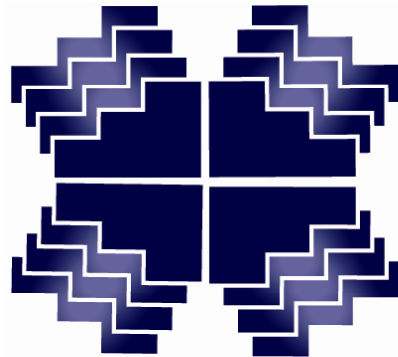# Multiscale Materials Modeling

Lecture 05

Proton Transport in Aqueous Systems

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Sustainable Technology through
Advanced Interdisciplinary Research
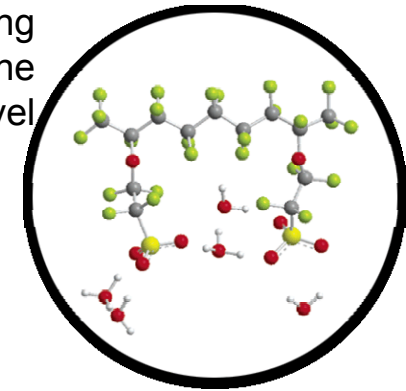
Fundamentals of Sustainable Technology

Proton Transport in Aqueous Systems

Moving toward fuel cell-powered vehicles

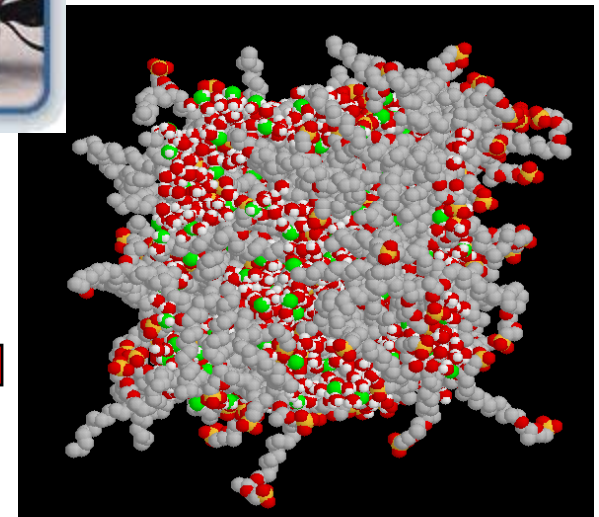understanding starts at the quantum level

H_2-powered autos become a reality

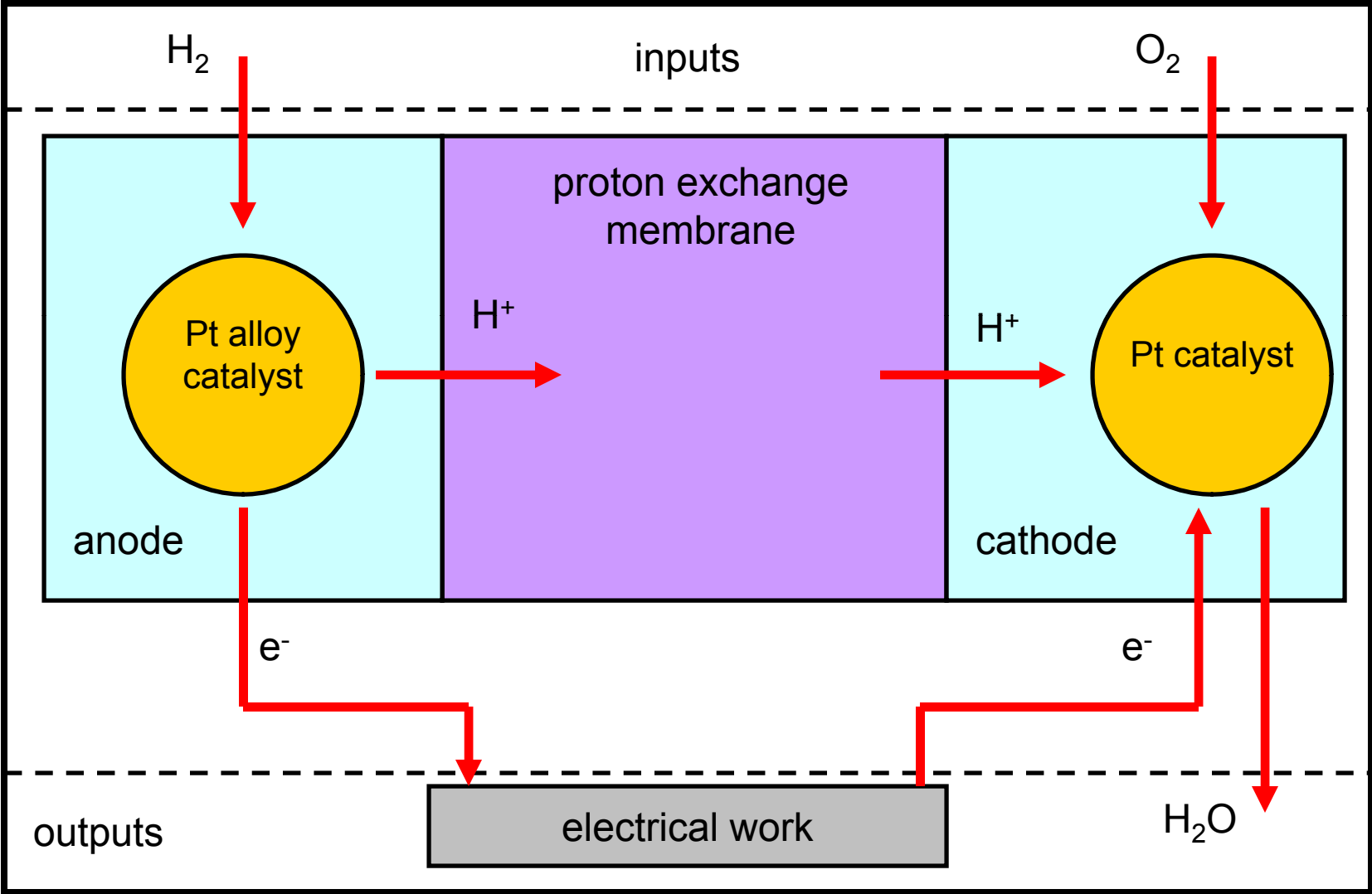leads to high-fidelity coarse-grained models

impacts fuel cell performance

improved nanoscale design of membrane/electrode assembly

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how fuel cells work: conceptual level

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industry standard:
Nafion (DuPont)
perfluorosulfonic acid

sulfonic acid at
end of side chain
provides protons

monomer backbone contains CF_2.
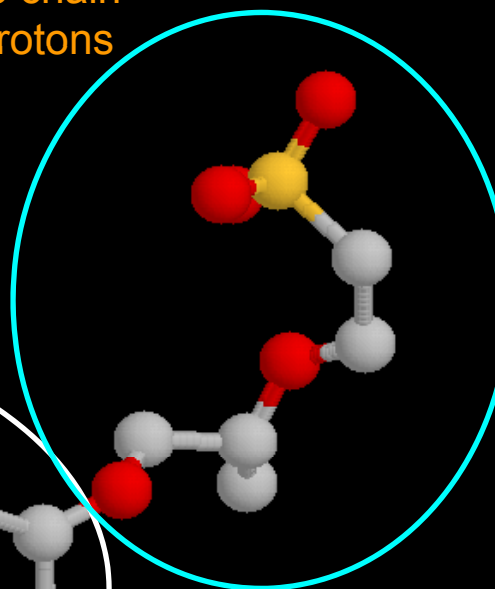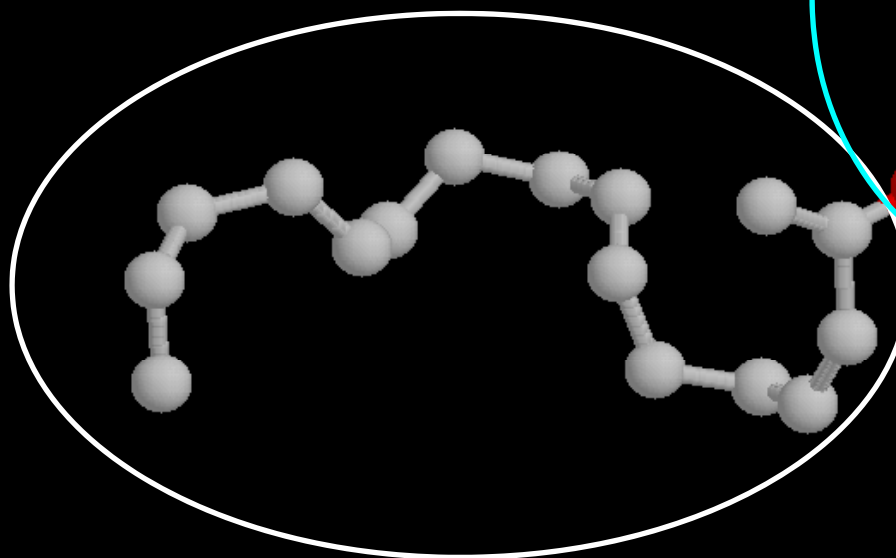
side chain

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

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self-diffusivity (m²/s)

bulk value = 9.7×10^{-9} m²/s

Robison, R. A.; Stokes, R. H. *Electrolyte Solutions*; 1959.

T = 300 K

Nafion (EW=1100) Kreuer, K. D. *Solid State Ionics* **1997.**

saturated value = 2.1×10^{-9} m²/s

Nafion 117

λ (water per sulfonic acid)
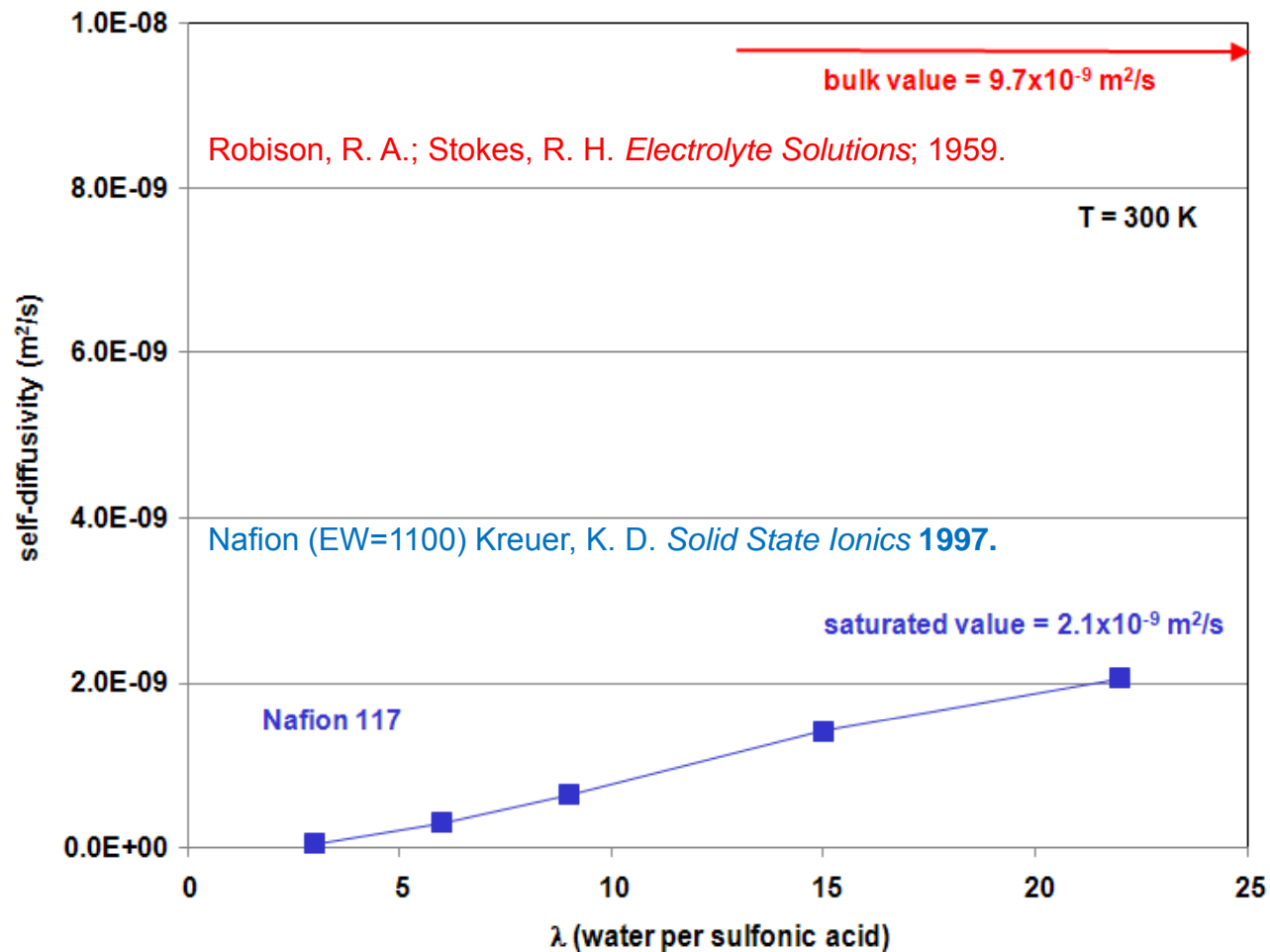
Even at saturation, the self-diffusivity of charge in Nafion is 22% of that in bulk water.

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morphology of bulk hydrated membrane

Nafion

EW = 1144
λ = 6 H_2O/HSO_3
T = 300 K
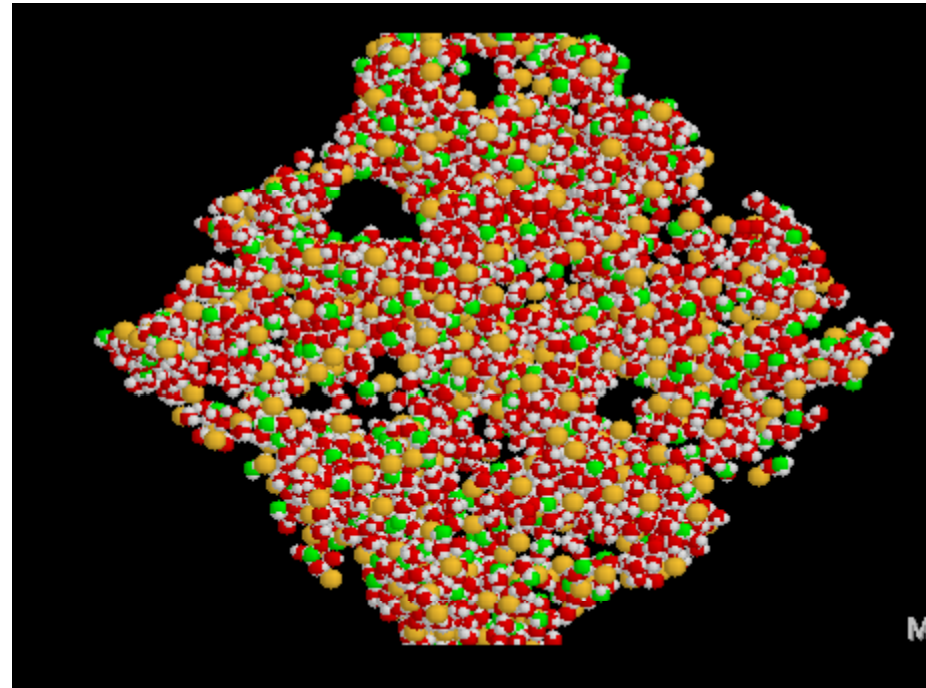
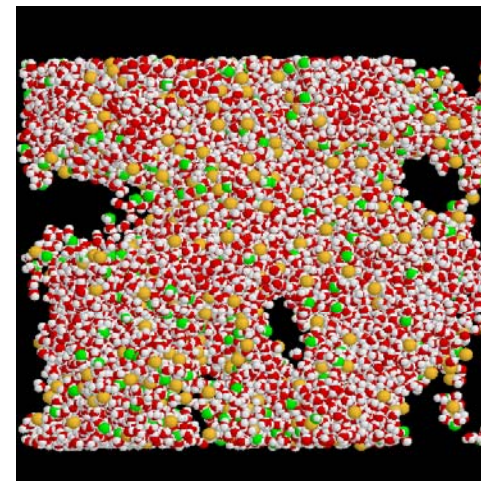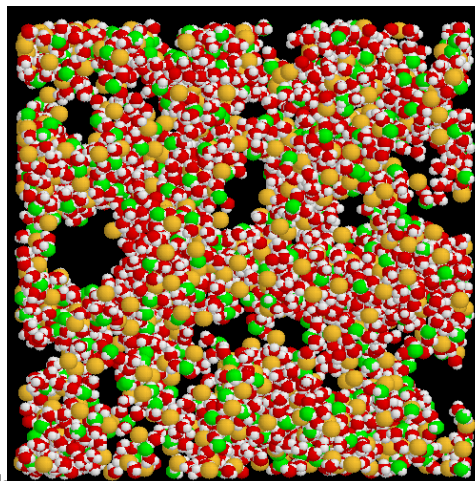Snapshots of the aqueous nanophase

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.

low water (λ = 6)
small aqueous channels

high water (λ = 22)
large aqueous channels

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Proton Transport – Two Mechanisms

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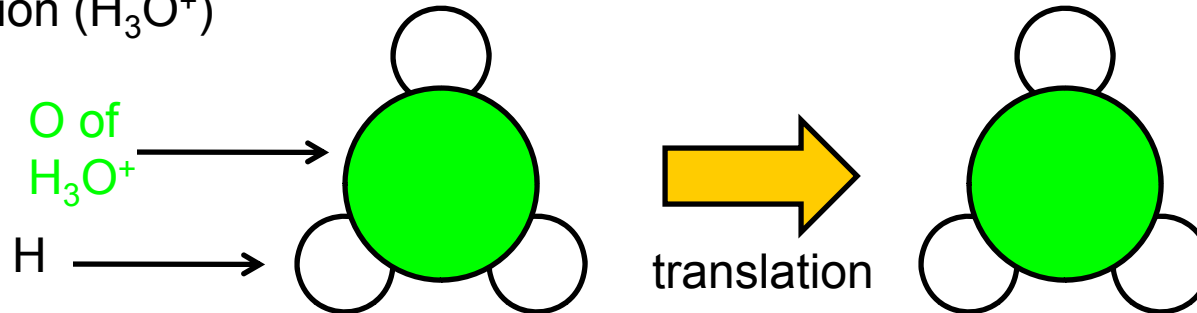
O of H_3O^+

H

translation

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

1 3 2

proton hops

1 3 2

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

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Outline
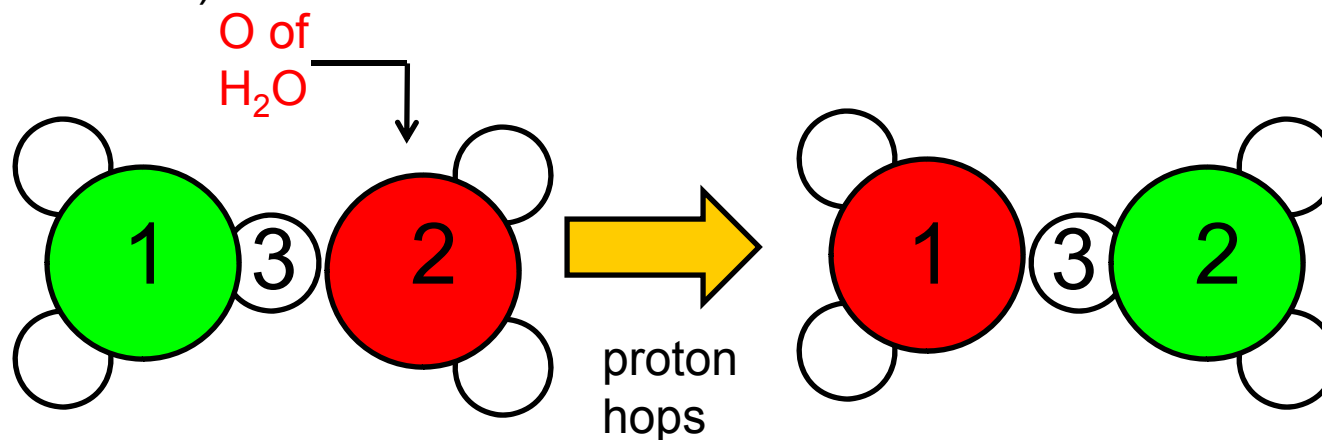
Proton Transport in Aqueous Systems

I. Introduction

II. Levels of Modeling

   II.A. Quantum Mechanics

   II.B. Reactive Molecular Dynamics

   II.C. Confined Random Walk Theory
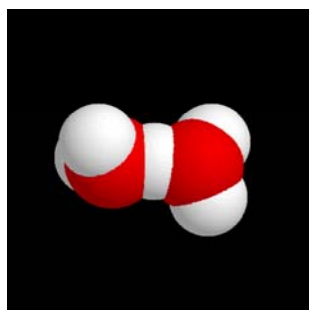
   II.D. Percolation Theory

III. Conclusions
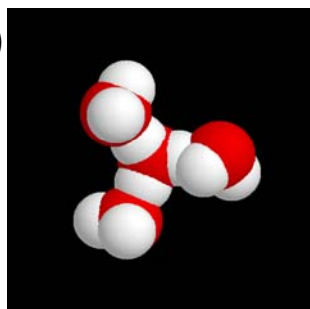
Understanding of fundamental mechanism of structural diffusion

Hydronium ions exist as hydrated ion complexes like

Zundel ions ($H_5O_2^+$)

and Eigen ions ($H_9O_4^+$)

structural diffusion or Proton hopping involves a reaction in which the ground state is likely an Eigen ion and the transition state is a Zundel ion.
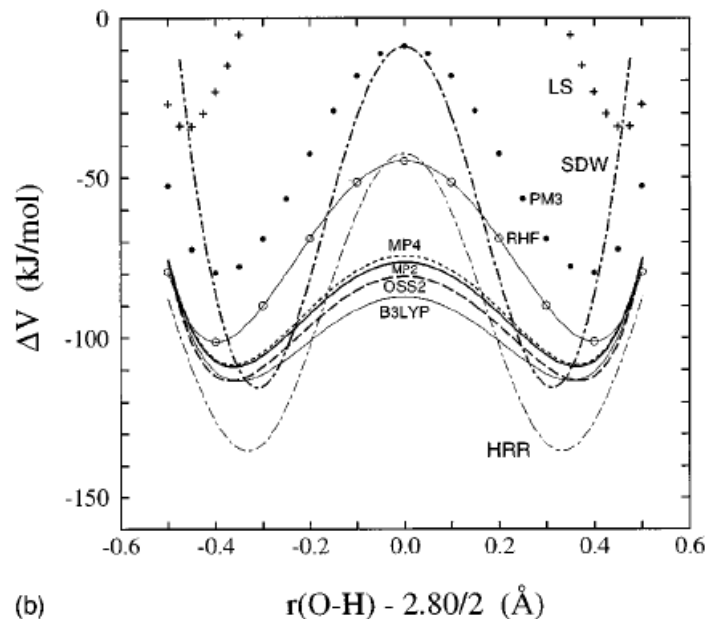

FIG. 3. Proton-transfer energy profiles in the $H_5O_2^+$ ion given by various methods. The distance between the two water molecules was fixed at (a) $R(O-O)=2.40$ Å (the optimized MP2 value at equilibrium) and (b) at $R=2.80$ Å. The proton is moved along and on the line connecting the two oxygen atoms. The other geometrical parameters are always fixed at the equilibrium MP2 values. The energy is given relative that of the free oxonium and water monomers. The potentials shown are OSS2 (dashed line), MP2 (solid line), MP4 (short dashes), B3LYP (thin solid line), RHF (thin solid line with open circles), PM3 (filled circles), LS (+), SDW (dash-dot line) and HRR (thin dash-dotted line). Corresponding results for the OSS1(p)–3(p) potentials are given in Fig. 4.

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Ojamäe, Shavitt, Singer
J. Chem. Phys. 1998

Zundel & Eigen Ions

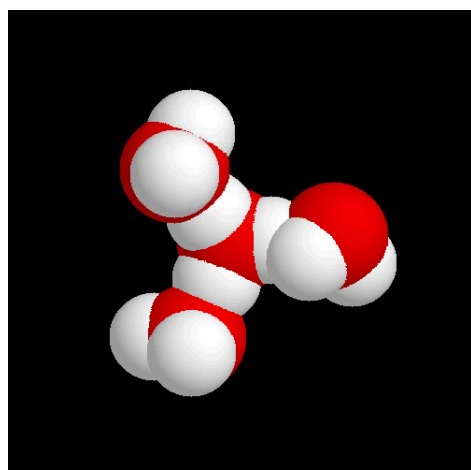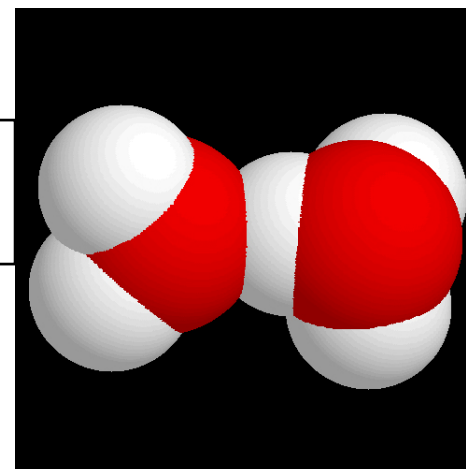**Quantum Mechanics**   **Molecular Dynamics**
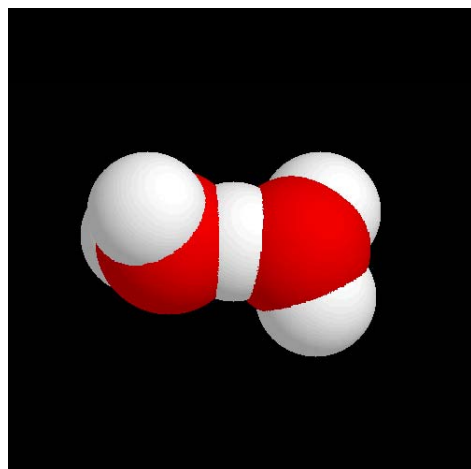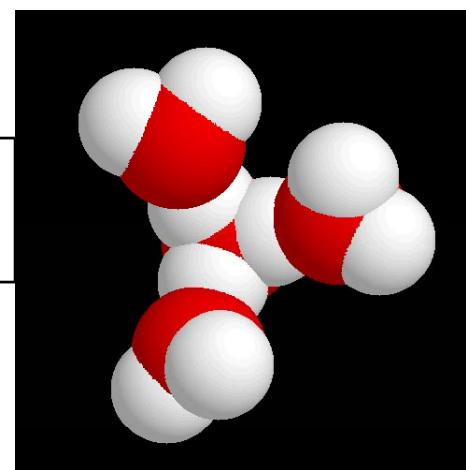
Zundel ion

MD at $\lambda = 4.4$

Huang, Braams, Bowman,
J. Chem. Phys. 2005

Eigen ion

MD at $\lambda = 4.4$
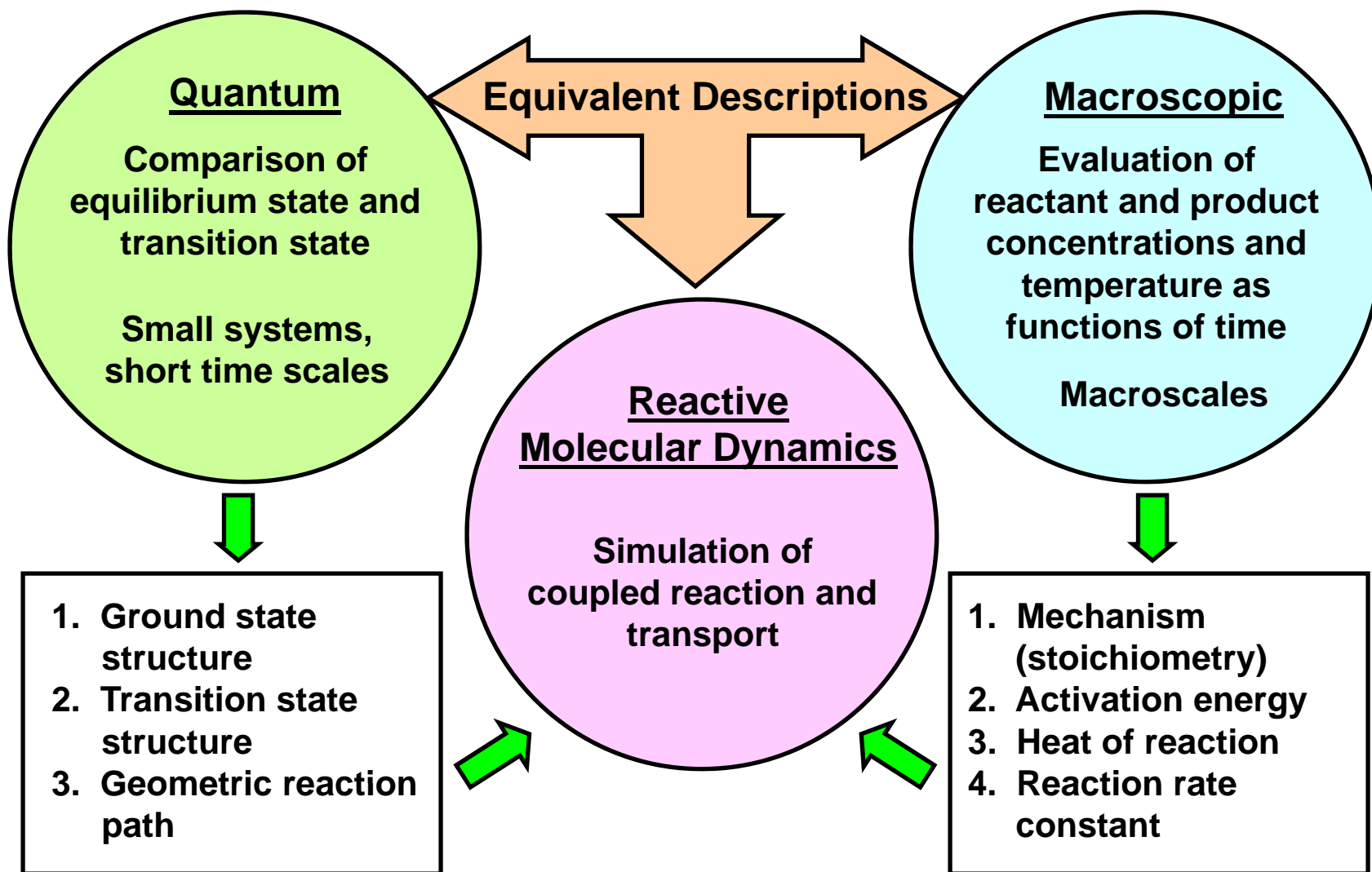
Ojamäe, Shavitt, Singer
J. Chem. Phys. 1998

MD simulations will only approximate the structures from Quantum Mechanics.

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Outline

Proton Transport in Aqueous Systems

Reactive Molecular Dynamics (RMD)

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Quantum

Comparison of equilibrium state and transition state

Small systems, short time scales

Equivalent Descriptions

Macroscopic

Evaluation of reactant and product concentrations and temperature as functions of time

Macroscales

Reactive Molecular Dynamics

Simulation of coupled reaction and transport

1. Ground state structure
2. Transition state structure
3. Geometric reaction path

1. Mechanism (stoichiometry)
2. Activation energy
3. Heat of reaction
4. Reaction rate constant

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Variety of Approaches of Simulation of Structural Diffusion

Author	Year	Method	Features	System
R. Car & M. Parinello [1]	1985	Car–Parrinello MD	• Computationally expensive • Restricted to small systems	• Excess H^+ in H_2O [2] • Nonaqueous hydrogen bonded media
A. Warshel [3]	1980	Empirical Valence Bond	• Charge transfer theory of hydrogen bonded complexes • Used to develop MS-EVB, SCI-MS-EVB, MS-EVB3	• Excess H^+ in H_2O [4,5] • Enzymes
R.G. Schmidt & J. Brickmann [6]	1997	Mixed MD and MC	• Proton hopping between titratable sites • Criteria - Distance between donor and acceptor	• Excess H^+ in H_2O • Proton in amino acid
M.A. Lill & V. Helms [7]	2001	Q-HOP MD	• Proton hopping between titratable sites • Criteria - Distance and environmental effect of the surrounding group	• Excess H^+ in H_2O • Aspartic acid in H_2O • Imidazole ring in H_2O

[1] R. Car and M. Parinello, *Phys.Rev.Lett.*, 55, 2471 (1985).

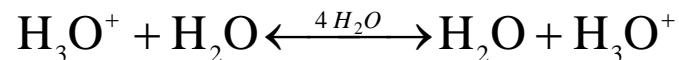[2] M. Tuckerman, et al., *J.Chem.Phys.*, 103, 150 (1995).

[3] A. Warshel and R.M. Weiss, *J. Am. Chem. Soc.*, 102, 6218 (1980).

[4] J. Lobaugh and G.A. Voth, *J. Chem. Phys.*, 104, 2056 (1996).

[5] D.E. Sagnella and M.E. Tuckerman, *J. Chem. Phys.*, 108, 2073 (1998).
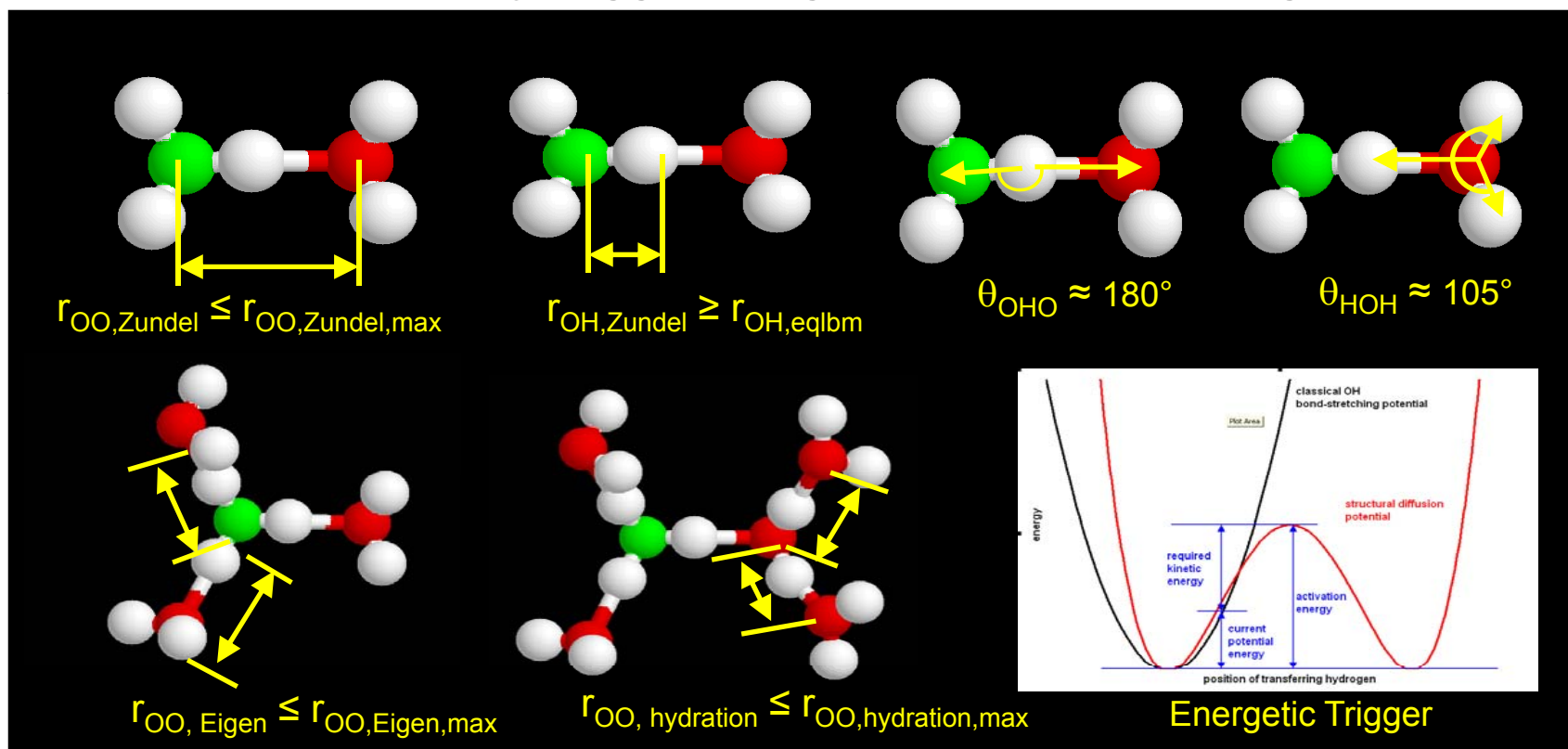
[6] R.G. Schmidt and J. Brickmann., *Ber. Bunsenges. Phys. Chem.*, 101, 1816 (1997).

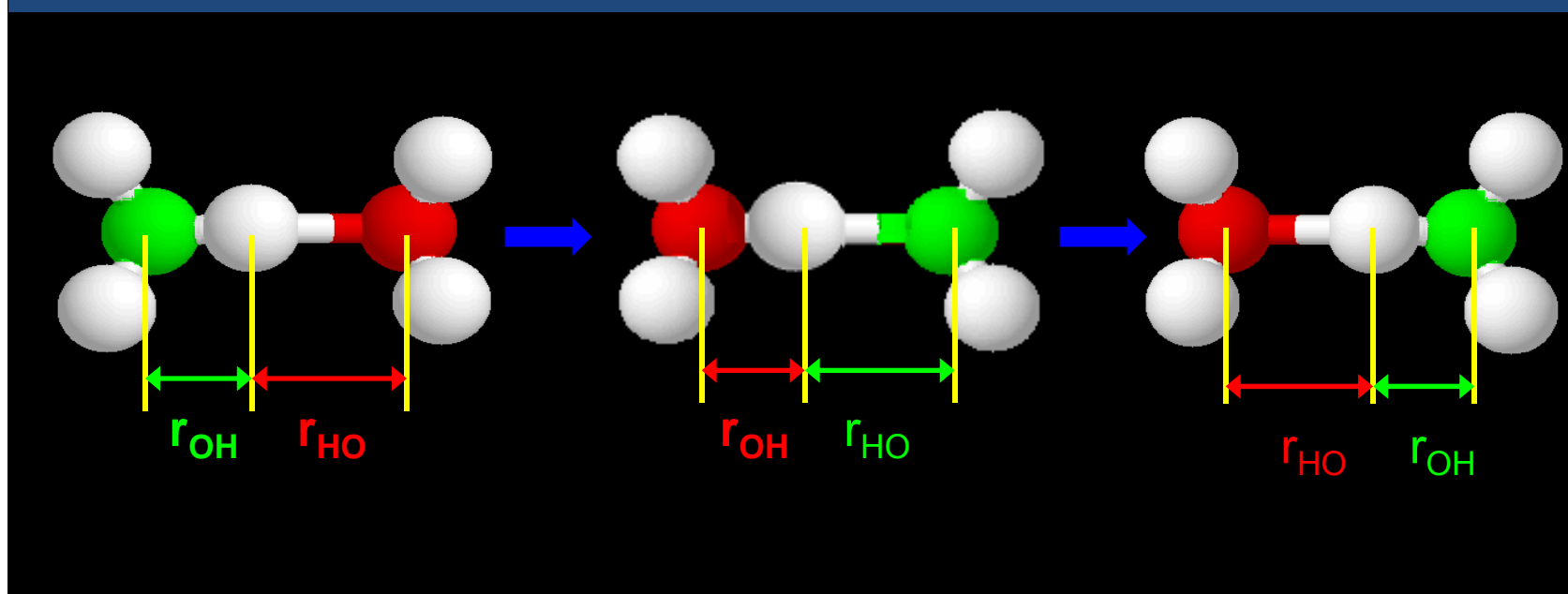[7] M.A. Lill and V. Helms, *J. Chem. Phys.*, 115, 7993 (2001).

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$$H_3O^+ + H_2O \xleftrightarrow{4\,H_2O} H_2O + H_3O^+$$

At each step of conventional MD simulation, check if reactant (H_3O^+) is in a reactive configuration.

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

$r_{OO,Zundel} \leq r_{OO,Zundel,max}$

$r_{OH,Zundel} \geq r_{OH,eqlbm}$

$\theta_{OHO} \approx 180°$

$\theta_{HOH} \approx 105°$

$r_{OO, Eigen} \leq r_{OO,Eigen,max}$

$r_{OO, hydration} \leq r_{OO,hydration,max}$

Energetic Trigger

Step 2. Instantaneous Reaction

O of H_3O^+ = green
O of H_2O = red
H = white
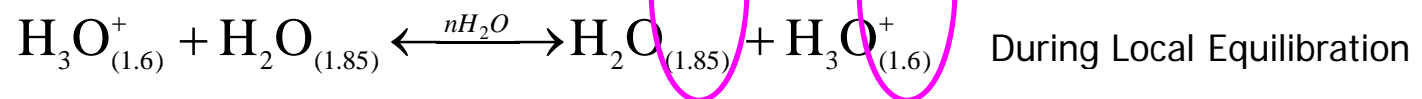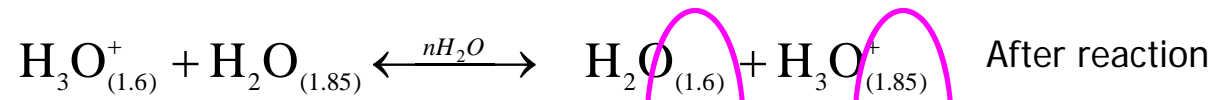

- Exchange identities of H_3O^+ and H_2O molecules

- Move proton over to the newly formed hydronium ion so that r_{OH} of the hydronium before and after reaction are the same

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Step 3. Local Equilibration

- There is an increase in the potential energy of the system and disturbance of structure

$$H_3O^+_{(1.6)} + H_2O_{(1.85)} \xleftrightarrow{nH_2O} H_2O_{(1.6)} + H_3O^+_{(1.85)}$$ After reaction

$$H_3O^+_{(1.6)} + H_2O_{(1.85)} \xleftrightarrow{nH_2O} H_2O_{(1.85)} + H_3O^+_{(1.6)}$$ During Local Equilibration

- Helps in restoring system structurally and maintaining the correct heat of reaction

Objective Function

energetic term   structural term

$$F_{obj} = w_1 \Delta U^{RMS} + w_2 \Delta g(r)^{RMS}$$

$$\Delta U^{RMS} = \sqrt{\left(\frac{U_{After} - U_{Before}}{U_{Before}}\right)^2}$$

$$\Delta g(r)^{RMS} = \sqrt{\frac{1}{N_{pairs}} \sum_{i=1}^{i=N_{pairs}} \left(\frac{r_{ij} - r_{ij}^{target}}{r_{ij}^{target}}\right)^2}$$
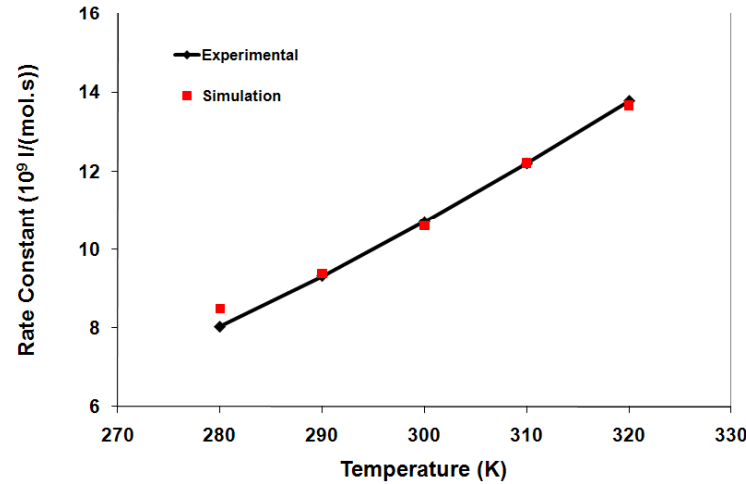
O of H_3O^+ = green
O of H_2O = red
H = white
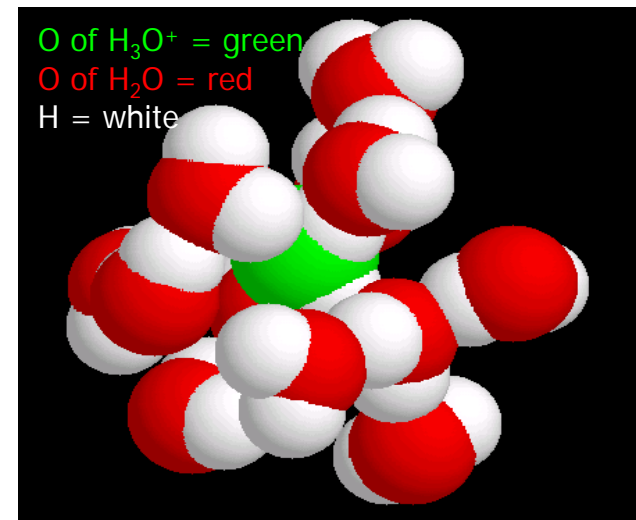
Snapshot representing the complex hydrogen bonding network

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Proton Transport in Bulk Water

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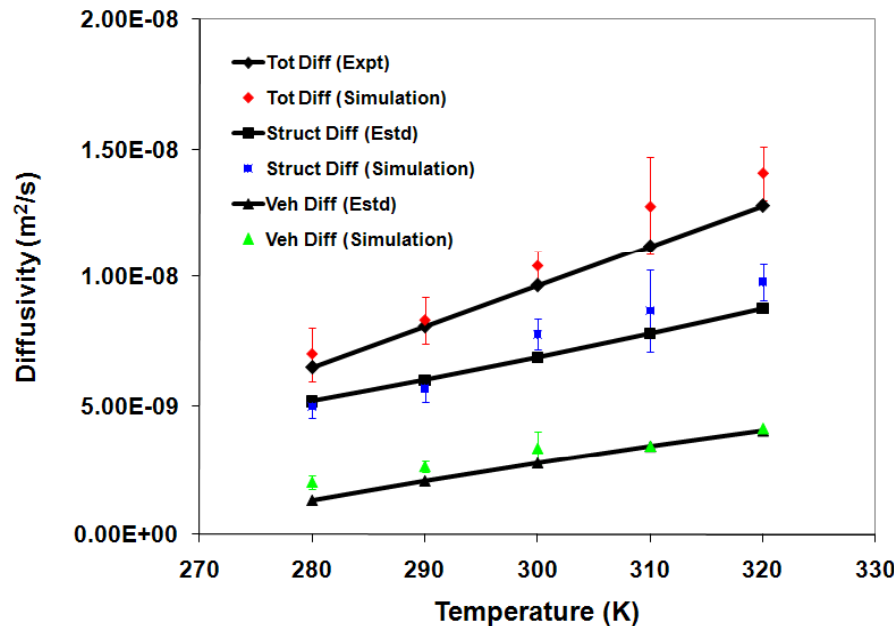
rate law: rate = k $[H_3O^+][H_2O]$

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

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

experimental data from
Luz, Z.; Meiboom, S. *J. Am. Chem. Soc.*, **1964**.
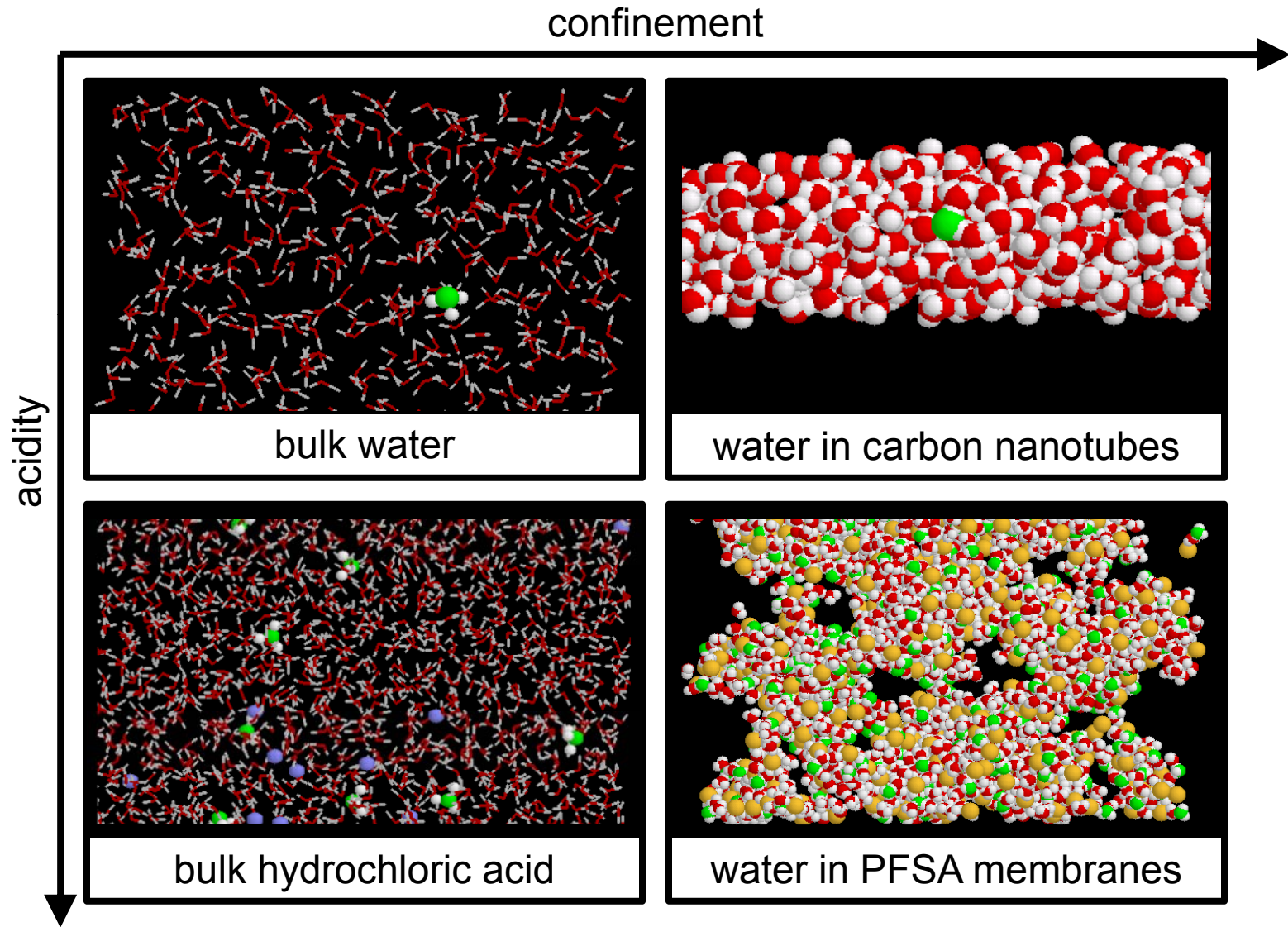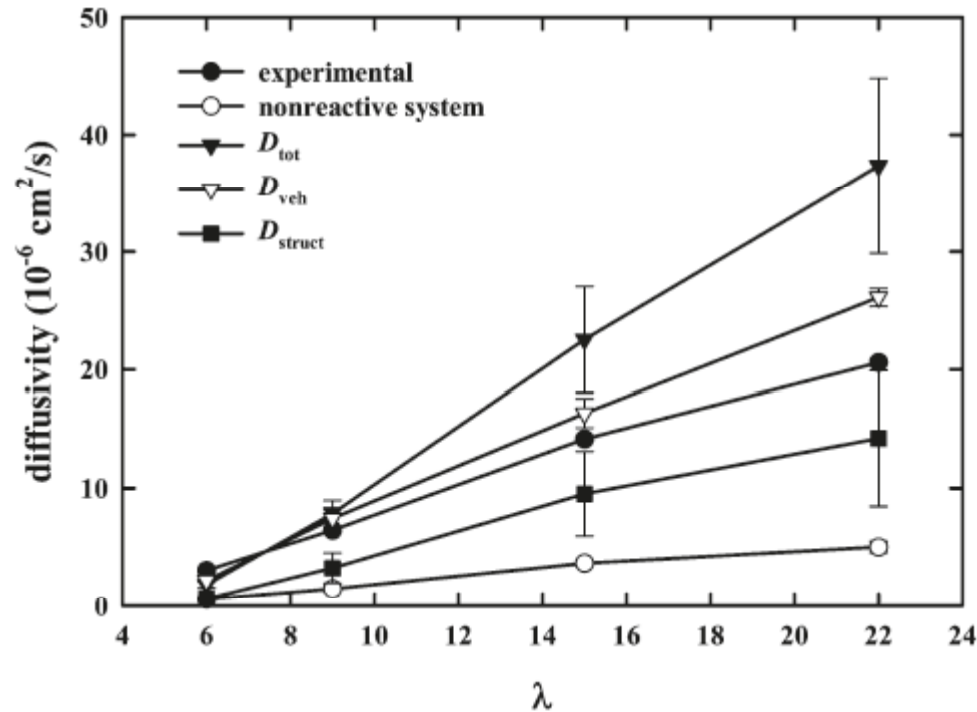
RMD rate constant within 6% of experiment.

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

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

Acidity and Confinement Effects on Proton Mobility

confinement →

acidity ↓

bulk water

water in carbon nanotubes

bulk hydrochloric acid
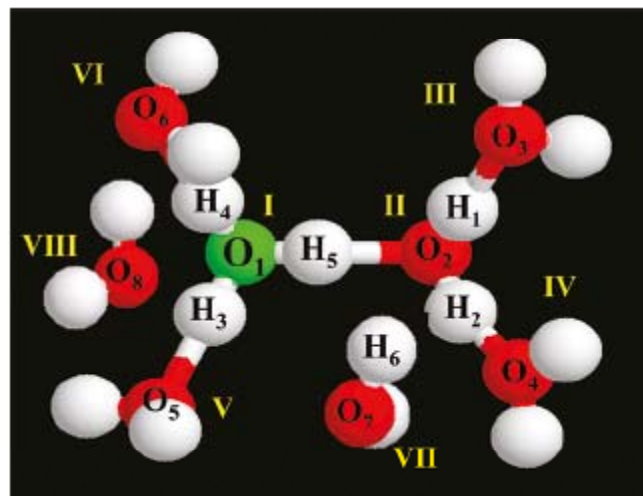

water in PFSA membranes

Introducing structural diffusion into the simulation via the same RMD algorithm that was used for bulk water, HCl solutions and water in carbon nanotubes
● provided a correct quantitative trend
● but the total charge diffusivity was too large
● the vehicular component significantly increased relative to nonreactive MD

The presence of reaction disturbs the local hydrogen-bonding network , resulting in higher mobility of protons (and water (not shown)).

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Figure 1. Typical structure of the reactants surrounded by six hydrating molecules in the bulk water system. Atom and molecule labels serve for identification purposes in Table 2. O of H_3O^+, green; O of H_2O, red; H, white.

Include more water molecules in local equilibration after instantaneous reaction.

Water and Proton Transport in Nafion (Method 2)
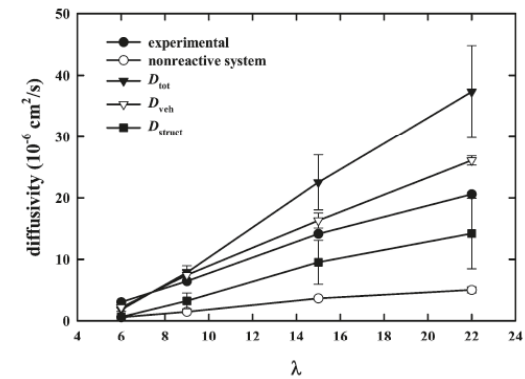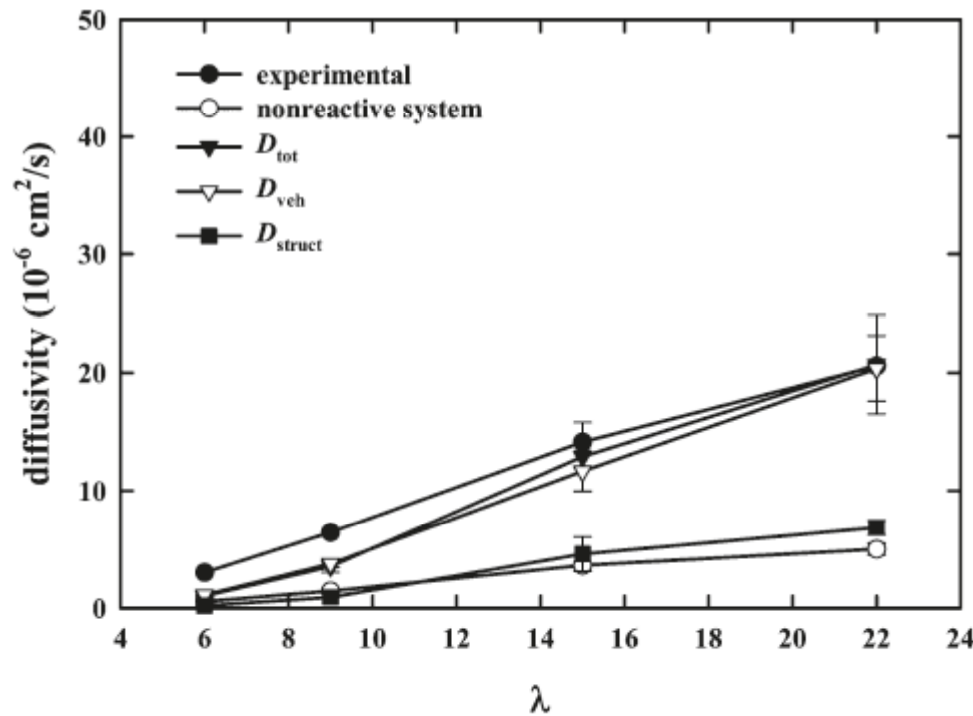
Method 1

Introducing a more stable hydrogen-bonding network after reaction
● provided a correct quantitative trend
● significantly improved quantiative agreement.
● the vehicular component now similar to nonreactive MD

Still observed higher water diffusivity.

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$$D_{tot} = \lim_{\tau \to \infty} \frac{\langle \Delta \vec{r}^2_{veh} \rangle + \langle \Delta \vec{r}^2_{struct} \rangle + 2 \langle \Delta \vec{r}_{veh} \Delta \vec{r}_{struct} \rangle}{2d\tau} \qquad (8)$$

The above definition can be decomposed as

$$D_{veh} \equiv \lim_{\tau \to \infty} \frac{\langle \Delta \vec{r}^2_{veh} \rangle}{2d\tau} \qquad (9a)$$

$$D_{struct} \equiv \lim_{\tau \to \infty} \frac{\langle \Delta \vec{r}^2_{struct} \rangle}{2d\tau} \qquad (9b)$$

$$D_{corr} \equiv \lim_{\tau \to \infty} \frac{2 \langle \Delta \vec{r}_{veh} \Delta \vec{r}_{struct} \rangle}{2d\tau} \qquad (9c)$$

The correlation term is zero in bulk water, HCl solutions and in carbon nanotubes.

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Outline

Proton Transport in Aqueous Systems

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Nafion

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

Snapshots of
the aqueous
nanophase
show a tortuous
path.

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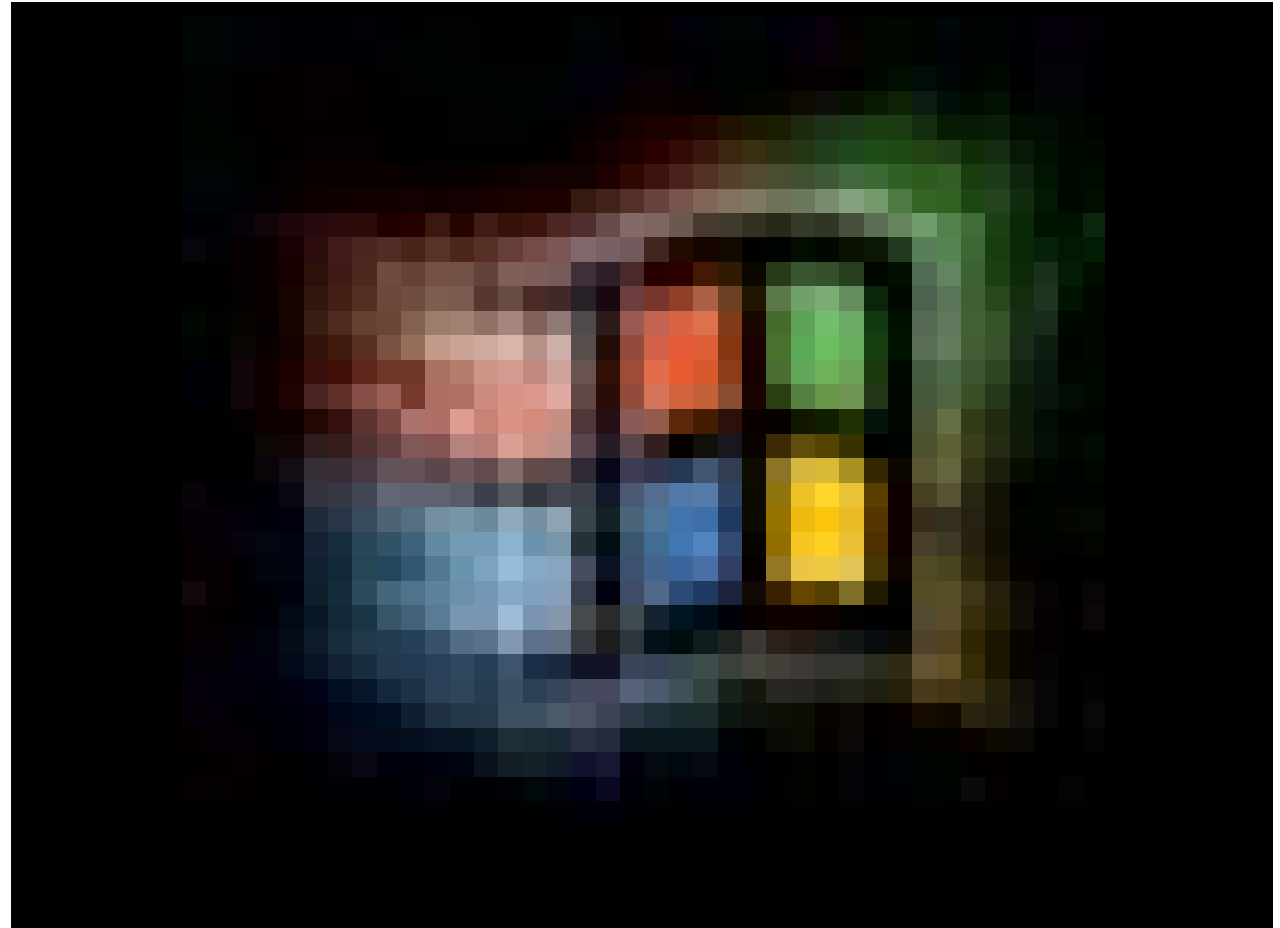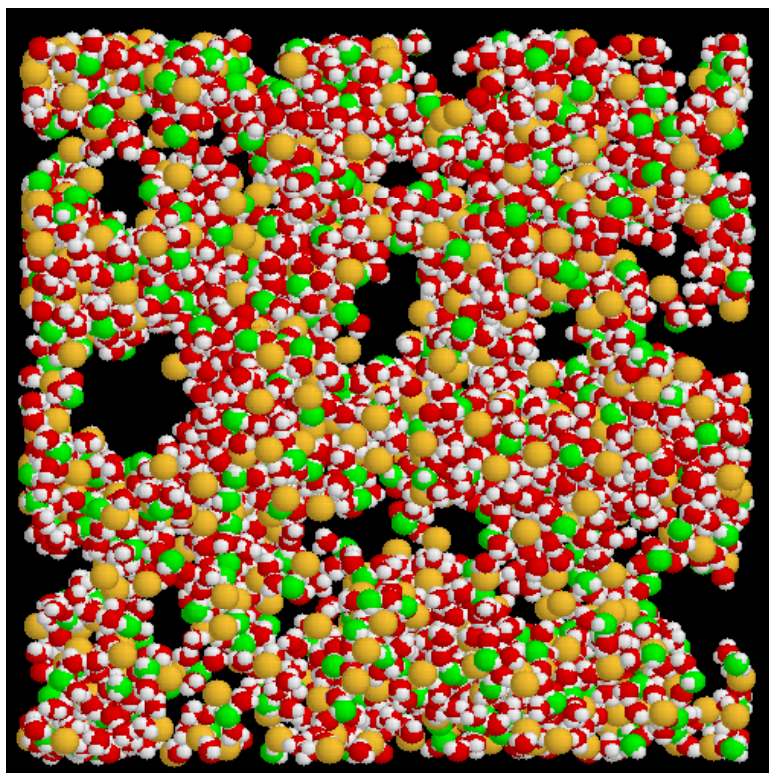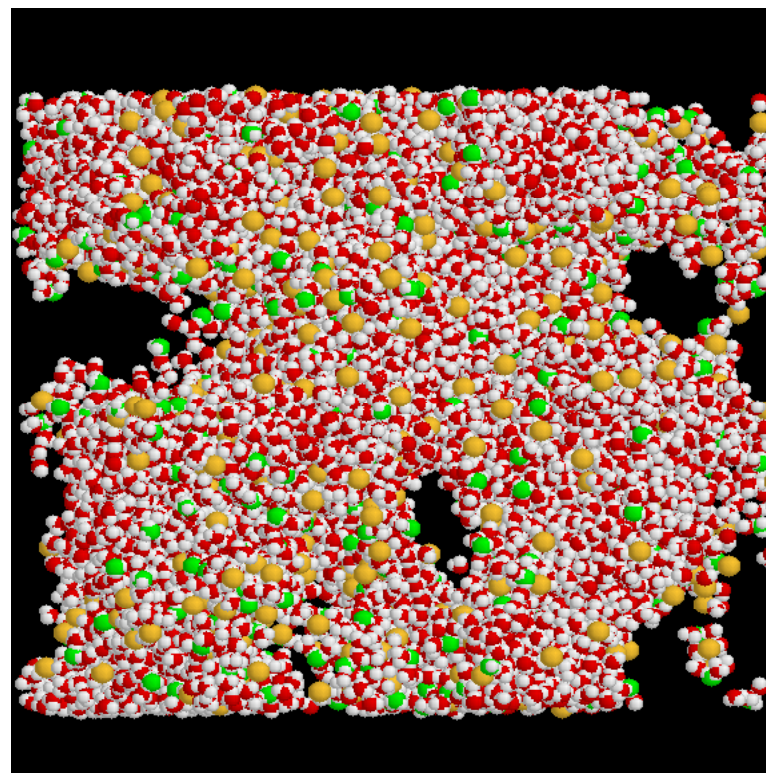O of H_2O = red
H = white
O of H_3O^+ = green
S = orange
remainder of polymer electrolyte not shown

PEM morphology is a function of water content

Nafion (EW = 1144) 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.)

Fundamentals of Sustainable Technology

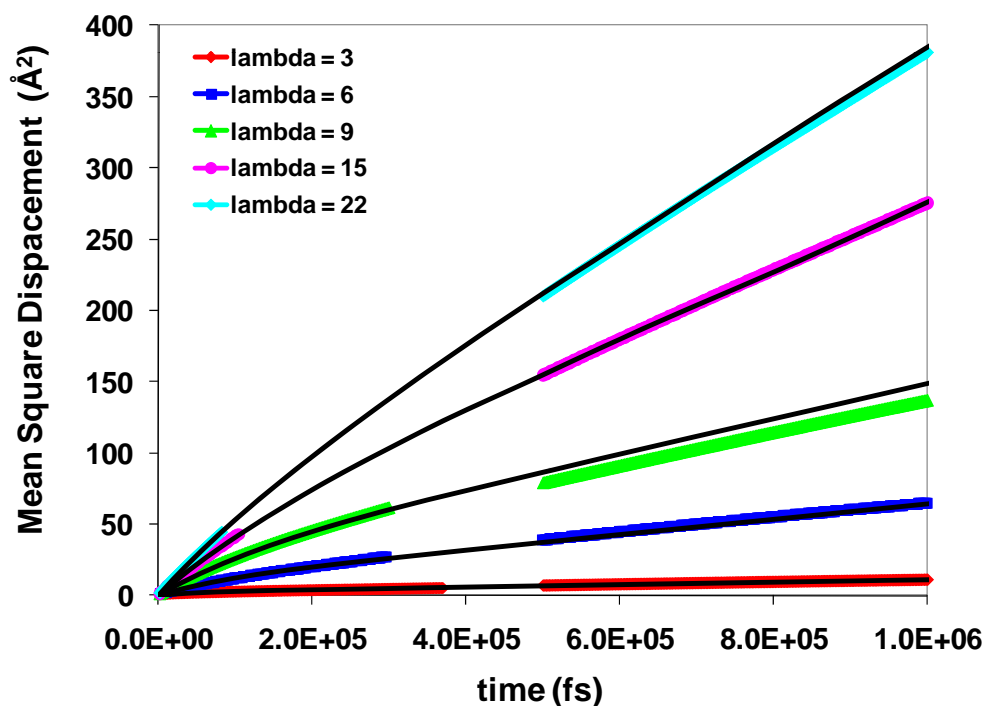Einstein Relation – long time slope of mean square displacement to observation time

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

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.

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

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

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
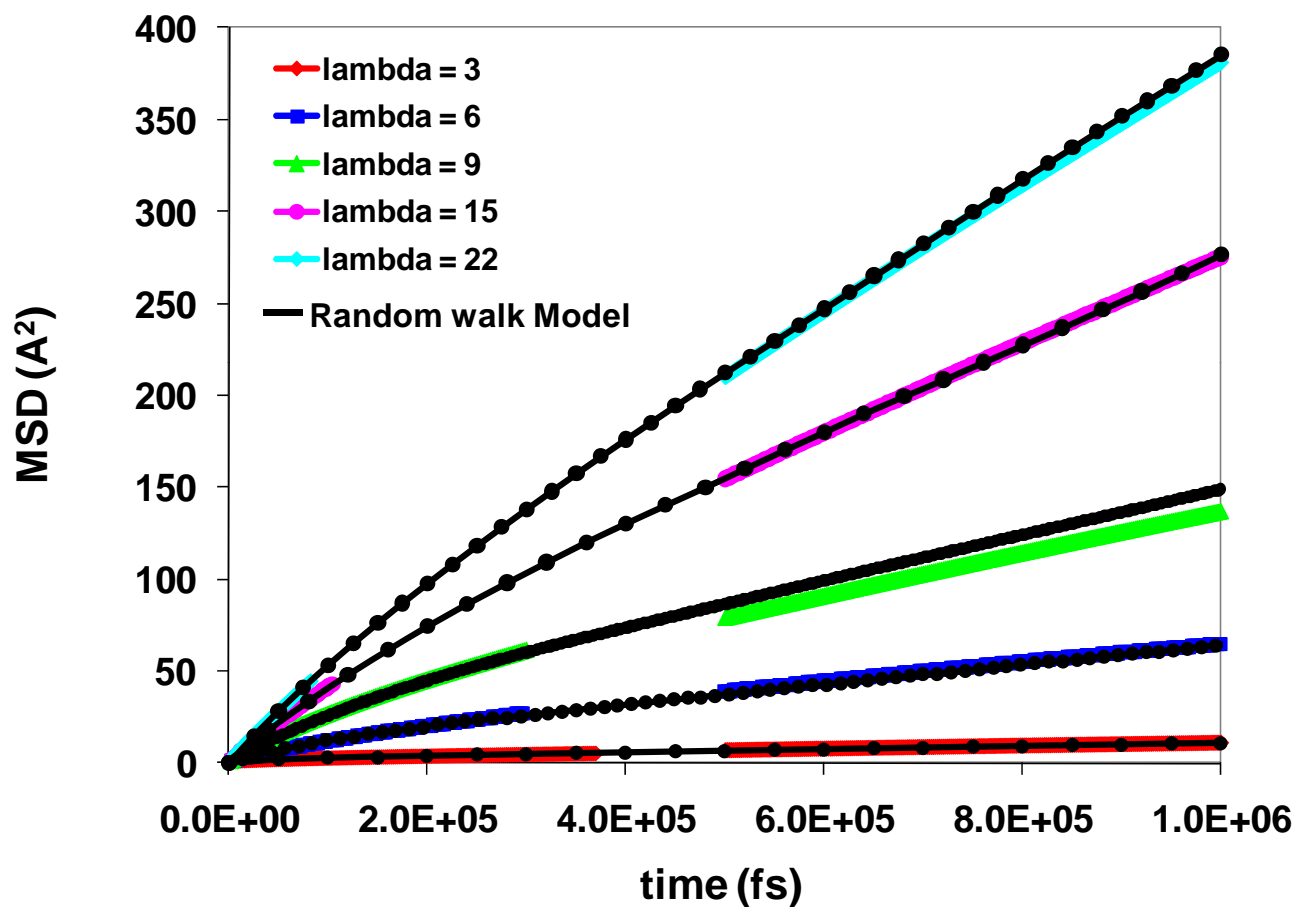- runs on a laptop in a few minutes
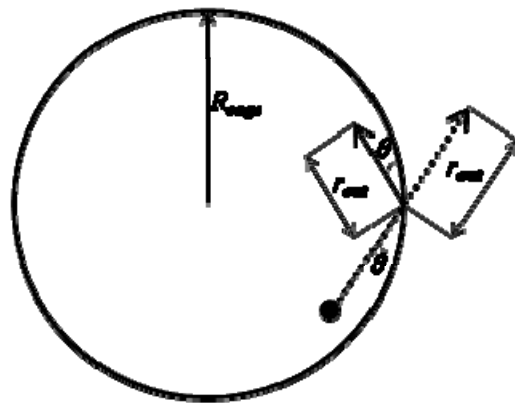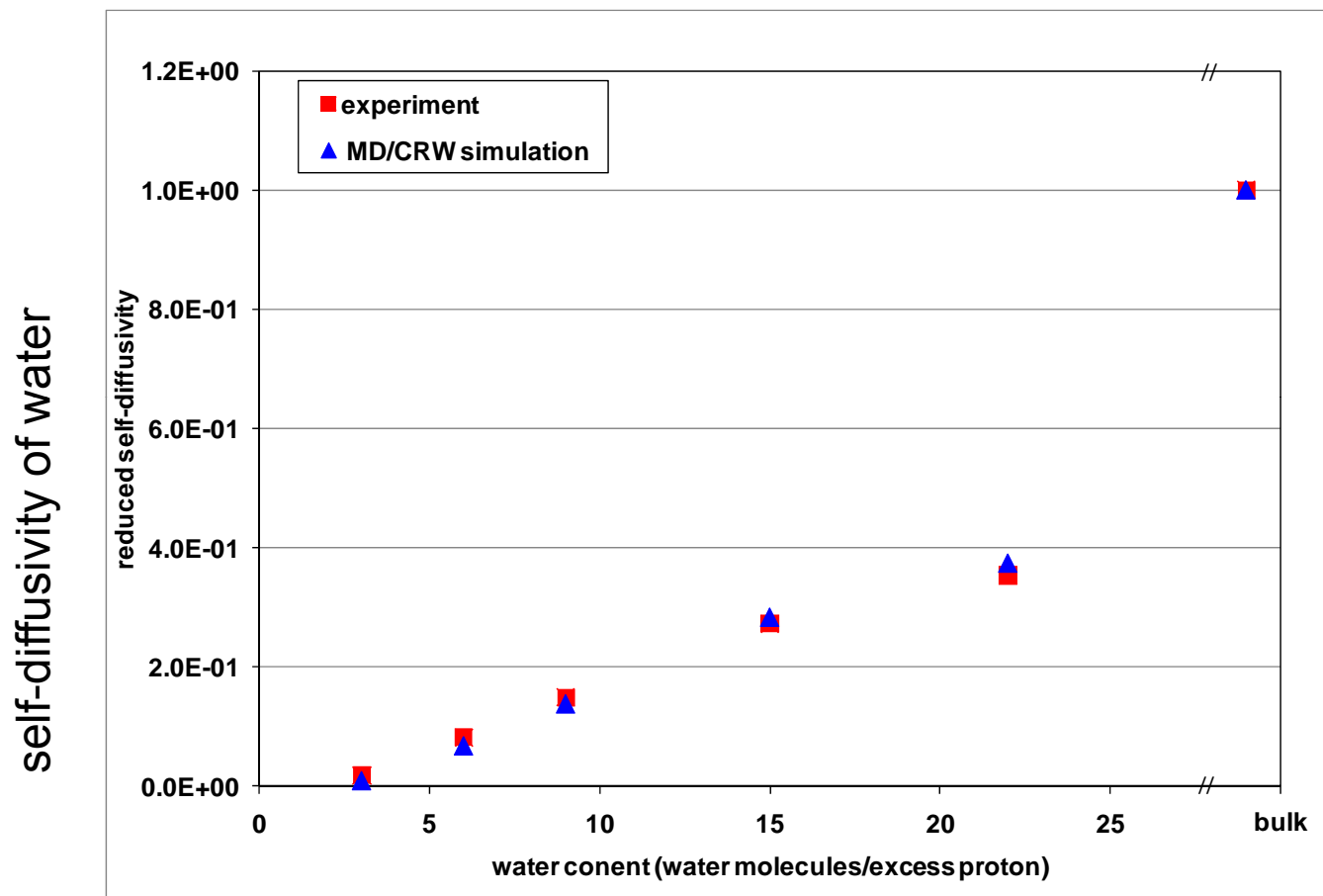
unsuccessful move   successful move
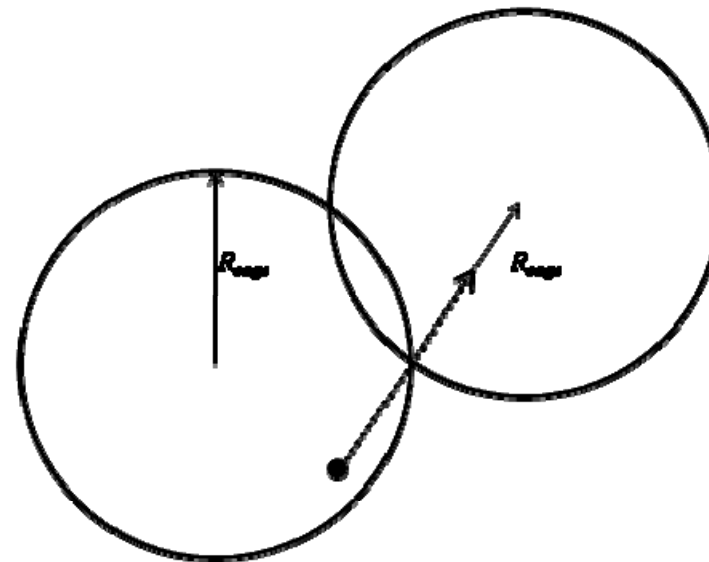
- Fit MD results (1 ns) to Confined Random Walk (CRW) Theory.
- Extend Mean Square Displacement to long-time limit (100 ns).
- Extract water diffusivity.

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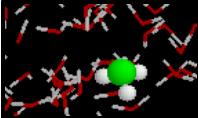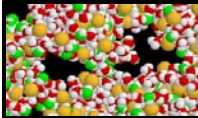
Robison, R. A.; Stokes, R. H. *Electrolyte Solutions*; 1959.
Nafion (EW=1100,) Kreuer, K. D. *Solid State Ionics* **1997.**
Esai Selvan, M., Calvo-Muñoz, E.M., Keffer, D.J., *J. Phys.*
Chem. B, dx.doi.org/10.1021/jp1115004 , 2011.

- 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?

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Proton Transport in Aqueous Systems

I. Introduction
II. Levels of Modeling
    II.A. Quantum Mechanics
    II.B. Reactive Molecular Dynamics
    II.C. Confined Random Walk Theory
    II.D. Percolation Theory
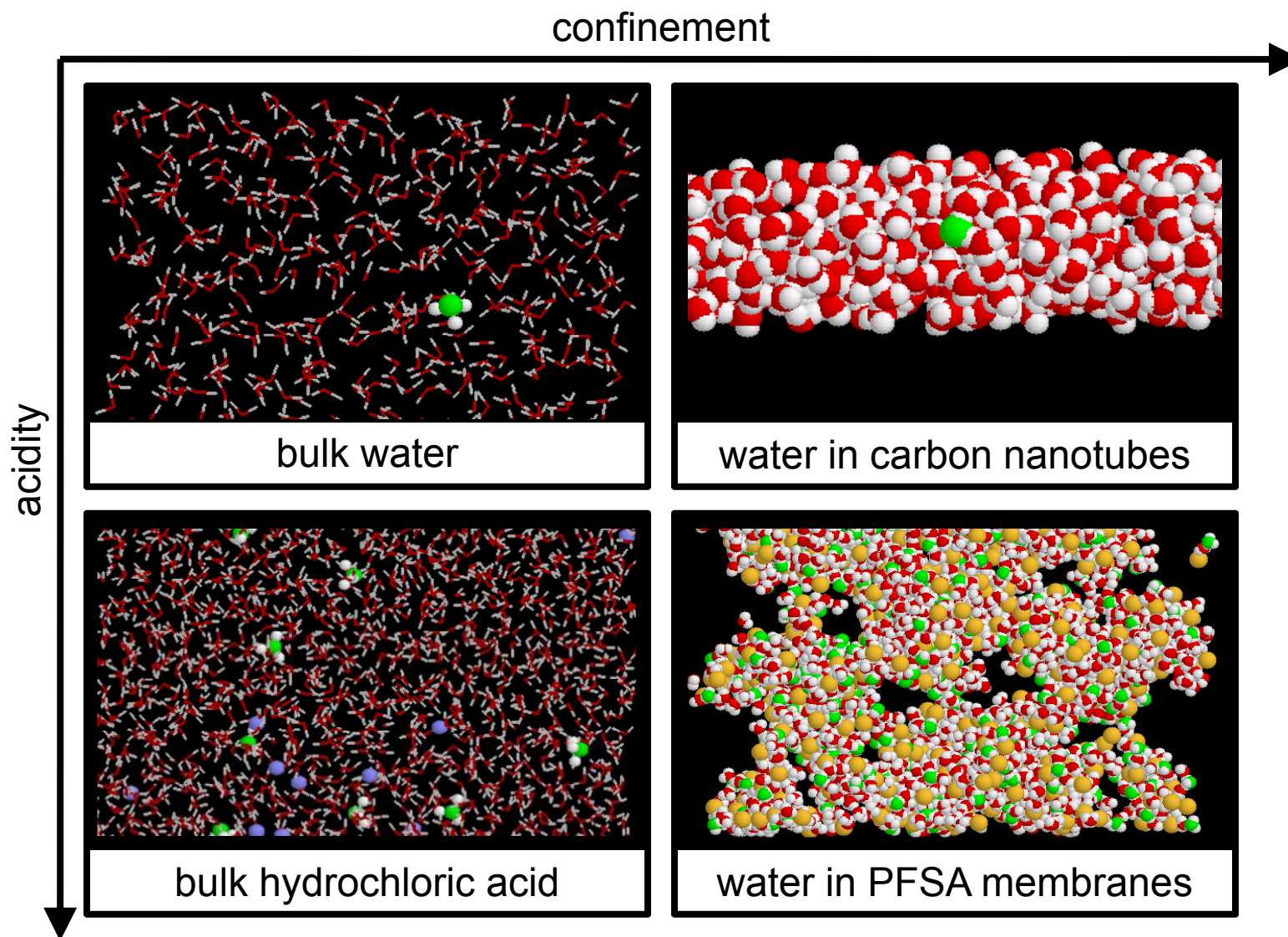III. Conclusions
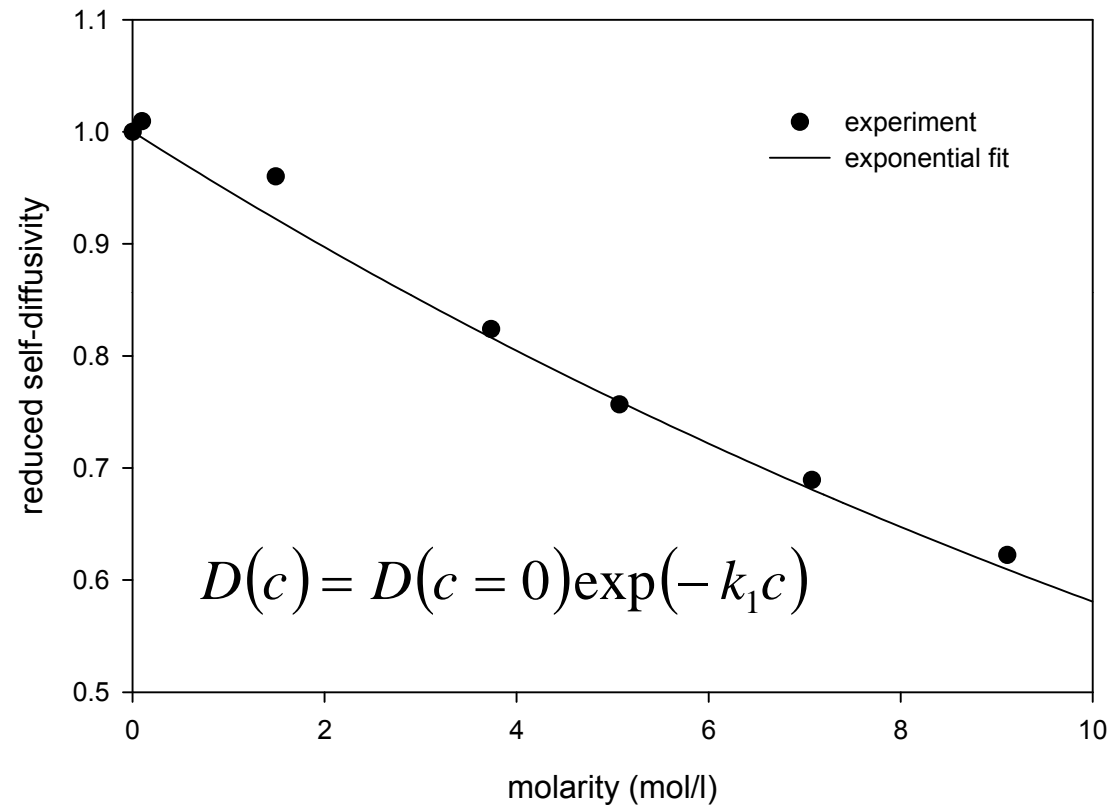
Three Factors: Acidity, Confinement & Connectivity

	bulk water	water in PFSA membranes
acidity	• H_3O^+ concentration is dilute $\lambda = 5.6 \cdot 10^8$ H_2O/H^+ (pH=7)	(Nafion EW=1144) H_3O^+ concentration • λ=3 H_2O/HSO_3, pH ≈ -0.59 (minimally hydrated) • λ=22, pH≈-0.22 (saturated)
confinement	• interfacial surface area is zero	interfacial surface area • 163 Å^2/H_2O or 2460 m^2/g (λ=3) • 23 Å^2/H_2O or 1950 m^2/g (λ=22)
connectivity	• no connectivity issues	• connectivity of aqueous domain deteriorates as water content decreases

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Acidity and Confinement Effects on Proton Mobility

confinement

acidity

bulk water

water in carbon nanotubes

bulk hydrochloric acid

water in PFSA membranes

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reduced self-diffusivity vs molarity (mol/l)

- experiment
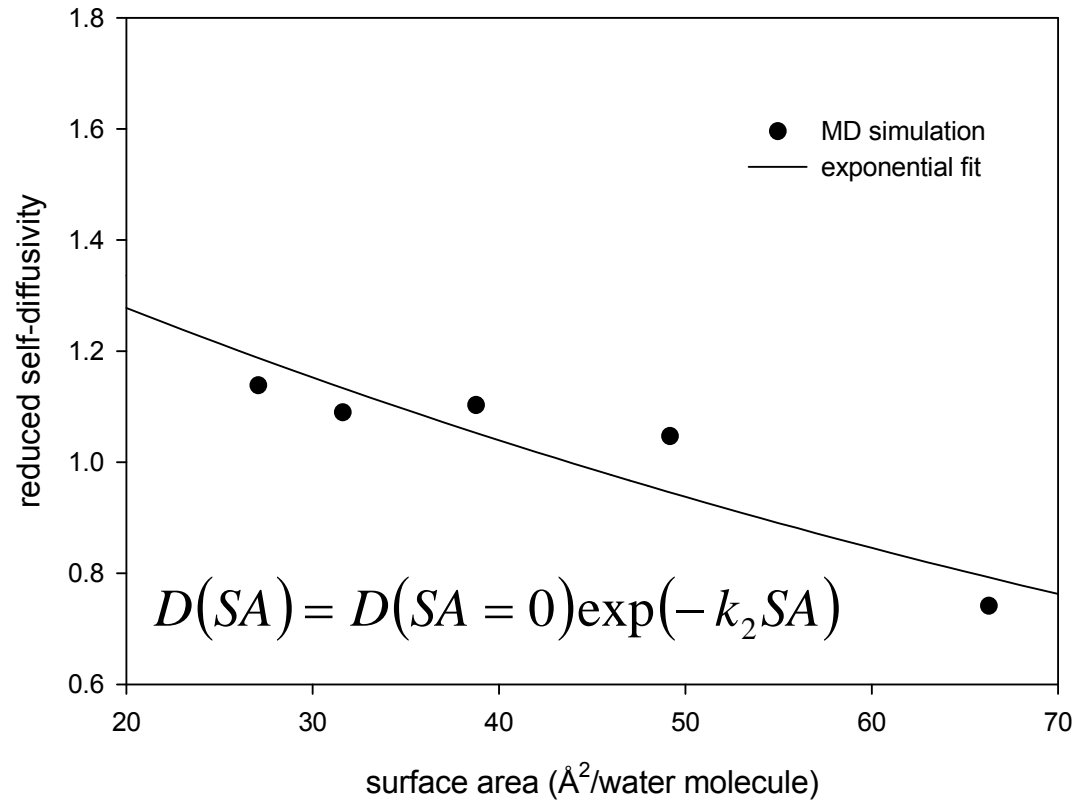— exponential fit

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

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.

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

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.
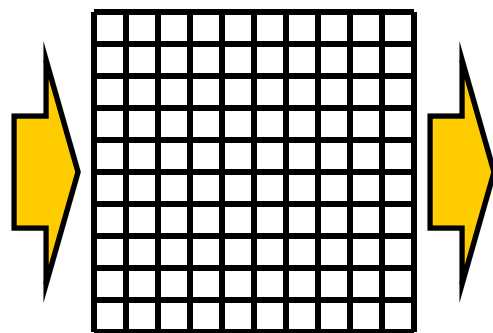- The behavior is fit by an exponential fit.

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Water Mobility in Bulk Systems – Effect of Connectivity

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

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

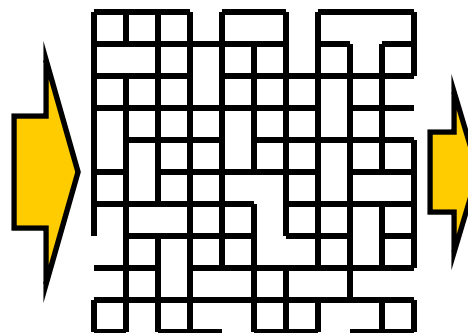$$g(D) = p_{EMA}\delta(D - D_b) + (1 - p_{EMA})\delta(D - D_o)$$
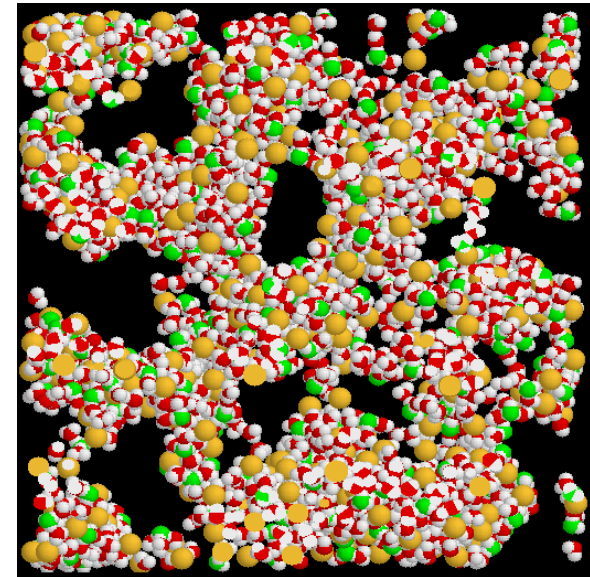
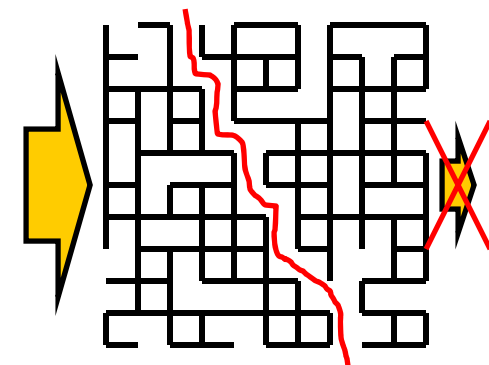Percolation theory relates the effective diffusivity to the fraction of bonds that are blocked to diffusion.

no blocked bonds
D = D$_{open}$

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

beyond threshold
D = 0

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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)

Esai Selvan, M., Calvo-Muñoz, E.M., Keffer, D.J., *J. Phys. Chem. B* **115**(12) 2011 pp 3052–3061.
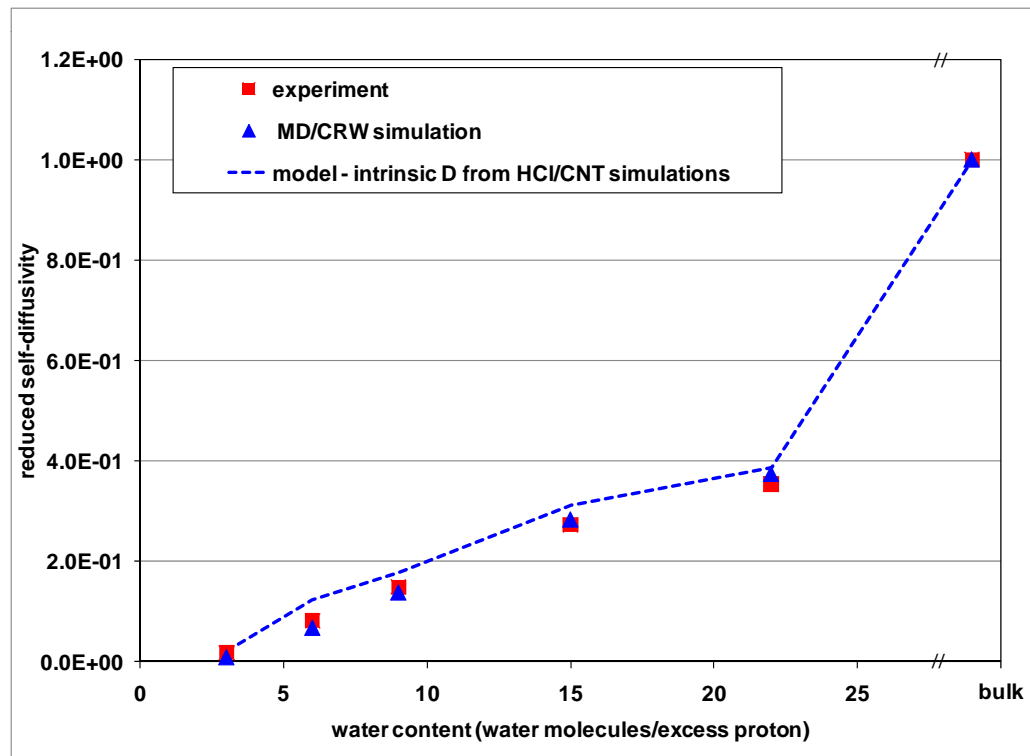
Excellent agreement of theory with both simulation and experiment.

Theory uses only structural information to predict transport property.

Water is solved! What about charge transport?

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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.
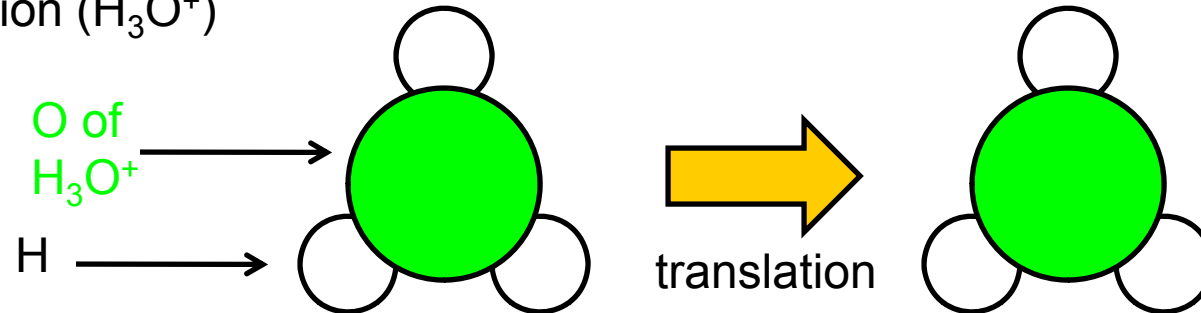
Why did we start with water?

Diffusion of water is easier to describe.

Water is transported only via vehicular diffusion (changes in the center of mass of the water molecules).
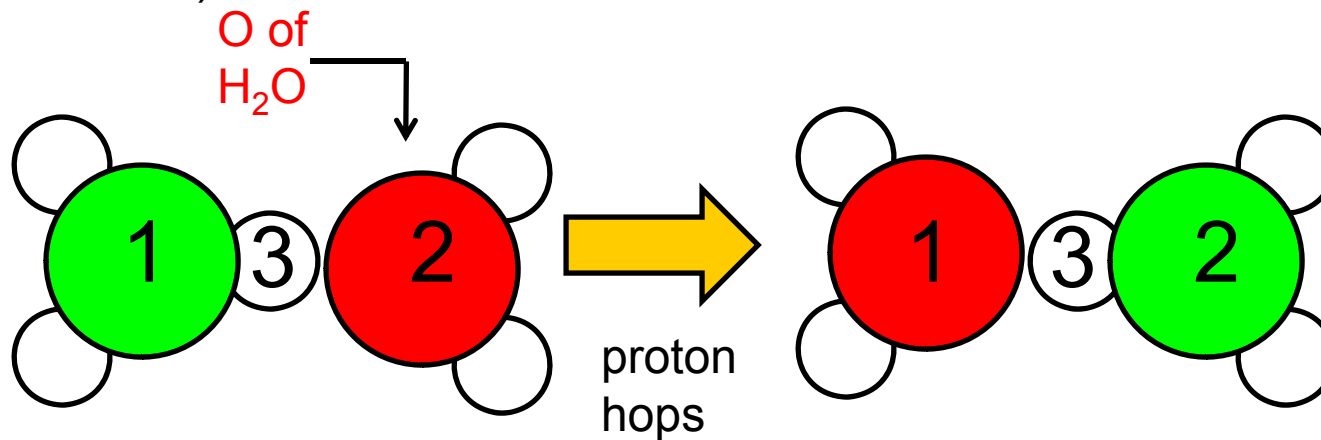
There are two mechanisms for proton transport.

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

O of
H_3O^+

H

translation

Structural diffusion (proton shuttling): passing of protons from water molecule to the next (a chemical reaction involving the breaking of a covalent bond)
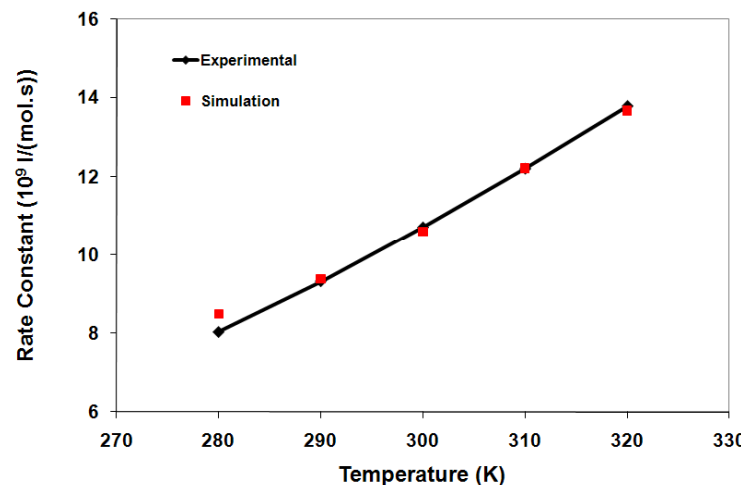
O of
H_2O

1 3 2

1 3 2

proton hops

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

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Proton Transport in Bulk Water

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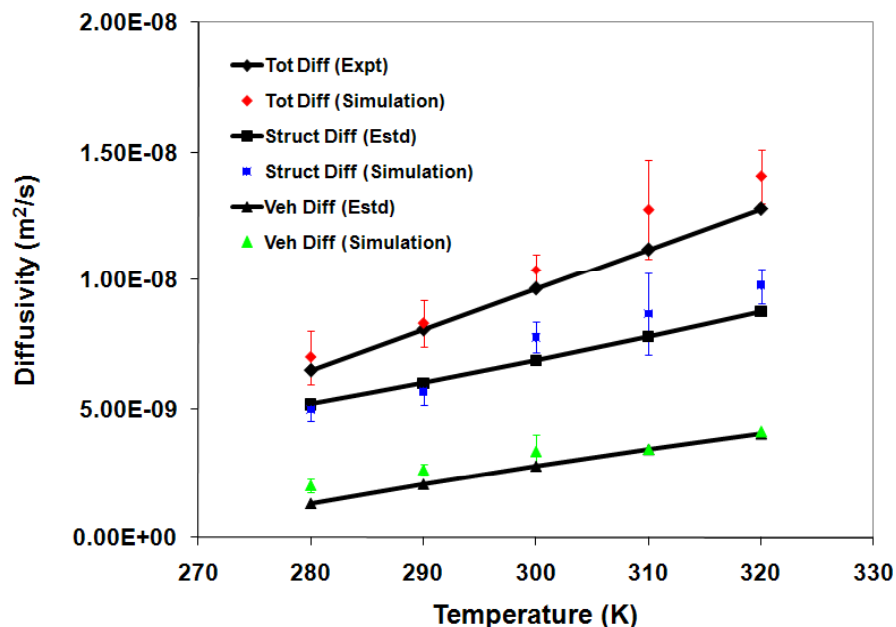
rate law: rate = k $[H_3O^+][H_2O]$

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

● 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

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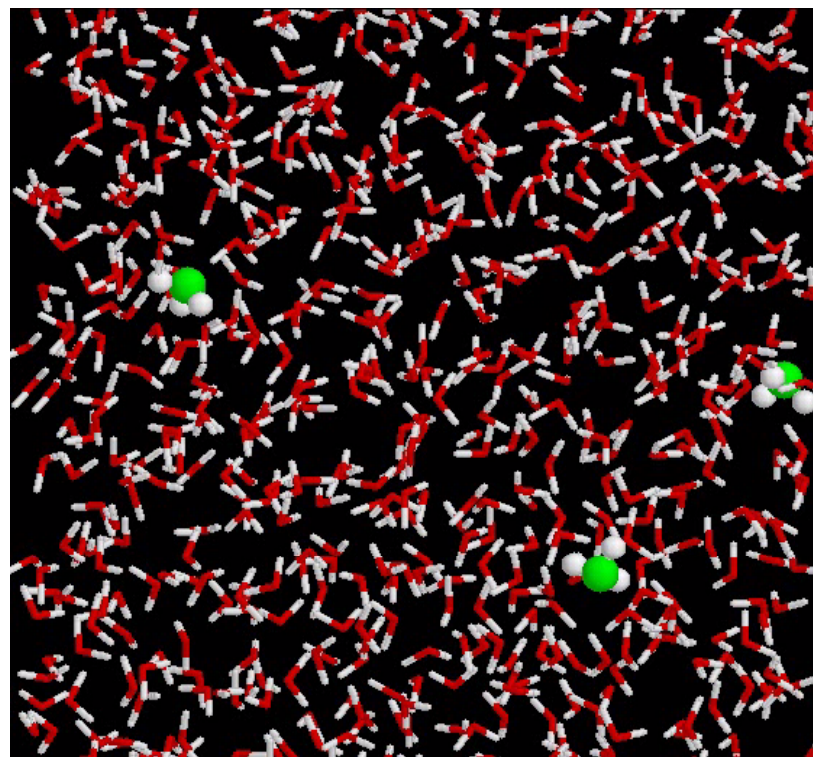
Proton Diffusion in Bulk Water

Non - Reactive System
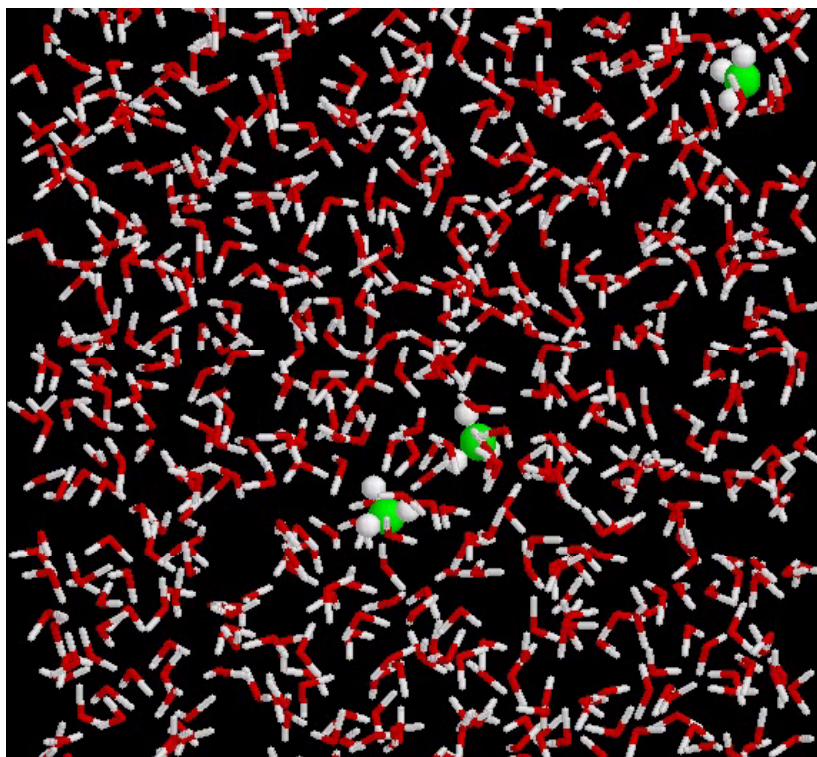
Reactive System

Vehicular Diffusion

Structural and Vehicular Diffusion

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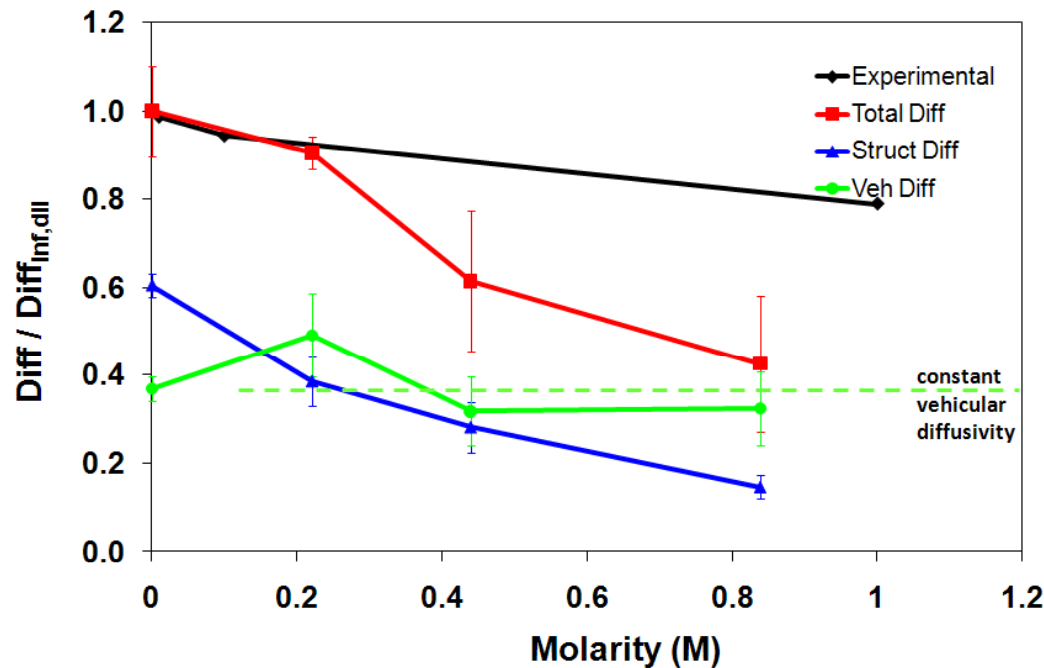
Bulk HCl Solution: Effect of High Acidity

simulation snapshot
periodic system
15 H^+
15 Cl^-
1875 H_2O
λ = 125
conc = 0.44 M
pH = 0.36
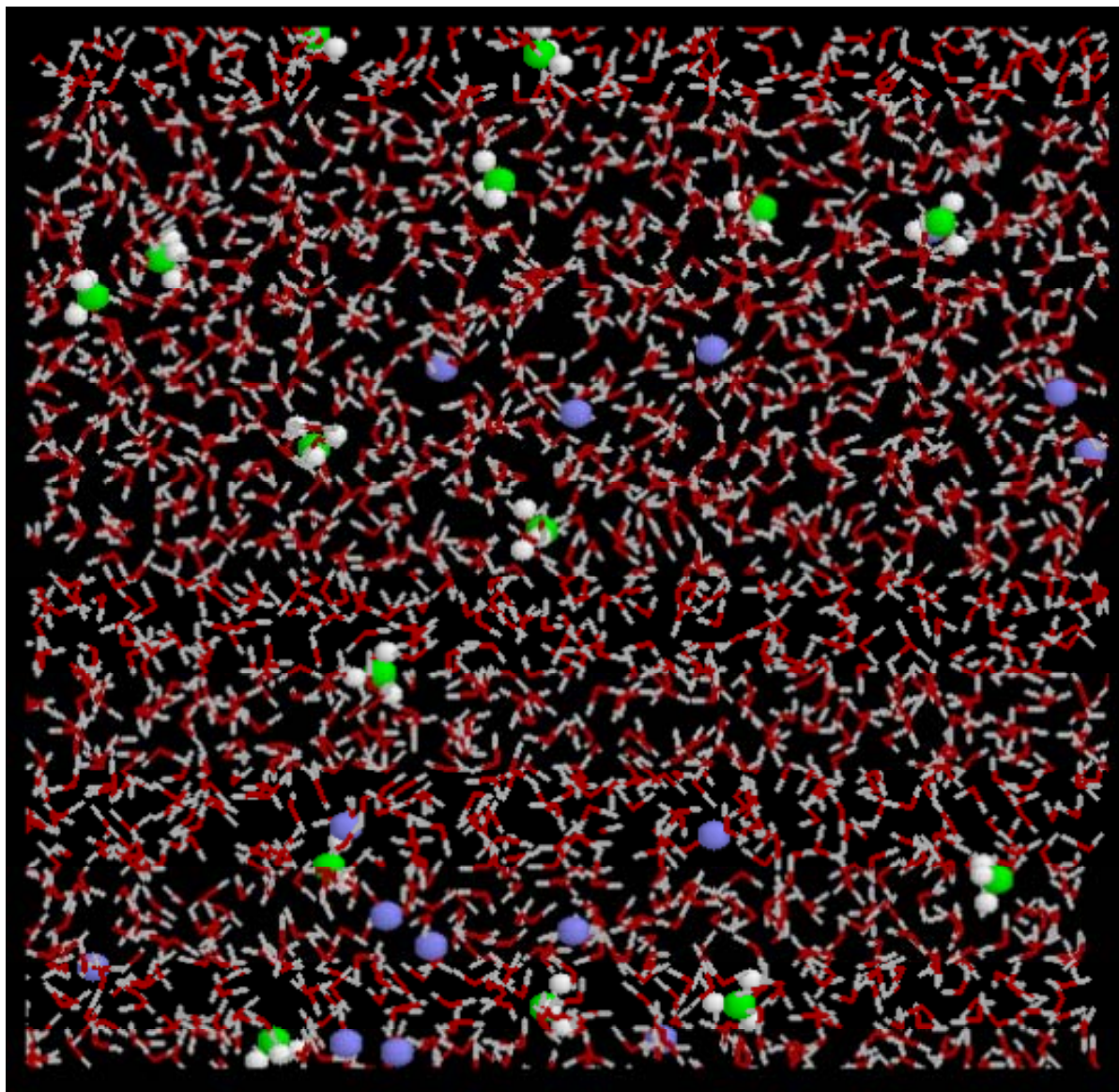
Legend
O of H_2O – red
O of H_3O^+ – green
H – white
Cl^- – blue

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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

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Bulk HCl Solution: Effect of Acidity in an Analytical Fit

- 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
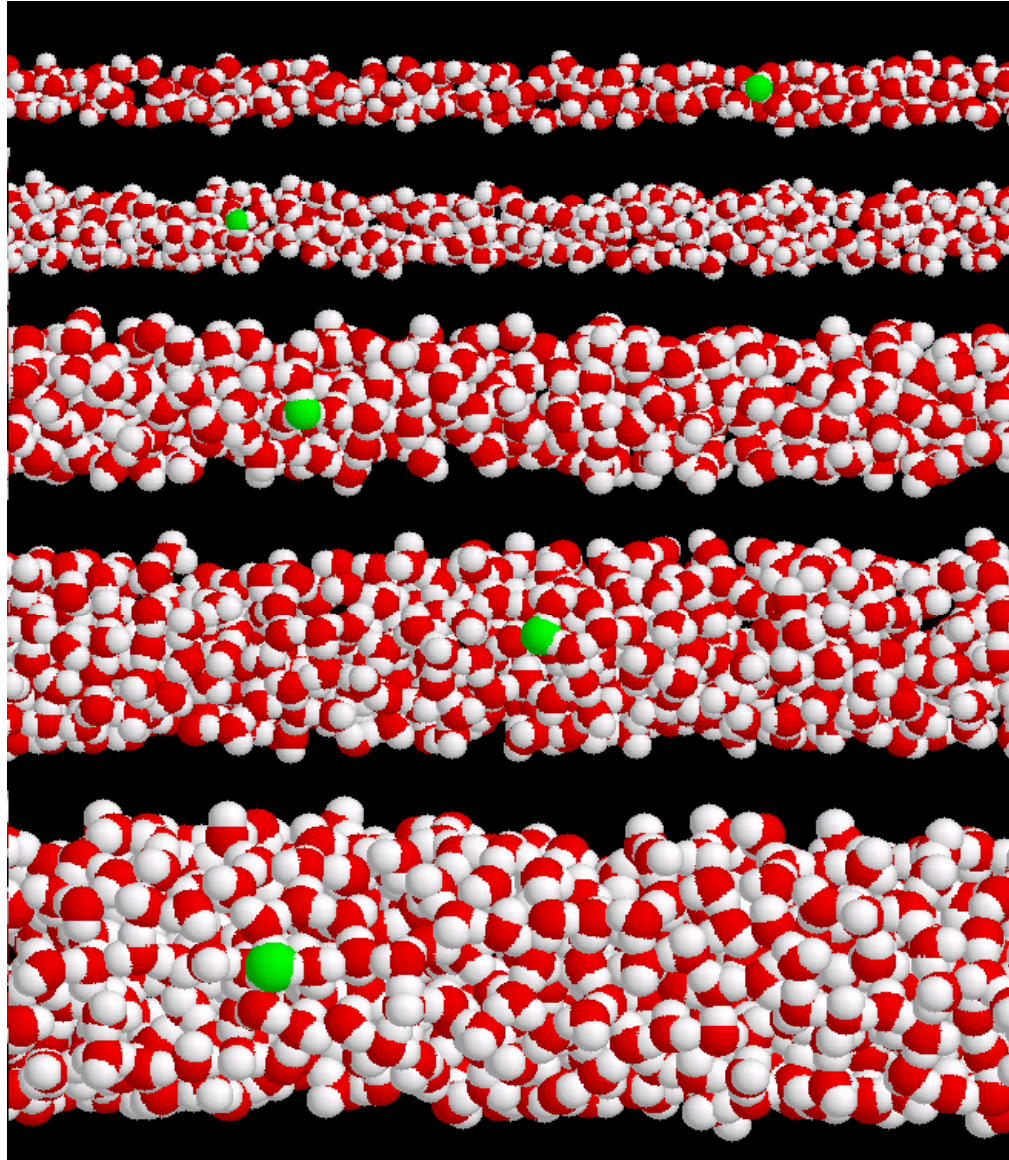
Nominal radii from 5.42 to 10.85 Å.

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.

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Proton Transport in Nanotubes: Effect of Confinement
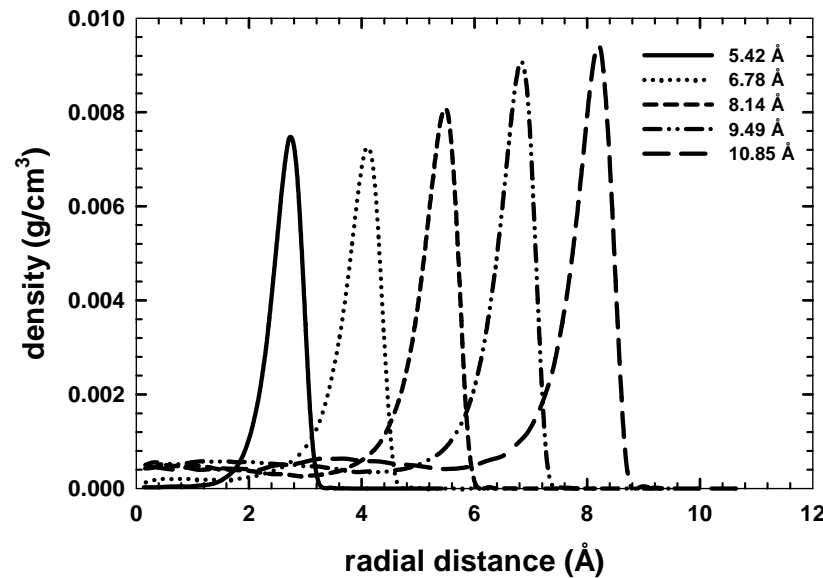
Density distribution of H_3O^+.

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.
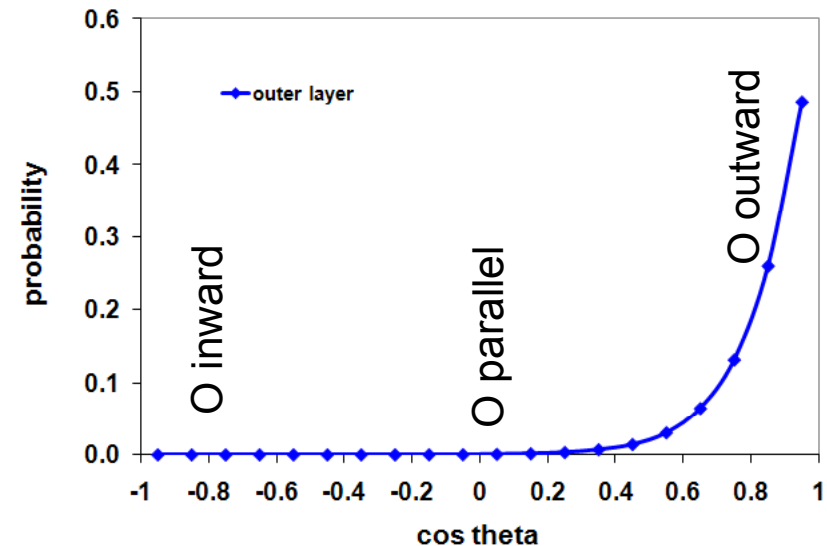
Fundamentals of Sustainable Technology

Proton Transport in Nanotubes: Effect of Confinement
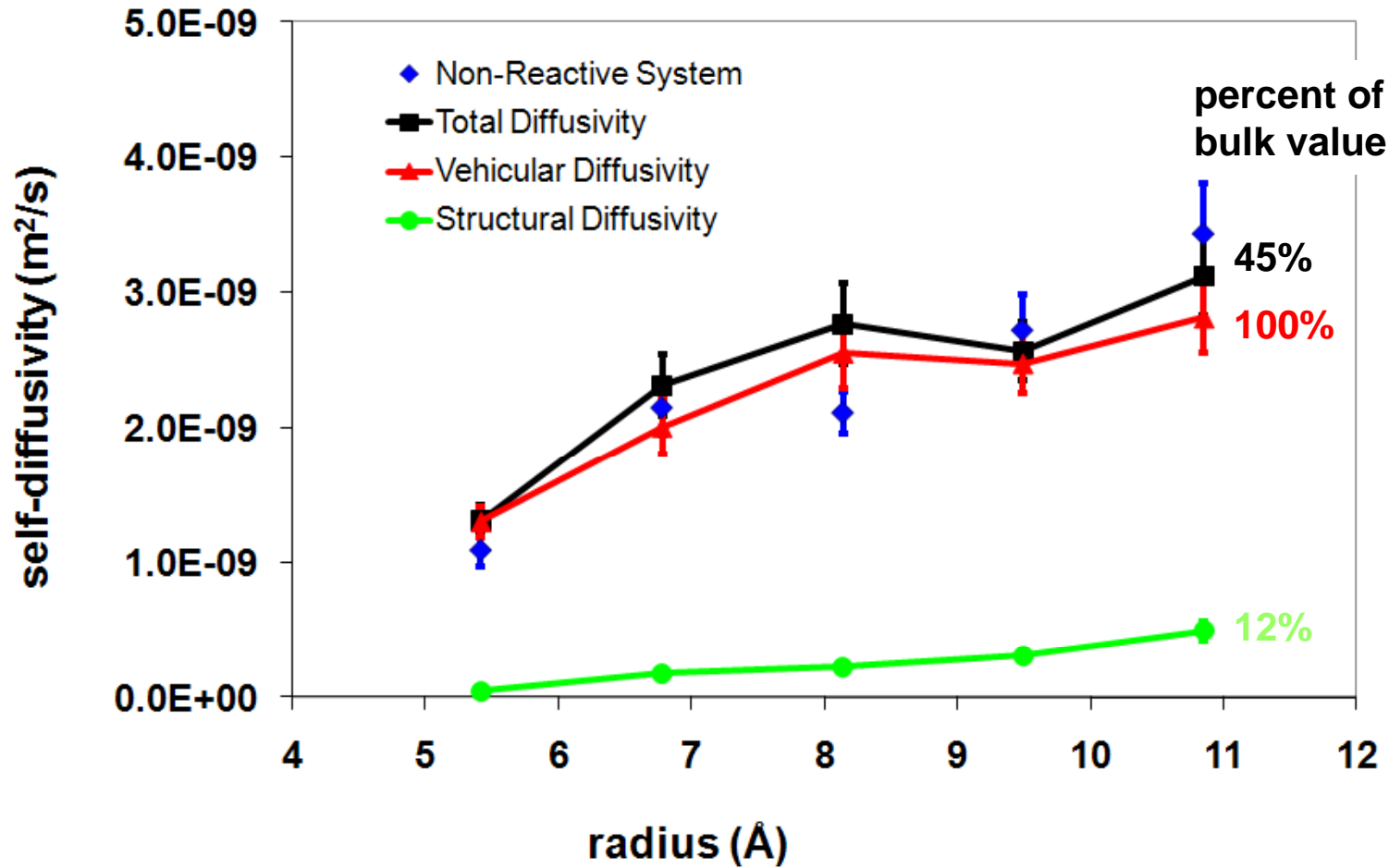
Confinement dramatically reduces structural diffusion.
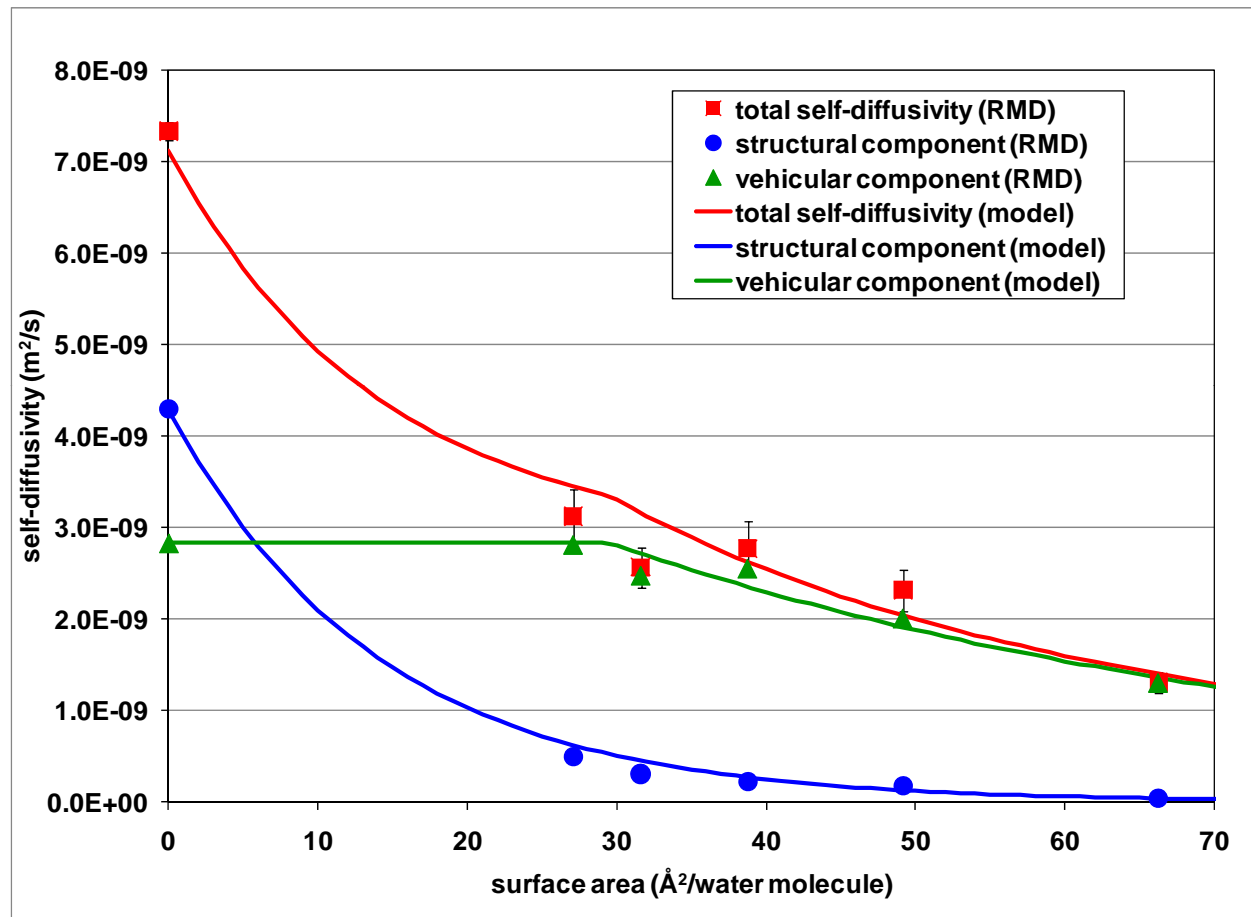
Fundamentals of Sustainable Technology

- 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

- 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)
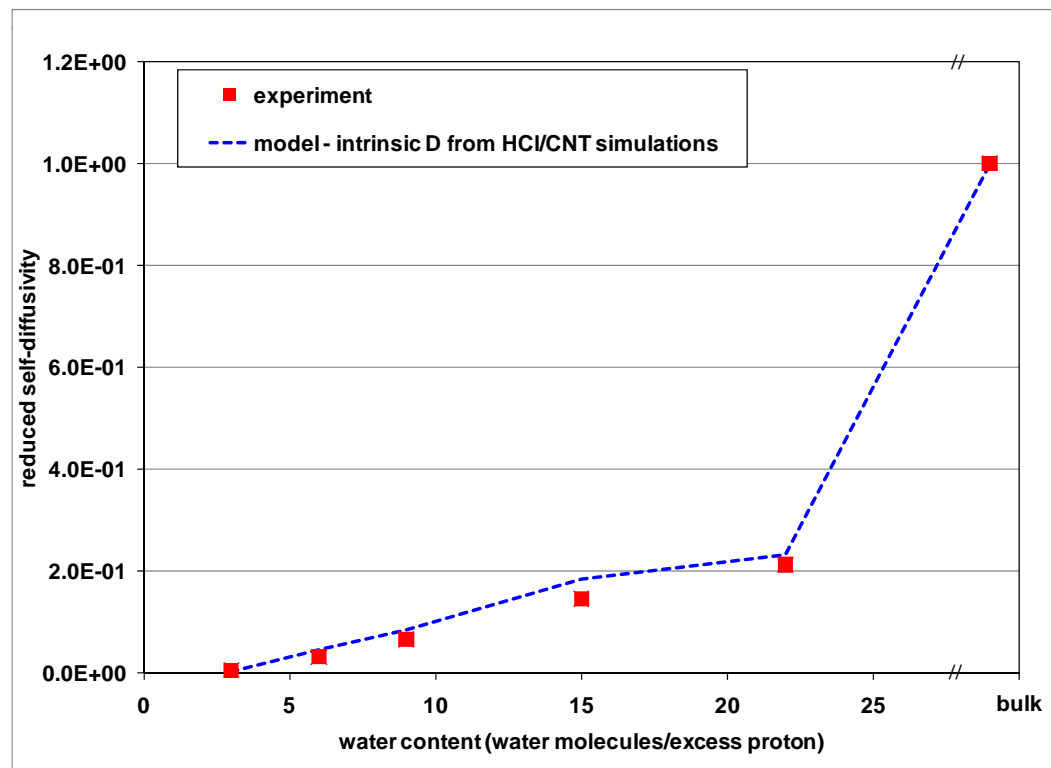
Good agreement of theory with experiment.

Theory uses only structural information to predict transport property.

Proton transport is well-described by this simple model.

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Conclusions

Quantum Mechanics calculations provide understanding of structure of ground state and transition state for structural diffusion, activation energy and rate constant

Reactive MD simulations provide molecular-level understanding of coupling of reaction and diffusion in aqueous systems, carbon nanotubes and proton exchange membranes, provides short time mean-square-displacements (MSDs)

Confined Random Walk theory extends MSDs from MD and 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

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PhD, 2012
Vol & Area Analysis

Elisa Calvo-Munoz
undergraduate
Confined Random Walks

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