PROTON BEHAVIOR AT GLASS/WATER INTERFACES: IMPLICATIONS ON REACTIONS AND PROTON TRANSPORT

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OUTLINE

• Motivation
• Dissociative Water Potential
• Interactions between Water and Silica Surfaces
• Proton Transport in Water
• Proton Adsorption Sites and Lifetimes on SiO$_2$
Motivation:

Experimental results regarding the surprisingly high thermal expansion of nanoconfined water.

But a second one developed based on our results that might be relevant to the electrochemical studies of Nogami, Abe, etc. showing high proton conductivity in nanoporous silica exposed to water.
ANOMALOUS EXPANSION OF NANOCONFINED WATER

Xu and Scherer, MRS Proc. Vol 790  2004
PREVIOUS SIMULATIONS OF WATER CONFINED IN SILICA PORES USED:

RIGID WATER MODELS (SPC/E, TIP4P, etc)

RIGID SILICA (glassy or crystalline)

Milischuk et al. JCP (2012)
Shaik et al. JCP (2010)
Thompson et al JPC B (2007)
Spohr et al J. Molec Liq (1999)
Gallo et al Phil Mag (1999)
SiO$_2$ network ring surface structure (important in proton transport…)
PREVIOUS SIMULATIONS OF WATER CONFINED IN SILICA PORES USED:

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However, these popular models do not match liquid equation of state.
New Multibody Dissociative Water Potential

![Graph showing density vs. temperature comparison between experiment and simulation.]

- Stern et al. JCP 2001
- Horn et al. JCP 2004
- Shaik et al. JCP 2010
- Jorgenson et al. JCC 1998
### OTHER BULK WATER PROPERTIES
Our MD simulations vs other MD and experiment

<table>
<thead>
<tr>
<th></th>
<th>MD (here)</th>
<th>MD*</th>
<th>EXP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{\text{vap}}^{\text{exp}}$ (kcal/mole)</td>
<td>10.5</td>
<td>10.0</td>
<td>10.5</td>
</tr>
<tr>
<td>$\mu$ (D)</td>
<td>2.6</td>
<td>2.1-3.0</td>
<td>2.6</td>
</tr>
<tr>
<td>D ($x10^{-5}$ cm$^2$/s) 298K</td>
<td>2.45</td>
<td>1.1-5.0</td>
<td>2.3</td>
</tr>
</tbody>
</table>

* TIP4P, SPC/E and other models
NEW WATER POTENTIAL MATCHES
EXPERIMENTAL DATA:

LIQUID DENSITY-TEMPERATURE CURVE
STRUCTURE
FREQUENCY SPECTRUM
HEAT OF VAPORIZATION
DIPOLE MOMENT
DIFFUSION CONSTANT

Mahadevan and Garofalini J Phys Chem B 111(2007)8919
Interactions between silicic acid molecule and a water molecule

Interaction energy

- MD simulation: 10.6 kcal/mole
- ab-initio calculations*: 9.0-11.6 kcal/mole

*Pelmenschikov et al, JPC 96 (1992) 7422

MO calc. gaussian, w and w/o MP2
Before we look at nanoconfined water,

Expose silica glass surface to water vapor
Simulations show expected mechanisms commonly considered.

BREAK UP NETWORK STRUCTURE

COORDINATE WITH UNDERSATURATED SURFACE IONS
Silanol concentrations as a f(time) approach experimental results
Put water between silica slabs (t=3nm and t=7nm)
Heat to various Temperatures under 1 atm pressure
Density near interface plays significant role in expansion behavior.

Minassian et al* showed that the CTE of bulk water increases as Pressure (density) increases.

Increase Density, Increase CTE

*Minassian et al JCP 75 (1981) 3064
NEW WATER POTENTIAL MATCHES EXPERIMENTAL DATA:

LIQUID DENSITY-TEMPERATURE CURVE STRUCTURE
FREQUENCY SPECTRUM
HEAT OF VAPORIZATION
DIPOLE MOMENT
DIFFUSION CONSTANT

and

TRANSFERABLE TO NANOCONFINED WATER
Simulations reproduce many features seen experimentally for bulk water and is transferable to nanoconfined water.

However, what are the molecular mechanisms of the reactions occurring in the simulations causing the silanol sites and how does this affect proton transport?
Simulations also show additional reaction mechanisms beyond these obvious ones.
H$_3$O formation at silica surface

Each takes ~150 fs

MD simulations match AIMD simulations

MD Mahadevan and Garofalini, JPCC 2008
AIMD Ma et al, JCP2005
Energy vs. Angle

Molecular Orbital (QM)

Our MD

Soooo…
We have protons on bridging oxygen sites,
protons on SiOH\textsubscript{2} sites,
and protons on SiOH sites

And excess H\textsubscript{3}O ions near the interface.
We need to know how well the simulations reproduce proton transport (PT) in bulk water.

Therefore, we need to add an $\text{H}_3\text{O}^+$ ion to bulk water...

But we first need some background regarding PT in water
Lot’s of background regarding Proton Transfer in water

But real molecular data comes from ab-initio MD simulations (AIMD) and classical simulations specifically designed for studying proton transport, the most advanced being MS-EVB models

So, we’ll compare to those.
PROTON TRANSPORT IN WATER

(a) Eigen $H_9O_4^+$
(b) Zundel $H_5O_2^+$
(c) Eigen $H_9O_4^+$
Free Energy decreases with decreasing O-O separation distance.

Marx CPC 2008
Our MD Simulations
H$_3$O$^+$ IN BULK WATER

Eigen

Zundel

MATCHES PROTON TRANSPORT VIA EIGEN AND ZUNDEL COMPLEXES
What causes a 1\textsuperscript{st} shell water to get close to the Hydronium ion to form the Zundel complex?

(a) Eigen $\text{H}_9\text{O}_4^+$
(b) Zundel $\text{H}_5\text{O}_2^+$
(c) Eigen $\text{H}_9\text{O}_4^+$
FIRST AND SECOND SHELL WATERS AROUND H$_3$O$^+$ ION

Schmitt JCP1999
FIRST AND SECOND SHELL WATERS AROUND H$_3$O$^+$ ION
FIRST AND SECOND SHELL WATERS AROUND $\text{H}_3\text{O}^+$ ION

Change in 2\textsuperscript{nd} shell waters HB to 1\textsuperscript{st} shell affects a 1\textsuperscript{st} shell water, enabling formation of the Zundel and proton transfer (see next slide).
MD result showing 1\textsuperscript{st} shell waters (blue O) around H\textsubscript{3}O ion (yellow) and two 2\textsuperscript{nd} shell waters (green), with arrow pointing to HB change in (b), but more dynamic than just HB rupture causing Zundel and PT in (d).
PROTON TRANSPORT IN WATER
MD SIMULATION

(a) Eigen
(b) Zundel
(c) Eigen
LIFETIME AUTOCORRELATION FUNCTIONS

Probability that hydronium O* (that formed at time 0) will be O* at some other time t

\[ c_c(t) = \frac{\langle h(0)H(t) \rangle}{\langle h \rangle} \quad \text{Continuous } c(t): \text{ continuously protonated from 0 to t} \]

\[ c_i(t) = \frac{\langle h(0)h(t) \rangle}{\langle h \rangle} \quad \text{Intermittent } c(t): \text{ protonated at 0 and } t, \text{ regardless of protonation state between 0 and } t \]
RESULTS OF ONE $\text{H}_3\text{O}$ IN BULK WATER AND $\text{H}_3\text{O}$ LIFETIMES

Chen and Voth MS-EVB3


Our MD results similar to the highly developed MS-EVB3 model for exponential behavior and long time $t^{-3/2}$ behavior.
Table 2. Comparison of the Diffusion Coefficient $D$ in Å²/ps of the Center of Excess Charge Resulting from Different Approaches

<table>
<thead>
<tr>
<th>Excess Proton</th>
<th>Value</th>
<th>Source</th>
</tr>
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<tbody>
<tr>
<td>Garofalini 283 K (NpT)</td>
<td>0.25</td>
<td>this work</td>
</tr>
<tr>
<td>Garofalini 283 K (NVE)</td>
<td>0.26</td>
<td>this work</td>
</tr>
<tr>
<td>Garofalini 296 K (NpT)</td>
<td>0.39</td>
<td>this work</td>
</tr>
<tr>
<td>Garofalini 298 K (NVE)</td>
<td>0.38</td>
<td>this work</td>
</tr>
<tr>
<td>Garofalini 323 K (NpT)</td>
<td>0.61</td>
<td>this work</td>
</tr>
<tr>
<td>Garofalini 325 K (NVE)</td>
<td>0.67</td>
<td>this work</td>
</tr>
<tr>
<td>MS-EVB2 298K</td>
<td>0.29</td>
<td>36</td>
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<tr>
<td>MS-EVB 298K</td>
<td>0.35</td>
<td>34</td>
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<tr>
<td>MS-EVB3 298K</td>
<td>0.36</td>
<td>36</td>
</tr>
<tr>
<td>aMS-EVB3 298K</td>
<td>0.41</td>
<td>37</td>
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<tr>
<td>qMS-EVB3 298K</td>
<td>0.50</td>
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<tr>
<td>MS-EVB 298K</td>
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<td>33</td>
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<tr>
<td>MS-EVB 298K</td>
<td>0.83</td>
<td>35</td>
</tr>
<tr>
<td>experimental</td>
<td>0.93</td>
<td>58, 59</td>
</tr>
</tbody>
</table>
SUMMARY

Exceedingly robust dissociative water potential for MD simulations.

_Unique_ly reproduces the trend of increased CTE of nanoconfined water as a function of pore size similar to experiment

Provides mechanism for high CTE of nanoconfined water

Shows appropriate reactions on silica surfaces

Shows proton transport in water via Eigen and Zundel complexes

Shows enhanced hydronium ion formation at silica surfaces, with reactions similar to AIMD

Shows lifetimes for protons in water similar to AIMD and MS-EVB, but at much less computational cost
Reactions between moisture and silica during irradiation

High energy PKA disrupts structure
But re-formation of bonds…’self-healing’…can occur

However, no atomistic models have included water
Presence of H$_2$O can inhibit bond re-formation
Insert either intact H$_2$O molecules within the silica structure or as already dissociated molecules (H$^+$ and OH$^-$) – then irradiate – Results are the same
H$_2$O 2.38%

DRY
Lockwood and Garofalini J Nucl Matl 400 (2010) 73
Destruction of 5- and 6-Member Rings

- **Dry six-membered rings**
- **Wet six-membered rings**

% change in 6-mem ring concentration

Time (ps)

-10% -9% -8% -7% -6% -5% -4% -3% -2% -1% 0%
3-mem Rings (Strained)

NOTE: Water inhibits formation of strained rings
What occurs during irradiation of silica in contact with a film of water?

Does the formation of larger rings allow for ingress of water into the glass?
SIDE VIEW – THIN SECTION INTO FIGURE
Effect of Water

Water reduces healing

Large voids, lower density

Water penetrates surface more easily
CONCLUSIONS

Without changing parameters in the potential

Simulations reproduce BULK and NANOCONFINED water
water REACTIONS on SiO$_2$ surfaces
PROTON transport and lifetimes in bulk water
and
Provide mechanism of high thermal expansion of nanoconfined water
and
Show that moisture inhibits self-healing in SiO$_2$ under irradiation, opening network to further ingress of protons and water