must solve a set of 3N coupled nonlinear ordinary differential equations.

$$F = ma$$

The force is completely determined by an interaction potential.

$$F \equiv -\nabla U$$

The ODE for particle i in dimension α is thus

$$\frac{d^2 x_{i,\alpha}}{dt^2} = -\frac{1}{m}\frac{\partial U}{\partial x_{i,\alpha}}$$

We must provide an interaction potential from either theory, quantum mechanical calculations or experiment.

- Numerically integrate the equations of motion.
- Limited to relatively small systems (10^6 particles) and short times (10 ns).
- Use MPI to parallelize code.

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.

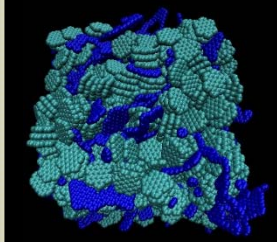
To solve systems of ODEs (largest system thus far is several million), we use the massively parallel supercomputers at ORNL.

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

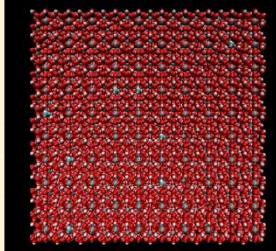
THE UNIVERSITY of TENNESSEE

STAIR
Sustainable Technology through Advanced Interdisciplinary Research

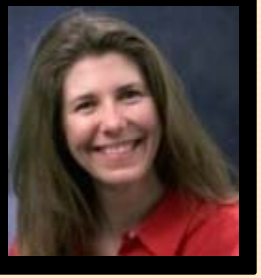
A Complementary Tool: Experimental Collaborators (2013)

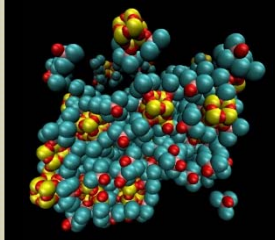


Orlando Rios
(ORNL)
nanostructured battery electrodes

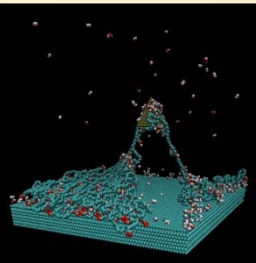


Claudia Rawn
(UT MSE)
methane & carbon dioxide hydrates



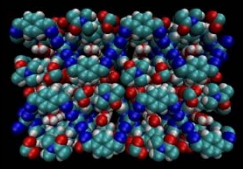


Craig Barnes
(UT Chem)
nanostructured single-site catalysts

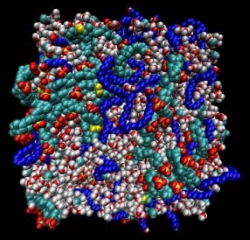


David Joy
(UT MSE/ORNL)

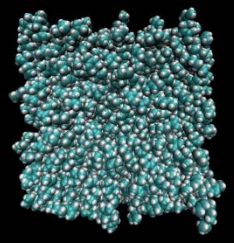
PEM fuel cell catalyst layer



David Jenkins
(UT Chem)
breathable metal-organic nanotubes

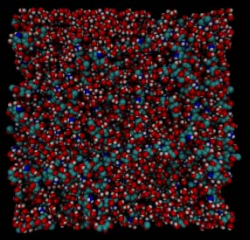


Jimmy Mays
(UT Chem/ORNL)
fuel cell proton exchange membranes



Bob Compton
(UT Phys)

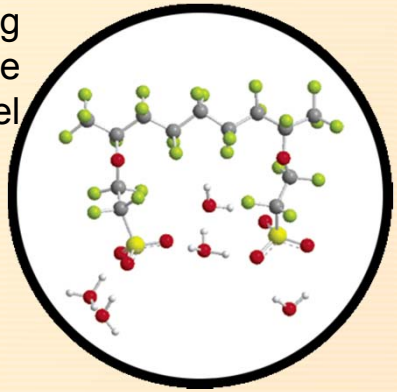
racemic mixtures



Kevin Kit
(UT MSE)
renewable polymer films

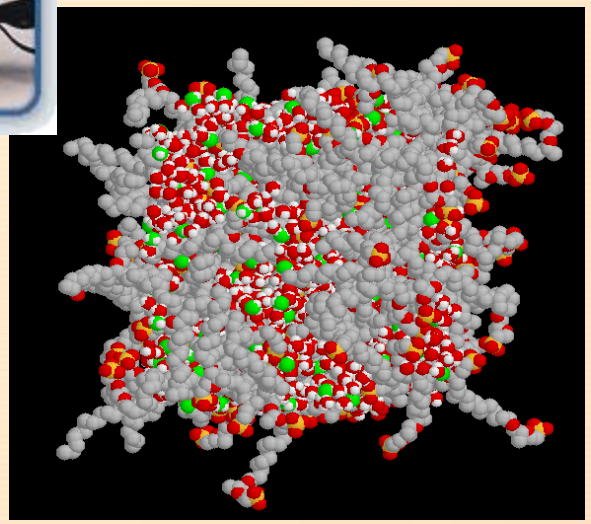
Moving toward fuel cell-powered vehicles

understanding starts at the quantum level



H_2-powered autos become a reality

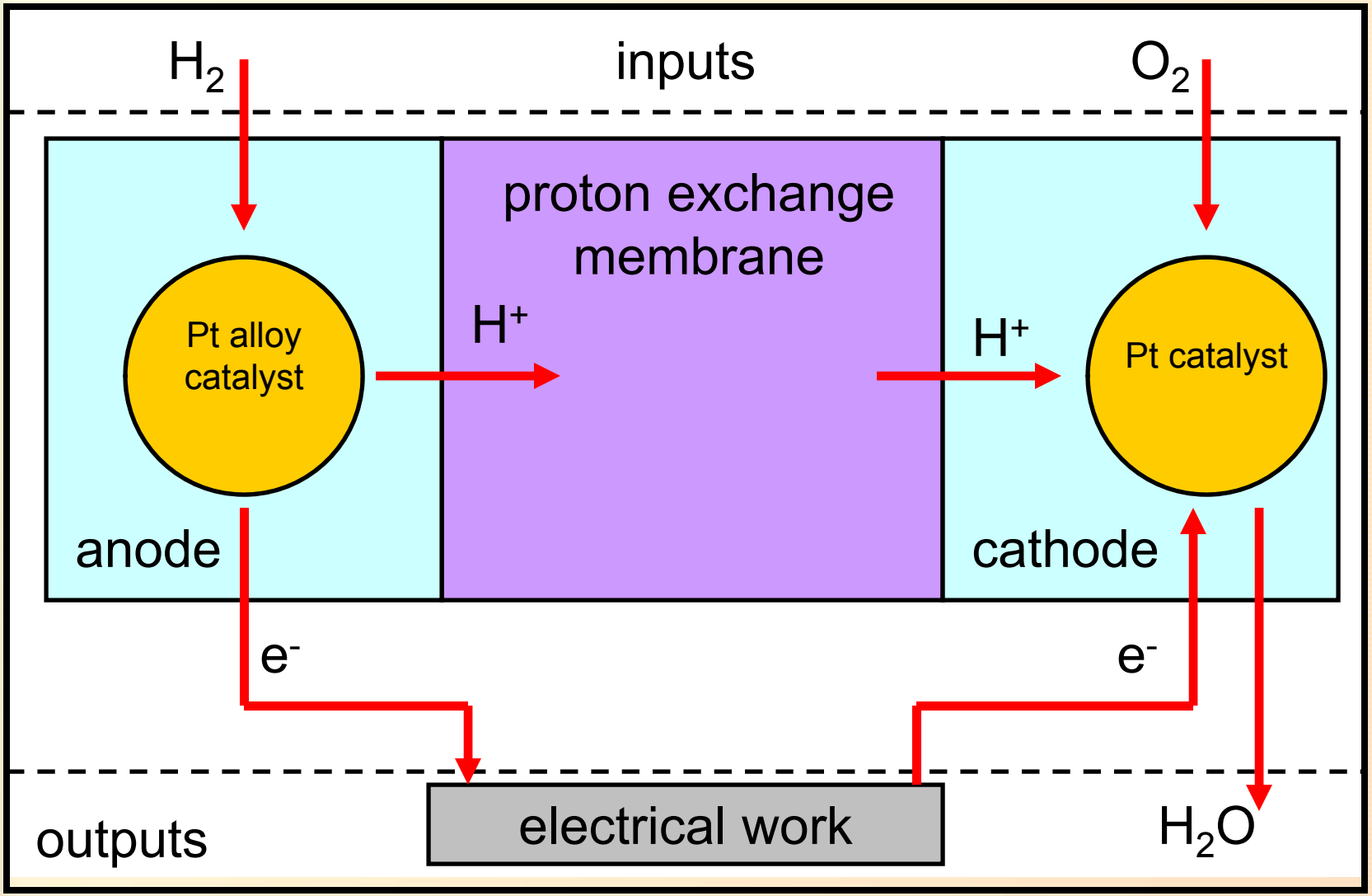
leads to high-fidelity coarse-grained models



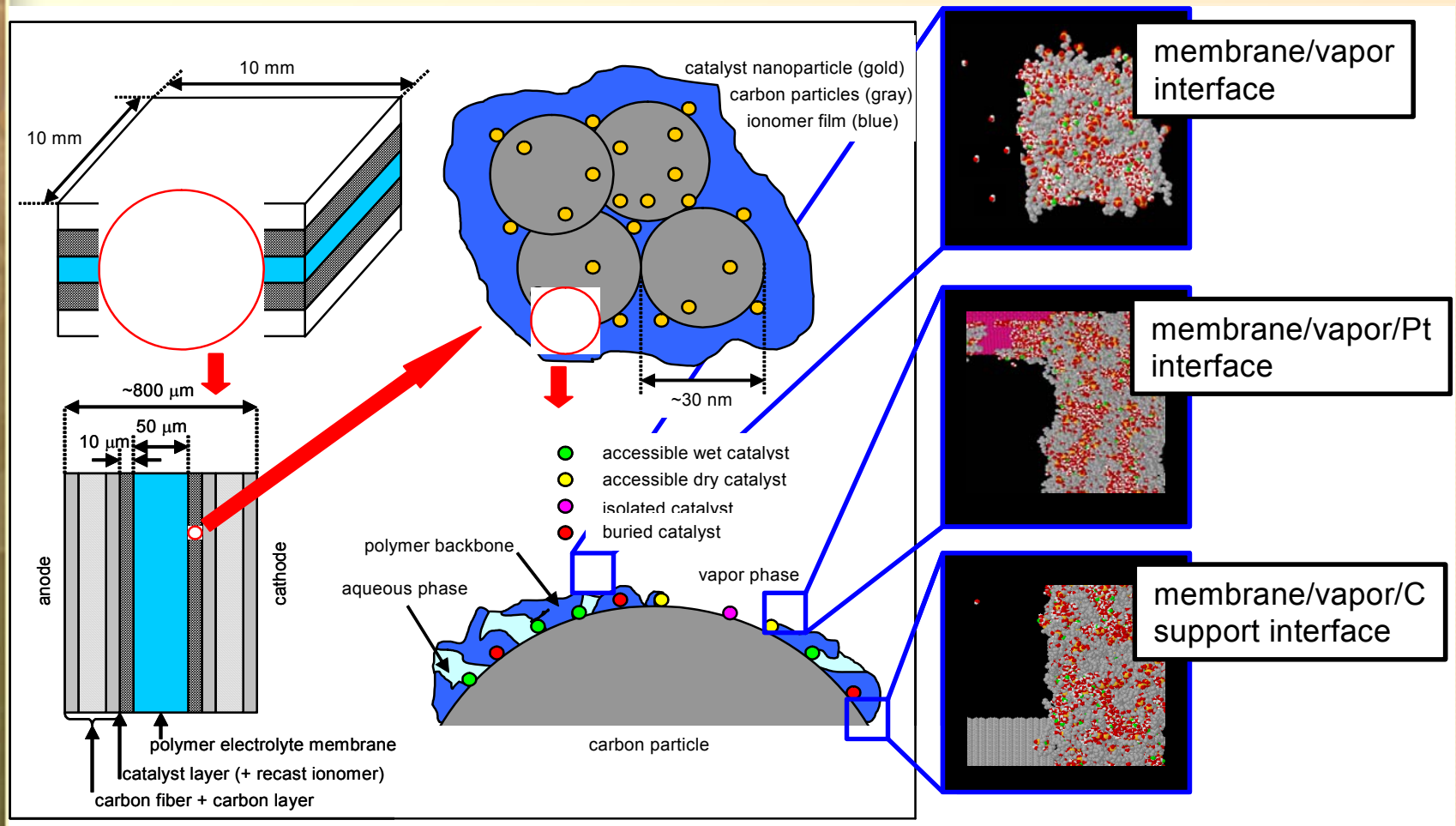
impacts fuel cell performance

improved nanoscale design of membrane/electrode assembly

how fuel cells work: conceptual level



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

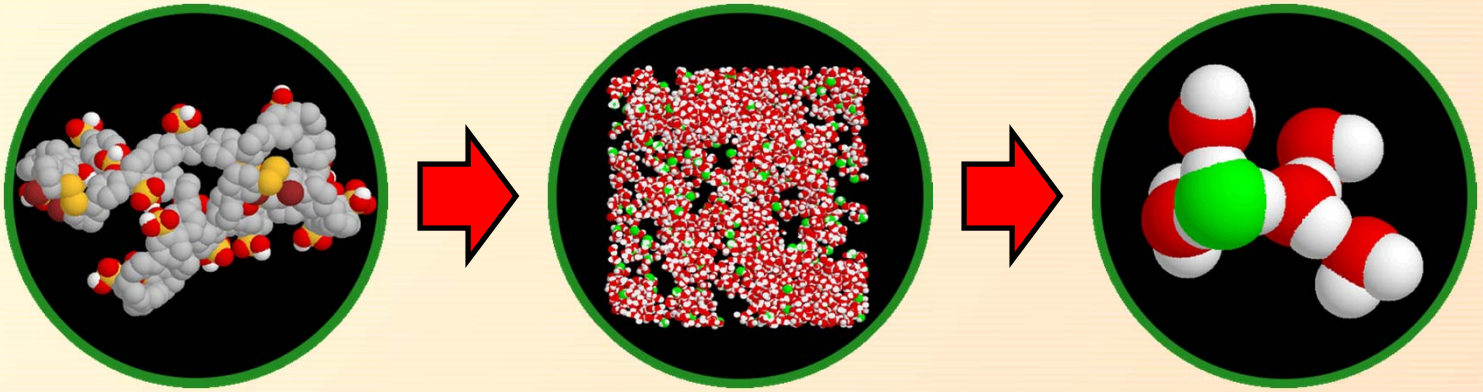


A membrane electrode assembly from the macroscale to the molecular scale.

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?**



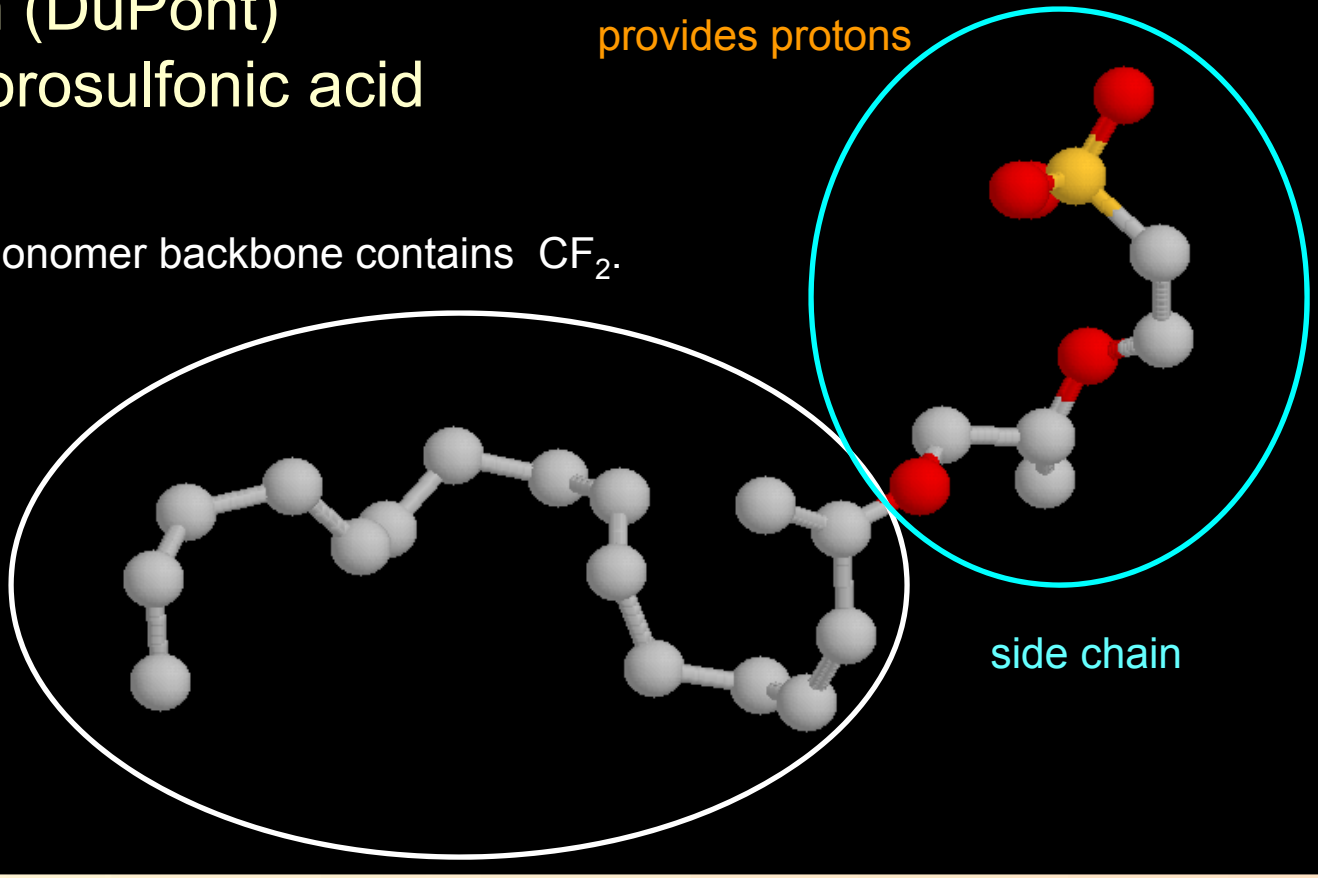
polymer chemistry **membrane morphology** **proton transport**

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.



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

Motivation for new proton exchange membranes

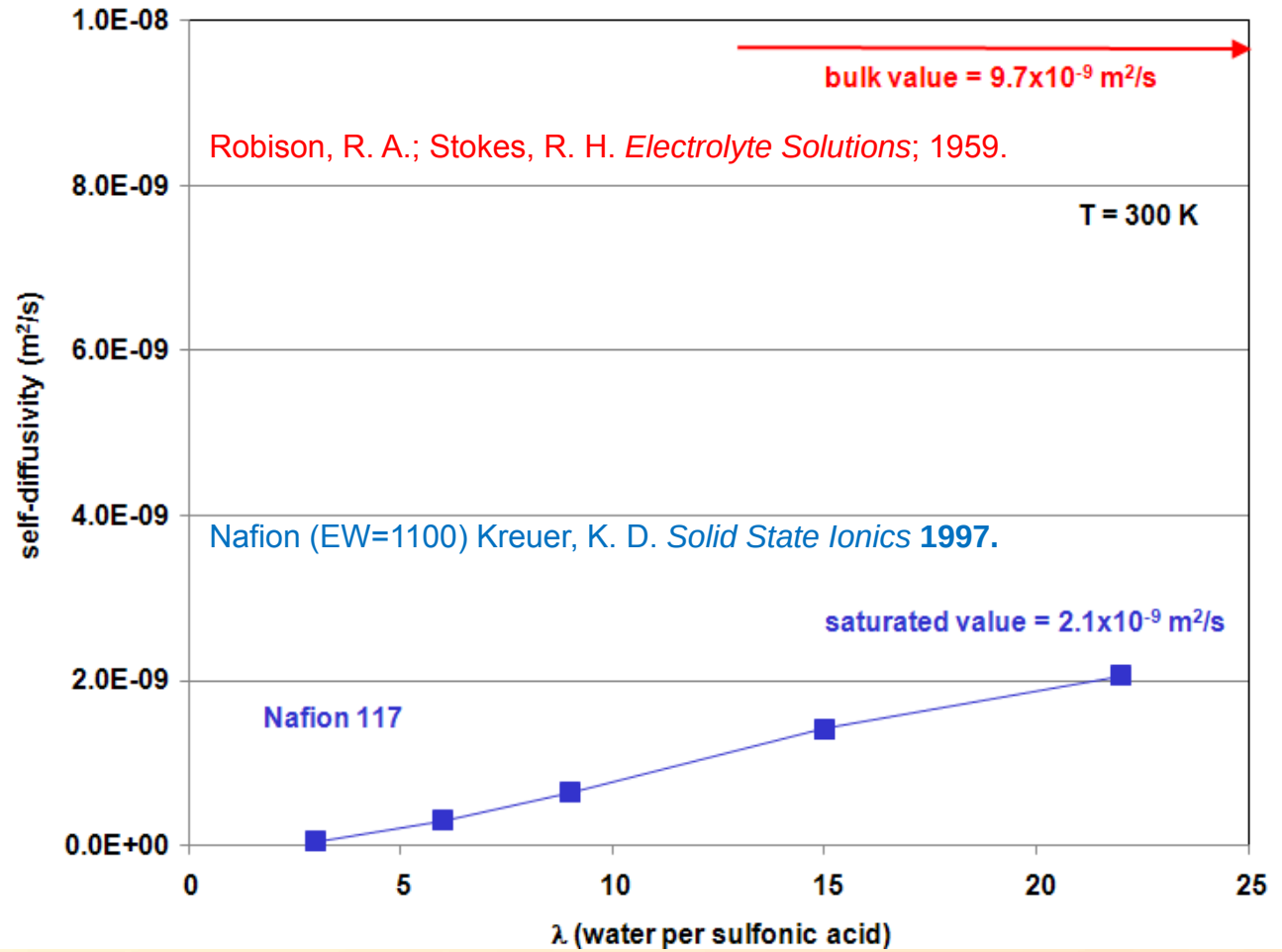
- Lower Cost
  reduce noble metal (Pt or Pt alloy) catalyst content

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

  - membrane
    - ► dries out
    - ► conductivity drops

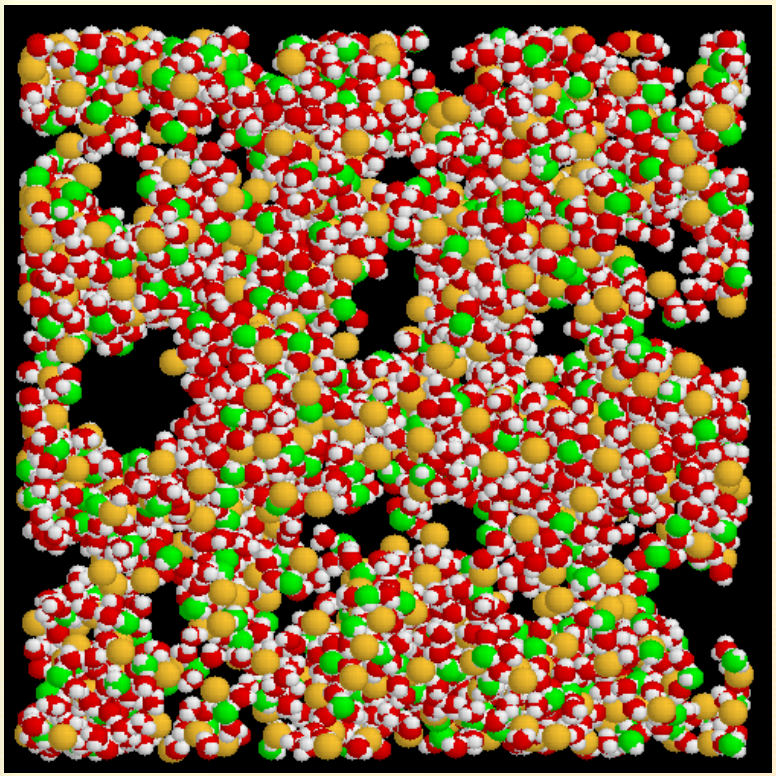
- High Temperature (120 °C) proton exchange membranes
  - retain moisture at higher temperatures
  - maintain high conductivity at lower water content

Proton Transport in Bulk Water and PEM Experimental Measurements

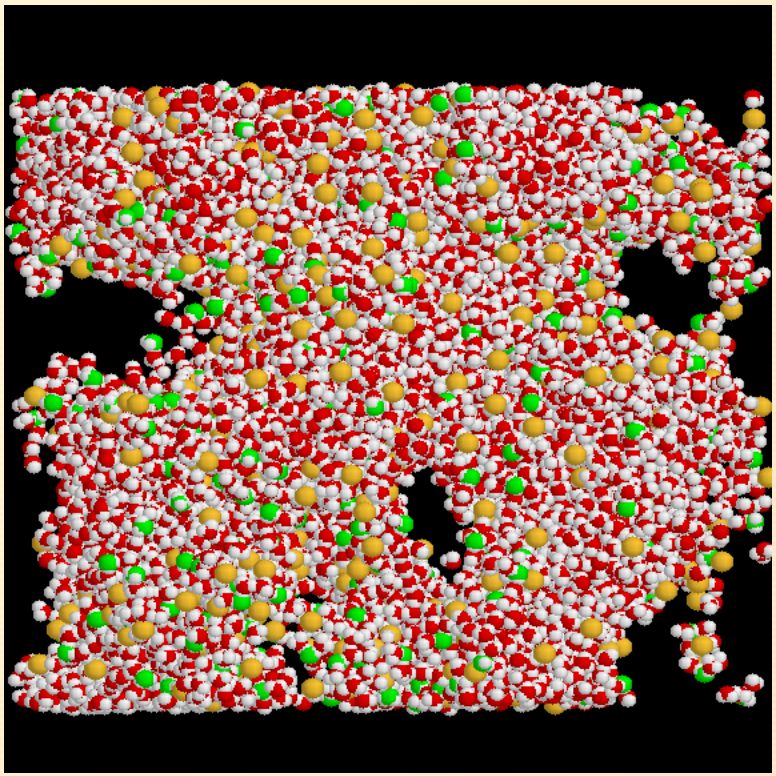


Even at saturation, the self-diffusivity of charge in Nafion is 22% of that in bulk water.

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

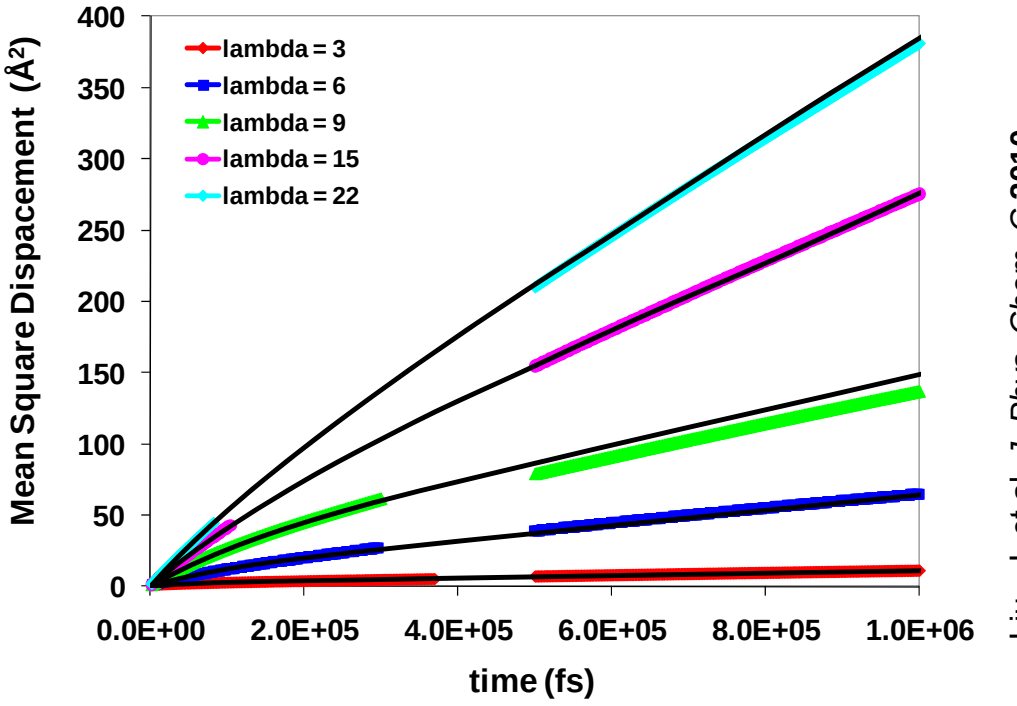
$$D = \lim_{\tau\to\infty} \frac{MSD}{2d\tau} = \lim_{\tau\to\infty} \frac{\left\langle \left[r_i(t+\tau) - r_i(t) \right]^2 \right\rangle}{2d\tau}$$

$r_i(t)$: 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.

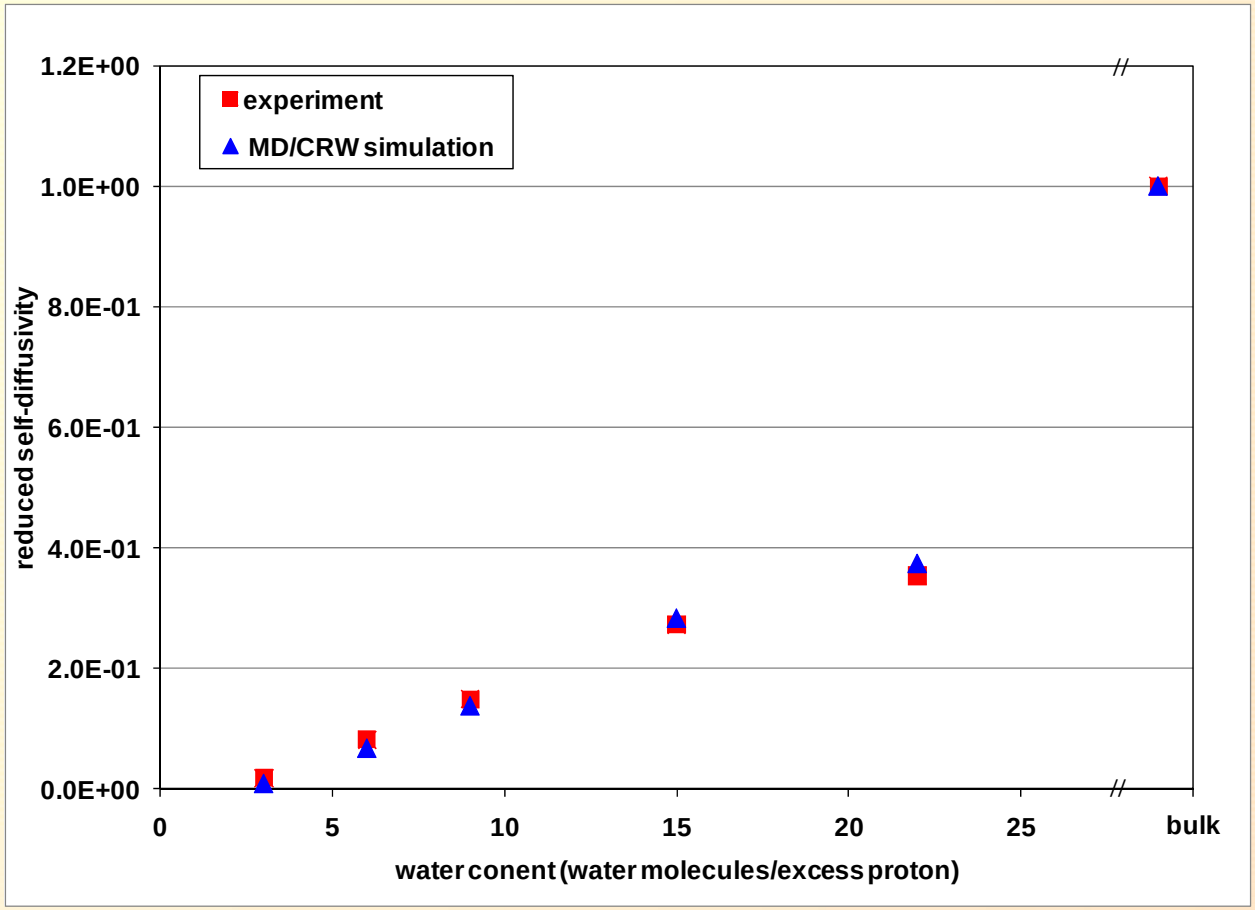
MD simulations alone are not long enough.



Liu, J. et al. *J. Phys. Chem. C* **2010**.

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

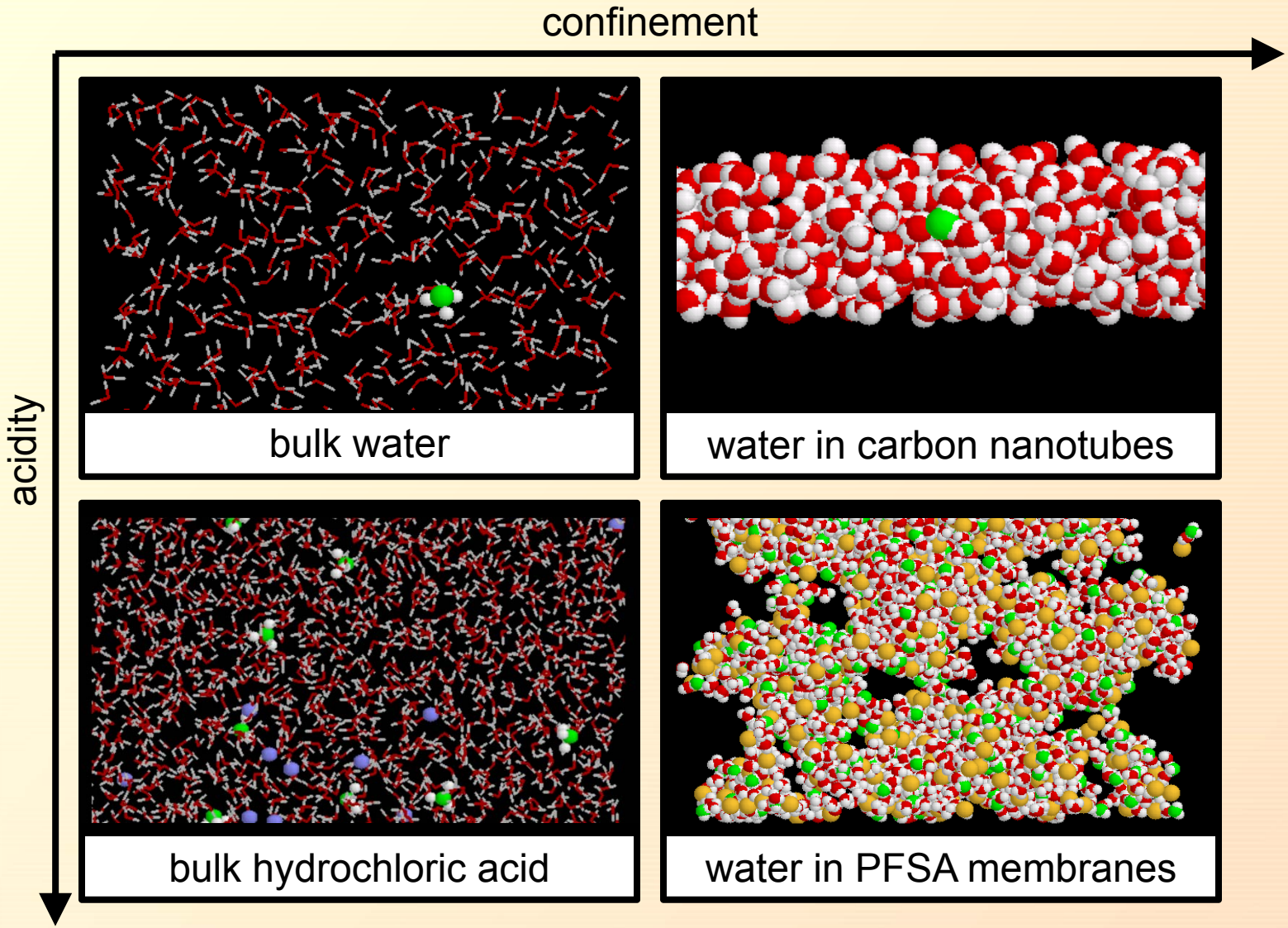
Comparison of MD/CRW Simulation with Experiment



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

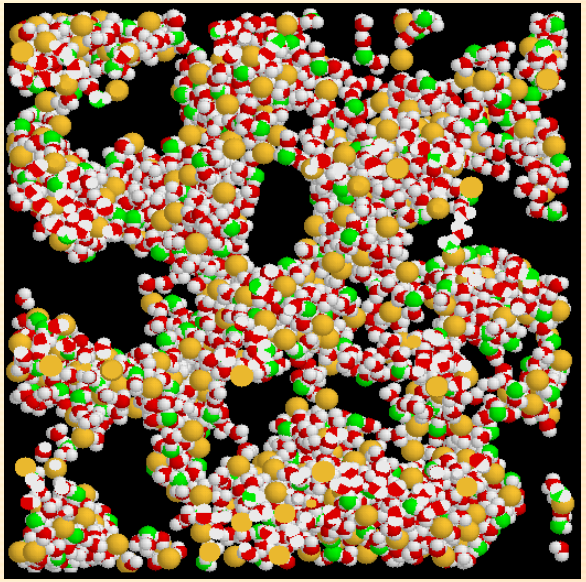


Water Mobility in Bulk Systems – Effect of Connectivity

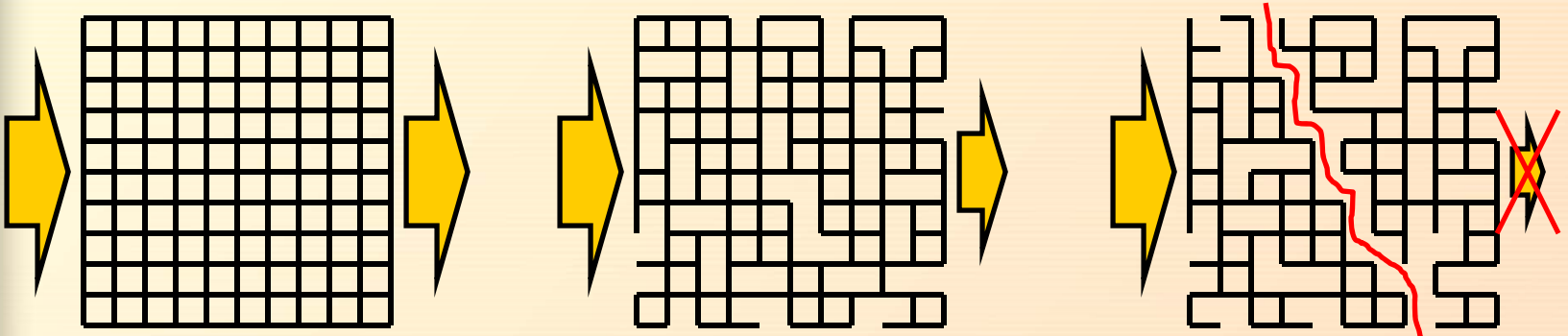
Invoke Percolation Theory to account for connectivity of aqueous domain within PEM and obtain effective diffusivity.

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

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



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



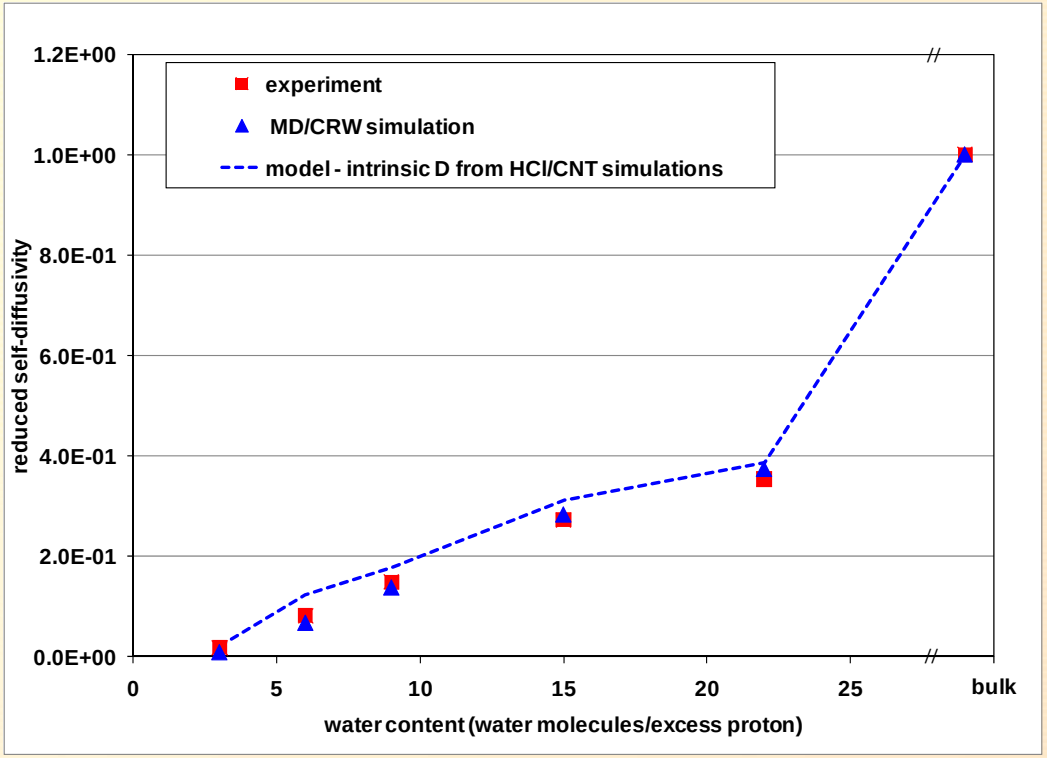
no blocked bonds
$D = D_{open}$

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.

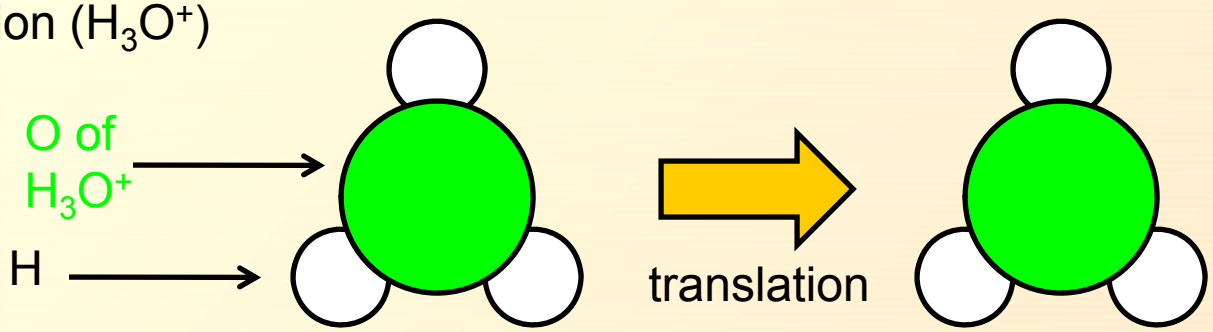
Theory uses only structural information to predict transport property.

Water is solved!
What about charge transport?

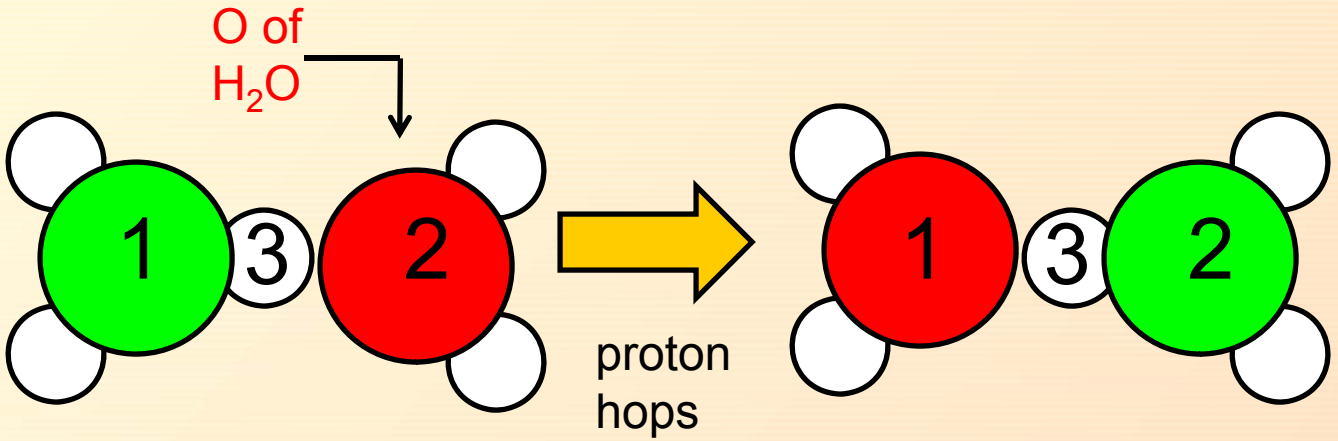
Esai Selvan, M., Calvo-Muñoz, E.M., Keffer, D.J., *J. Phys. Chem. B* **115**(12) 2011 pp 3052–3061.

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)

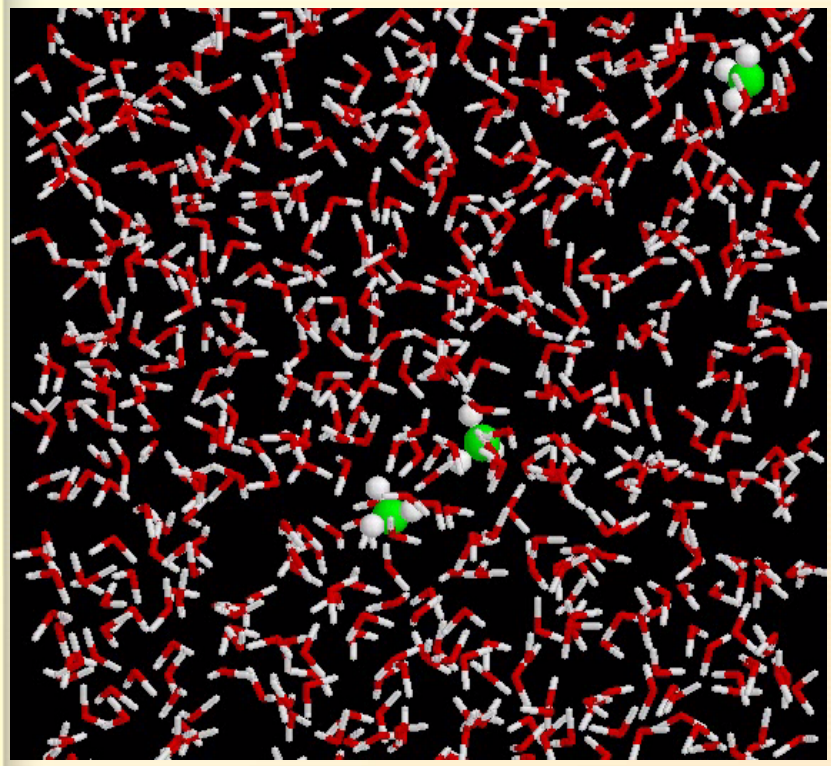


In bulk water, structural diffusivity is about 70% of total diffusivity.

RMD In Water

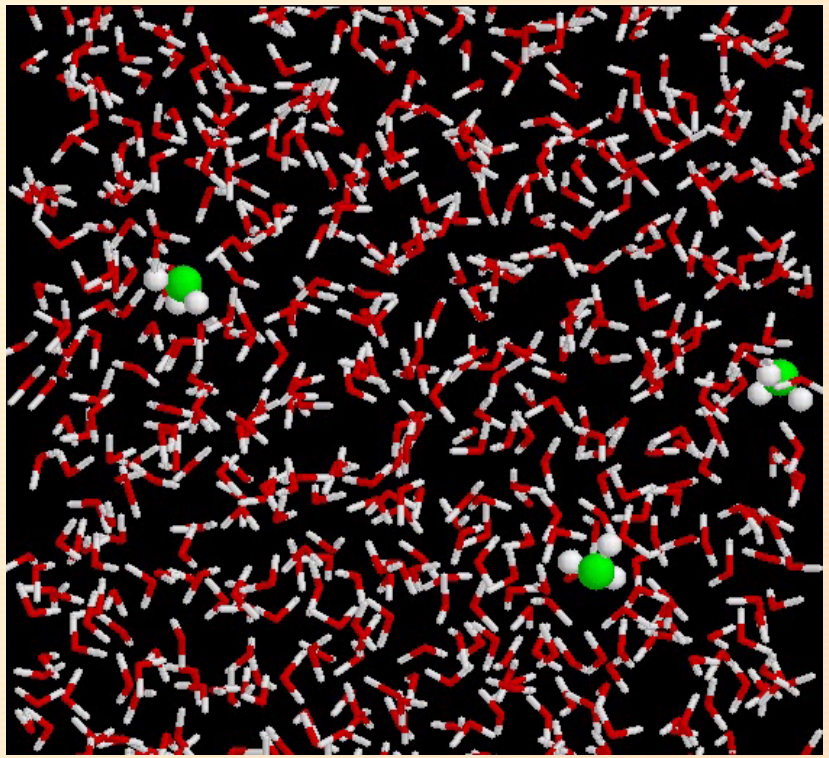
Proton Diffusion in Bulk Water

Non - Reactive System



Vehicular Diffusion

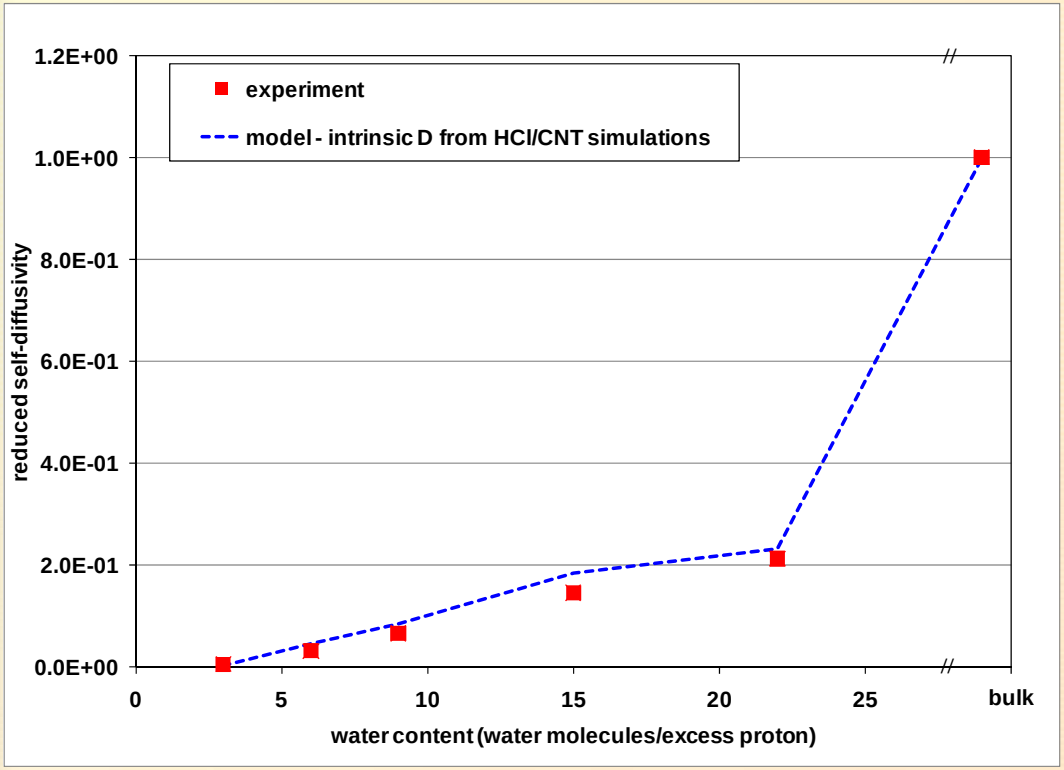
Reactive System



Structural and Vehicular Diffusion

Structure-Based Analytical Prediction of Self-diffusivity

- 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)



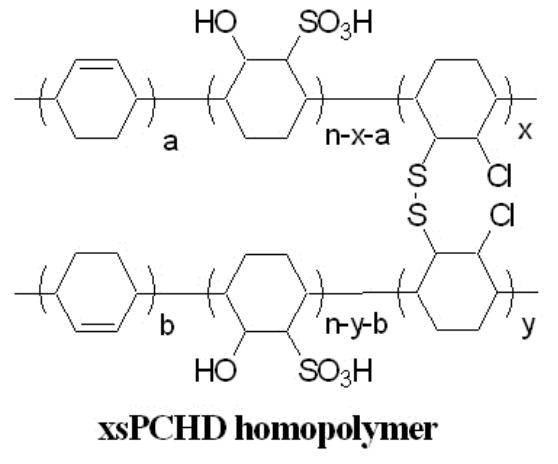
Good agreement of theory with experiment.

Theory uses only structural information to predict transport property.

Proton transport is well-described by this simple model.

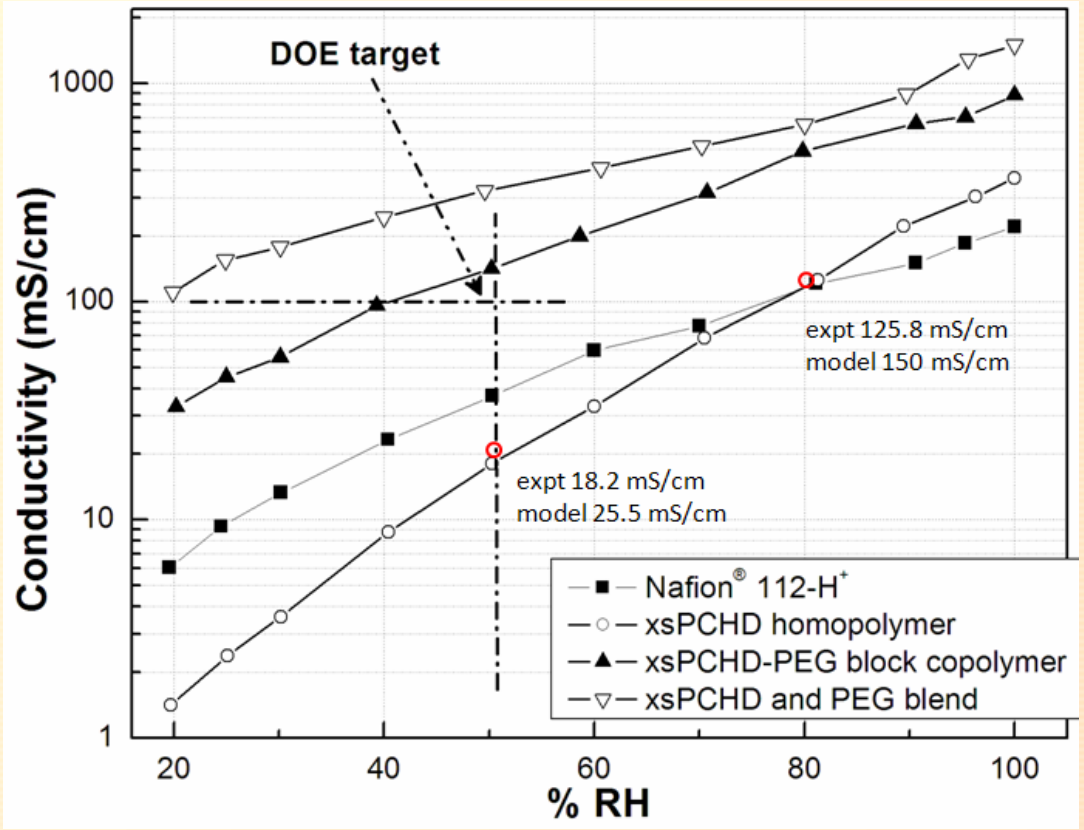
Esai Selvan, M., Calvo-Muñoz, E.M., Keffer, D.J., *J. Phys. Chem. B*, dx.doi.org/10.1021/jp1115004 , 2011.

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

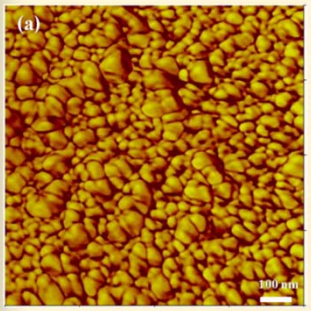


xsPCHD homopolymer

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.

THE UNIVERSITY of TENNESSEE

STAIR
Sustainable Technology through Advanced Interdisciplinary Research

Acknowledgments

Office of Basic Energy Sciences

This work is supported by the United States Department of Energy Office of Basic Energy Science through grant number DE-FG02-05ER15723.

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

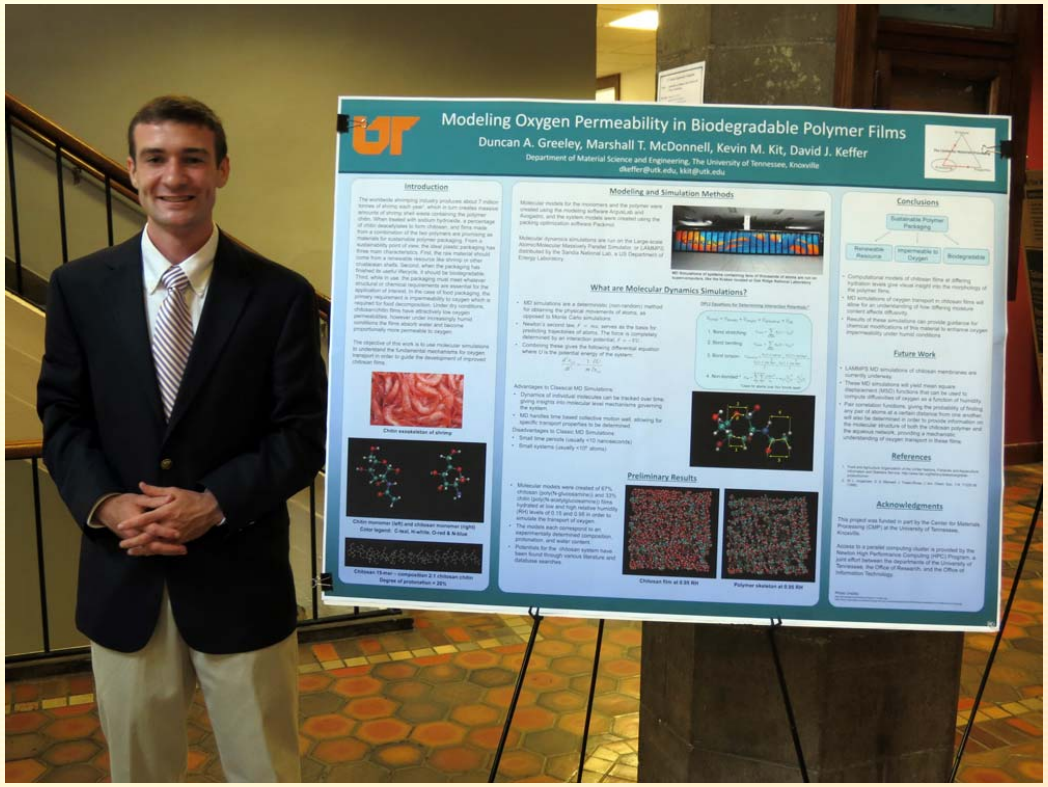
Conclusions

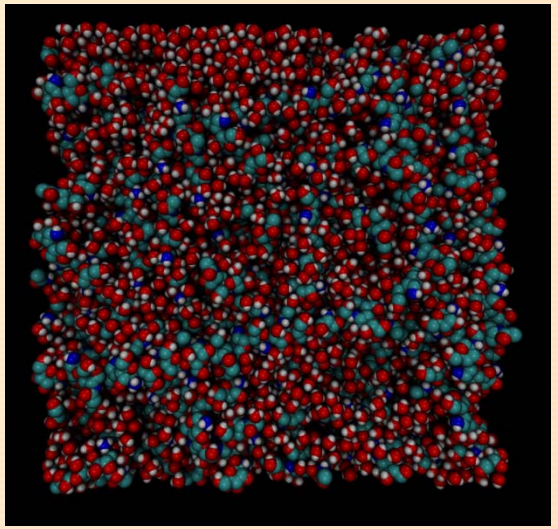
- The search for renewable energy sources and systems is the defining challenge of your generation.
- Materials Scientists & Engineers play a critical role in this search for sustainability.
- Students in the Materials Science & Engineering Department at the University of Tennessee are performing state-of-the-art 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!

THE UNIVERSITY of TENNESSEE

STAIR
Sustainable Technology through Advanced Interdisciplinary Research

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)

Questions?