# Investigations of Material Structure-Property Relationships in Fuel Cells Through Molecular-Level Simulation

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# molecular-level process and materials modeler

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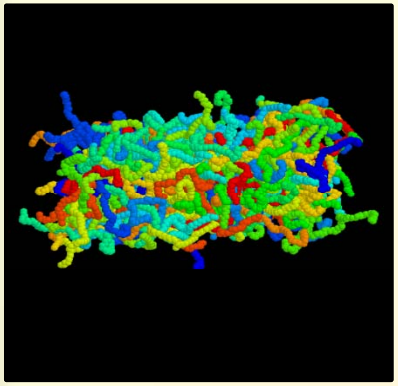
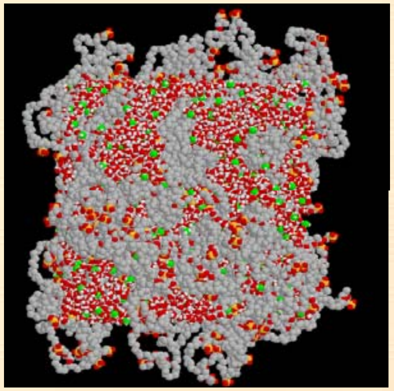
# Apply molecular simulation to develop structure/property relationships

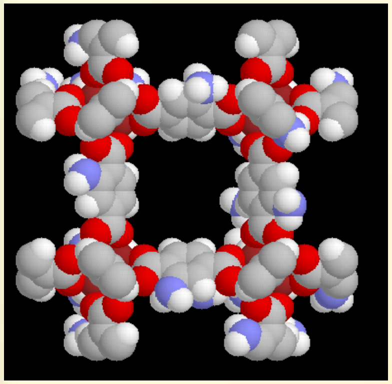


## polymeric materials

polymers at equilibrium and under flow (PE, PET)

polymer electrolyte membranes (PEMs) in fuel cells

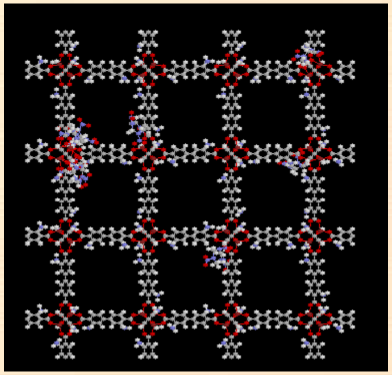


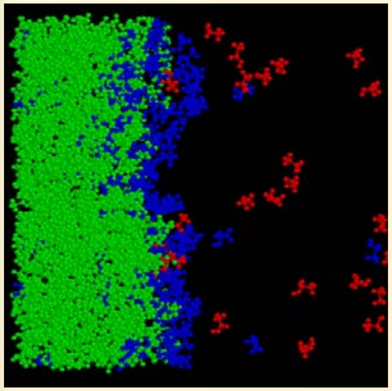


## nanoporous materials

hydrogen sorption in metal organic frameworks (MOFs)

Sensing of RDX, TATP and other explosives in MOFs

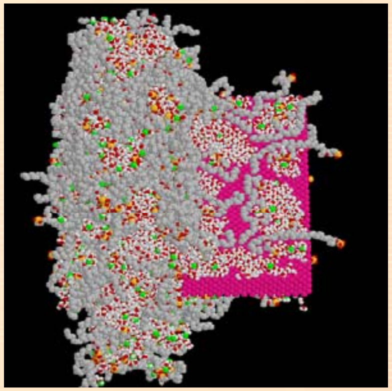




## interfacial systems

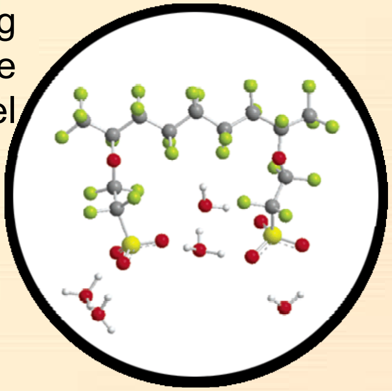
near critical vapor-liquid interface structure

fuel cell electrode/ electrolyte interfaces



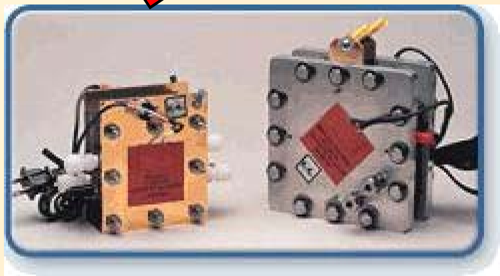
# Moving toward fuel cell-powered vehicles

understanding starts at the quantum level

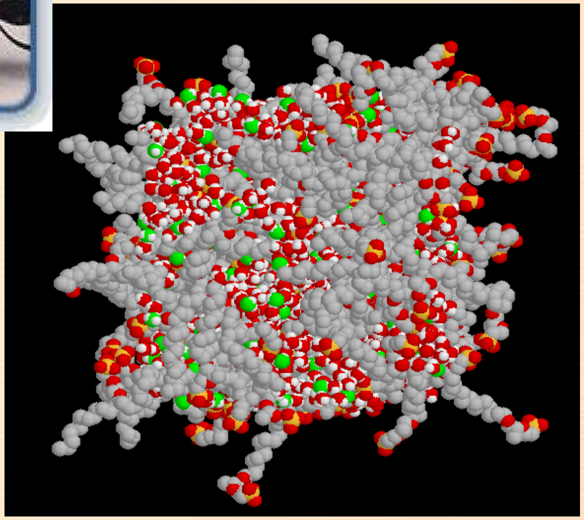


$H_2$-powered autos become a reality

leads to high-fidelity coarse-grained models

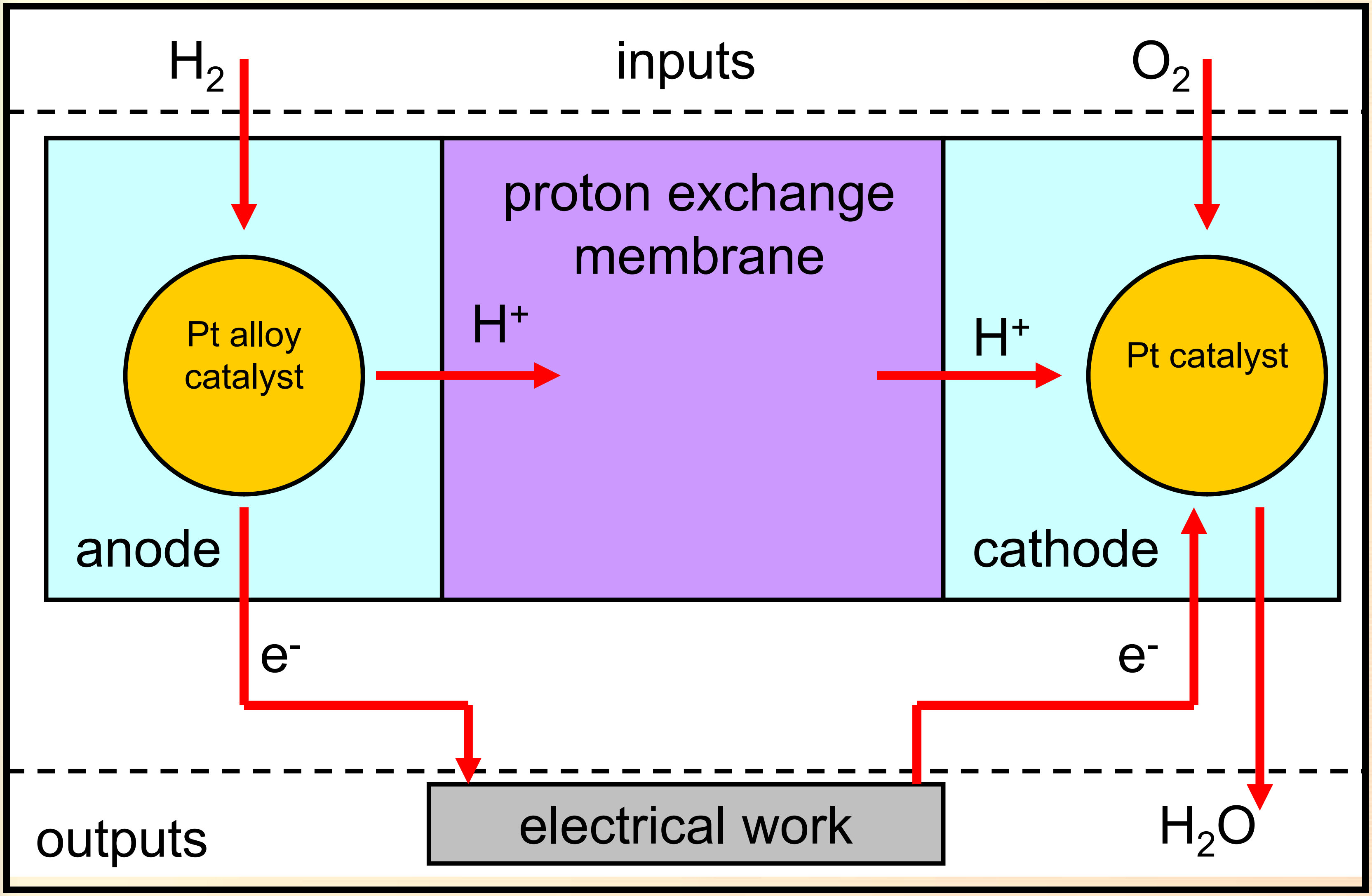


impacts fuel cell performance



improved nanoscale design of membrane/electrode assembly

# how fuel cells work: conceptual level



inputs

$H_2$

$O_2$

anode

Pt alloy catalyst

proton exchange membrane

$H^+$

$H^+$

Pt catalyst

cathode

$e^-$

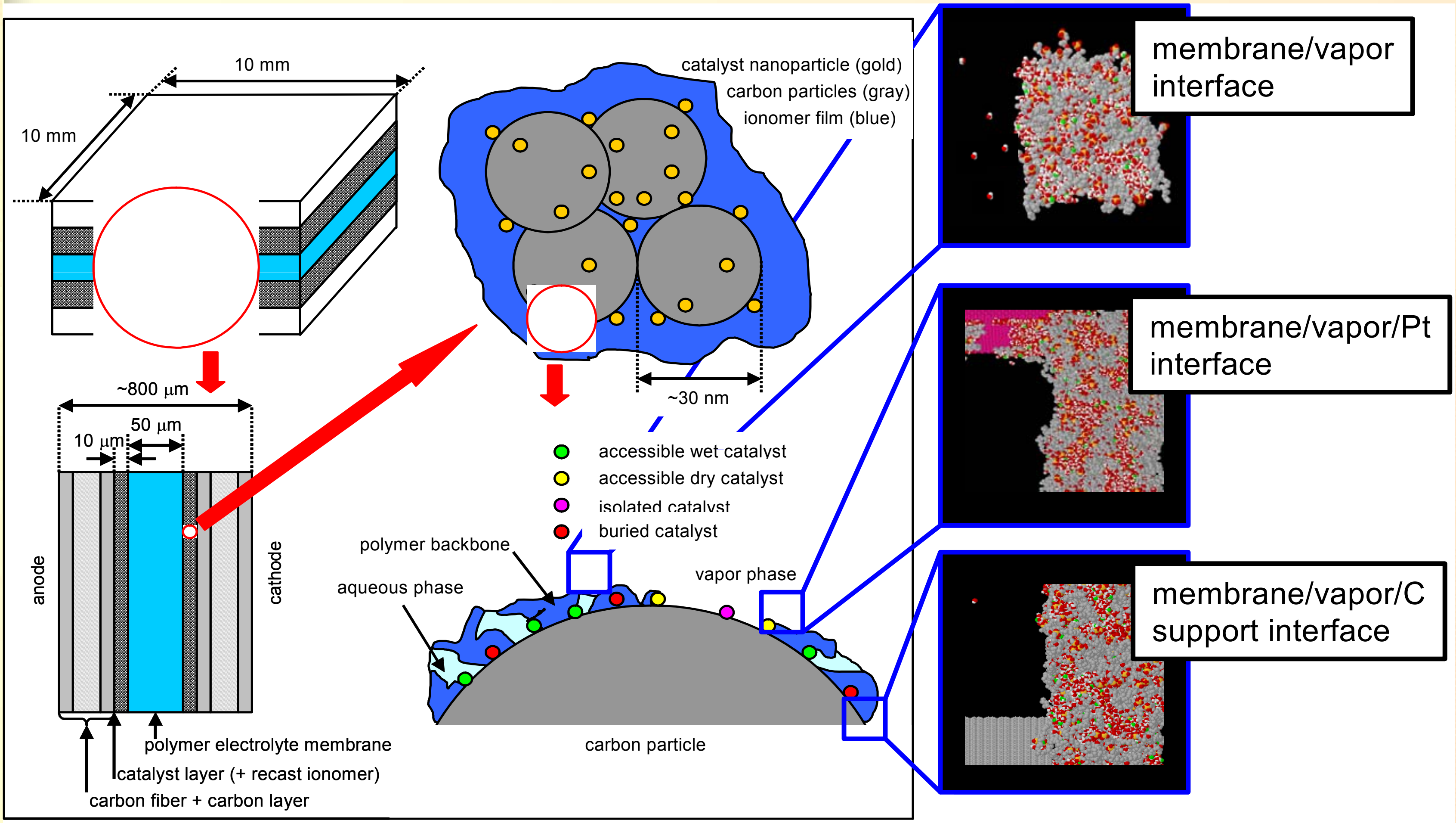
$e^-$

outputs

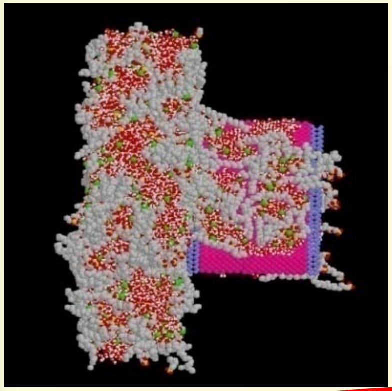
electrical work

$H_2O$

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

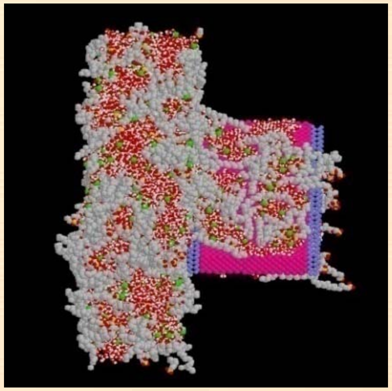


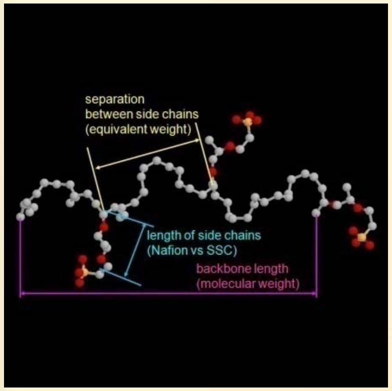
# Research Questions



1. What is the molecular-level structure electrode/electrolyte interfaces in the MEA of PFSA PEM fuel cells?

2. What are the molecular-level mechanisms for proton transport through these systems?

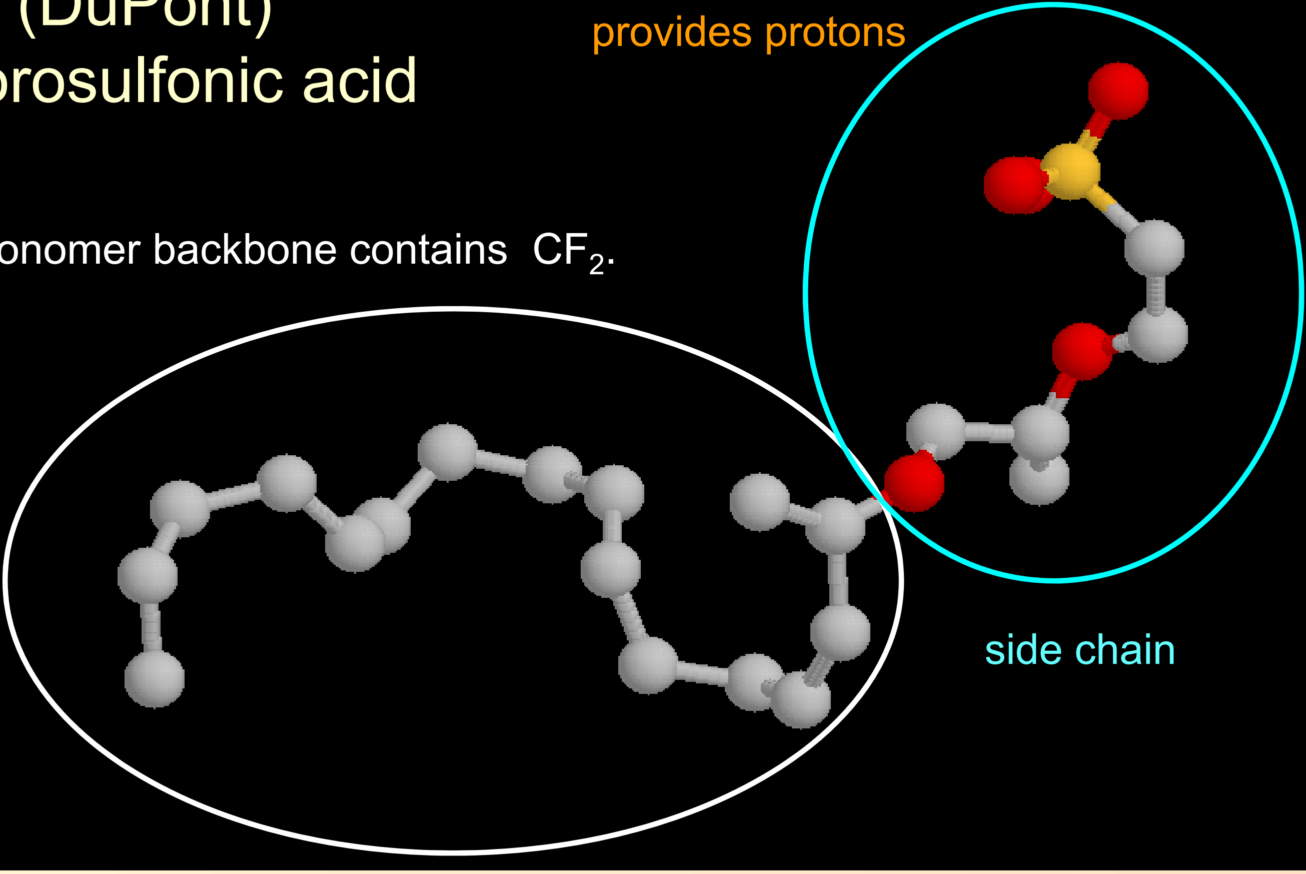




3. How can one control the structure and transport properties of the interface through changes in polymer chemistry?

# proton exchange membranes are polymer electrolytes

industry standard:
Nafion (DuPont)
perfluorosulfonic acid



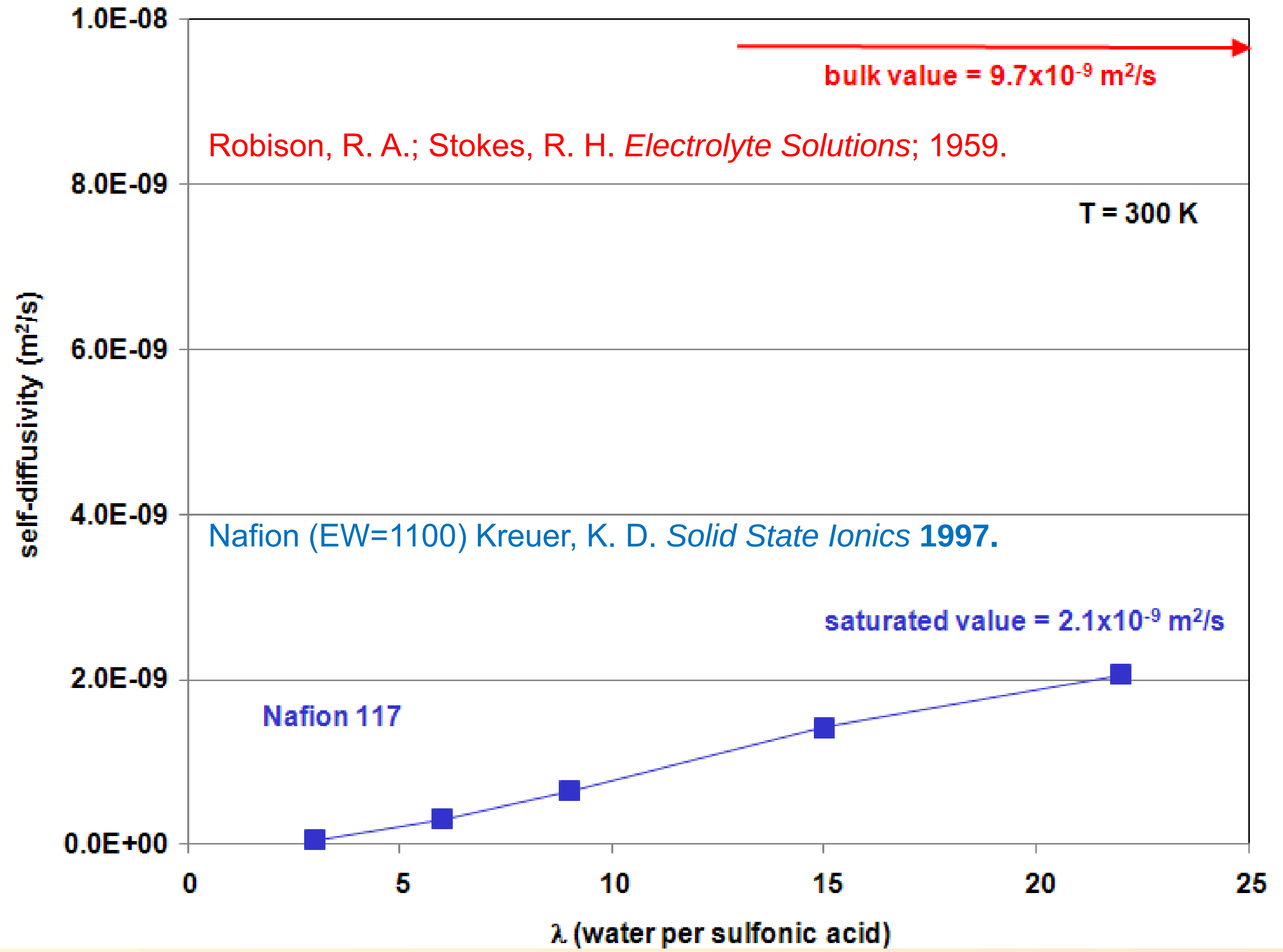
sulfonic acid at end of side chain provides protons

monomer backbone contains $CF_2$.

side chain

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

# Proton Transport in Bulk Water and PEM Experimental Measurements



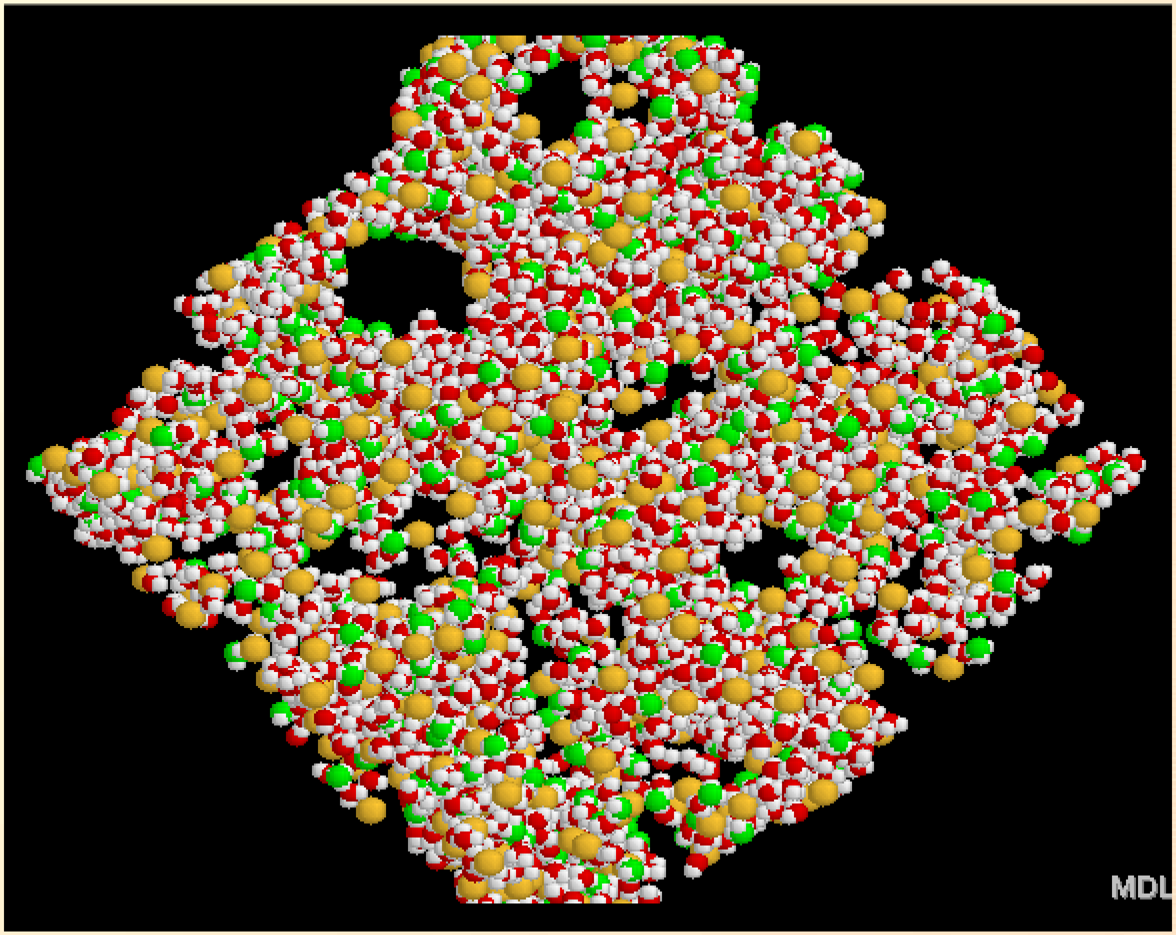
Even at saturation, the self-diffusivity of charge in Nafion is 22% of that in bulk water.

# morphology of bulk hydrated membrane

Nafion

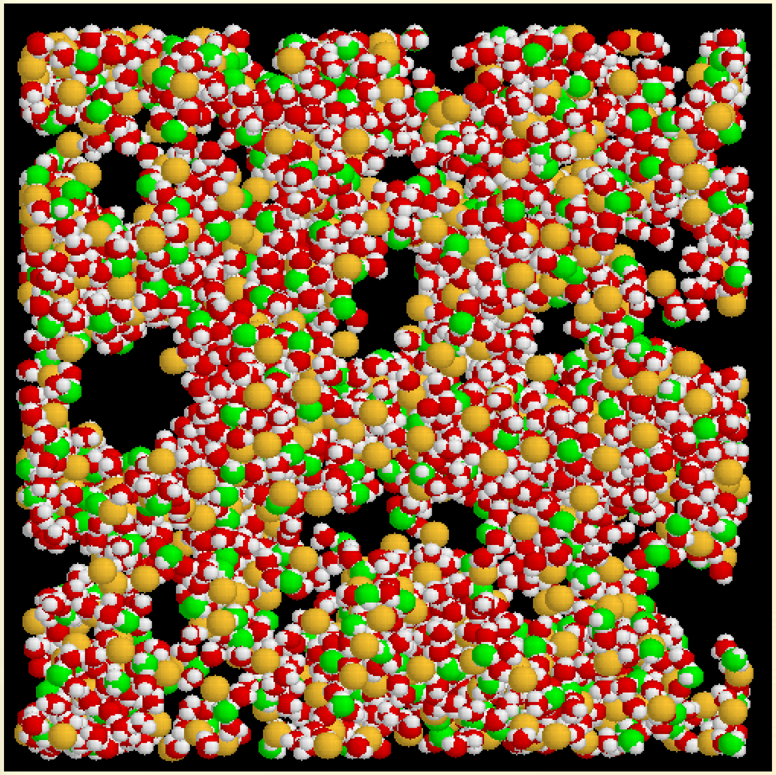
EW = 1144
$\lambda$= 6 $H_2O/HSO_3$
T = 300 K

Snapshots of the aqueous nanophase show a tortuous path.

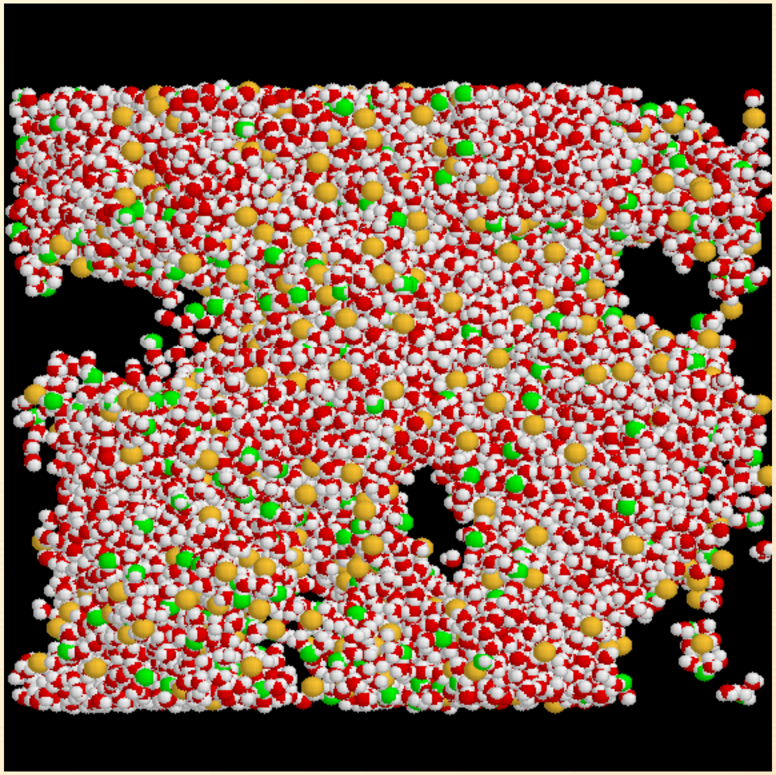


legend:
O of $H_2O$ = red
H= white
O of $H_3O^+$ = green
S = orange
remainder of polymer electrolyte not shown

# PEM morphology is a function of water content



Nafion (EW = 1144) $\lambda = 6\ H_2O/HSO_3$
small aqueous channels



Nafion (EW = 1144) $\lambda = 22\ H_2O/HSO_3$
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.)

# 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 $\alpha$ 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.

# Strengths and Weaknesses of Classical MD simulation

## Advantages

- The primary advantage of MD simulation is that the structure and dynamics of individual molecules can easily be tracked, giving insight into the molecular-level mechanisms governing the system.
- Materials with nanostructure and interfacial systems are particularly suited for investigation via MD simulation

## Disadvantages

- small systems (less than $10^6$ atoms typically)
- short simulation duration (less than 10 nanoseconds typically)
- classical MD does not model chemical reaction (needs quantum mechanics)

## Requirements

- requires knowledge of atomic level interactions
- results are only as good as the interaction potential

## Optimal Use

- simulation is complementary to theory and experiment
- MD simulation should be coupled with finer models (QM) and coarser models (mesocale, continuum)

# Determination of Diffusivities from MD Simulation

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

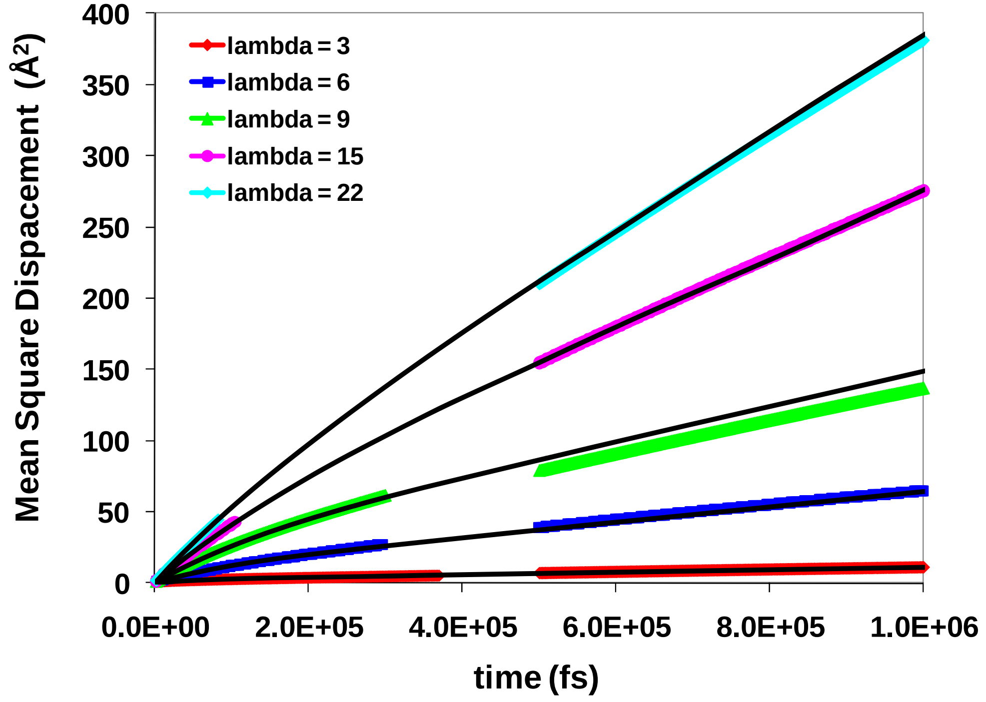
$$D = \lim_{\tau \to \infty} \frac{MSD}{2d\tau} = \lim_{\tau \to \infty} \frac{\left\langle \left[ r_i(t+\tau) - r_i(t) \right]^2 \right\rangle}{2d\tau}$$

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.



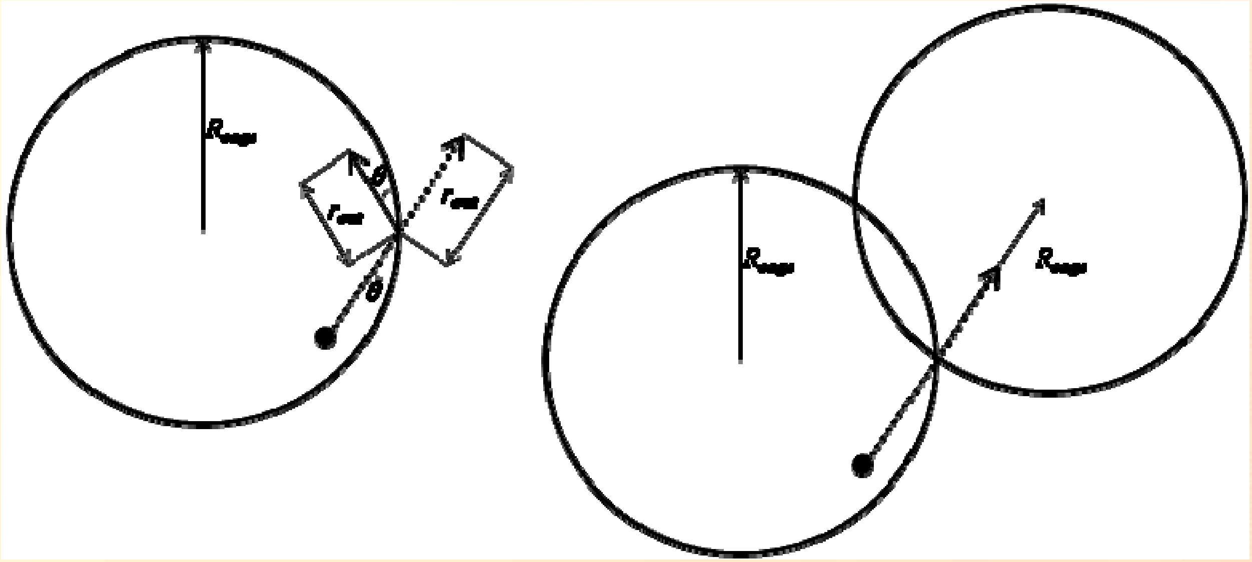
Liu, J. et al. *J. Phys. Chem. C* 2010.

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

# Confined Random Walk Simulation

## Mesoscale Model

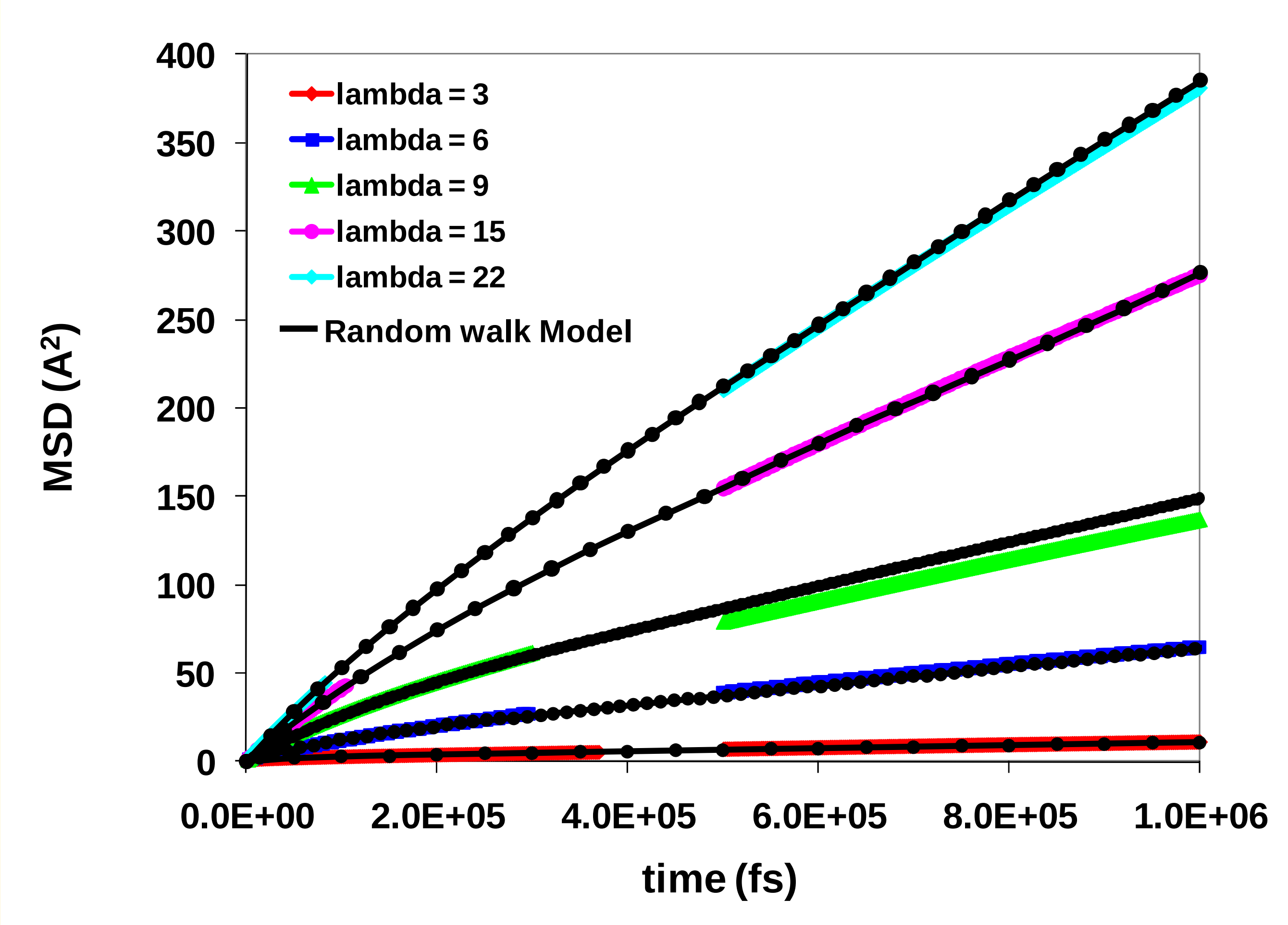
- non-interacting point particles (no energies, no forces)
- sample velocities from a Maxwell-Boltzmann distribution
- two parameters
    - cage size
    - cage-to-cage hopping probability
- parameters fit to MSD from Molecular Dynamics Simulation
- runs on a laptop in a few minutes



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

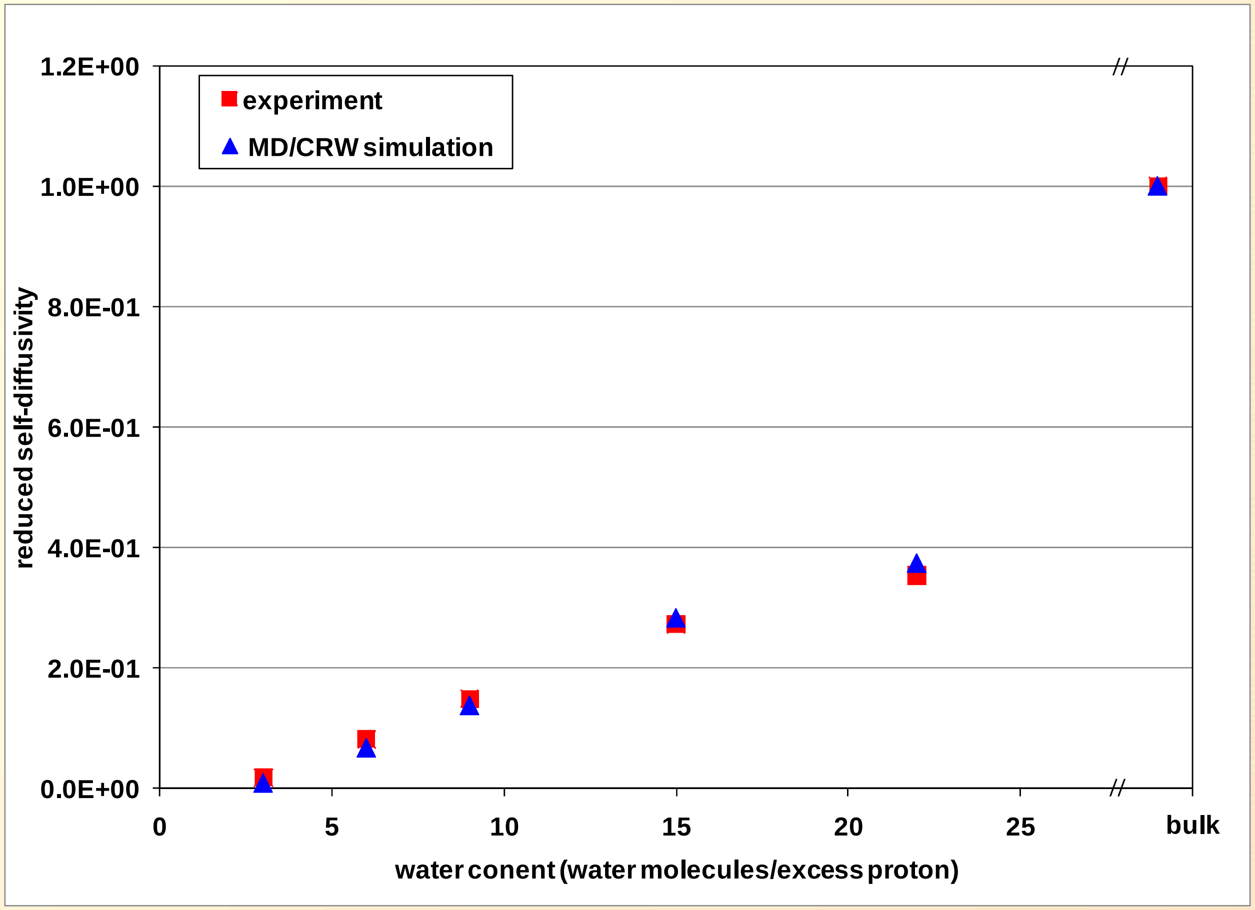


Calvo-Muñoz, E.M., Esai Selvan, M., Xiong, R., Ojha, M., Keffer, D.J., Nicholson, D.M., Egami, T”, *Phys. Rev. E*, **83**(1) 2011 article # 011120.

- 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

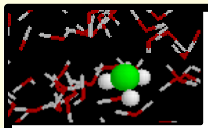
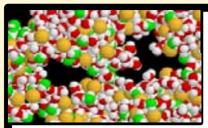
self-diffusivity of water



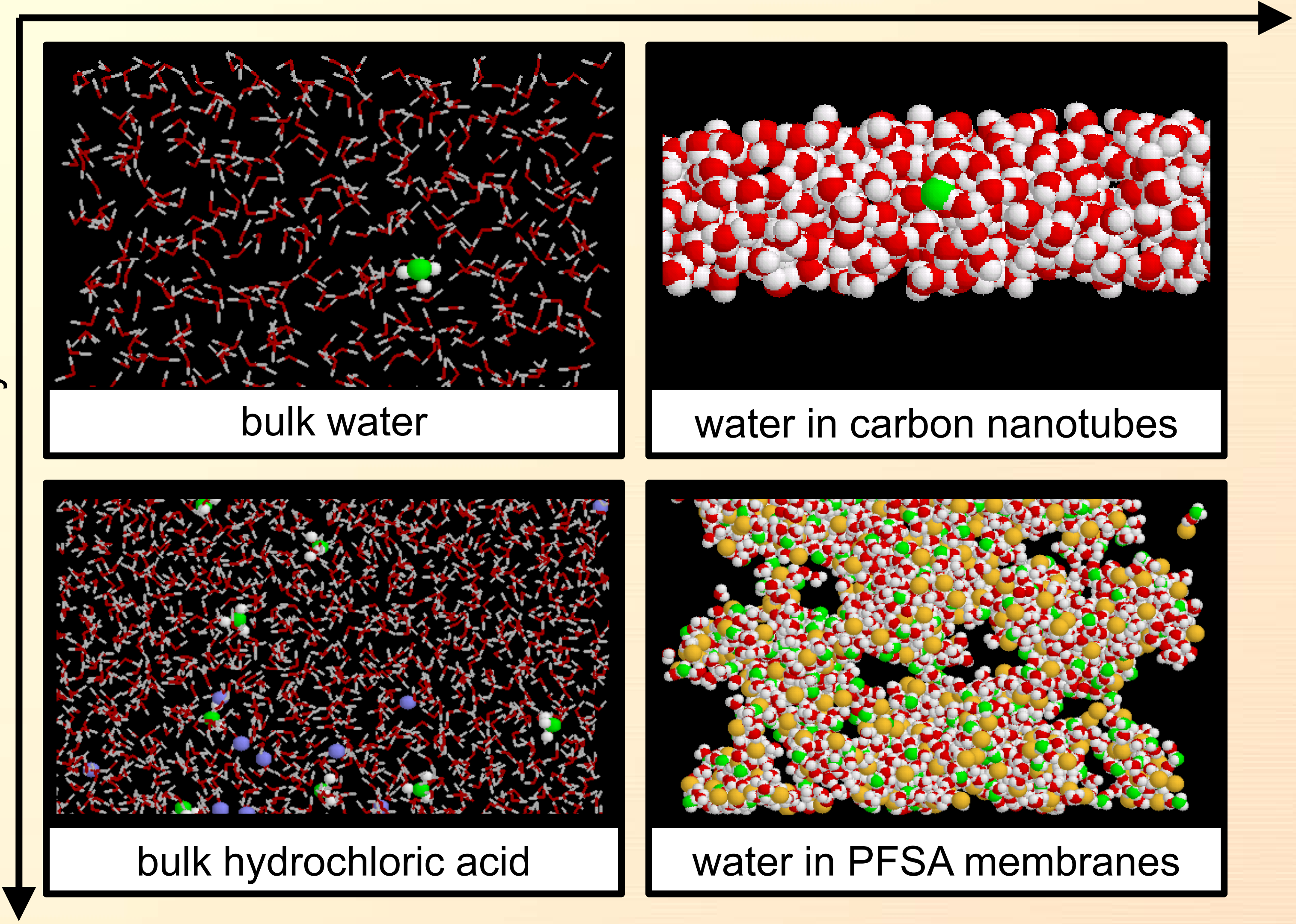
Robison, R. A.; Stokes, R. H. *Electrolyte Solutions*; 1959.
Nafion (EW=1100,) Kreuer, K. D. *Solid State Ionics* **1997.**
Esai Selvan, M., Calvo-Muñoz, E.M., Keffer, D.J., *J. Phys. Chem. B*, dx.doi.org/10.1021/jp1115004 , 2011.

- 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?

# Three Factors: Acidity, Confinement & Connectivity

| | bulk water | water in PFSA membranes |
|---|---|---|
| acidity | <br>● $H_3O^+$ concentration is dilute<br>$\lambda=5.6\cdot10^8\ H_2O/H^+$ (pH=7) | <br>(Nafion EW=1144)<br>$H_3O^+$ concentration<br>● $\lambda=3\ H_2O/HSO_3$, pH ≈ -0.59 (minimally hydrated)<br>● $\lambda=22$, pH≈-0.22 (saturated) |
| confinement | ● interfacial surface area is zero | interfacial surface area<br>● 163 $Å^2/H_2O$ or 2460 $m^2/g$ ($\lambda=3$)<br>● 23 $Å^2/H_2O$ or 1950 $m^2/g$ ($\lambda=22$) |
| connectivity | ● no connectivity issues | ● connectivity of aqueous domain deteriorates as water content decreases |

# Acidity and Confinement Effects on Proton Mobility


confinement

acidity

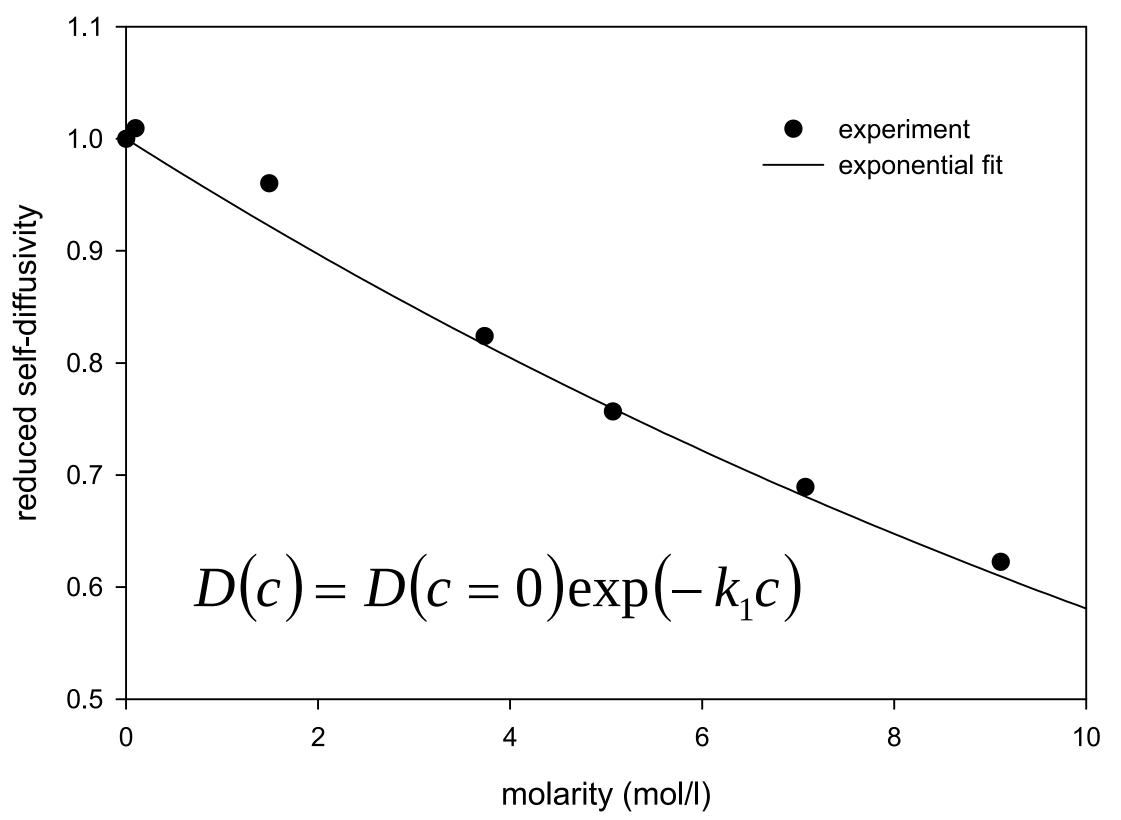
bulk water

water in carbon nanotubes

bulk hydrochloric acid

water in PFSA membranes

# Water Mobility in Bulk HCl solutions – Effect of Acidity

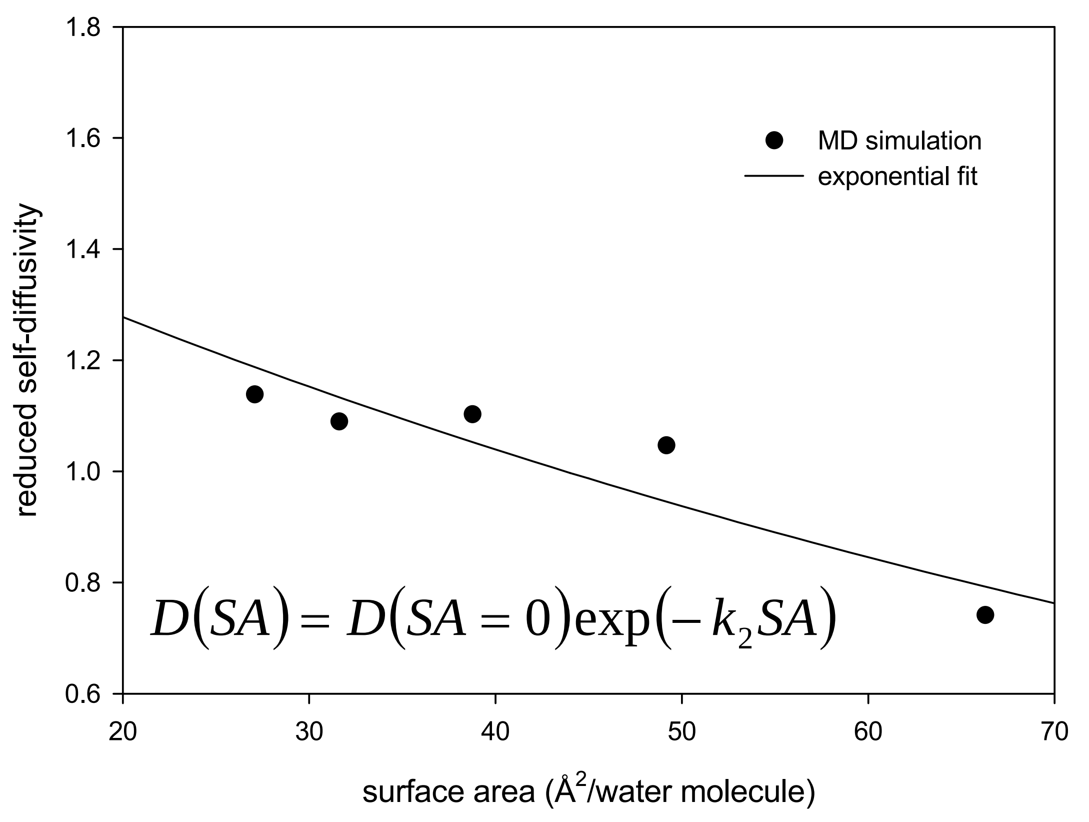


$$D(c) = D(c=0)\exp(-k_1 c)$$

Dippel, T.; Kreuer, K. D. *Solid State Ionics* **1991**, *46*, 3-9.

- In bulk systems, the diffusivity of water decreases as the concentration of HCl increases.
- The behavior is well fit by an exponential fit.

# Water Mobility in Nanotubes – Effect of Confinement



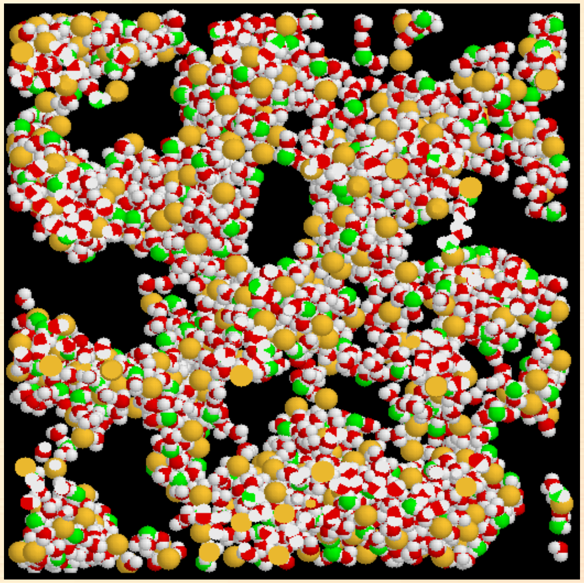
$$D(SA) = D(SA = 0)\exp(-k_2 SA)$$

Esai Selvan, M.; Keffer, D. J.; Cui, S.; Paddison, S. J. *Molec. Sim.* **2010**.

- In carbon nanotubes, the diffusivity of water decreases as the radius of the nanotube decreases.
- The behavior is fit by an exponential fit.

# Water Mobility in Bulk Systems – Effect of Connectivity

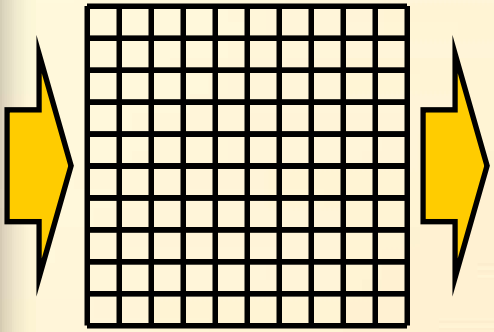
Invoke Percolation Theory to account for connectivity of aqueous domain within PEM and obtain effective diffusivity.



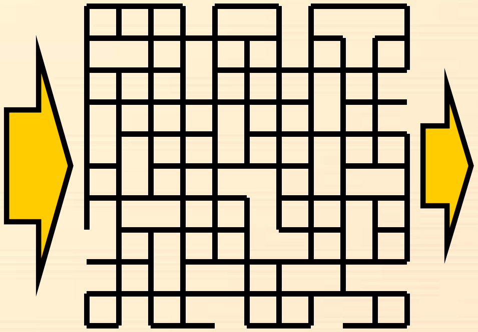
$$\int_0^\infty \frac{D_{eff} - D}{\left(\frac{z}{2}-1\right)D_{eff} + D}\, g(D)\,dD = 0$$

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

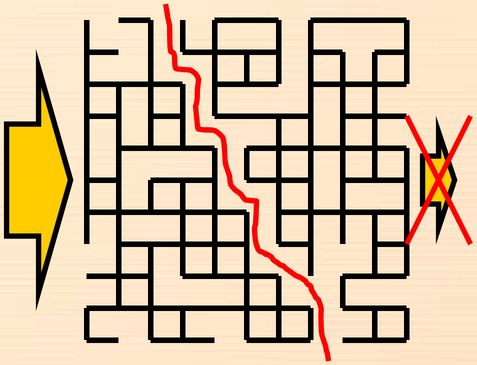
Percolation theory relates the effective diffusivity to the fraction of bonds that are blocked to diffusion.



no blocked bonds
$D = D_{open}$



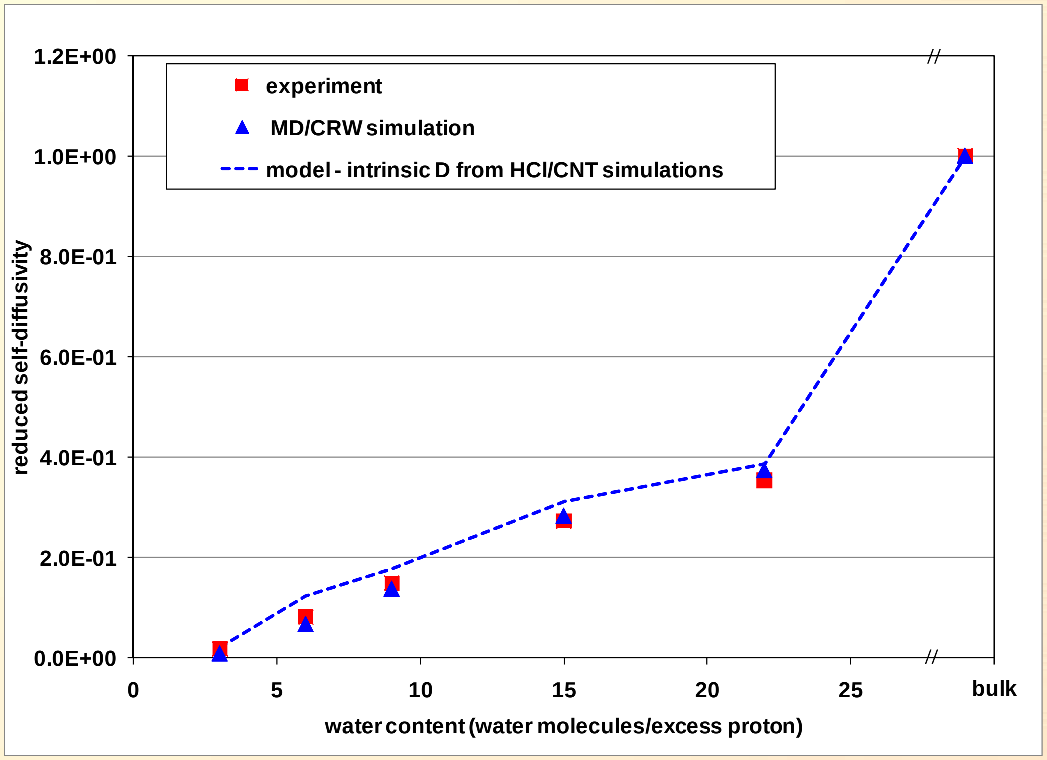
some blocked bonds
$0 < D < D_{open}$



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*, dx.doi.org/10.1021/jp1115004 , 2011.

# What about Proton Transport?

We have shown thus far that we can model the transport of water fairly accurately using either

1. detailed MD/CRW simulation (months on a supercomputer)
2. analytical model based on acidity, confinement & connectivity (minutes on a laptop computer)

We now want to repeat this process for protons. After all, it is the transport of protons that completes the electrical circuit in a fuel cell.

Why did we start with water?

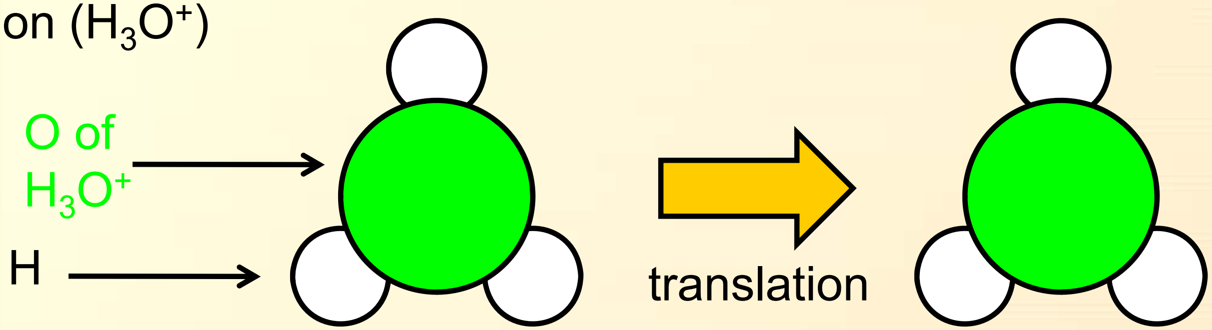
Diffusion of water is easier to describe.

Water is transported only via vehicular diffusion (changes in the center of mass of the water molecules).

There are two mechanisms for proton transport.

# Proton Transport – Two Mechanisms

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



O of $H_3O^+$

H

translation

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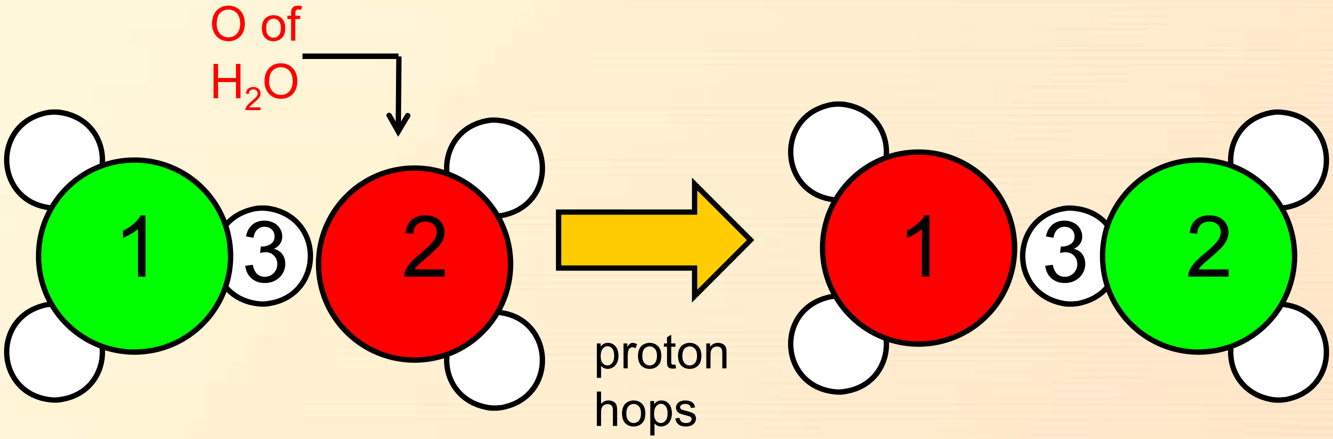
Structural diffusion (proton shuttling): passing of protons from water molecule to the next (a chemical reaction involving the breaking of a covalent bond)



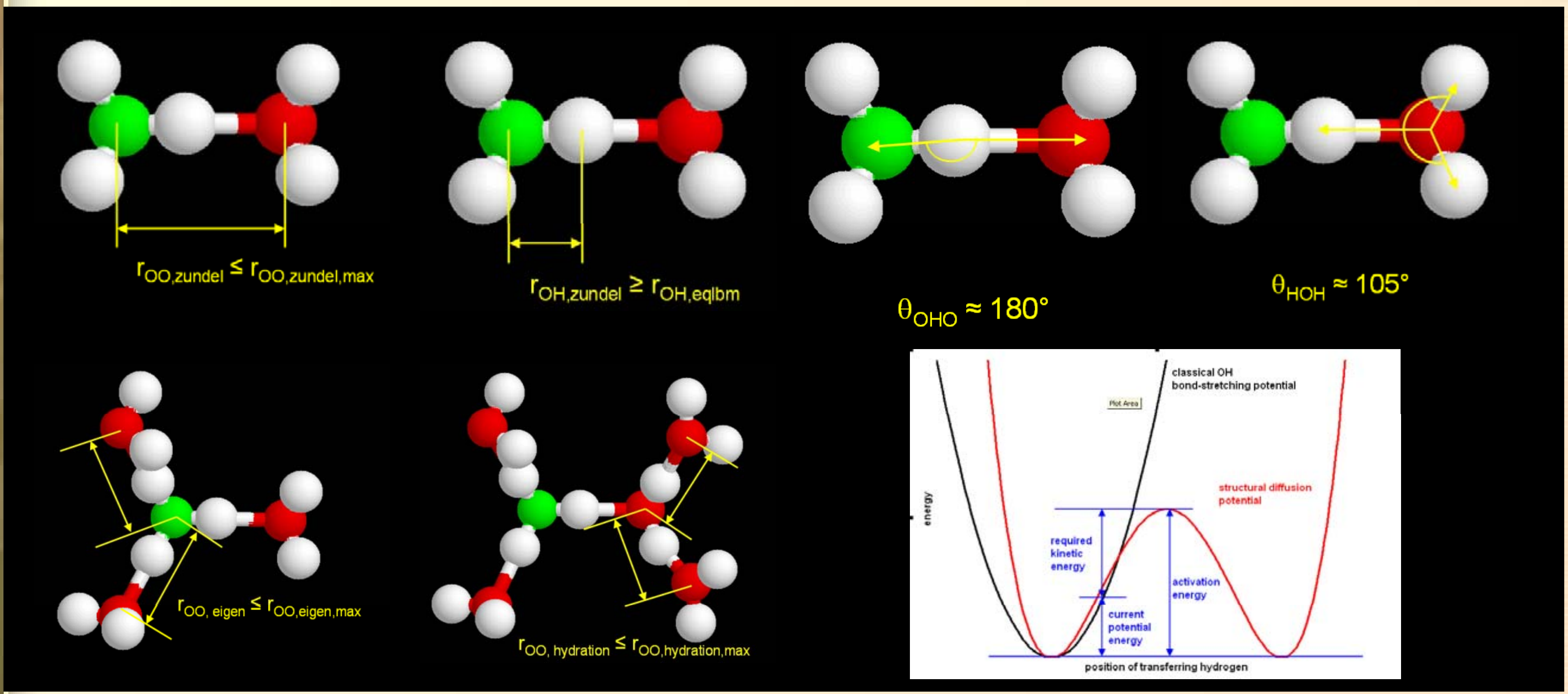
O of $H_2O$

proton hops

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

# Reactive Molecular Dynamics of Proton Transport

Step 1. Satisfy Triggers (6 geometric and 1 energetic)



Step 2. Instantaneously exchange proton.
Step 3. Locally equilibrate to stable structure.
Resume conventional MD simulation.

Esai Selvan *et al.*, *J. Phys. Chem. C*, *2010.*

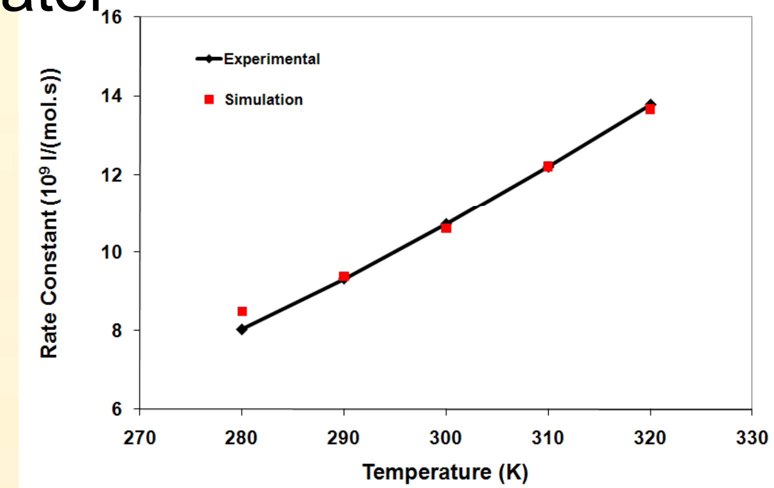
# Proton Transport in Bulk Water

reaction: $H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$

rate law: rate = k $[H_3O^+][H_2O]$

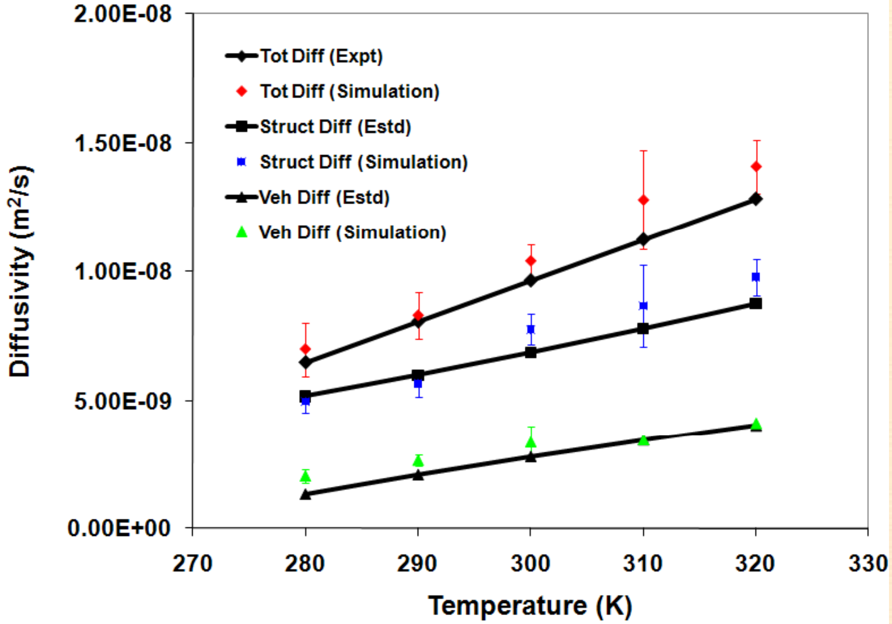
$$k = k_o \exp\left(-\frac{E_a}{RT}\right)$$

- Adjust triggers to fit experimental rate.
- Predict transport properties.



experimental data from Luz, Z.; Meiboom, S. *J. Am. Chem. Soc.*, **1964**.

**RMD rate constant within 6% of experiment.**



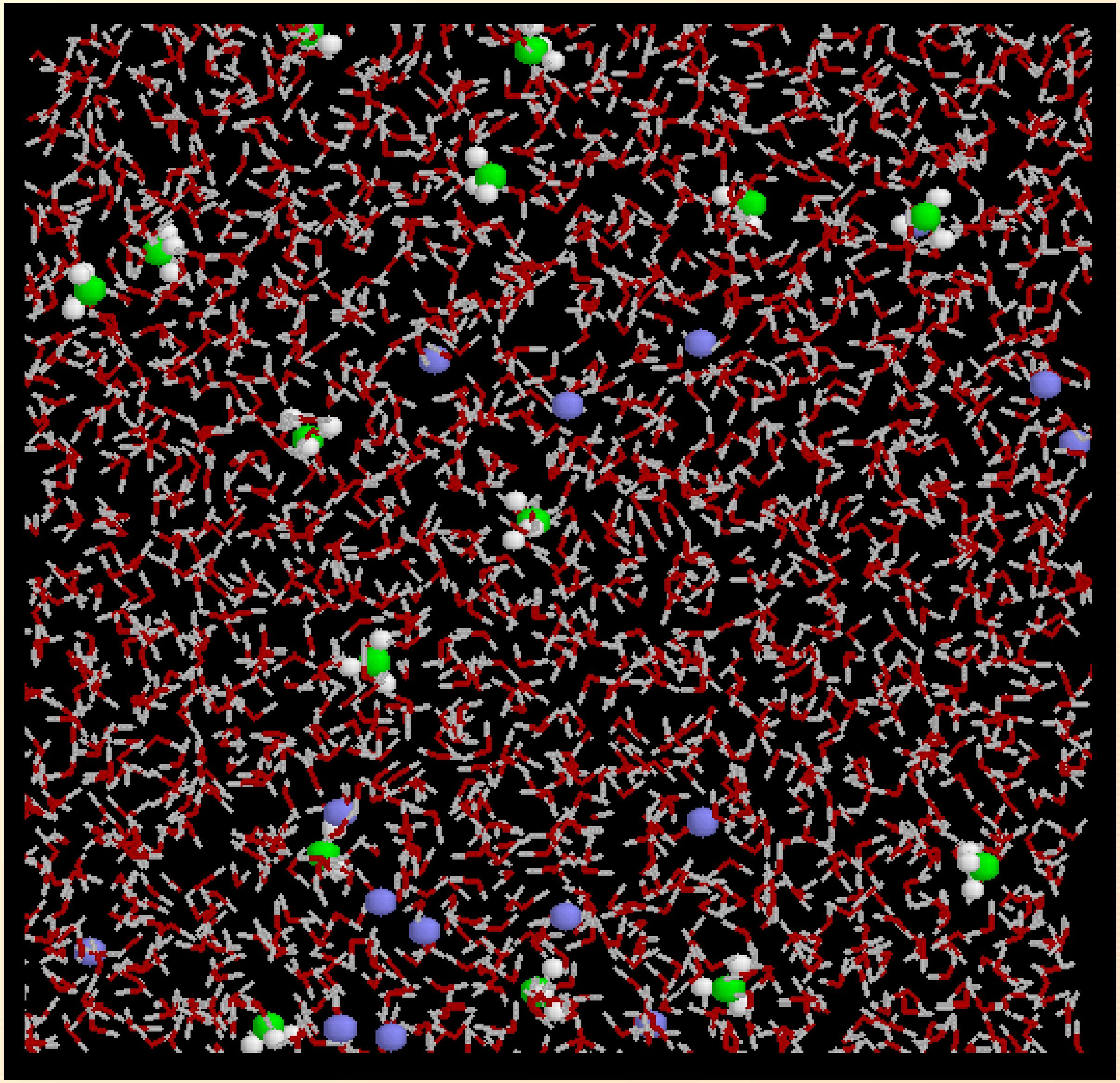
Charge self-diffusivity prediction

- semi-quantitative agreement with experiment
- decomposition into structural and vehicular components
- structural is 60-70% of total
- correct temperature dependence
- structural and vehicular components are uncorrelated

$$D_{tot} = \lim_{\tau \to \infty} \frac{\left\langle \Delta \vec{r}_{veh}^{\,2} \right\rangle + \left\langle \Delta \vec{r}_{struct}^{\,2} \right\rangle + 2\left\langle \Delta \vec{r}_{veh} \Delta \vec{r}_{struct} \right\rangle}{2d\tau}$$

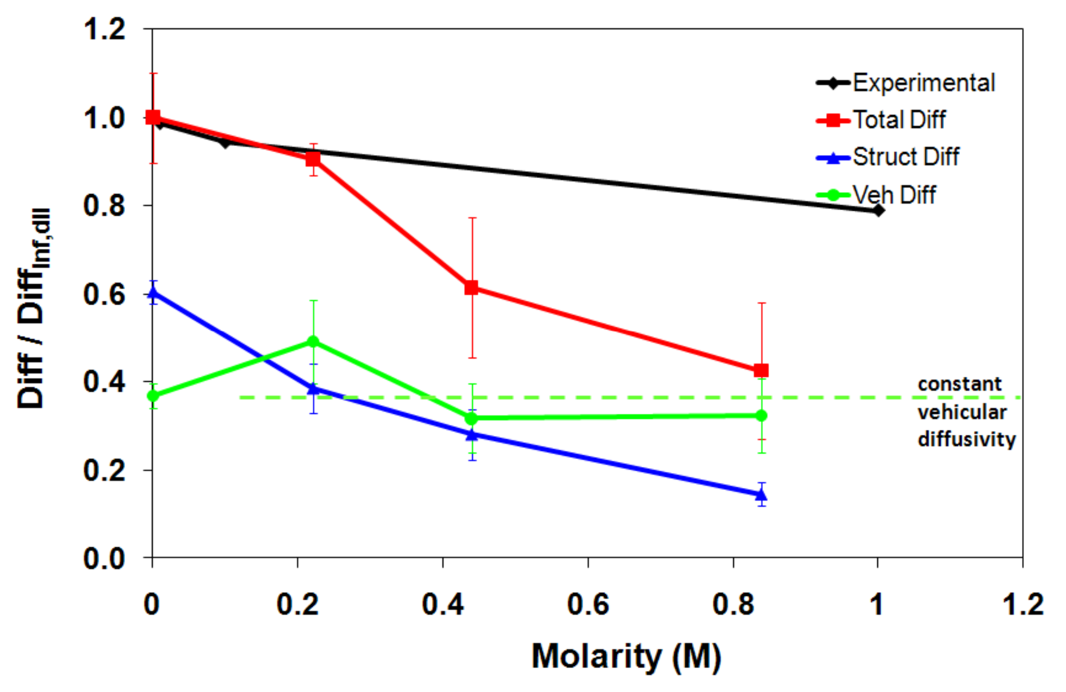
# Bulk HCl Solution:  Effect of High Acidity

simulation snapshot
periodic system
15 $H^+$
15 $Cl^-$
1875 $H_2O$
$\lambda = 125$
conc = 0.44 M
pH = 0.36



Legend
O of $H_2O$ – red
O of $H_3O^+$ – green
H – white
$Cl^-$ – blue

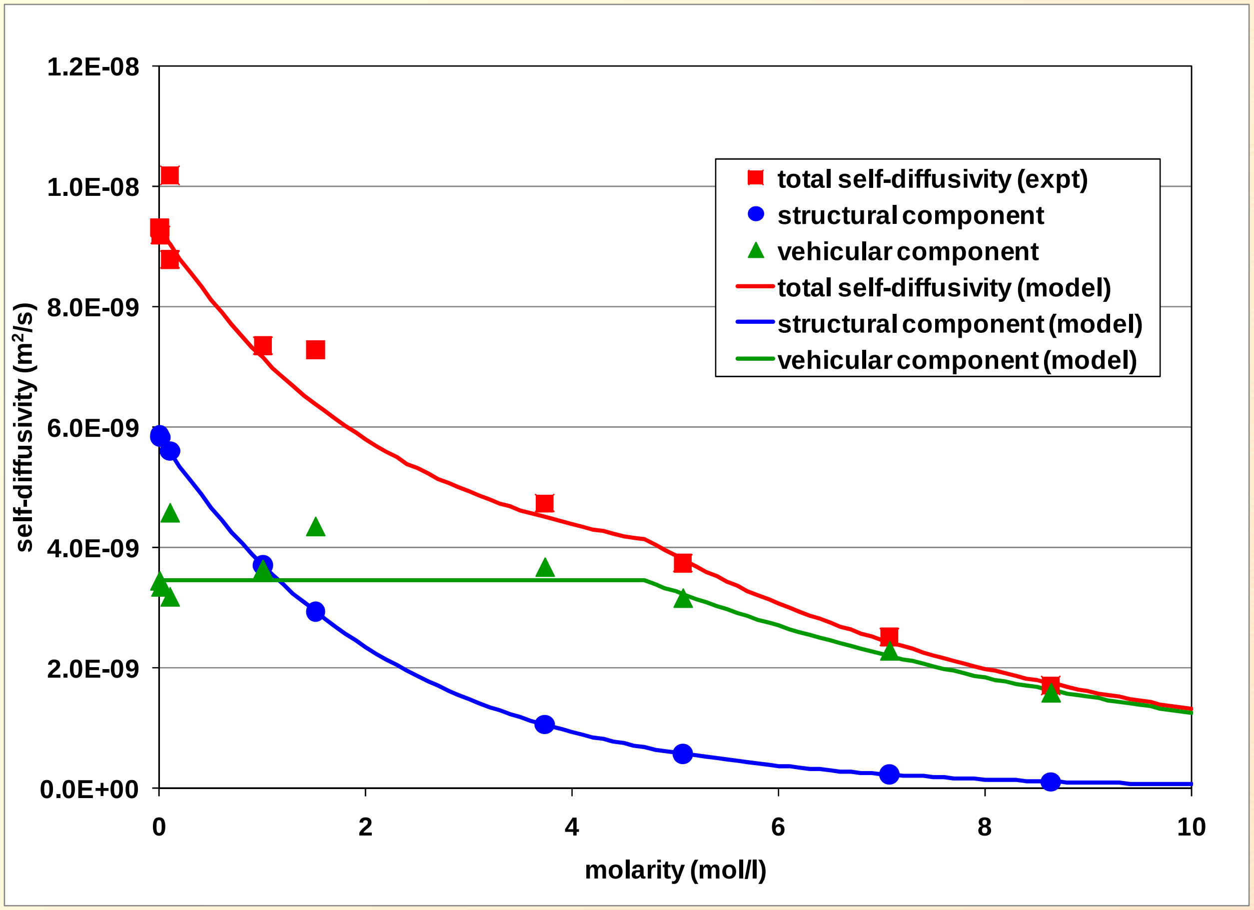
# Bulk HCl Solution: Effect of High Acidity



experimental data from.
Cornish, B. D.; Speedy, R. J. *J. Phys. Chem.*, *1984*, *88*, 1888.

- Total charge diffusivity follows the same trend as experimental value but is a bit steeper
- Vehicular component of the charge diffusion is almost constant irrespective of the concentration
- Structural diffusion decreases with increases in HCl concentration and plays a major role in determining the dependence of charge diffusion on the concentration

# Bulk HCl Solution: Effect of Acidity in an Analytical Fit

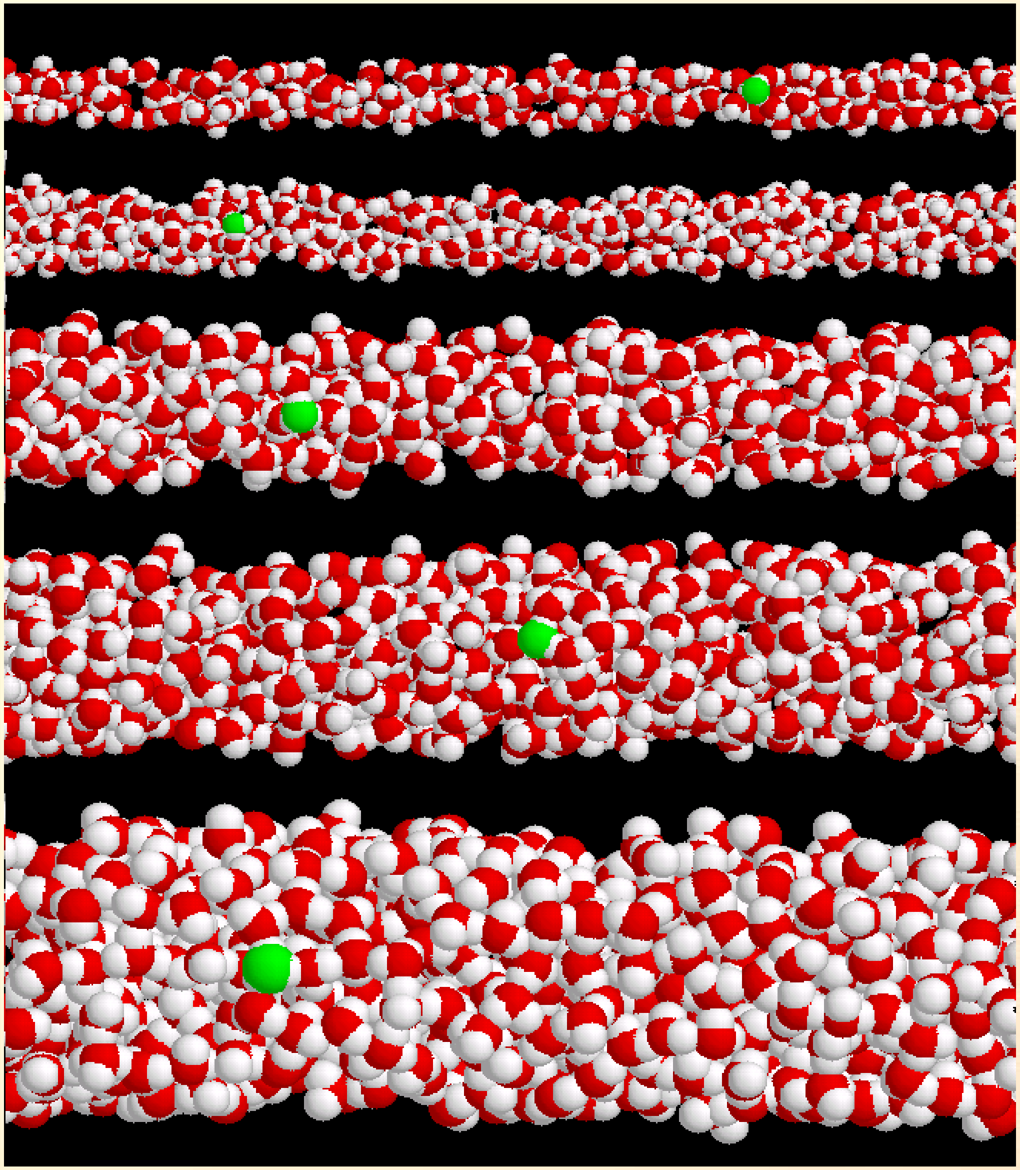


Esai Selvan, M., Calvo-Muñoz, E.M., Keffer, D.J., *J. Phys. Chem. B*, dx.doi.org/10.1021/jp115004 , 2011.

experimental data from.
Cornish, B. D.; Speedy, R. J. *J. Phys. Chem.*, 1984.
Dippel, Th.; Kreuer, K.D., *Solid State Ionics*, 1991.

- Experimental data for total value
- Two assumptions (validated by RMD) for structural and vehicular components
  - Decline in diffusivity due to pH is in the structural component
  - Structural and diffusive components remain uncorrelated

# Proton Transport in Nanotubes: Effect of Confinement



Nominal radii from 5.42 to 10.85 Å.

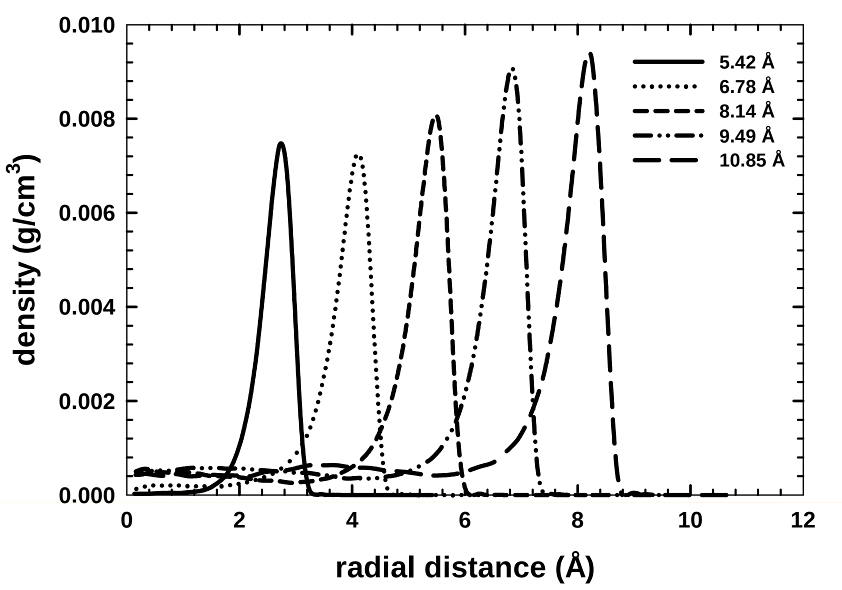
Infinitely dilute simulations (1 excess $H^+$)

Results averaged over 144 independent simulations.

Snapshots show $H_3O^+$ at pore wall with O atom extended outward.

Esai Selvan, M. *et al*.
*Mol. Simul.*, 2010.

# Proton Transport in Nanotubes: Effect of Confinement

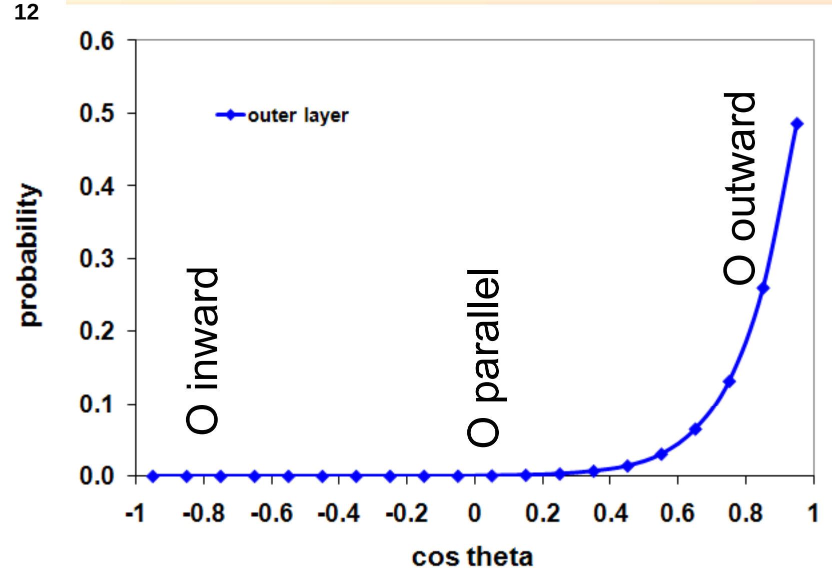


**Density distribution of $H_3O^+$.**

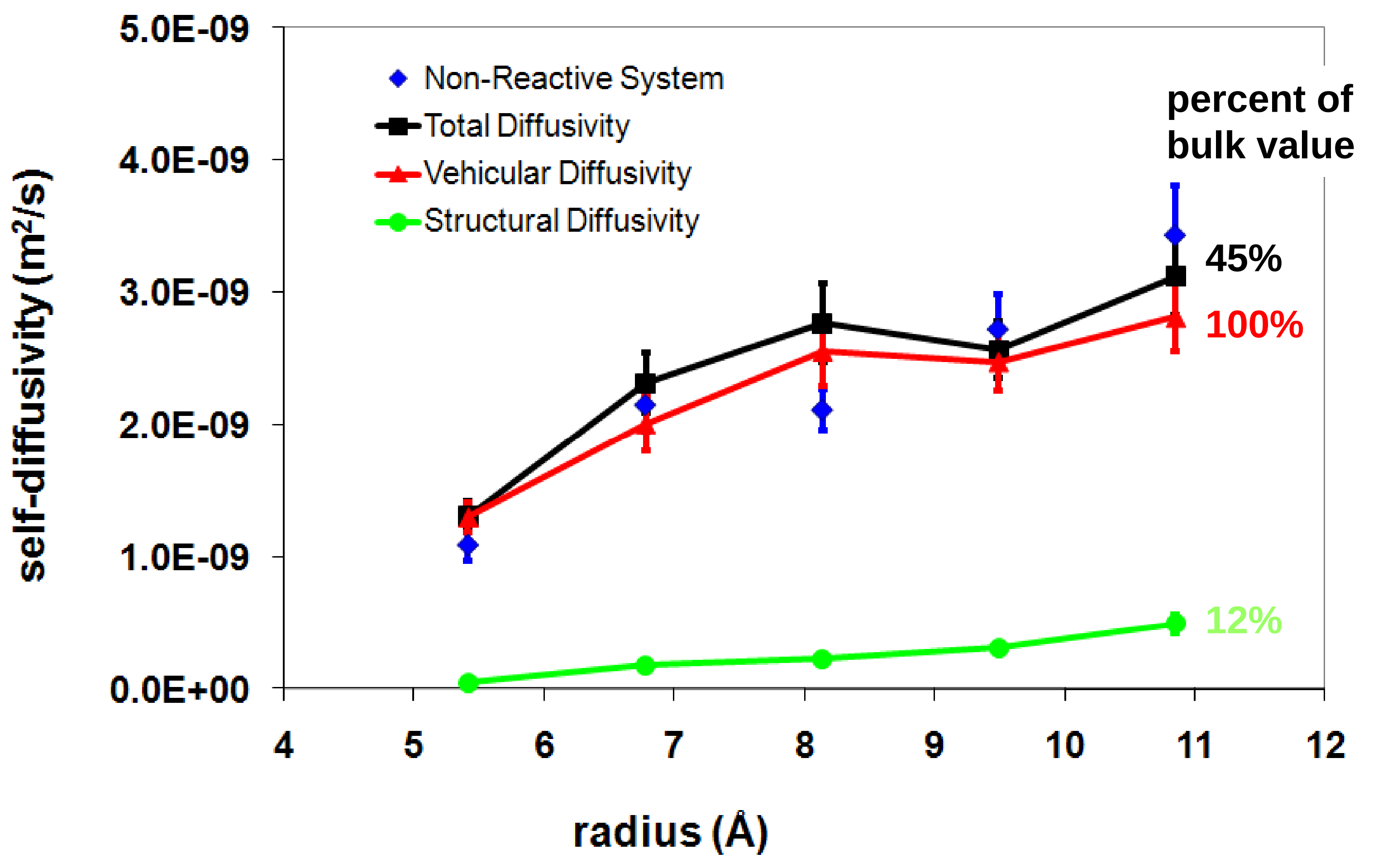
$H_3O^+$ is preferentially located at pore wall.

**orientation distribution of $H_3O^+$.**

$H_3O^+$ is preferentially oriented with oxygen at the pore wall, so as to maximize hydrogen bonding network with 3 hydrogen.



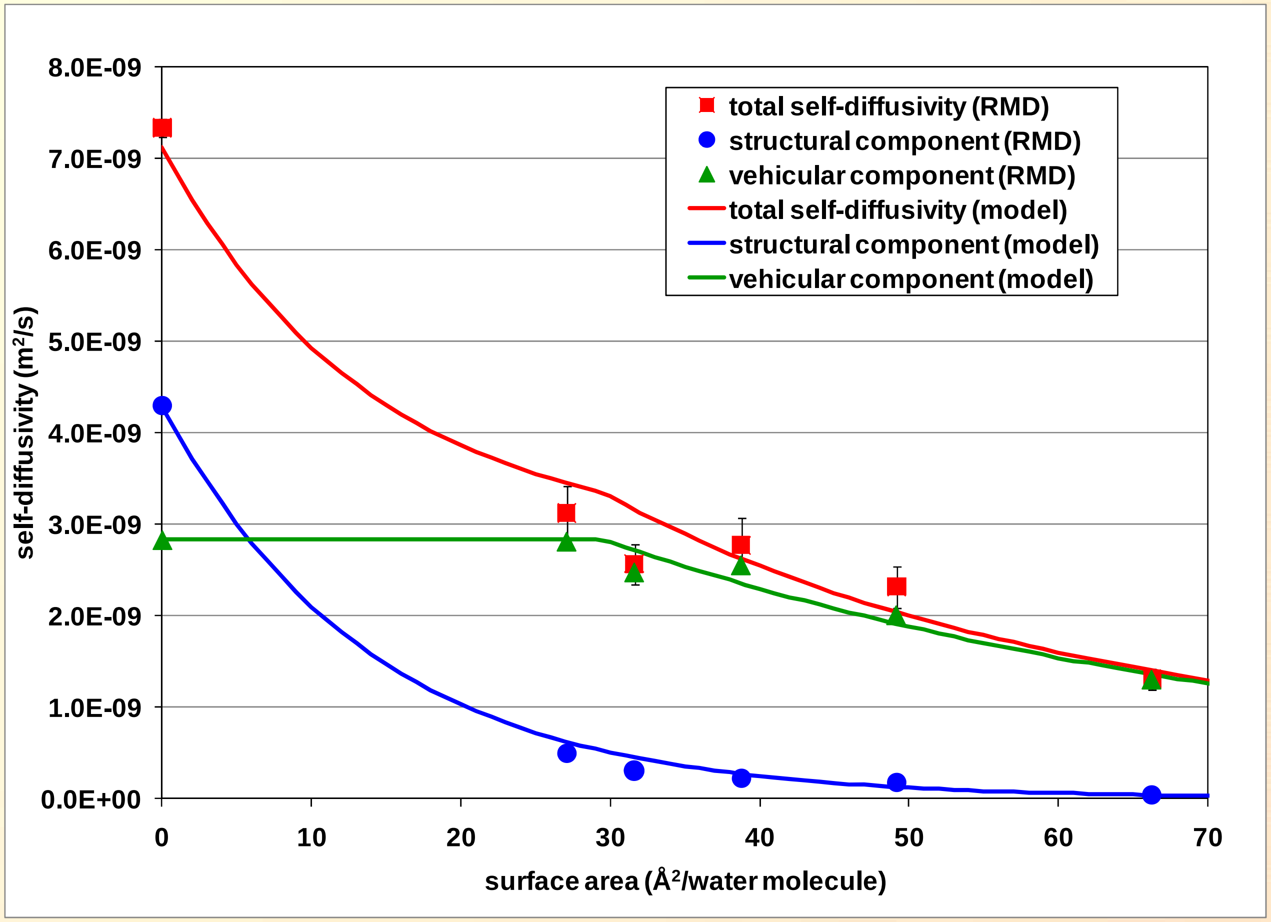
# Proton Transport in Nanotubes: Effect of Confinement



Esai Selvan, M., Keffer, D.J., Cui, S., Paddison, S.J., **36**(7-8), *Molec. Sim.* pp. 568–578.

Confinement dramatically reduces structural diffusion.

# Nanotubes:  Effect of Confinement in an Analytical Fit

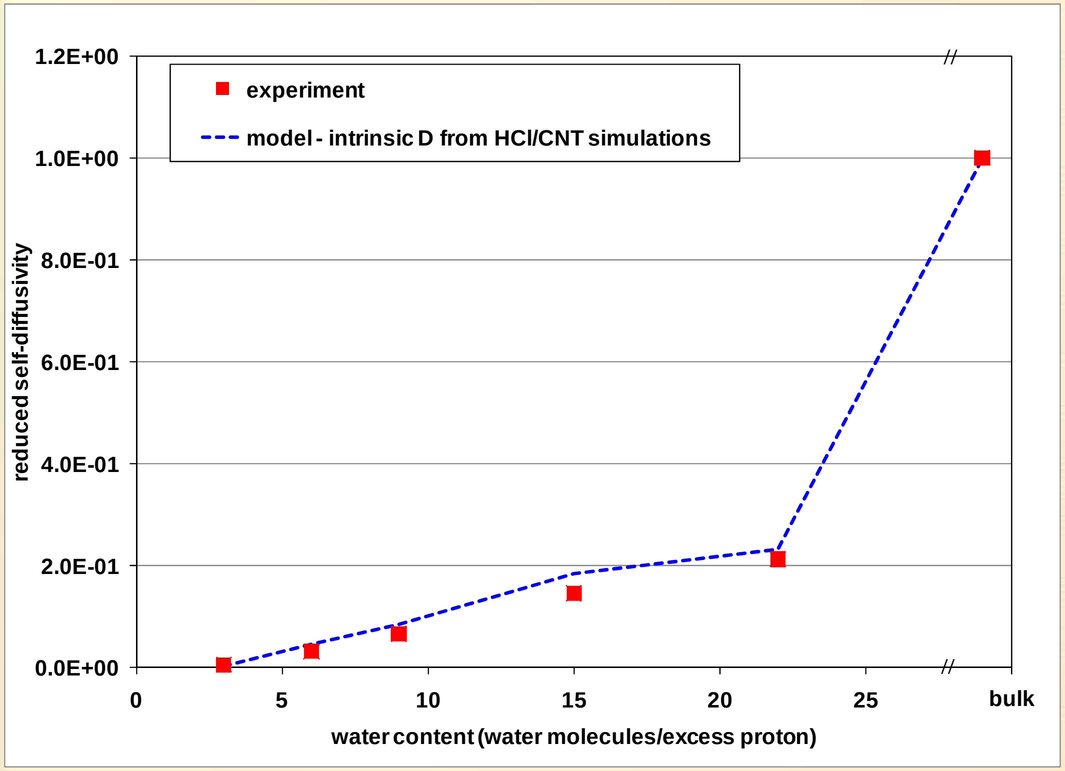


Esai Selvan, M., Calvo-Muñoz, E.M., Keffer, D.J., *J. Phys. Chem. B*, dx.doi.org/10.1021/jp1115004 , 2011.

- Two assumptions (validated by RMD) for structural and vehicular components
  - Decline in diffusivity due to confinement is in the structural component
  - Structural and diffusive components remain uncorrelated

# 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.

# Conclusions

Reactive Molecular Dynamics simulations were used to model water and proton transport in four systems:

- bulk water
- bulk HCl sol'n
- water in carbon nanotubes
- hydrated Nafion

MD simulations & Confined Random Walk theory

- yield water self-diffusivities in excellent agreement with expt

An analytical model incorporating

- acidity (concentration of $H_3O^+$ in aqueous domain)
- confinement (interfacial surface area per $H_2O$)
- connectivity (percolation theory based on $H_2O$ transport)

is capable of quantitatively capturing the self-diffusivity of both water and charge as a function of water content

Future Work: Apply this approach to other systems with novel nanostructures.

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# Questions?