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

Lecture 06. Multiscale Modeling of Water & Charge Transport

Dept. of Chemical & Biomolecular Engineering
Yonsei University
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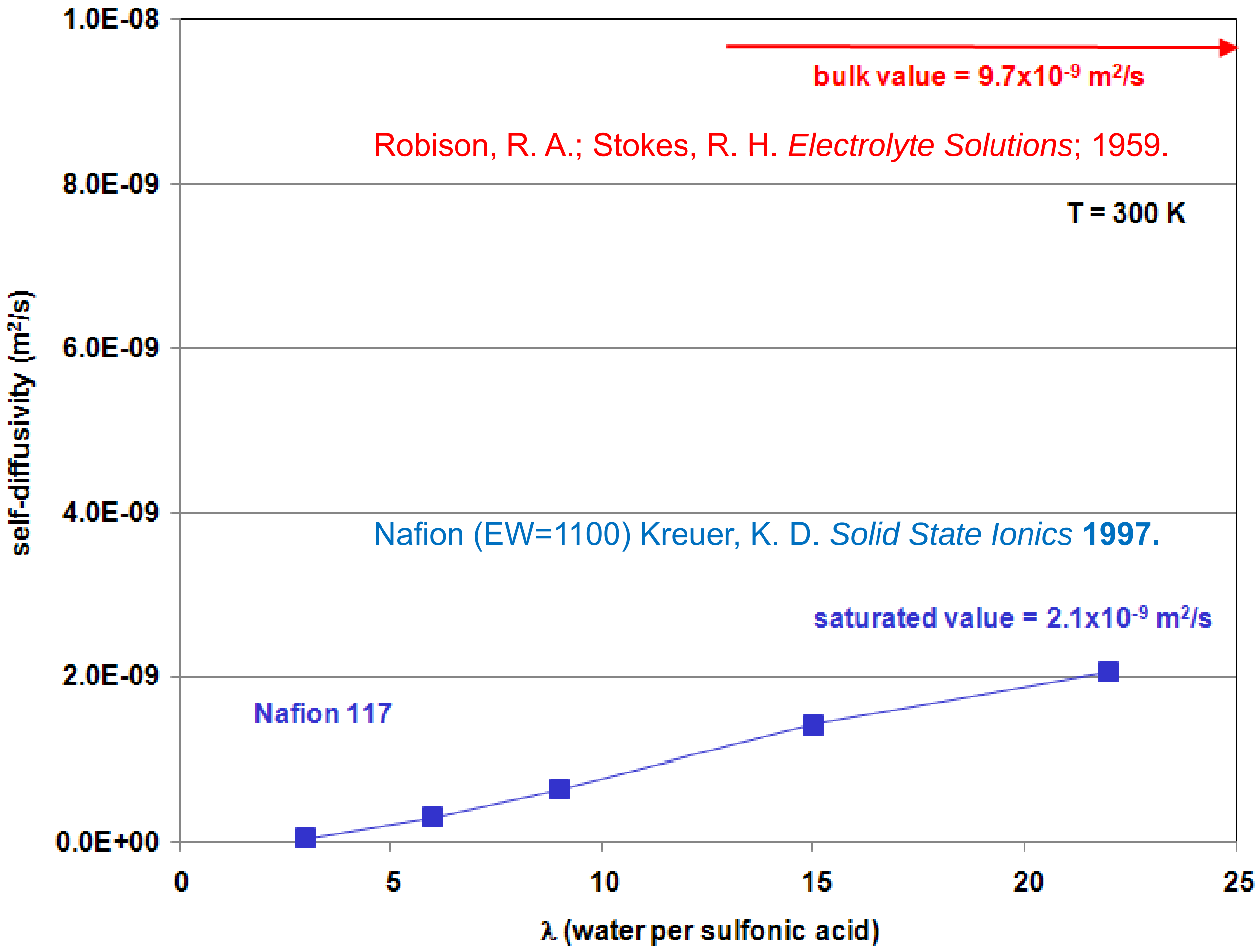
Lecture Outline

- Review: Obtaining Diffusivities in Molecular Dynamics Simulation
- Mesoscale Models: Confined Random Walk Simulations
- Percolation Theory
- Analytical Theory – Applications to Water and Charge
    - Acidity
    - Confinement
    - Connectivity

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.

Diffusivities from MD Simulation

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

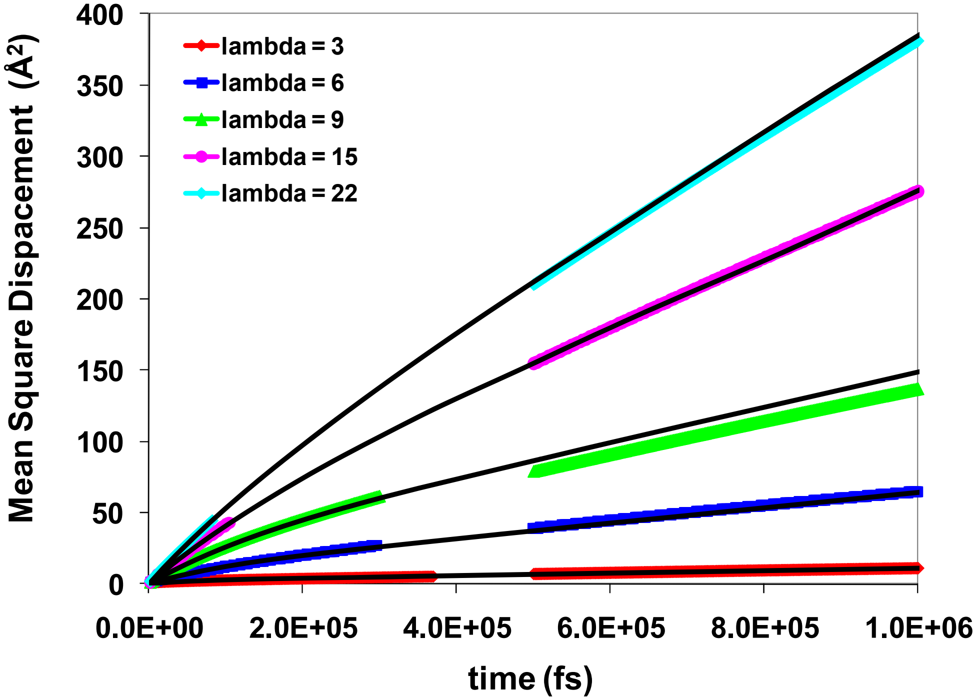
$$D = \lim_{\tau \to \infty} \frac{MSD}{2d\tau} = \lim_{\tau \to \infty} \frac{\left\langle \left[r_i(t+\tau) - r_i(t) \right]^2 \right\rangle}{2d\tau}$$

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**.

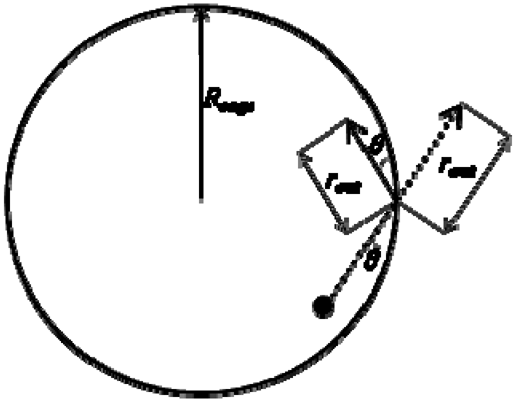
MSDs don't reach the long-time (linear) regime.

Confined Random Walk Simulation

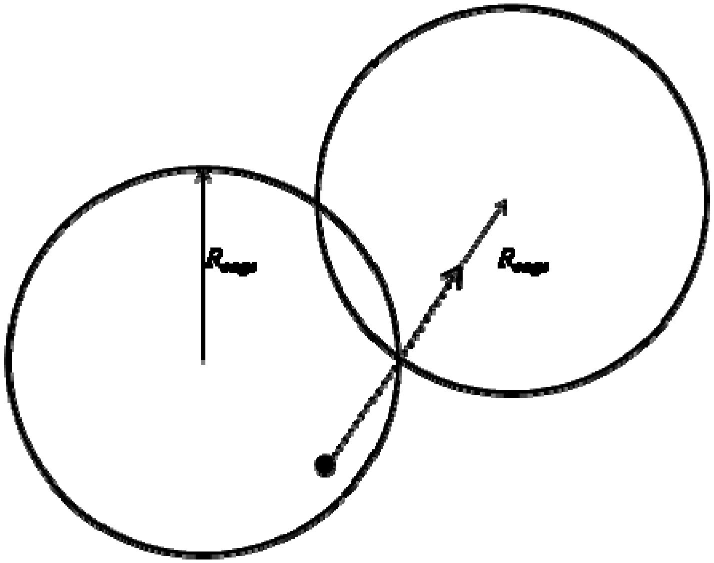
Mesoscale Model

- 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

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.



unsuccessful move



successful move

Confined Random Walk Simulation

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Impact of cage-to-cage hopping probability

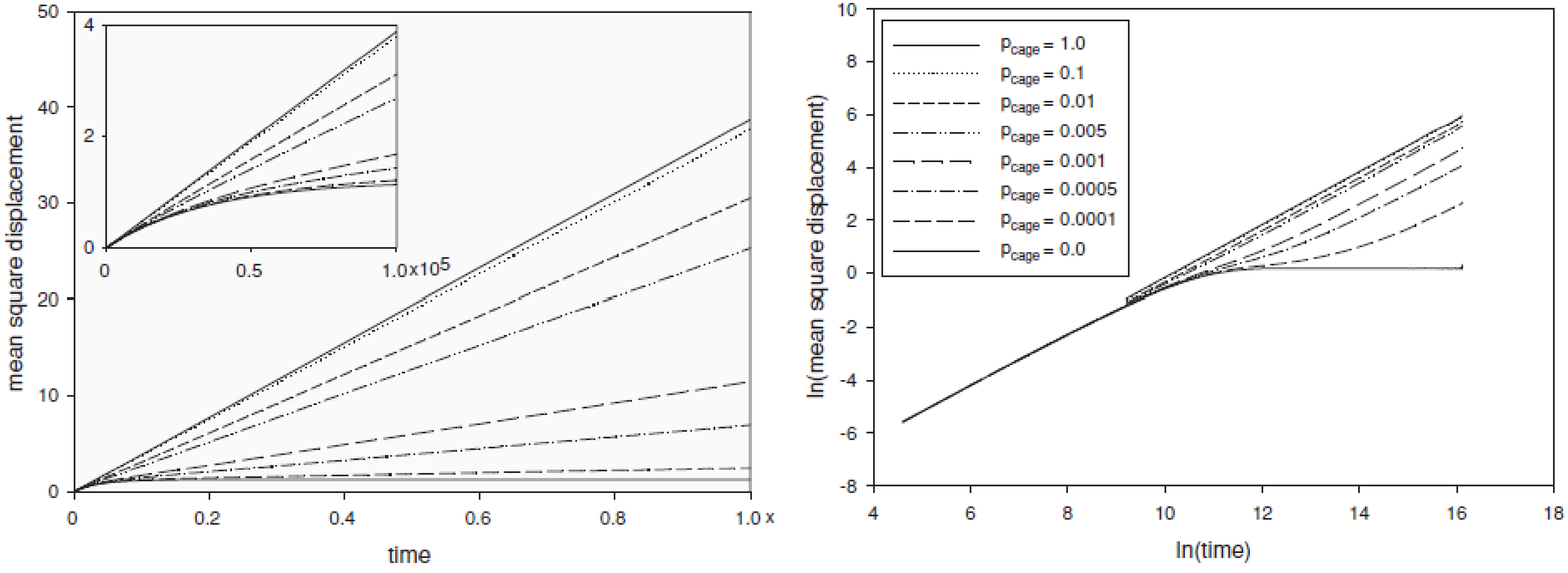


FIG. 4. Impact of cage-to-cage hopping probability p_{cage}. Plot of the mean square displacement as a function of observation time on linear (a) and logarithmic (b) scales for a dimensionless system in which $\langle \Delta r \rangle = 2.87 \times 10^{-3}$, $\Delta t = 1$, $R_{\text{cage}} = 1$, and p_{cage} is varied from 0 to 1.

Low cage-to-cage hopping probability slows diffusion but doesn't eliminate the Einstein infinite-time limit linear behavior.

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.

Confined Random Walk Simulation

Impact of cage size

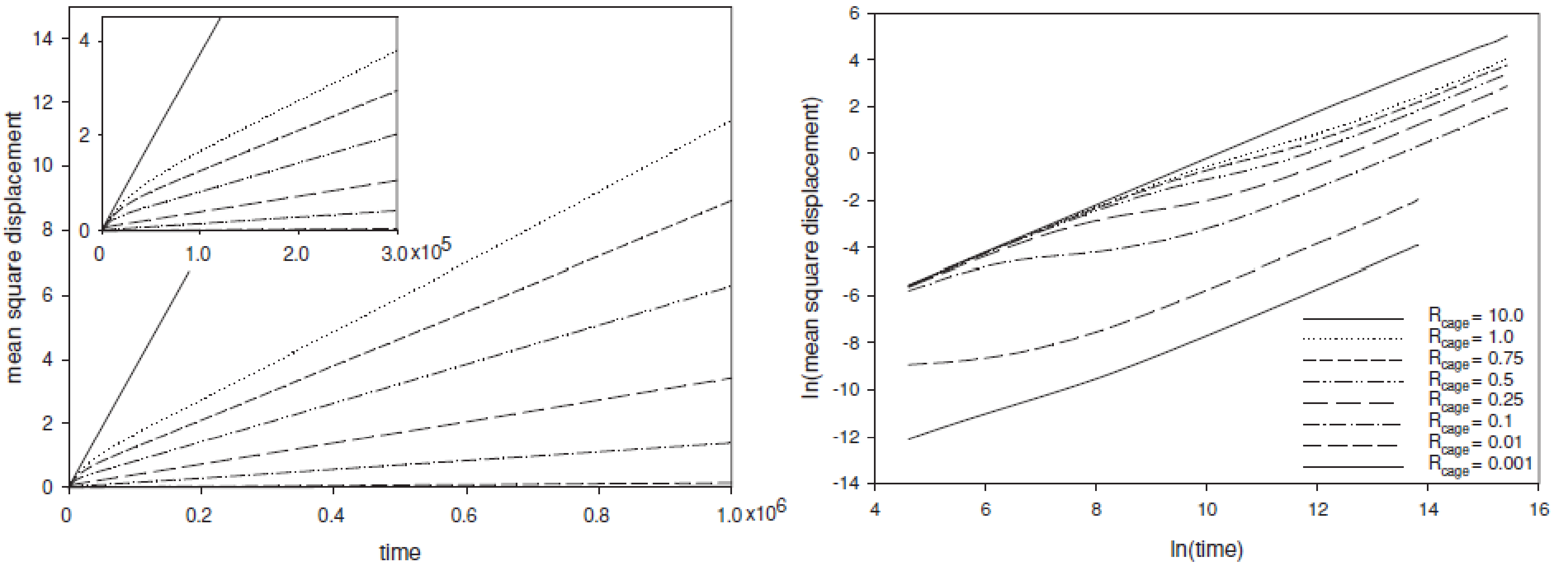
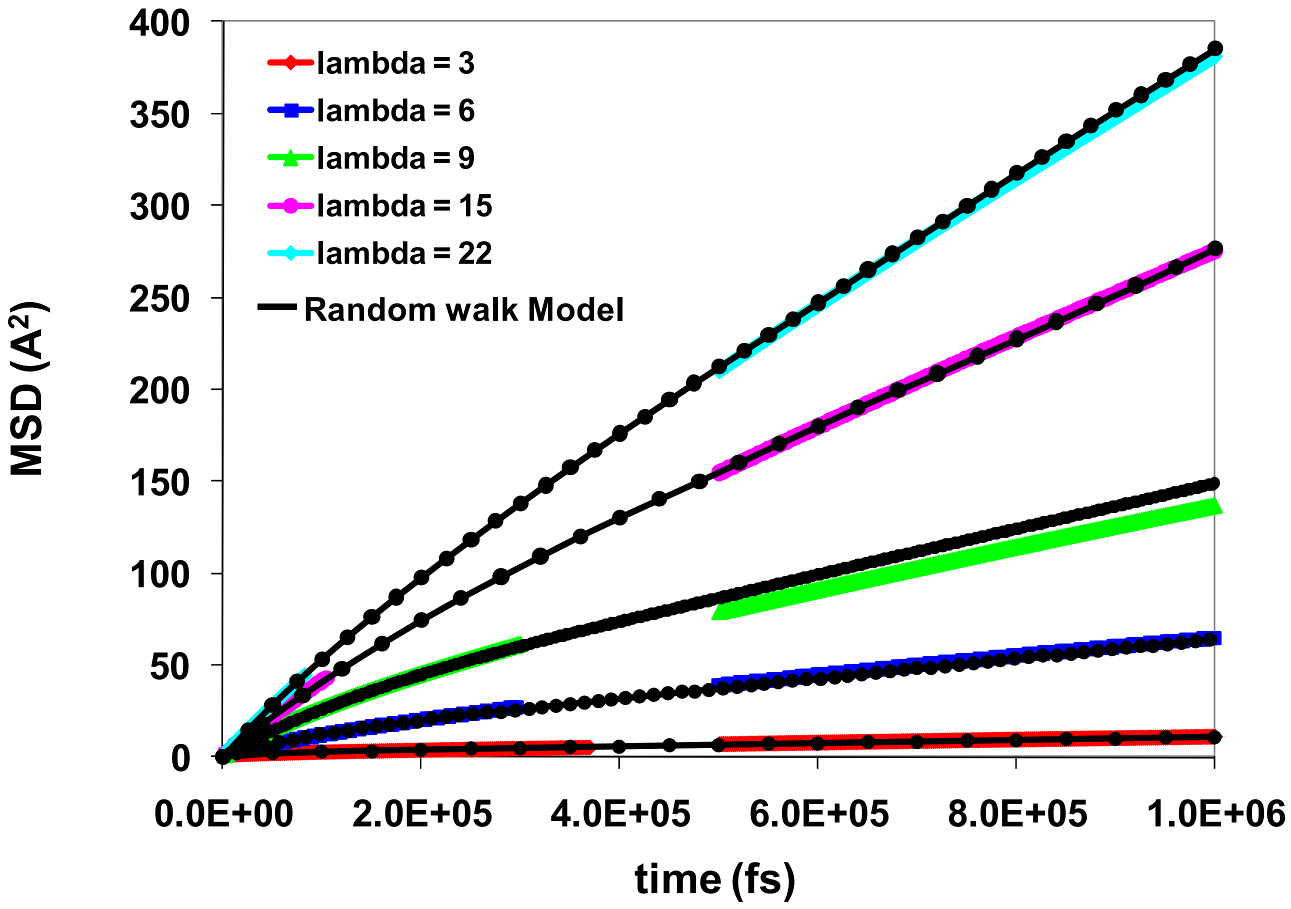


FIG. 5. Impact of cage radius R_{cage}. Plot of the mean square displacement as a function of observation time on linear (a) and logarithmic (b) scales for a dimensionless system in which $\langle \Delta r \rangle = 2.87 \times 10^{-3}$, $\Delta t = 1$, $p_{\text{cage}} = 0.001$, and R_{cage} is varied from 0 to 10.

Small cage size reduces the diffusivity.

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 Simulations with Confined Random WalkTheory

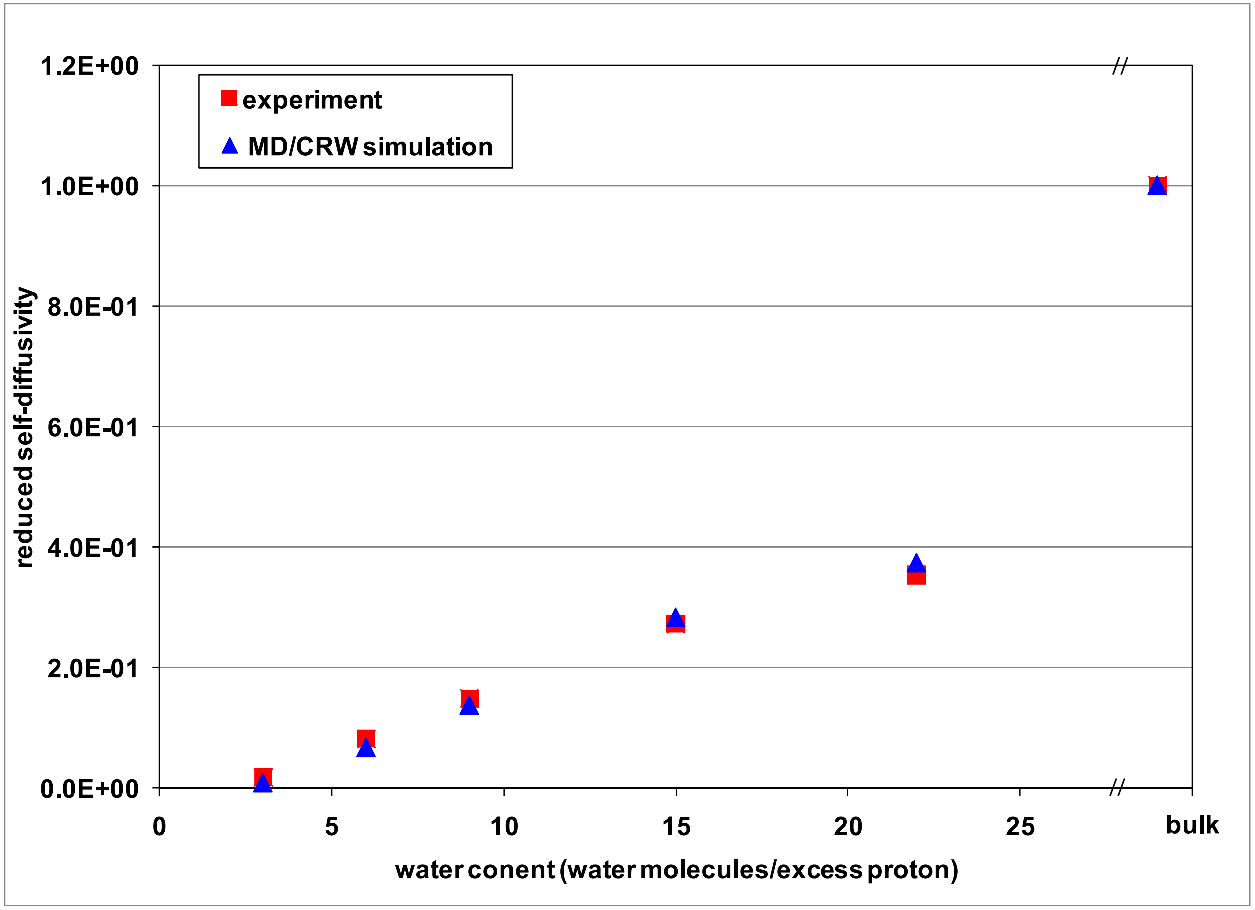


Calvo-Muñoz, E.M., Esai Selvan, M., Xiong, R., Ojha, M., Keffer, D.J., Nicholson, D.M., Egami, T", *Phys. Rev. E*, **83**(1) 2011 article # 011120.

- 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?

Confined Random Walk Simulation

Combined MD simulations and Confined Random Walk simulations do not only yield the effective diffusivity of the system, but they also yield intrinsic diffusivities of the unconfined system, D_o, and the cage size, R_{cage}., and the probability of a successful cage-to-cage hop, p_{cage}.

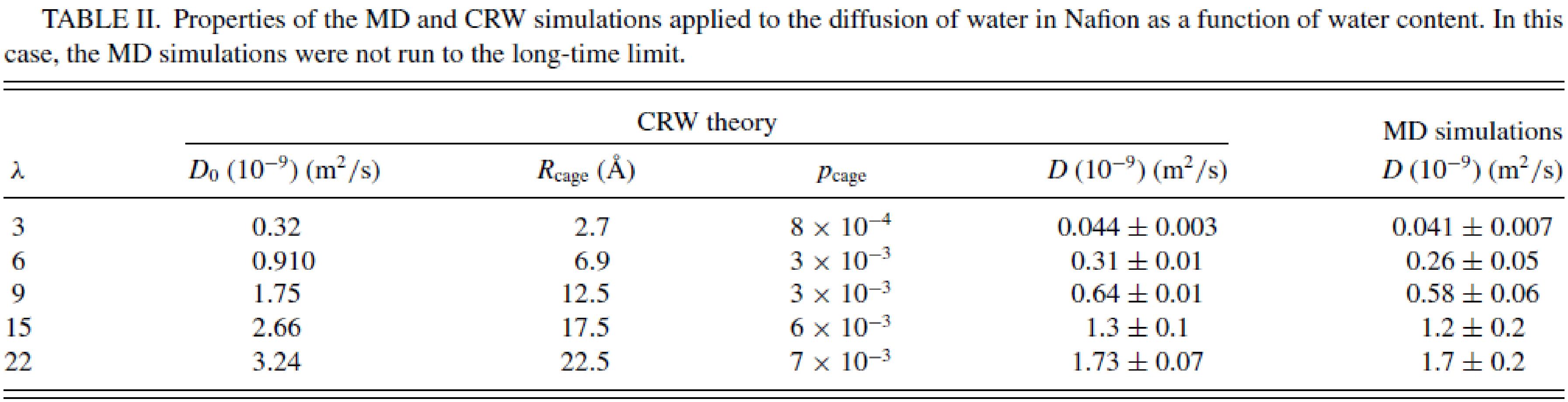


TABLE II. Properties of the MD and CRW simulations applied to the diffusion of water in Nafion as a function of water content. In this case, the MD simulations were not run to the long-time limit.

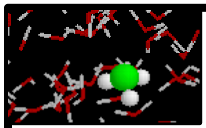
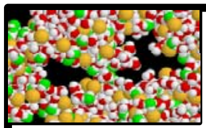
	CRW theory				MD simulations
λ	D_0 (10^{-9}) (m^2/s)	R_{cage} (Å)	p_{cage}	D (10^{-9}) (m^2/s)	D (10^{-9}) (m^2/s)
3	0.32	2.7	8×10^{-4}	0.044 ± 0.003	0.041 ± 0.007
6	0.910	6.9	3×10^{-3}	0.31 ± 0.01	0.26 ± 0.05
9	1.75	12.5	3×10^{-3}	0.64 ± 0.01	0.58 ± 0.06
15	2.66	17.5	6×10^{-3}	1.3 ± 0.1	1.2 ± 0.2
22	3.24	22.5	7×10^{-3}	1.73 ± 0.07	1.7 ± 0.2

We will use the intrinsic diffusivities of the unconfined system, D_o, in an analytical theory of diffusion in hydrated PEMs.

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.

Analytical Theory

Three Factors: Acidity, Confinement & Connectivity

	bulk water	water in PFSA membranes
acidity	 ● H_3O^+ concentration is dilute λ=5.6·10^8 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

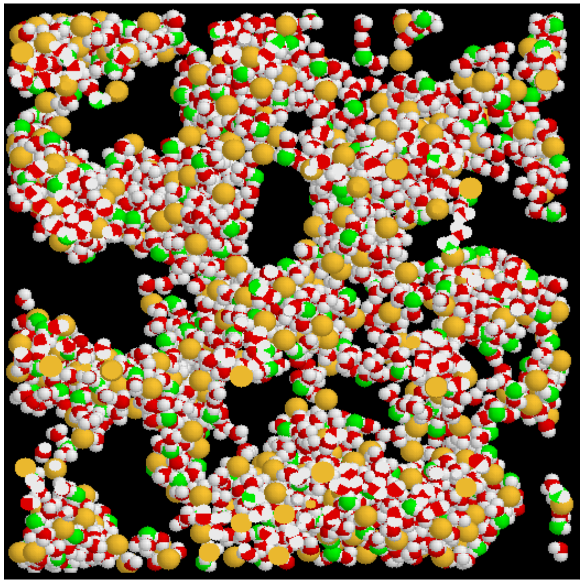
Percolation Theory

Water Mobility in Bulk Systems – Effect of Connectivity

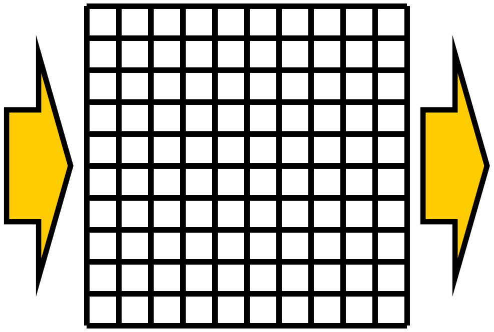
Invoke Percolation Theory to account for connectivity of aqueous domain within PEM and obtain effective diffusivity.

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

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

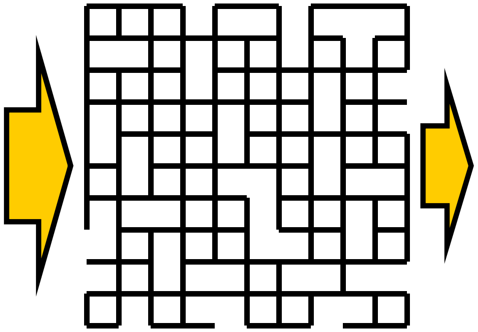


Percolation theory relates the effective diffusivity to the fraction of bonds that are blocked to diffusion.



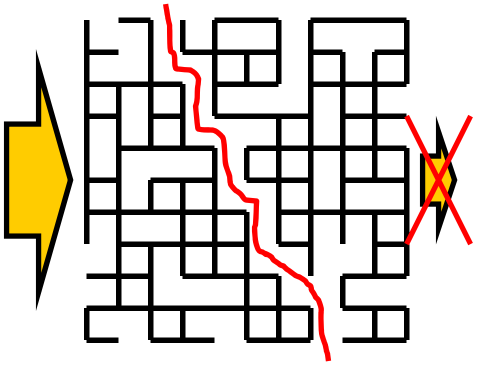
no blocked bonds

$D = D_{open}$



some blocked bonds

$0 < D < D_{open}$



beyond threshold

$D = 0$

Percolation Theory

This percolation theory has four variables

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

D_o = diffusivity through an open pore
(or D of the unconfined system)

D_b = diffusivity through a blocked pore

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

z = connectivity of the porous network

p_{EMA} = probability of a pore is blocked

It has an analytical solution
for the effective diffusivity,
D_{eff}

$$\frac{D_{\mathrm{eff}}}{D_{\mathrm{o}}} = \frac{1}{2}\left(A + \sqrt{A^2 + \frac{4f}{\frac{z}{2}-1}}\right)$$

where $f = D_{\mathrm{b}}/D_{\mathrm{o}}$ and

$$A = 1 - p_{\mathrm{EMA}} + f p_{\mathrm{EMA}} - \frac{f + p_{\mathrm{EMA}} - f p_{\mathrm{EMA}}}{\frac{z}{2}-1}$$

Percolation Theory

D_o = diffusivity of the unconfined system

Determined from empirical fits to experimental and simulation data as a function of acidity and confinement.
The acidity data is experimental data from bulk HCl solutions.
The confinement data is simulated data for water in model carbon nanotubes.
The fits are exponential.

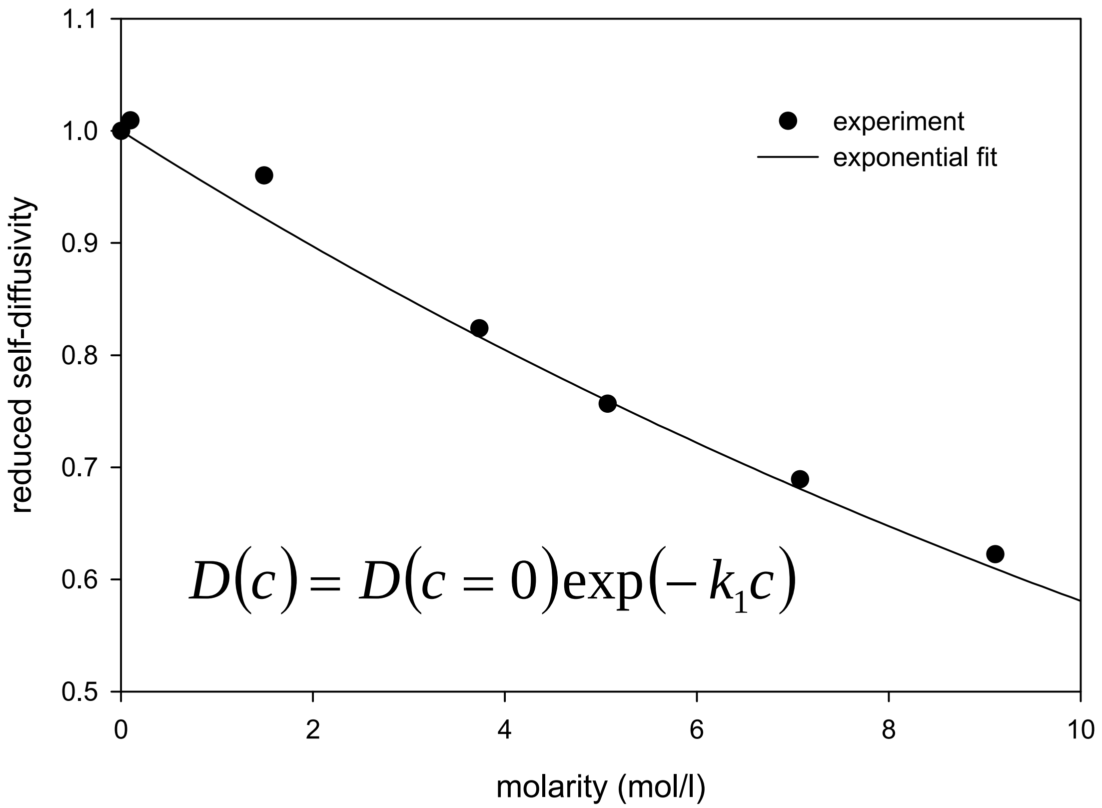
$$D_o(c, SA) = D_o(c = 0, SA = 0)\exp\left(-k_{c,H_2O}c\right)\exp\left(-k_{SA,H_2O}SA\right)$$

where c is concentration of hydronium ions and SA is surface area per water molecule.

$D_o(c = 0, SA = 0)$ is the diffusivity of bulk water.

Water Mobility in Bulk HCl solutions – Effect of Acidity

This experimental data is used to obtain the behavior of water diffusivity on 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

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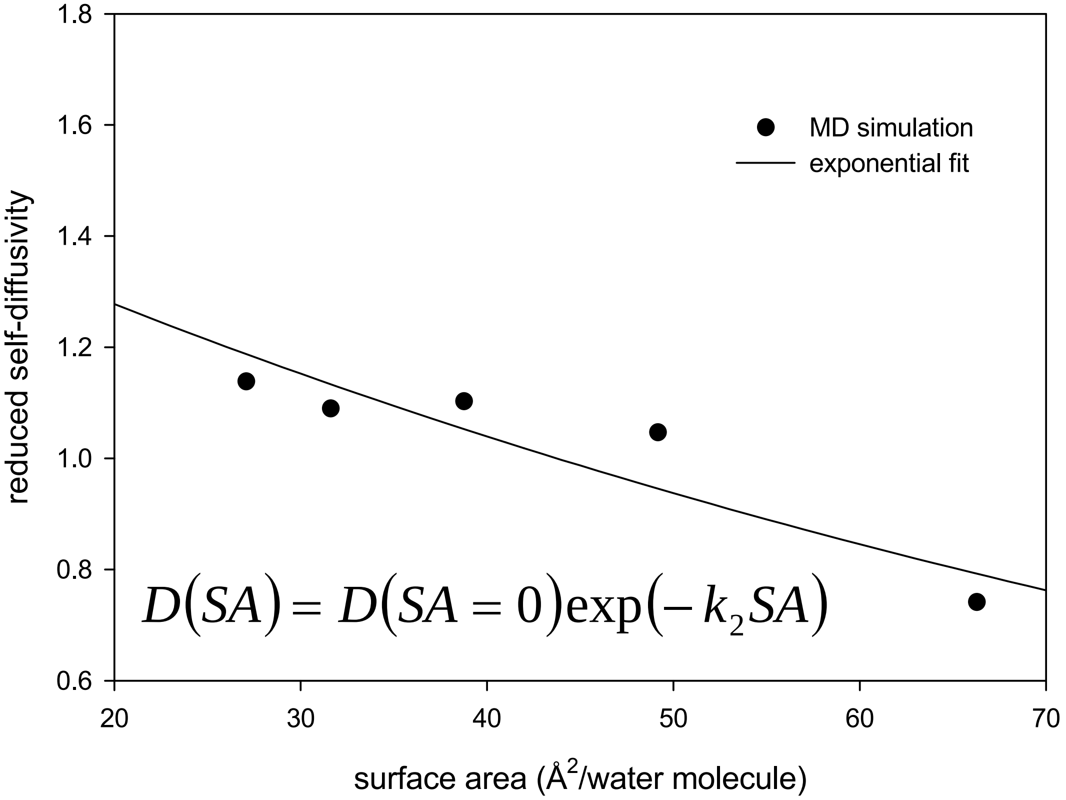
This simulated data is used to obtain the behavior of water diffusivity on acidity.



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

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.

Percolation Theory

D_b = diffusivity through a the blocked pore

$$D_b(c, SA) = p_{cage} D_o(c, SA)$$

where p_{cage} is the cage-to-cage hopping probability obtained when fitting the confined random walk theory to the mean square displacements from MD simulations of water diffusion in Nafion.

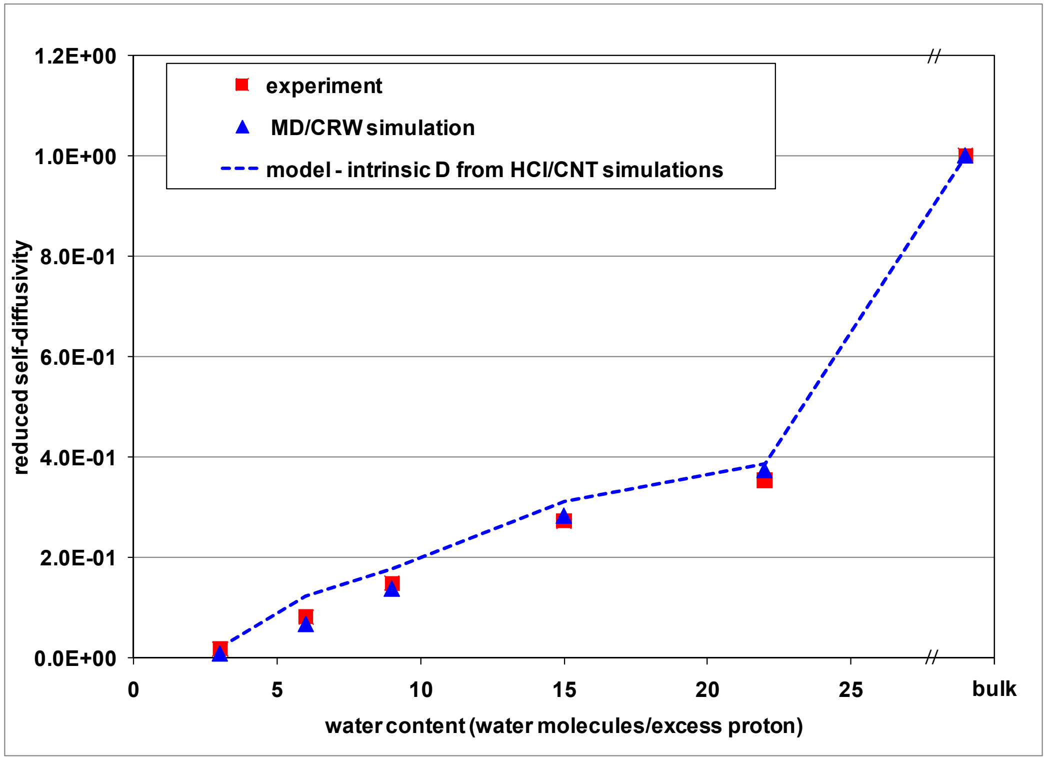
It turns out that, in this case, the remaining two parameters for the percolation theory, z and p_{EMA}, are not independent. We fit this remaining parameter to the effective diffusivities obtained from the MD/CRW simulations.

Result is shown on the next page.

Analytical Theory

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

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?

Analytical Theory

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?

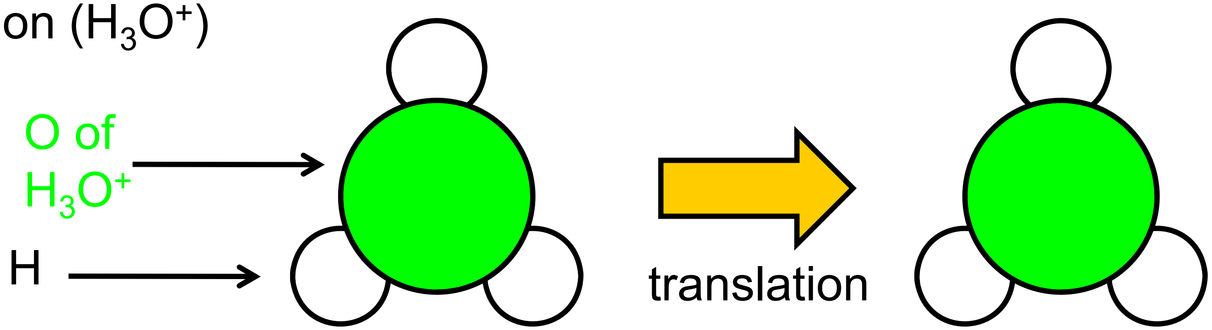
Diffusion of water is easier to describe.

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

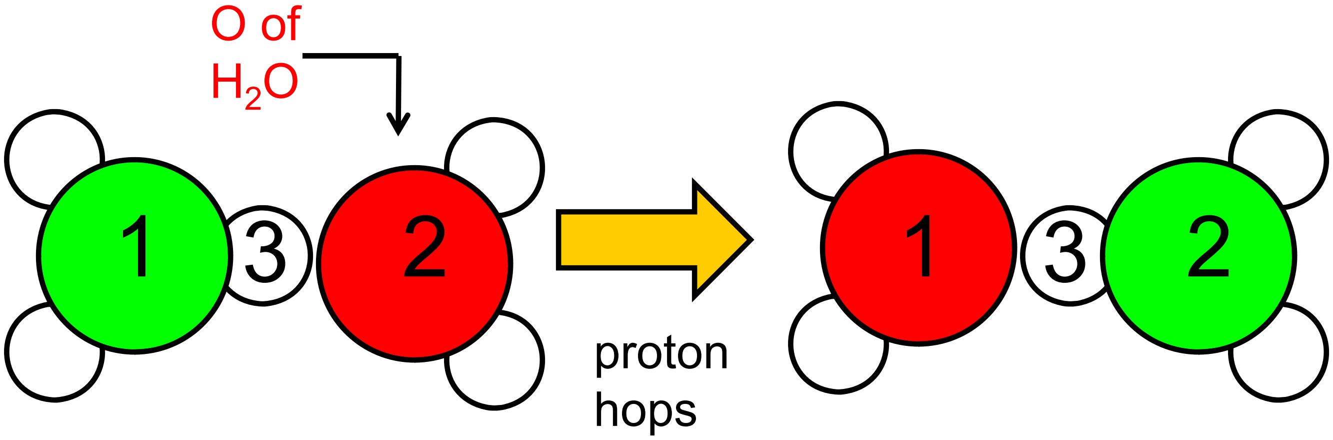
There are two mechanisms for proton transport.

Proton Transport – Two Mechanisms

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



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.

Bulk HCl Solution:
Effect of Acidity in an Analytical Fit

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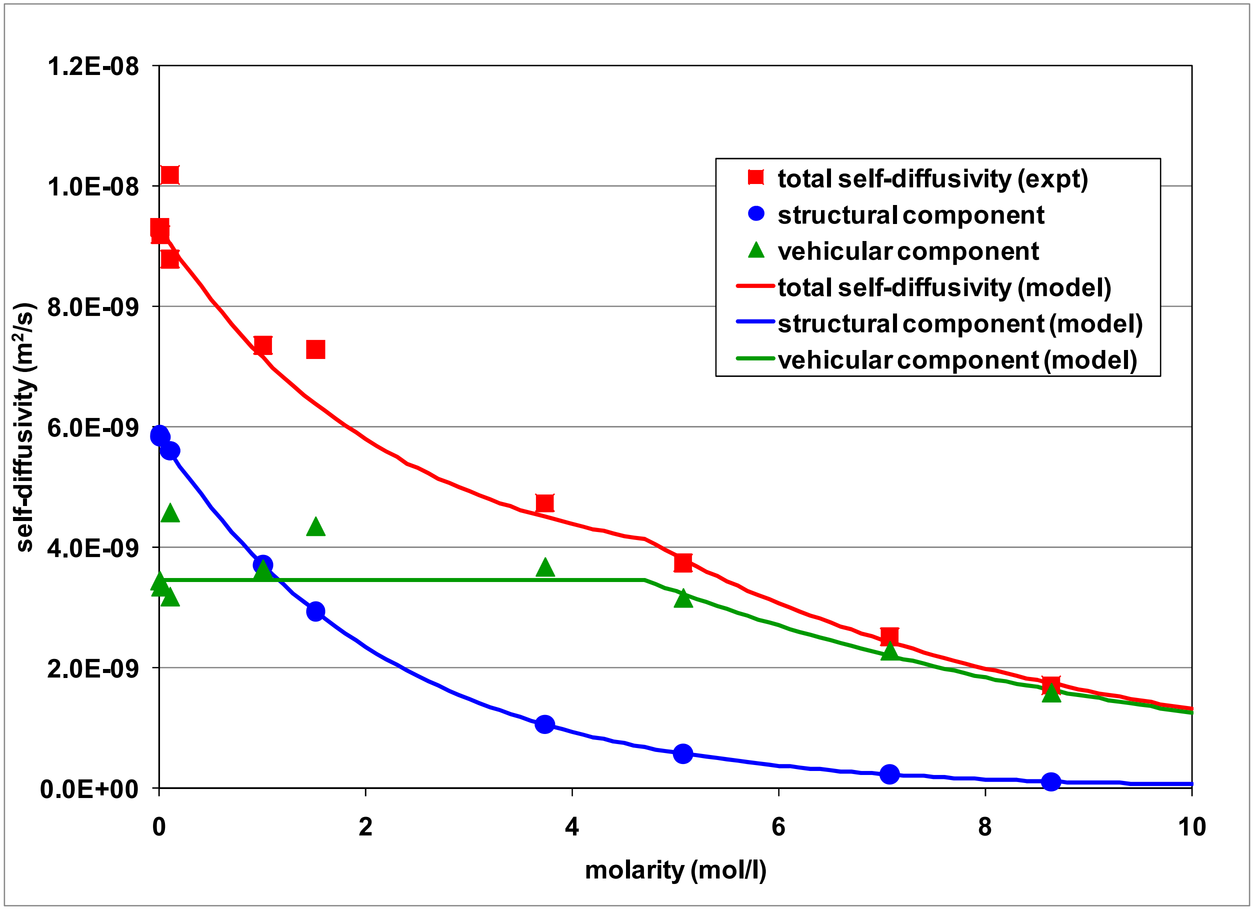
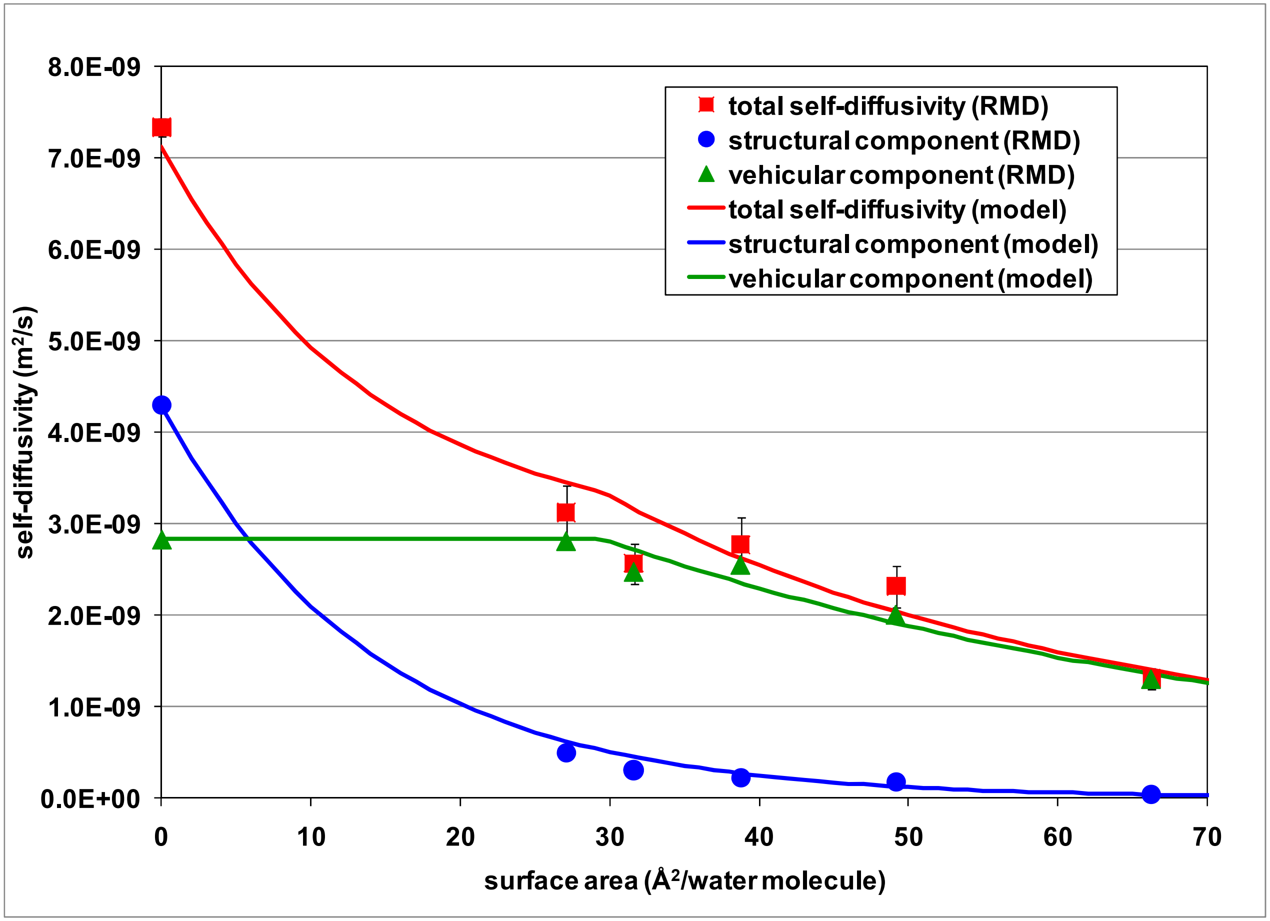


Esai Selvan, M., Calvo-Muñoz, E.M., Keffer, D.J., *J. Phys. Chem. B*, dx.doi.org/10.1021/jp1115004 , 2011.

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

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

Percolation Theory:
Effect of Connectivity

This percolation theory has four variables

D_o = diffusivity through an open pore
(or D of the unconfined system)

Obtained from exponential fit to experimental and simulated data for bulk HCl solutions and carbon nanotubes (last two slides).

D_b = diffusivity through a blocked pore

z = connectivity of the porous network

p_{EMA} = probability of a pore is blocked

Use the same parameters as for water, Since the structure of the aqueous domain through which both water and charge transport occurs is the same.

Structure-Based Analytical Prediction of Self-diffusivity of Charge

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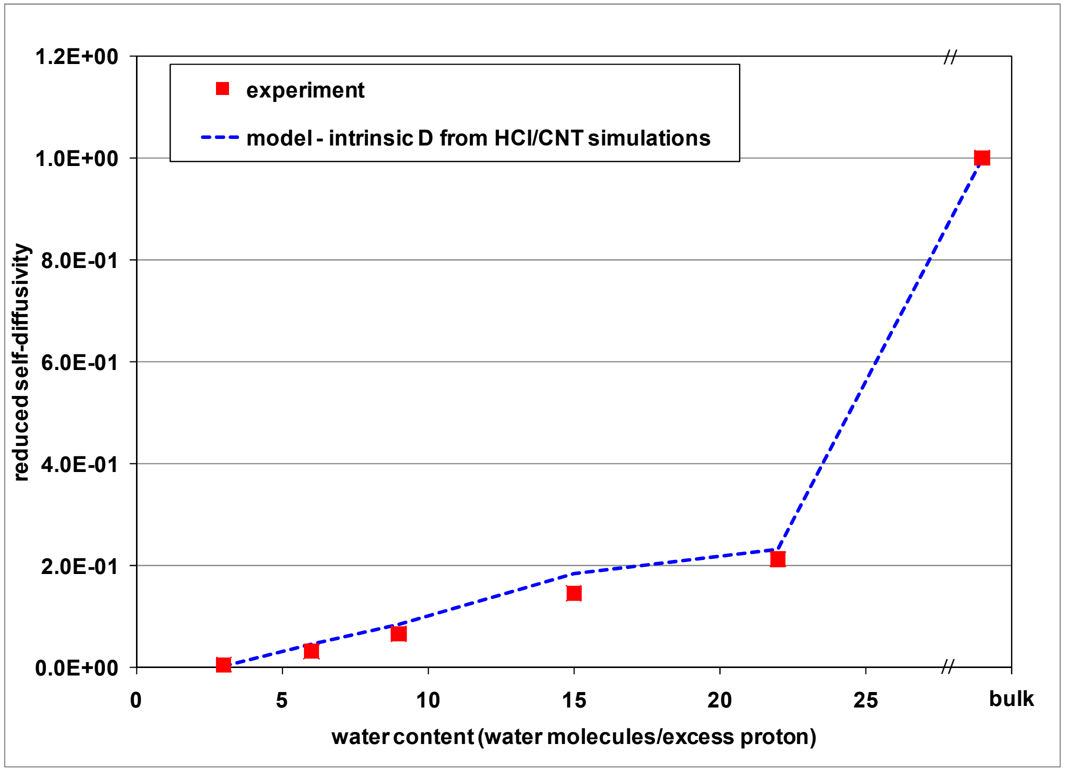
- Acidity – characterized by concentration of H_3O^+ in aqueous domain (exponential fit of HCl data)
- Confinement – characterized by interfacial surface area (exponential fit of carbon nanotube data)
- Connectivity – characterized by percolation theory (fit theory to MD/CRW water diffusivity in PEMs)

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



Good agreement of theory with experiment.

Theory uses only structural information to predict transport property.

Proton transport is well-described by this simple model.

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.

Acknowledgments:

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Office of Basic Energy Sciences

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

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

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
Confined Random Walks

Relevant Publications 2007-2011

1. Esai Selvan, M., Calvo-Muñoz, E.M., Keffer, D.J., “Toward a Predictive Understanding of Water and Charge Transport in Proton Exchange Membranes”, J. Phys. Chem. B 115(12) 2011 pp 3052–3061.
2. Calvo-Muñoz, E.M., Esai Selvan, M., Xiong, R., Ojha, M., Keffer, D.J., Nicholson, D.M., Egami, T., “Applications of a General Random Walk Theory for Confined Diffusion”, *Phys. Rev. E*, **83**(1) 2011 article # 011120.
3. Esai Selvan, M., Keffer, D.J., Cui, S., Paddison, S.J., “Proton Transport in Water Confined in Carbon Nanotubes: A Reactive Molecular Dynamics Study”, **36**(7-8), *Molec. Sim.* pp. 568–578.†
4. Esai Selvan, M., Keffer, D.J., Cui, S., Paddison, S.J., “A Reactive Molecular Dynamics Algorithm for Proton Transport in Aqueous Systems”, *J. Phys. Chem. C* **114**(27) 2010 pp. 11965–11976.
5. Liu, J., Suraweera, N., Keffer, D.J., Cui, S., Paddison, S.J., “On the Relationship Between Polymer Electrolyte Structure and Hydrated Morphology of Perfluorosulfonic Acid Membranes”, *J. Phys. Chem. C* **114**(25) 2010 pp 11279–11292.
6. Esai Selvan, M., Keffer, D.J., “Molecular-Level Modeling of the Structure and Proton Transport within the Membrane Electrode Assembly of Hydrogen Proton Exchange Membrane Fuel Cells”, in “Modern Aspects of Electrochemistry, Number 46: Advances in Electrocatalysis”, Eds. P. Balbuena and V. Subramanian, Springer, New York, 2010.†
7. Liu, J., Cui, S., Keffer, D.J., “Molecular-level Investigation of Critical Gap Size between Catalyst Particles and Electrolyte in Hydrogen Proton Exchange Membrane Fuel Cells”, *Fuel Cells* **6** 2008 pp.422-428.
8. Cui, S., Liu, J., Esai Selvan, M., Paddison, S.J., Keffer, D.J., Edwards, B.J., “Comparison of the Hydration and Diffusion of Protons in Perfluorosulfonic Acid Membranes with Molecular Dynamics Simulations”, *J. Phys. Chem. B* **112**(42) 2008 pp. 13273–13284.
9. Liu, J., Esai Selvan, M., Cui, S., Edwards, B.J., Keffer, D.J., Steele, W.V., “Molecular-Level Modeling of the Structure and Wetting of Electrode/Electrolyte Interfaces in Hydrogen Fuel Cells” *J. Phys. Chem. C* **112**(6) 2008 pp. 1985-1993.
10. Esai Selvan, M., Liu, J., Keffer, D.J., Cui, S., Edwards, B.J., Steele, W.V., “Molecular Dynamics Study of Structure and Transport of Water and Hydronium Ions at the Membrane/Vapor Interface of Nafion”, *J. Phys. Chem. C* **112**(6) 2008 pp. 1975-1984.
11. Cui, S.T., Liu, J., Esai Selvan, M., Keffer, D.J., Edwards, B.J., Steele, W.V., “A Molecular Dynamics Study of a Nafion Polyelectrolyte Membrane and the Aqueous Phase Structure for Proton Transport”, *J. Phys. Chem. B* **111**(9) 2007 p. 2208-2218.