Modeling of Electrochemical Cells:
Proton Exchange Membrane Fuel Cells
HYD7007 – 01

Lecture 05. Molecular-level Modeling of Water & Charge Transport

Dept. of Chemical & Biomolecular Engineering
Yonsei University
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Prof. David Keffer
dkeffer@utk.edu

Lecture Outline

- Mechanisms for Water Transport
- Obtaining Diffusivities in Molecular Dynamics Simulation
- Mechanisms for Proton Transport
- Reactive Molecular Dynamics Simulation
    - Bulk Water
    - Bulk Hydrochloric Acid Solution
    - Carbon Nanotubes
    - Nafion

Einstein Relation

Water molecules diffuse via translation of their center of mass.

$$D \equiv \frac{1}{2d} \lim_{t \to \infty} \frac{\left\langle \left[\underline{r}(t_o + t) - \underline{r}(t_o)\right]^2 \right\rangle}{t}$$

The Einstein Relation states that the self-diffusion coefficient, **D**, is a proportionality constant between the mean square displacement and the observation time, **t**. (**d** is the dimensionality of the system).

The mean square displacement is based on the average value in the change of positions, **r**, over time **t**.

Einstein Relation

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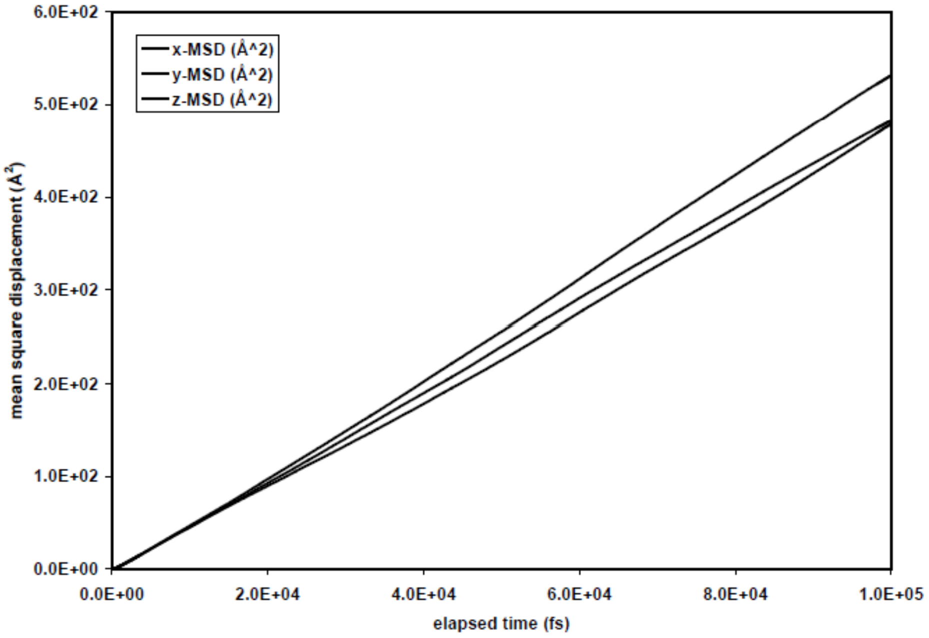
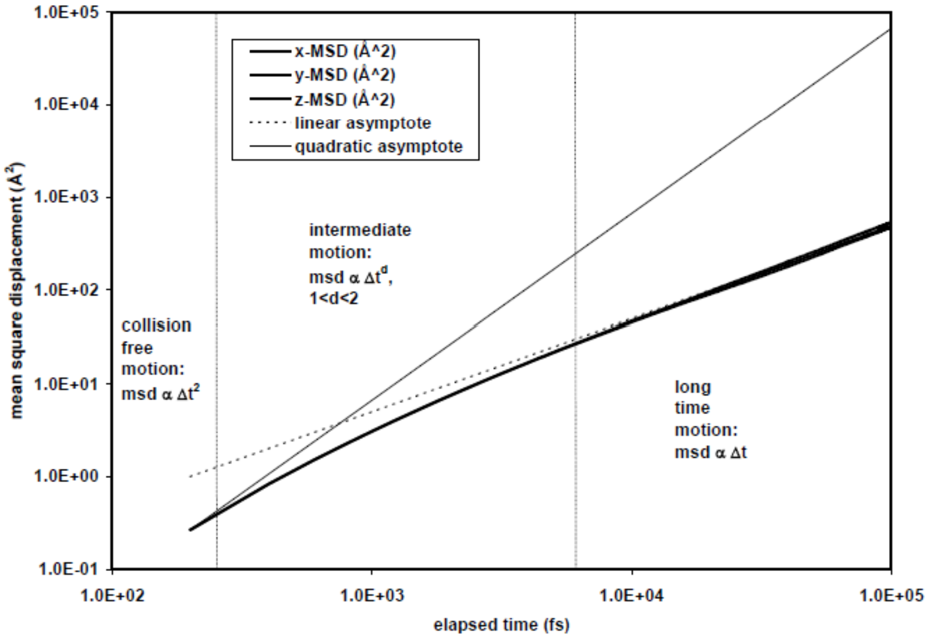
The Einstein relation is valid in the infinite-time limit.



linear plot



log plot

At very short times, there is a ballistic (quadratic) relationship.
As collisions occur, there is a transition region.
At long times, the linear relationship is established.

The infinite-time limit occurs for this example (liquid methane at 150 K) at 100,000 fs (0.1 ns).

Fickian Diffusivities

Macroscopic material balances, such as

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A - \nabla \cdot \mathbf{j}_A$$

invoke Fick's law as a constitutive equation,

$$\mathbf{j}_A = -\rho D_{AB} \nabla w_A$$

for a binary system, where
$\mathbf{j}_A$ is the diffusive mass flux of component A relative to the center-of-mass velocity,
ρ is the mass density
D_{AB} is the Fickian diffusivity
w_A is the mass fraction of component A

Einstein's relation provides self-diffusivities not Fickian diffusivities, but is still an excellent measure of the mobility of a species.

Fickian Diffusivities from MD

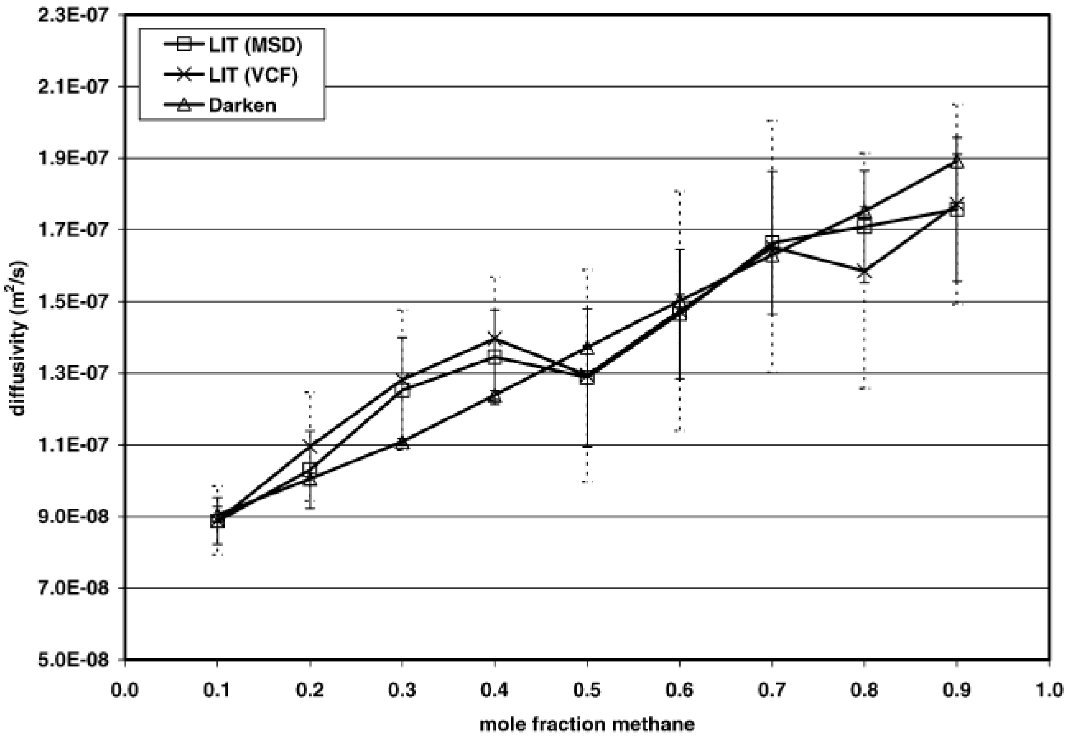
It is possible to rigorously obtain Fickian diffusivity from MD simulation,
But it is subject to statistical error.
It is often times better to use the Darken approximation to relate the Fickian diffusivity in terms of self-diffusivities measured from MD.

Darken equation:

$$D = \left(\frac{\partial \ln a_\alpha}{\partial \ln x_\alpha} \right)_{T,p} (x_\alpha D_{\mathrm{self},\beta} + x_\beta D_{\mathrm{self},\alpha}),$$

(Darken, 1948)

where
a_α is the activity of α
x_α is the mole fraction of α

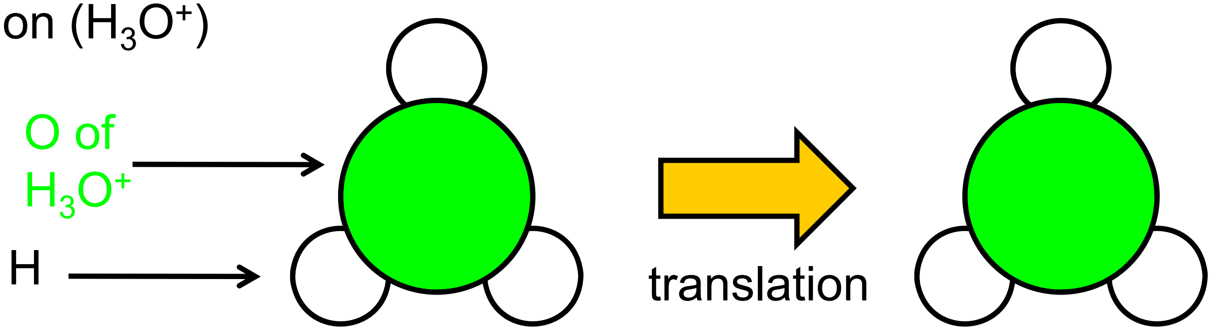


This example for gaseous methane/ethane at 100 atm and 350 K illustrates that the theoretical approximation of the Darken equation is less than the statistical uncertainty of the more theoretically rigourous method. (Keffer, J. Non-Newtonian Fluid Mech., 2004)

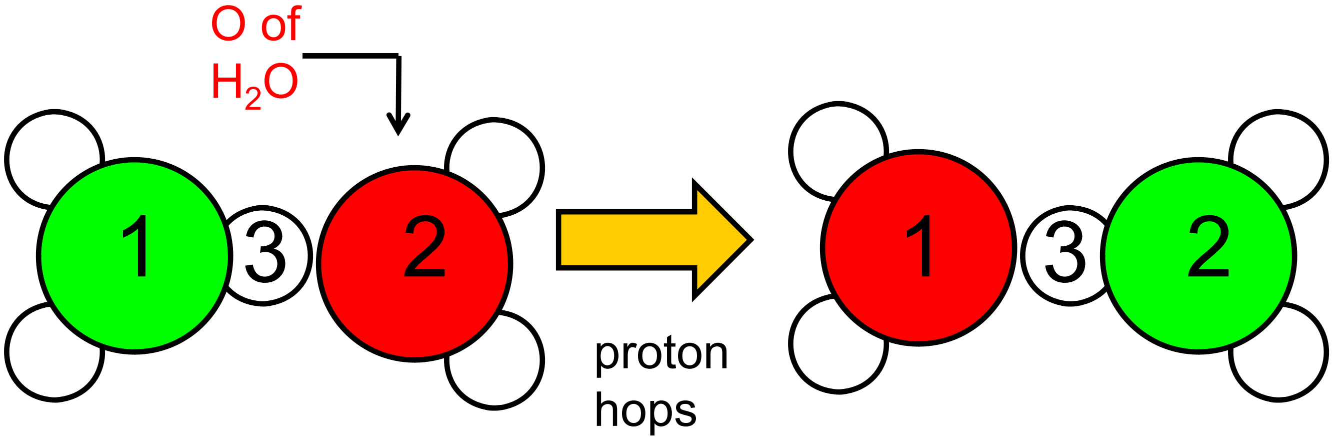
Proton Transport

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)

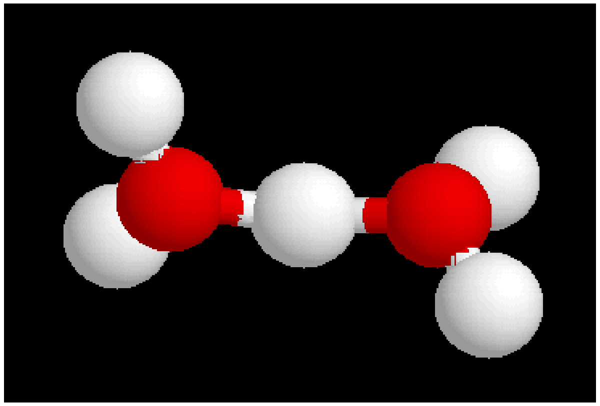


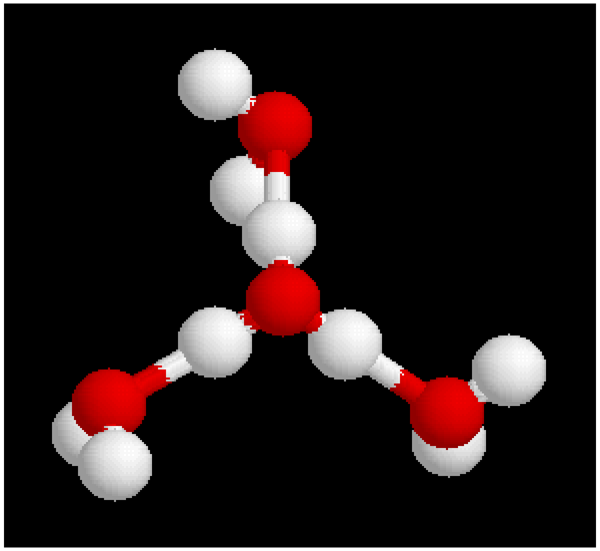
In bulk water, structural diffusivity is about 70% of total diffusivity.
Structural diffusion aka proton shuttling aka the Grotthuss mechanism (1806).

Proton Transport

In aqueous systems, we think of excess protons as existing as hydronium ions, H_3O^+.

But aqueous systems are hydrogen bonding networks and there are other entities that have been names, such as the



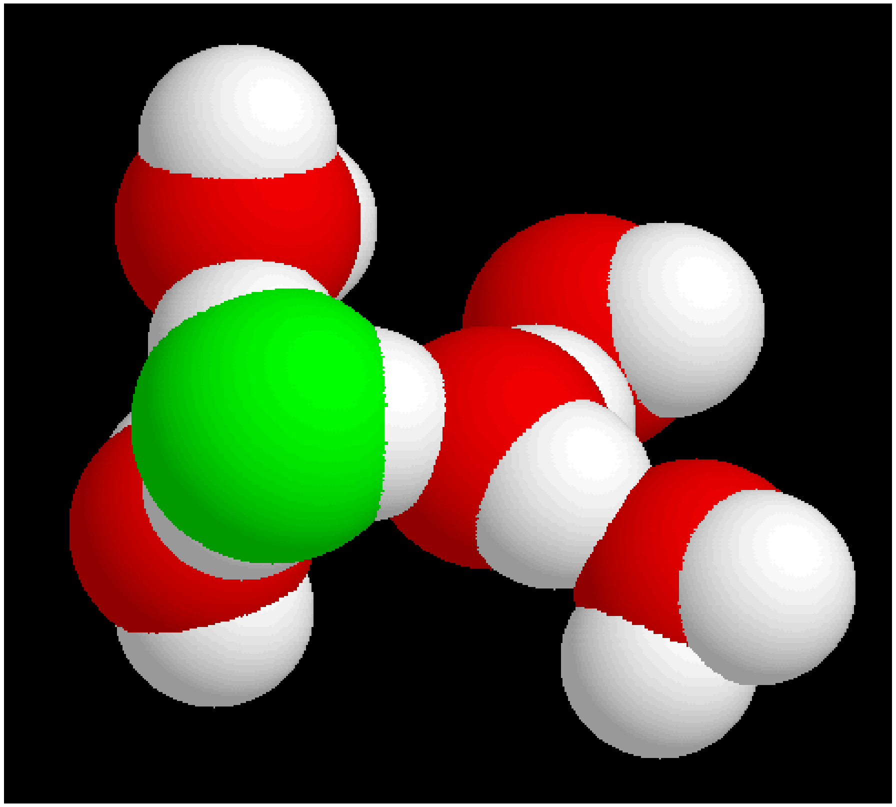


Zundel ion, $H_5O_2^+$
2 water share the excess H^+

Eigen ion, $H_9O_4^+$
3 water hydrogen-bound to each hydrogen atom of the hydronium ion

Proton Transport

Proton shuttling is a transition from an Eigen ion through a Zundel ion to another Eigen ion.



This process is most accurately described through expensive quantum mechanical calculations. However, we need to model large systems on the timescale at which not only reaction but also diffusion is occurring.

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. Parrinello, *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).

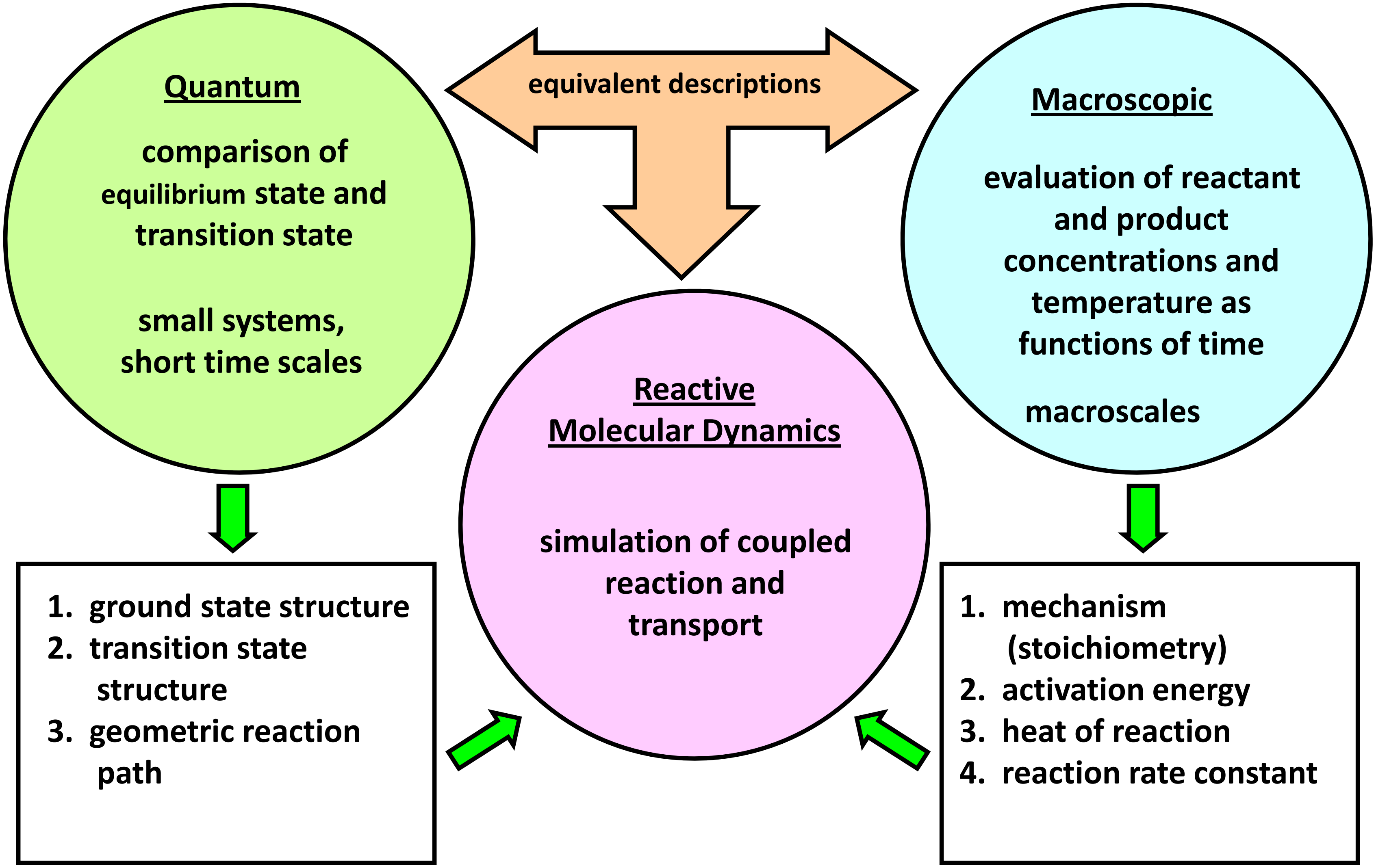
[4] J. Lobaugh and G.A. Voth, *J. Chem. Phys.*, 104, 2056 (1996).

[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).

Reactive Molecular Dynamics



equivalent descriptions

Quantum

comparison of equilibrium state and transition state

small systems, short time scales

1. ground state structure
2. transition state structure
3. geometric reaction path

Reactive Molecular Dynamics

simulation of coupled reaction and transport

Macroscopic

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

macroscales

1. mechanism (stoichiometry)
2. activation energy
3. heat of reaction
4. reaction rate constant

Macroscopic Model

A chemical reaction is completely defined by four parameters

- stoichiometry

$$H_3O^+ + H_2O \longleftrightarrow H_2O + H_3O^+$$

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

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

- activation energy [1]

$$E_a = 2.4 - 2.6 \ \ kcal/mol$$

- heat of reaction

$$\Delta H_R = 0 \quad (isothermal\ reaction)$$

- rate constant in bulk water at 300 K

$$self-diffusivity\ of\ \ proton = 9.3x10^{-9}\ m^2/s$$

$$reaction\ rate\ \mathrm{constant} = 6.0x10^{-11} e^{\left(\frac{-2.4}{RT}\right)}\ liter/mole/s$$

Reactivity of the model is implemented through the simulation algorithm rather than through potential

[1] N. Agmon, J. Chim. Phys. Phys.-Chim. Biol., 93, 1714 (1996).

[2] R. A. Robinson and R. H. Stokes, Electrolyte Solutions (Butterworths, London, 1959).

[3] Z. Luz and S. Meiboom J. Am. Chem. Soc., 86, 4768 (1964).

Reactive Molecular Dynamics

- Treats chemical reaction in a coarse-grained fashion
- Map Quantum Mechanics (QM) transition state onto a non-reactive potential

Algorithm

- Begin with conventional molecular dynamics algorithm using existing well-parameterized non-reactive potentials
- At the end of each MD simulation step – *Reactive Molecular Dynamics Algorithm*

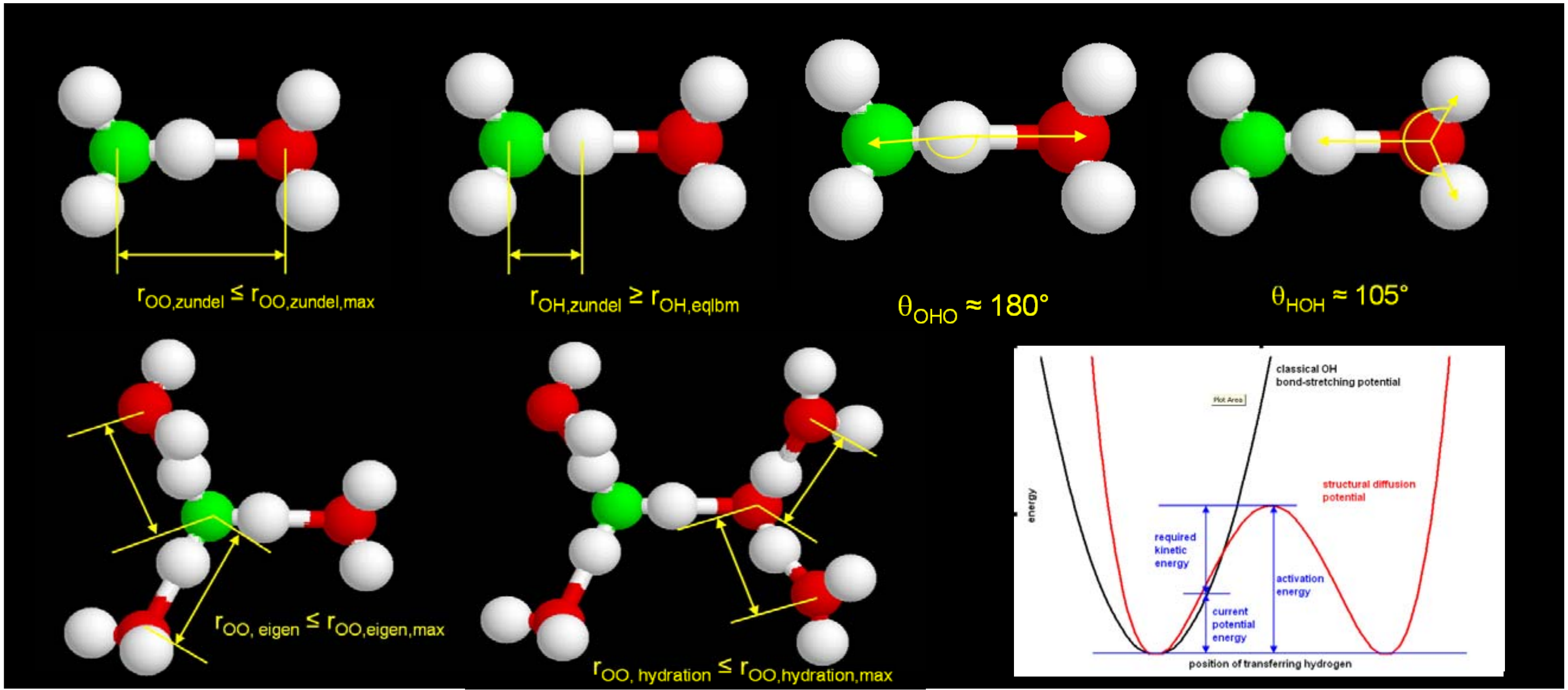
Step	Concept	Detail
Reaction Trigger	good start configuration favorable for reaction	satisfy set of triggers geometric – QM transition state energetic – QM or experiment
Instantaneous Reaction	coarse grained out reaction path	instantaneous transfer of H^+
Local Equilibration	good final configuration	maintain the model of isothermal reaction

- Reaction is complete
- Continue with next step of conventional MD simulation

RMD Algorithm – Step 1

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)



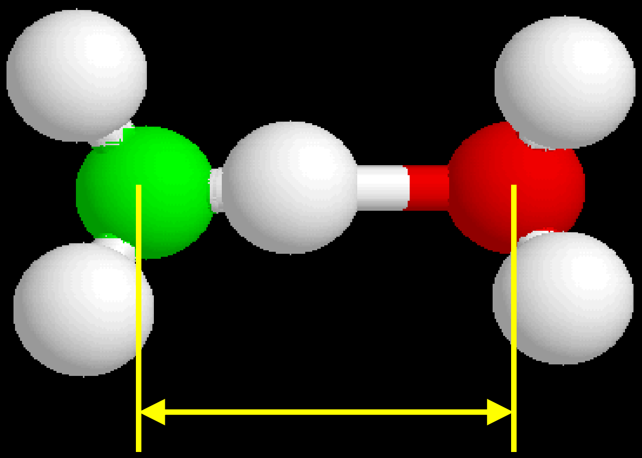
O of H_3O^+ = green

O of H_2O = red

H = white

Reaction Trigger #1

Zundel ion O-O separation



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

O of H_3O^+ = green

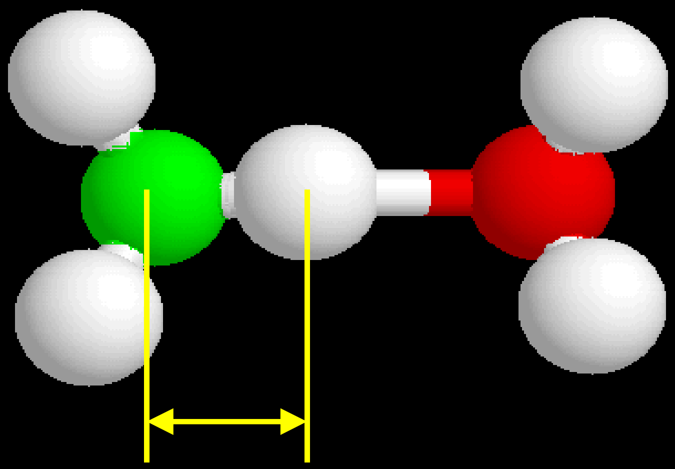
O of H_2O = red

H = white

Trigger #1. O-O separation must form a Zundel ion

Reaction Trigger #2

Zundel ion O-H separation

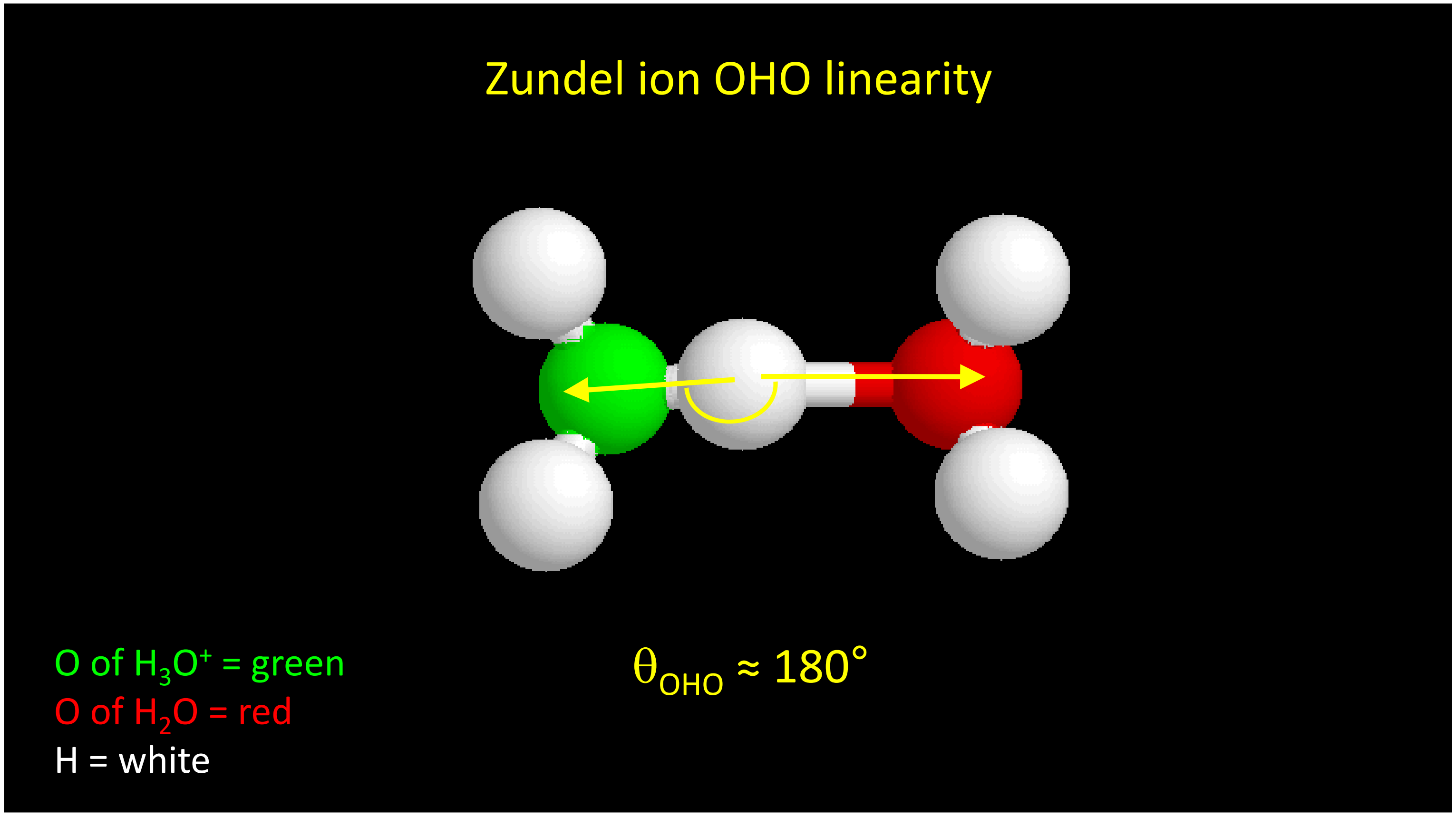


$r_{OH,Zundel} \geq r_{OH,eqlbm}$

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

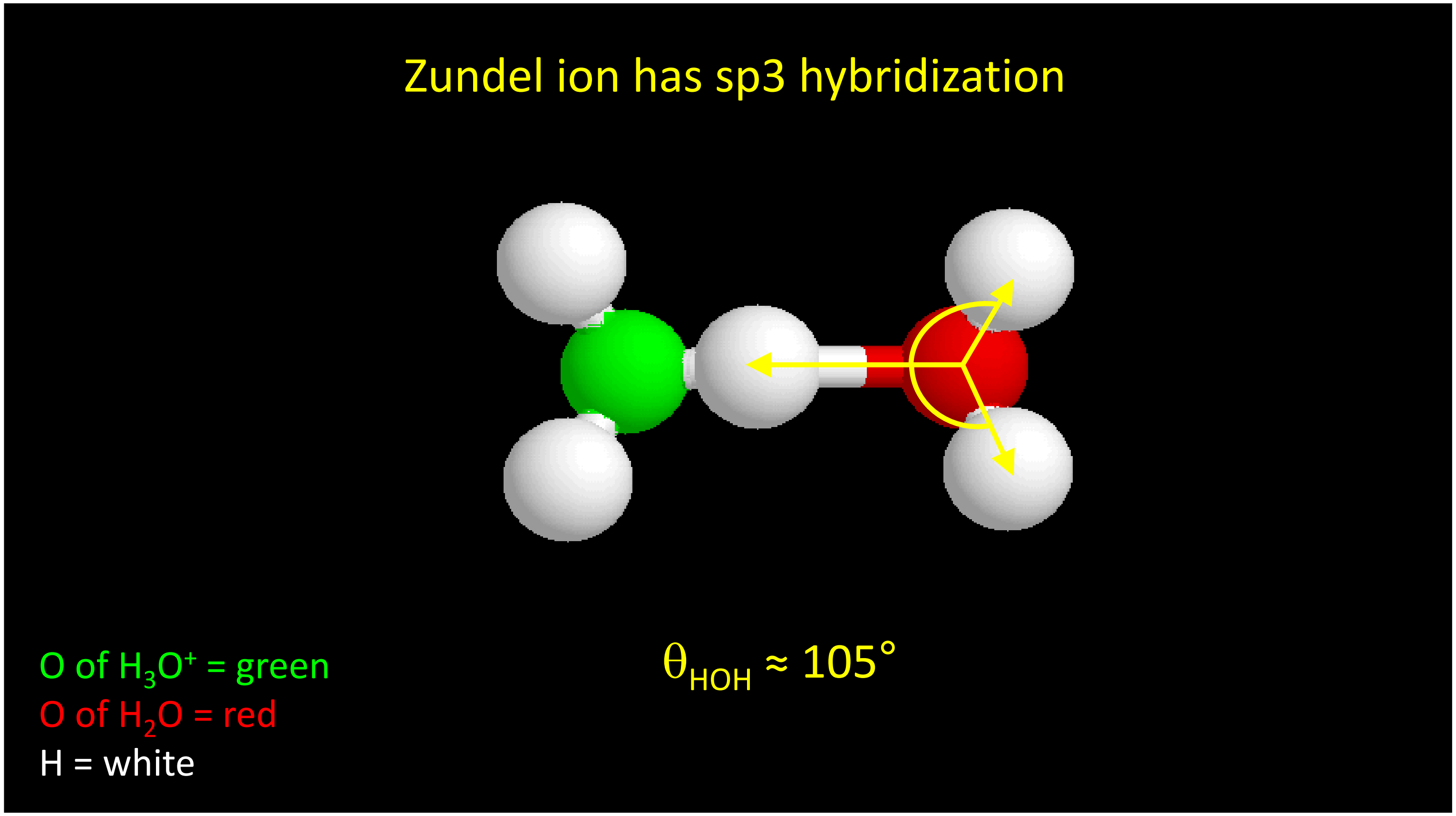
Trigger #2. O-H separation must exceed equilibrium bond

Reaction Trigger #3



Trigger #3. OHO angle is nearly linear in a Zundel ion

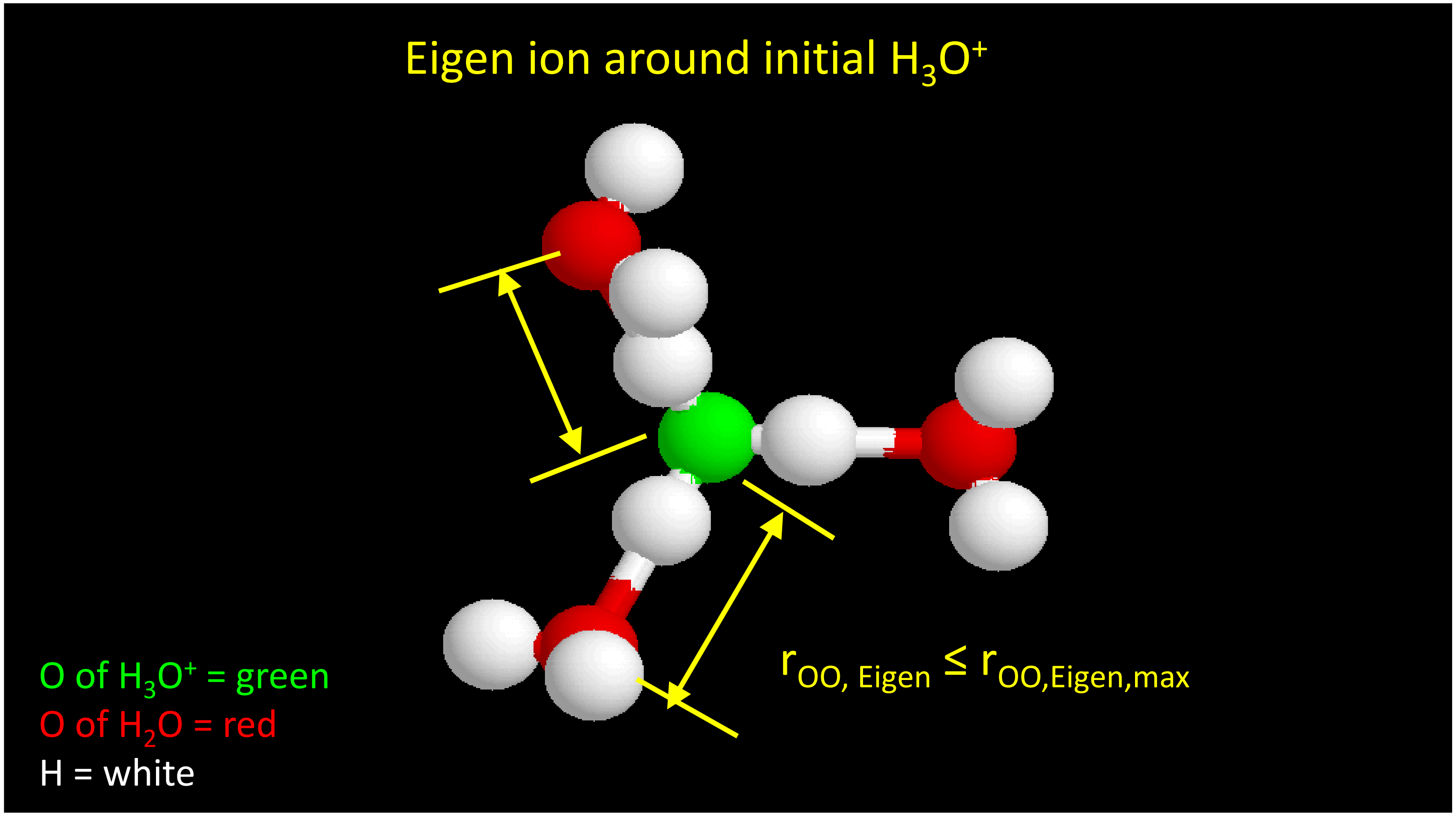
Reaction Trigger #4



Trigger #4. Zundel ion has sp3 hybridization

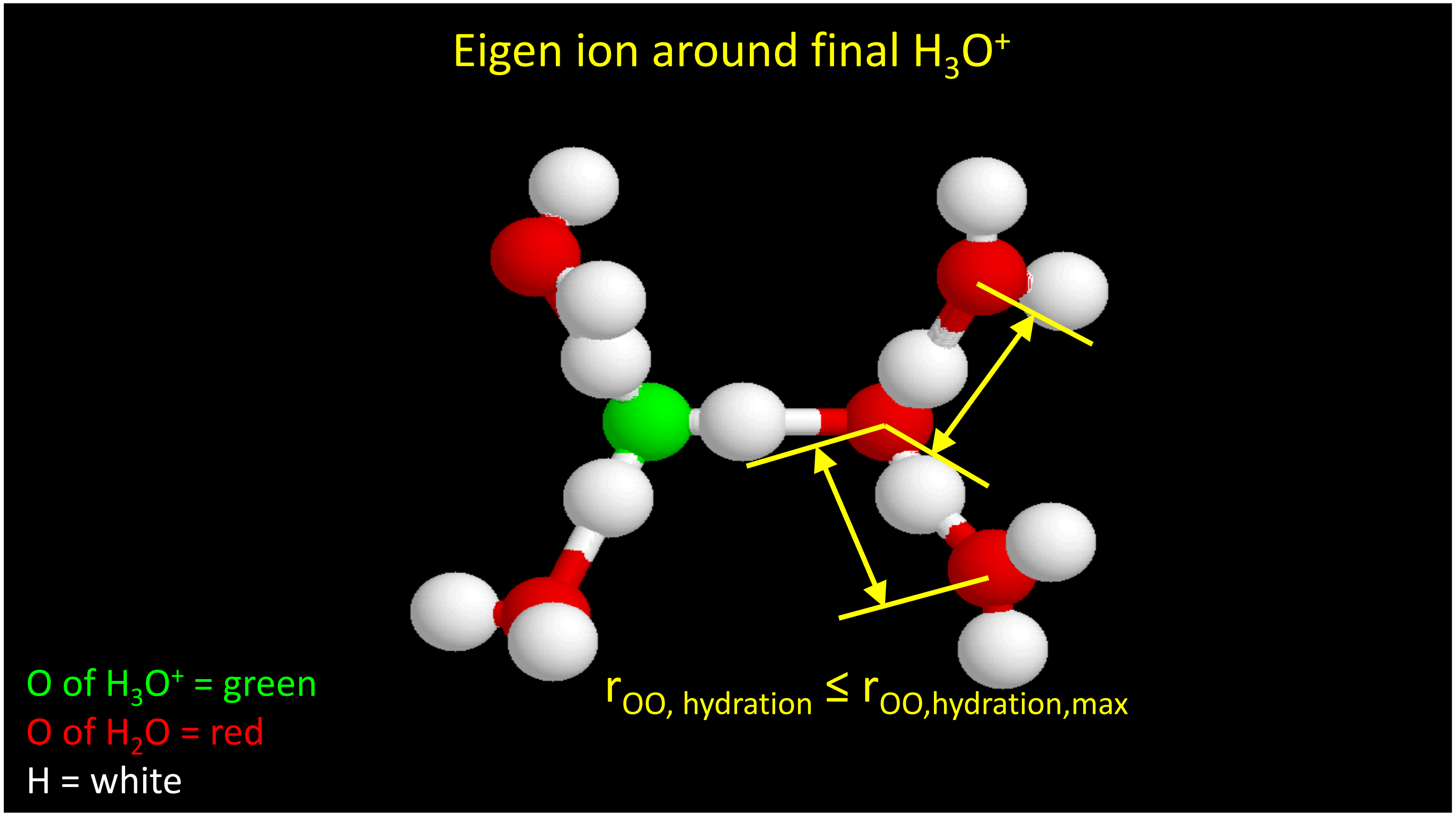
(Lone pair of electrons in H_2O is pointed toward H)

Reaction Trigger #5



Trigger #5. Initial hydronium ion forms an Eigen ion

Reaction Trigger #6



Eigen ion around final H_3O^+

Trigger #6. H_2O in Zundel ion is hydrated

Reaction Trigger #7

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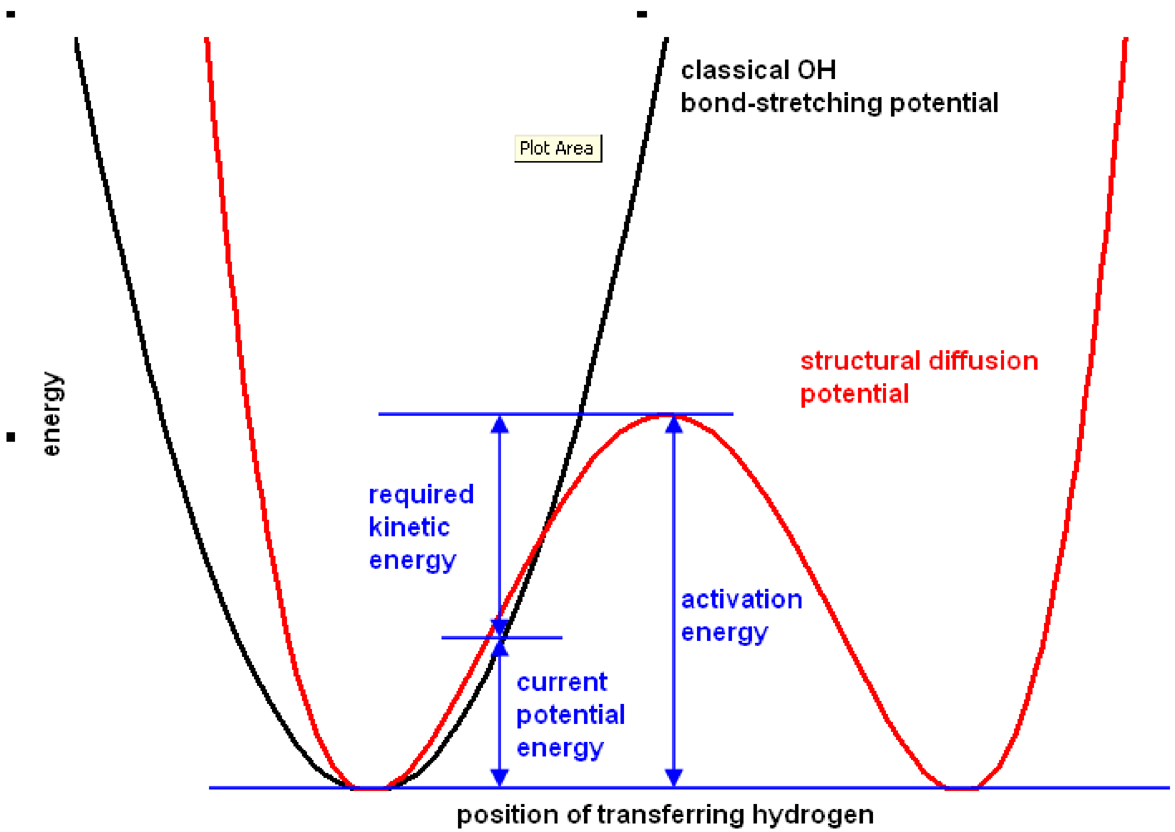
H must exceed activation energy



Trigger #7. H kinetic energy projected along OHO axis must be sufficient to overcome activation barrier

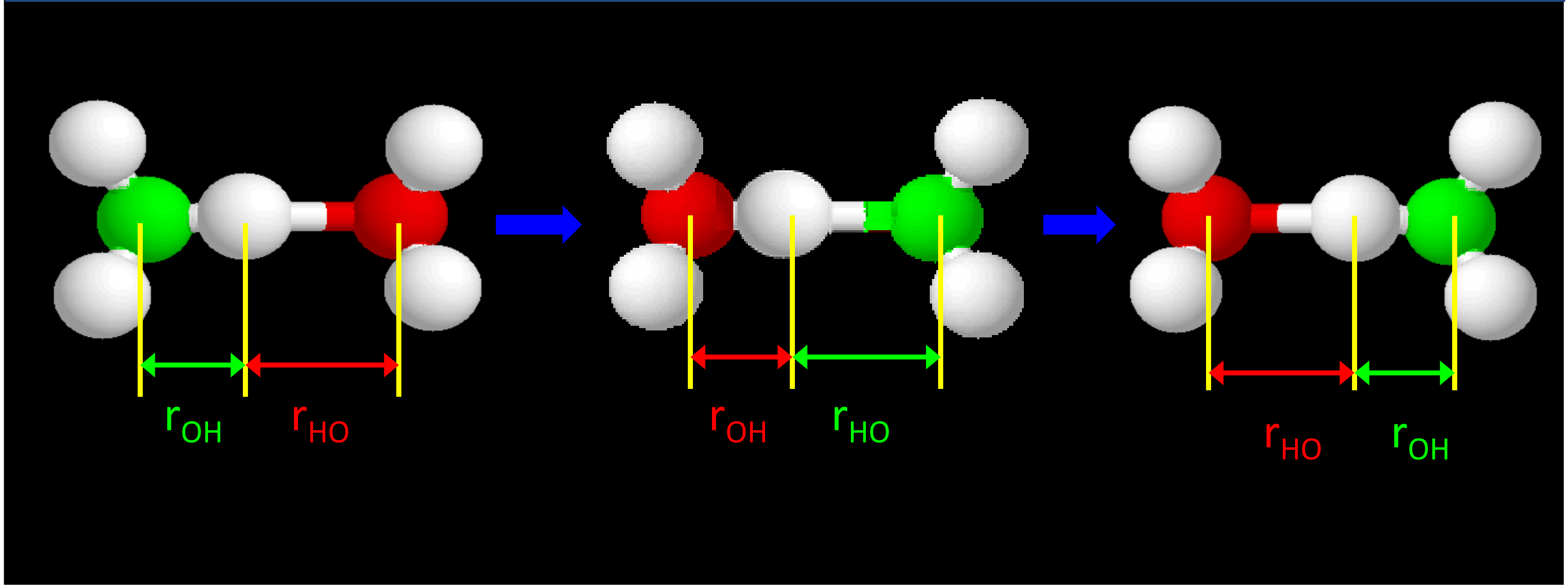
Algorithm – Step 2

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

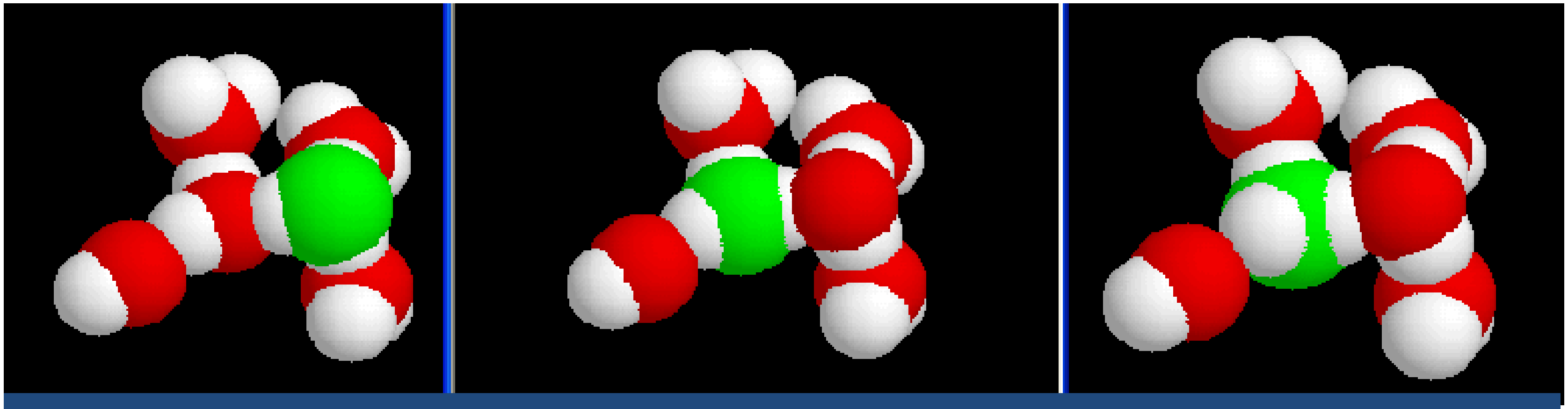
- Move proton over to the newly formed hydronium ion so that r_{OH} of the hydronium before and after reaction are the same

Algorithm – Step 3

Step 3. Local Equilibration

- There is an increase in the potential energy of the system
- Helps in maintaining the correct heat of reaction

Summary



Step 1. **Step 2.** **Step 3.**

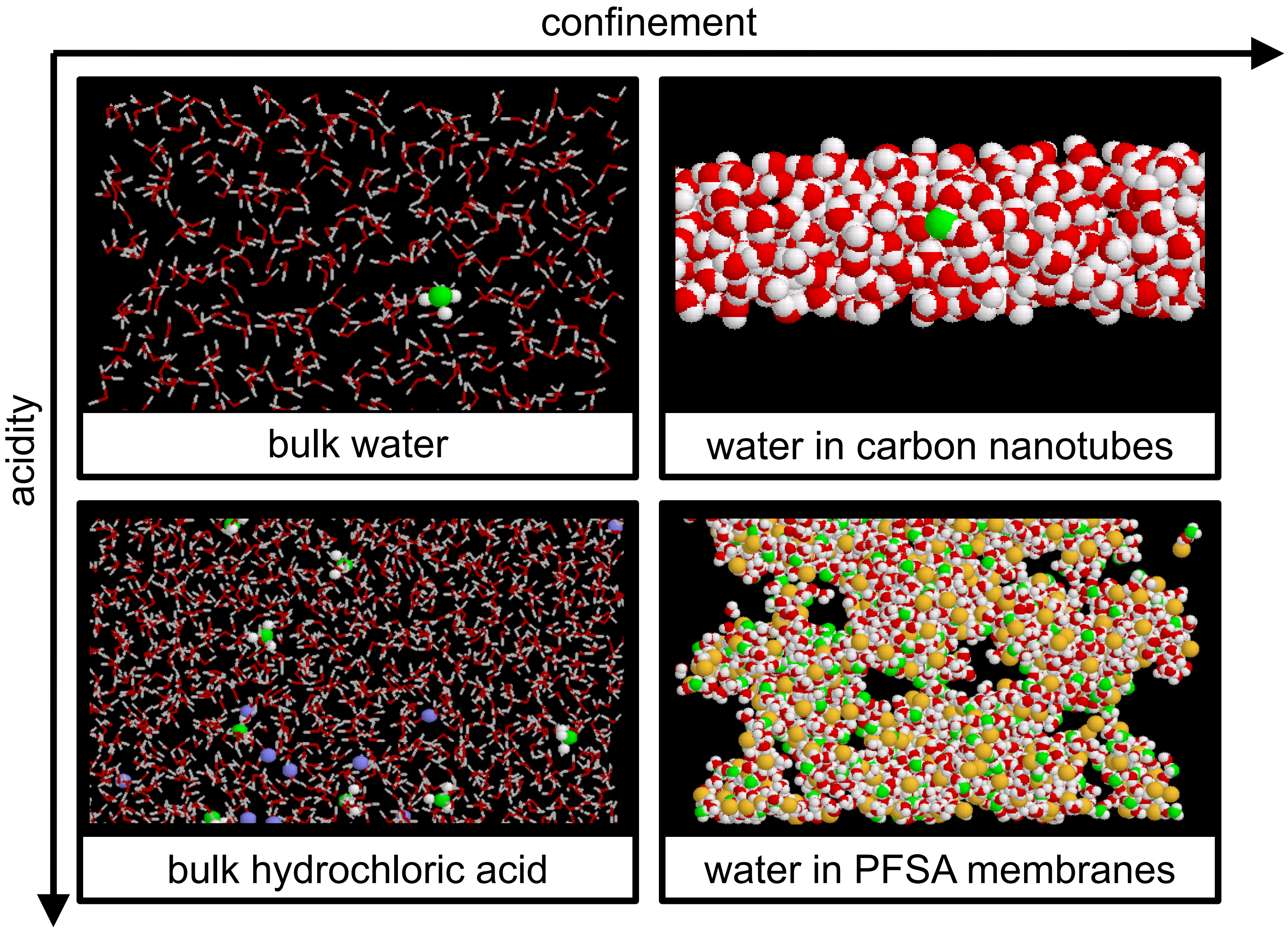
O of H_3O^+ = green

O of H_2O = red

H = white

4 RMD Applications

Acidity and Confinement Effects on Proton Mobility



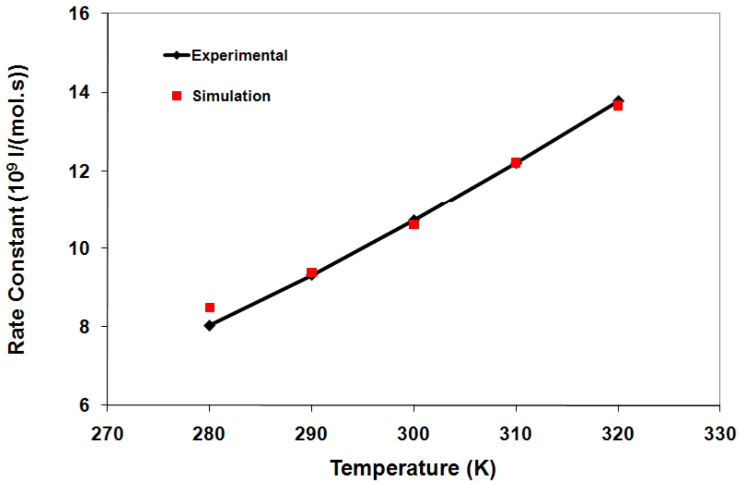
Proton Transport in Bulk Water

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

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

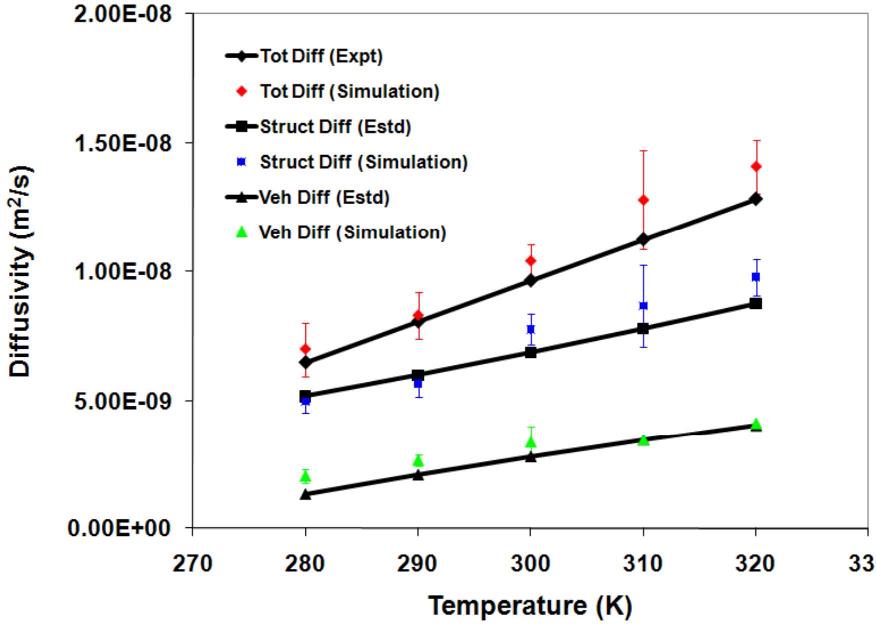
$$k = k_o \exp\left(-\frac{E_a}{RT}\right)$$

- 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.



Esai Selvan, J. Phys. Chem. C, 2010.

Charge self-diffusivity prediction

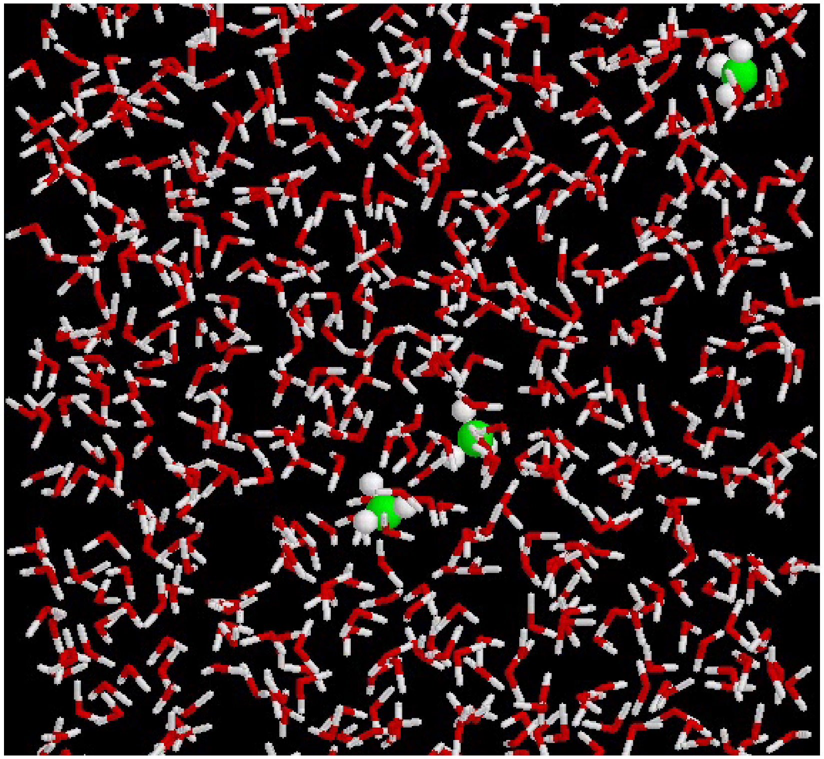
- semi-quantitative agreement with experiment
- decomposition into structural and vehicular components
- structural is 60-70% of total
- correct temperature dependence
- structural and vehicular components are uncorrelated

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

RMD In Water

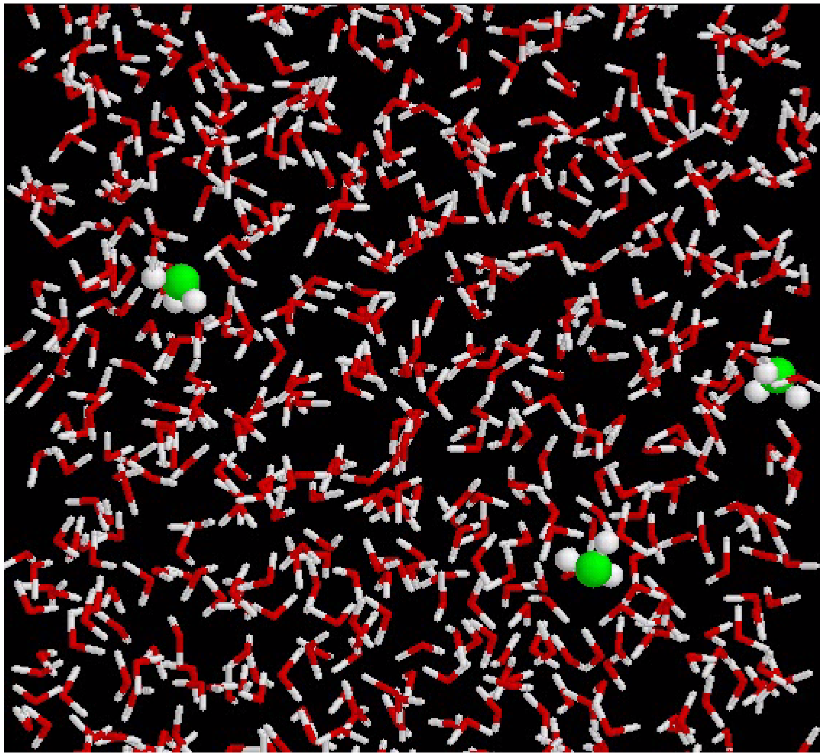
Proton Diffusion in Bulk Water

Non - Reactive System



Vehicular Diffusion

Reactive System



Structural and Vehicular Diffusion

View diffusion movies online at
https://trace.lib.utk.edu/home/davidkeffer/sites/atoms/RMD/text/rmd_h3o_03.html

Bulk HCl Solution: Acidity Effect

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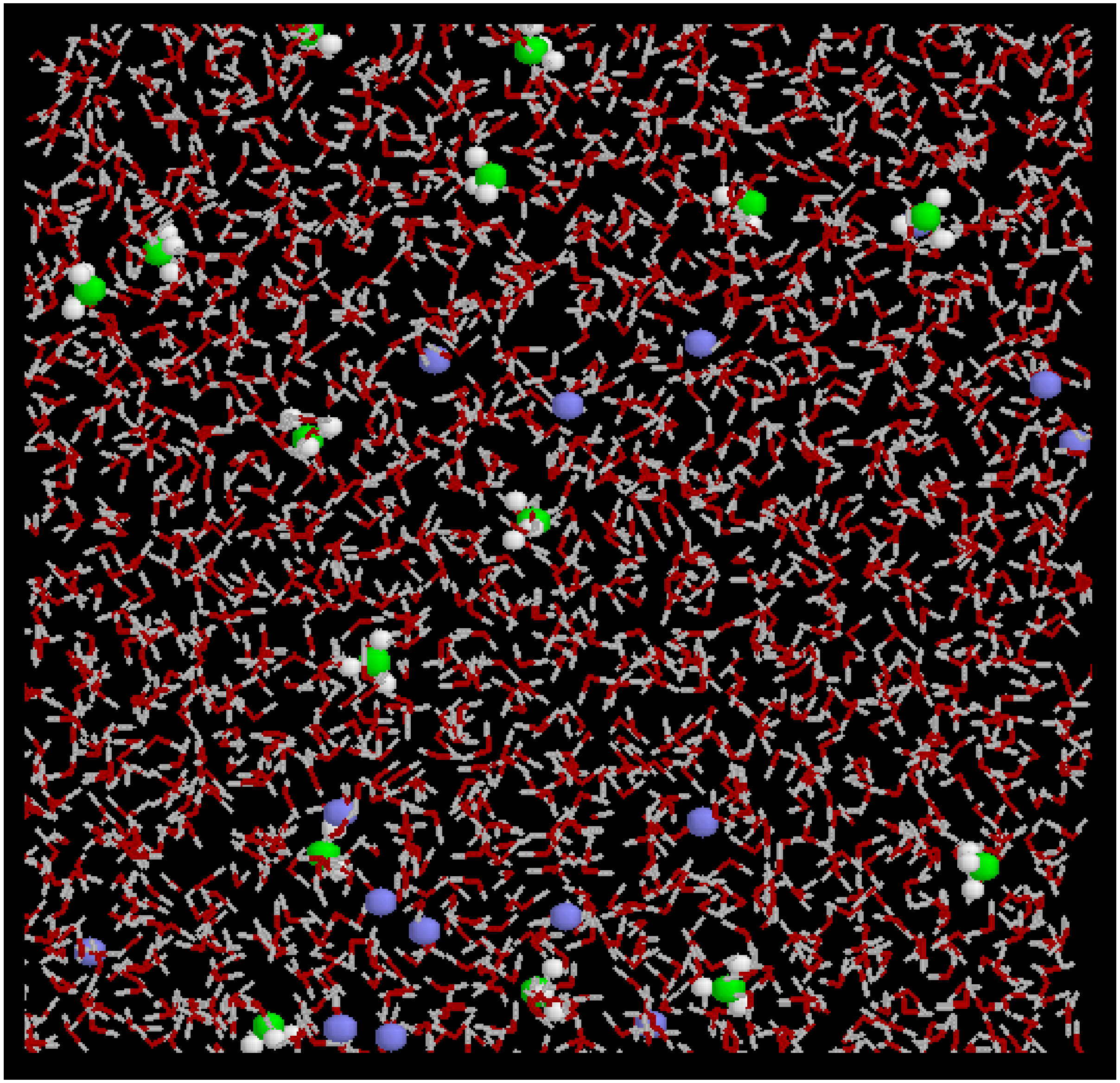
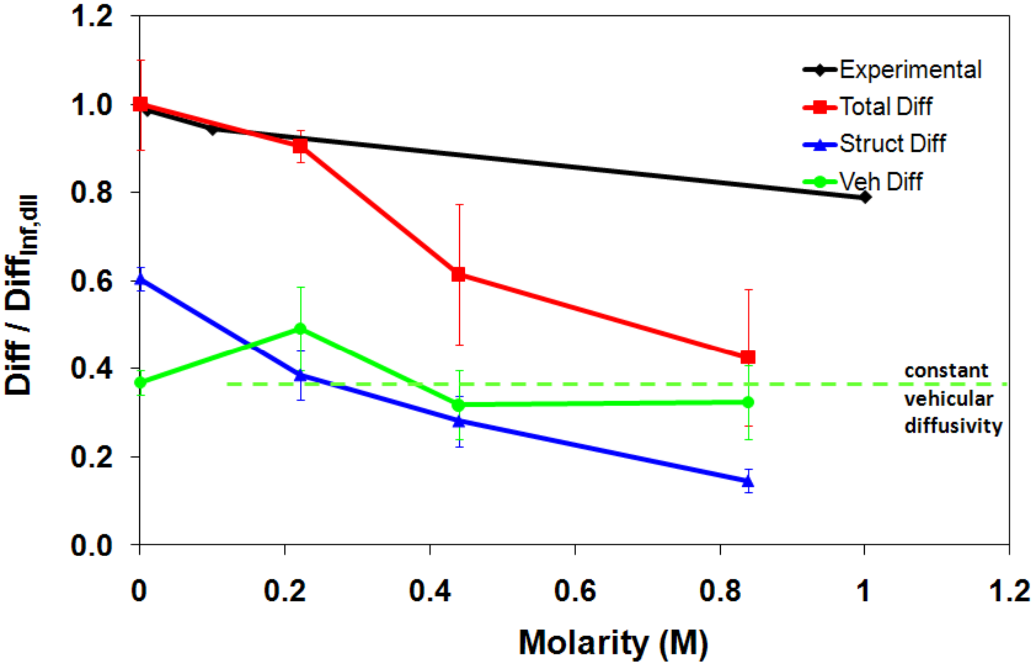
simulation snapshot
periodic system
15 H^+
15 Cl^-
1875 H_2O
λ= 125
conc = 0.44 M
pH = 0.36



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

Bulk HCl Solution: Acidity Effect

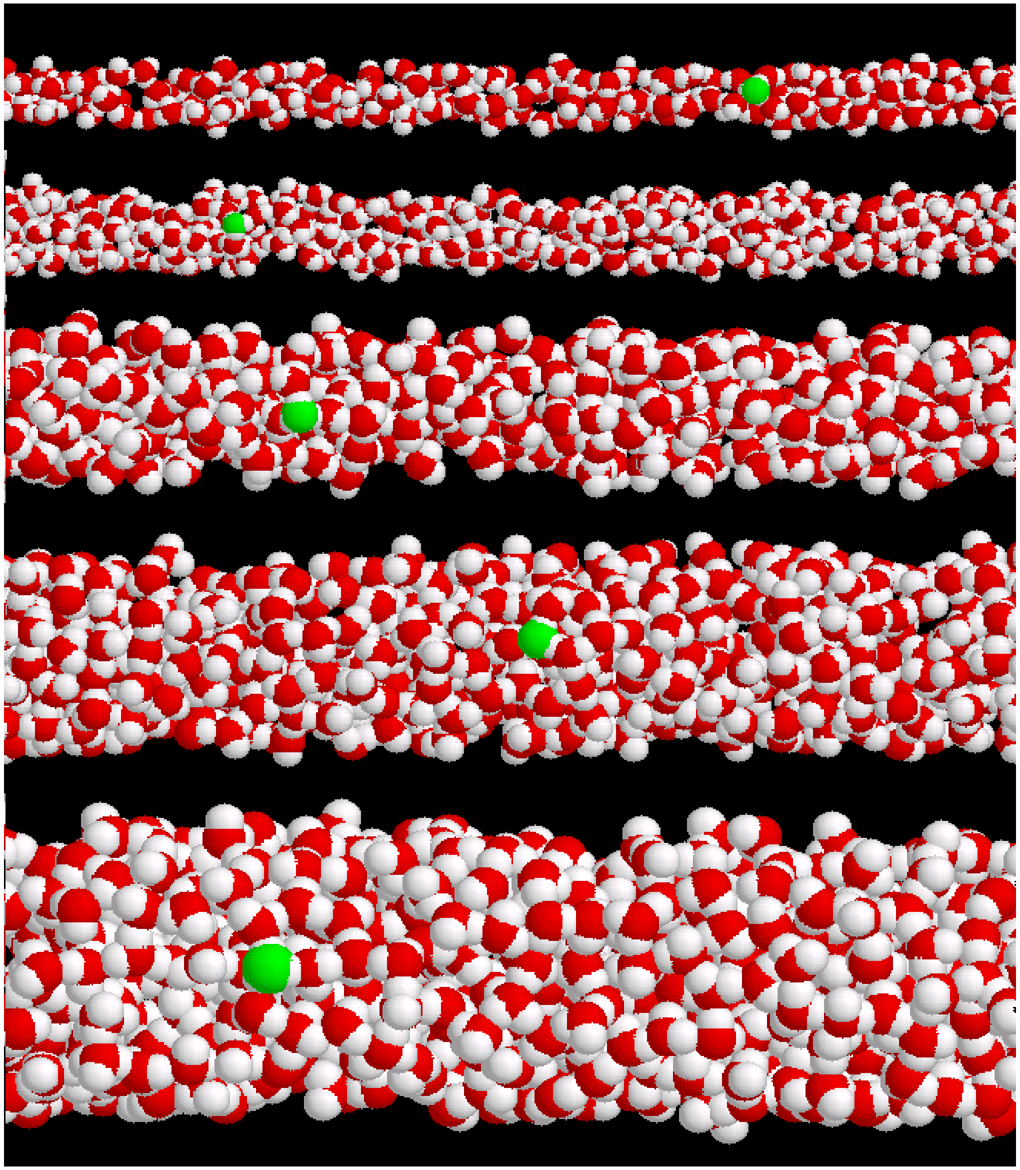


Esai Selvan, J. Phys. Chem. C, 2010.

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

Proton Transport in Nanotubes: Effect of Confinement



Nominal radii from 5.42 to 10.85 Å.

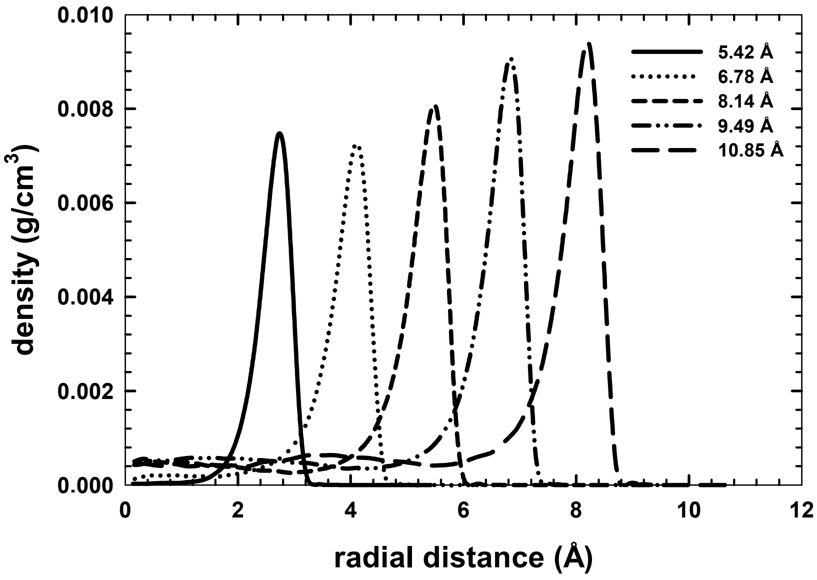
Infinitely dilute simulations (1 excess H^+)

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

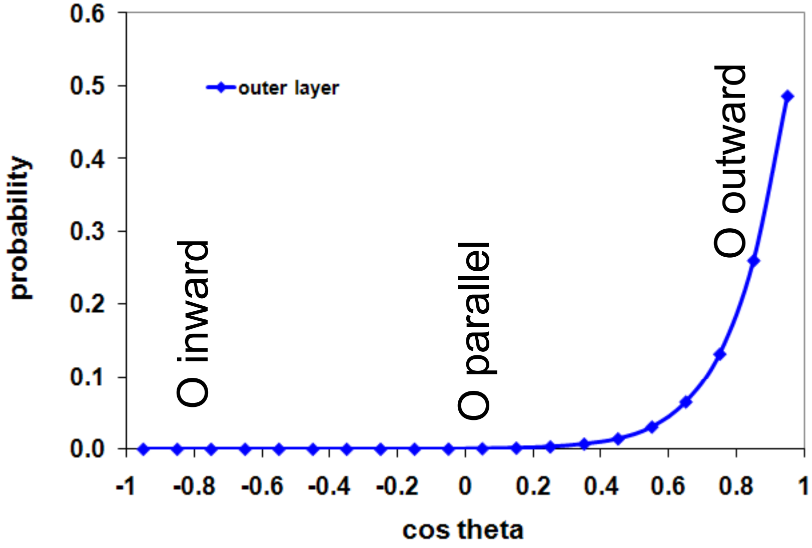


Density distribution of H_3O^+.

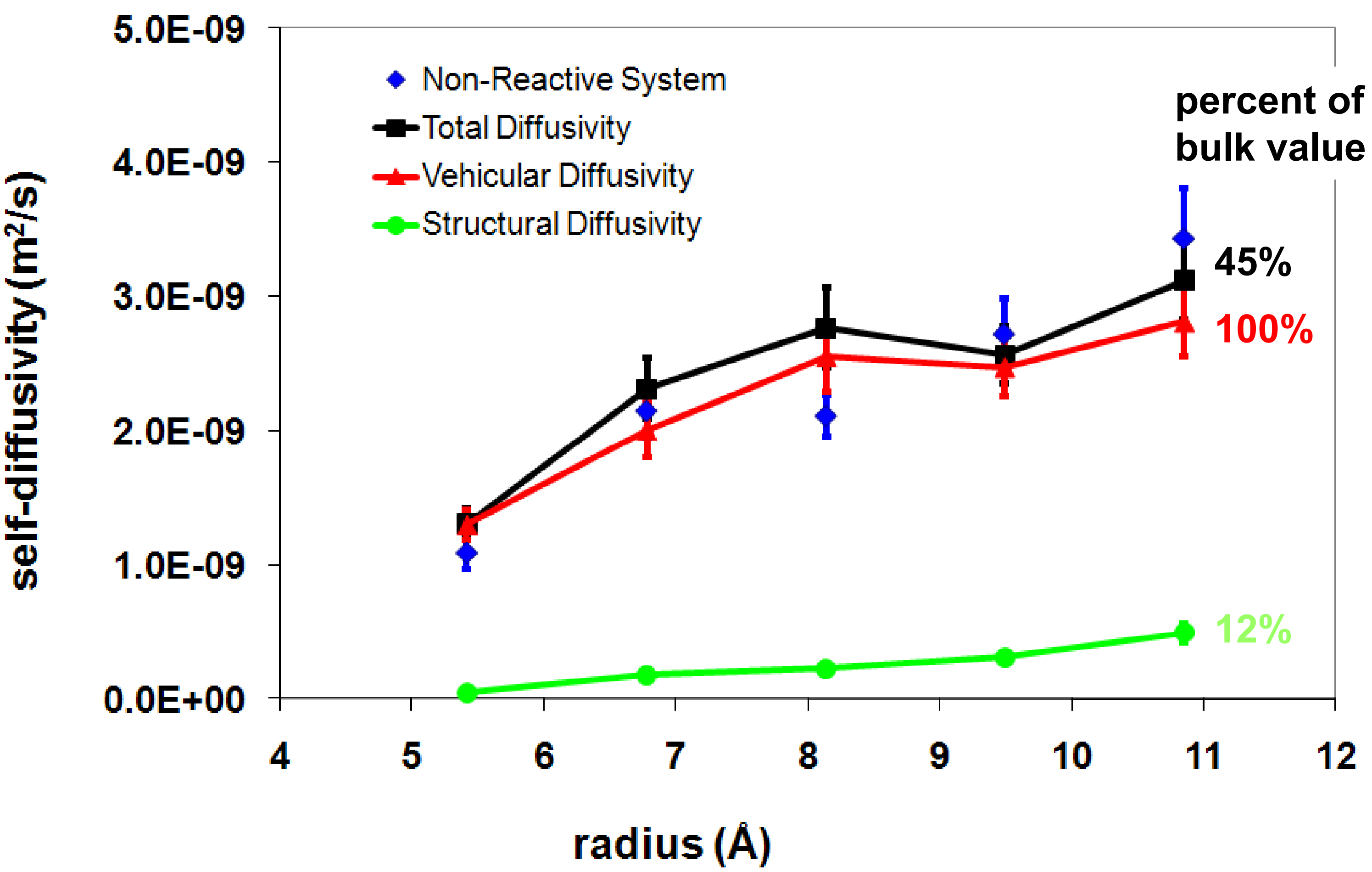
H_3O^+ is preferentially located at pore wall.

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.



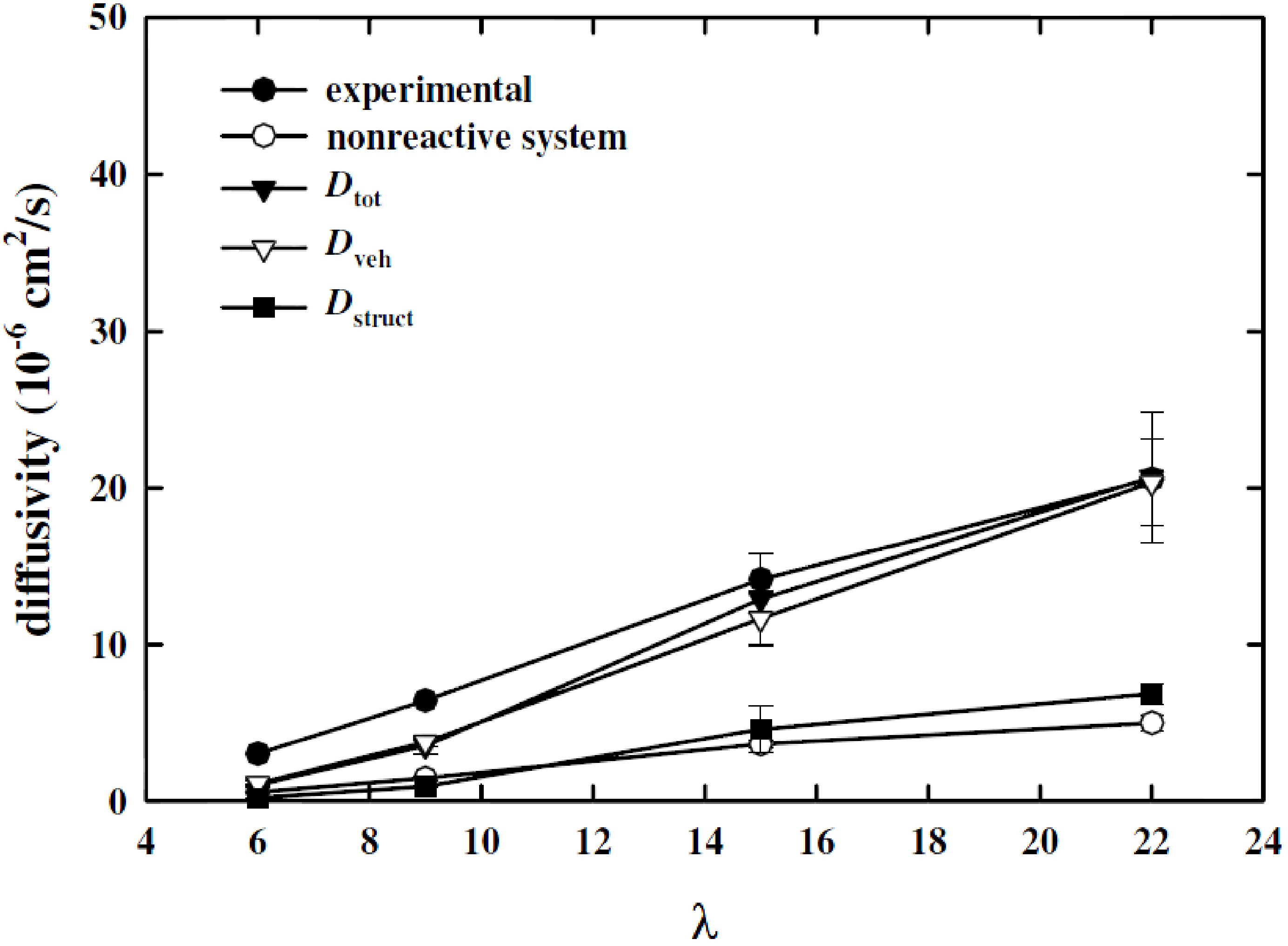
Proton Transport in Nanotubes: Effect of Confinement



Confinement dramatically reduces structural diffusion.

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

Proton Transport in Nafion



Simulation results are in reasonable agreement with experiment.
Structural component is drastically reduced in Nafion.

Manuscript currently under review, J. Phys. Chem. C, 2011.

Proton Transport in Nafion

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Correlation term was near zero in bulk systems and in carbon nanotubes.

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

The above definition can be decomposed as,

$$D_{\mathrm{veh}} \equiv \lim_{\tau\to\infty} \frac{\left\langle \Delta\vec{r}_{\mathrm{veh}}^{\,2} \right\rangle}{2d\tau}$$

$$D_{\mathrm{struct}} \equiv \lim_{\tau\to\infty} \frac{\left\langle \Delta\vec{r}_{\mathrm{struct}}^{\,2} \right\rangle}{2d\tau}$$

$$D_{\mathrm{corr}} \equiv \lim_{\tau\to\infty} \frac{2\left\langle \Delta\vec{r}_{\mathrm{veh}} \Delta\vec{r}_{\mathrm{struct}} \right\rangle}{2d\tau}$$

What about in Nafion?
Correlation term is negative.
Total diffusivity is less than sum of structural and vehicular components.
Structural diffusion on average moves protons to immobile sulfonate anions.
Structural diffusion on average moves protons away from sulfonate anions.

Manuscript currently under review, J. Phys. Chem. C, 2011.

Future Work

Other proton transport rxns in Nafion

Aqueous domains

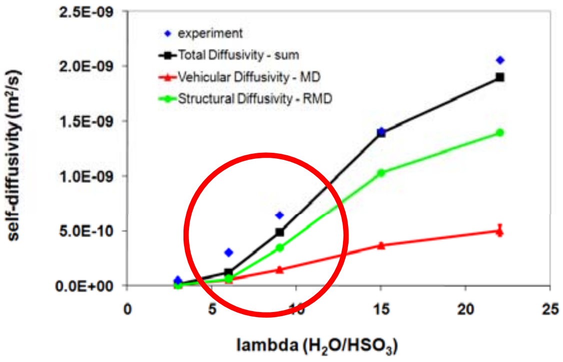
$$H_3O^+ + H_2O \xleftrightarrow{4\,H_2O} H_2O + H_3O^+ \qquad (1)$$

Hydrophilic/Hydrophobic interfacial regions

$$H_3O^+ + H_2O \xleftrightarrow{n\,H_2O/(4-n)\,SO_3^-} H_2O + H_3O^+ \qquad (2)$$

Dissociation of proton (λ < 3)

$$SO_3H + H_2O \xleftrightarrow{2\,H_2O} SO_3^- + H_3O^+ \qquad (3)$$



Expected to have impact at low λ.

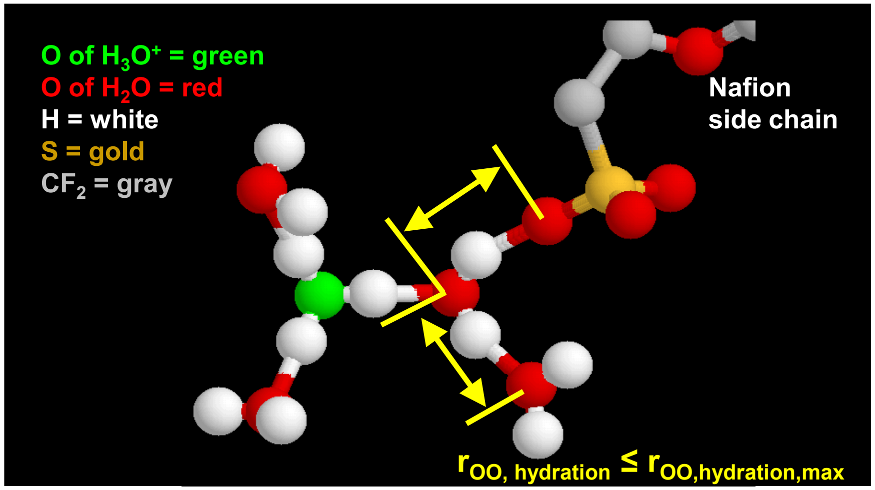


Figure 1: The two reacting molecules with three water molecules and one SO_3^- (eq 2)

Trigger #6. Eigen ion around final H_3O^+. H_2O in Zundel ion can be hydrated by H_2O or SO_3^-.

Trigger #7. Energetic trigger can automatically register differences in forces due to presence of the SO_3^- groups.

Quantum calculations have been performed.

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

Bulk water

- RMD parameterized to match diffusivity data

Bulk HCl solutions

- acidity causes a decrease in diffusivity, mostly to the structural component

Carbon nanotubes

- confinement causes a decrease in diffusivity, mostly to the structural component

Nafion

- combination of acidity, confinement and connectivity causes a drastic decrease in diffusivity