Water Diffusion in NaCl/CsI Solutions

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June 11th, 2014
• What is diffusion coefficient?

• How do we calculate coefficient?

• How is simulation compared to the experiment?

• How to parameterize the ions?

• How to judge the new parameters? Which reference should I choose to compare with?

• How will the new parameters affect my target — water diffusion coefficient in salt solution?
What is diffusion coefficient?

- Flux goes from high concentration region to low concentration region, described by Fick’s first law.

\[
\frac{dn}{dt}/A = -D \frac{d\rho}{dx}
\]

*E.g.* $n$: mol; $t$: s; $A$: m$^2$; $D$: m$^2$/s;

$\rho$: mol/m$^3$; $x$: m.

- The coefficient $D$ is diffusion coefficient.
How to calculate $D$?

• Fick’s second law.

• Fick’s second law: concentration/density/probability density/etc. in space change with time.

$$\frac{\partial \rho(x,t)}{\partial t} = D \frac{\partial^2 \rho(x,t)}{\partial x^2}$$

$$\lim_{x \to \infty} \rho(x,t) = \lim_{t \to \infty} \rho(x,t) = 0 \quad \rho(x,0) = \delta(0)$$

$$\rho(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}$$

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \rho(x,t)x^2 \, dx = 2Dt$$

$$D = \frac{\langle r^2 \rangle}{6t}$$

• Why we can, and how we can calculate $D$ in 3 dimensional space.
Experiments and Simulations

<table>
<thead>
<tr>
<th></th>
<th>3 M NaCl</th>
<th>Water</th>
<th>3M CsI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment</strong></td>
<td>1.87</td>
<td>2.299</td>
<td>2.79</td>
</tr>
<tr>
<td><strong>AIMD</strong></td>
<td>1.412↓</td>
<td>2.135</td>
<td>2.305↑</td>
</tr>
<tr>
<td><strong>AMOEBA09</strong></td>
<td>1.8193↓</td>
<td>2.1317</td>
<td>1.8897↓</td>
</tr>
</tbody>
</table>

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\(D\) of Water at 25 °C (10 M)

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\(^c\) Y. Ding, A. A. Hassanali and M. Parrinello, *Proceedings of the National Academy of Sciences*, **2014**, 111, 3310

\(^d\) NPT ensemble
### Parametrization and Energy References

#### Parameters of Cs

<table>
<thead>
<tr>
<th></th>
<th>vDW Radius</th>
<th>Depth of Energy Well</th>
<th>Polarizability</th>
<th>Damping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>4.37</td>
<td>0.53</td>
<td>2.26</td>
<td>0.39</td>
</tr>
<tr>
<td>I</td>
<td>4.66</td>
<td>0.52</td>
<td>7.25</td>
<td>0.39</td>
</tr>
</tbody>
</table>

#### Energy References

- **Quantum**
  - $X + H$: $-10.0256$

- **TINKER**
  - $X + H$: $-9.7898$

- **Experiments**
  - solvation free energy
    - Cs: $-61.66$
    - I$: $-67.64$

  - TINKER
    - solvation free energy
      - Cs: $-58.5$
      - I$: $-69.2$
Problems

Energy References

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Cs</th>
<th>I⁻</th>
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</thead>
<tbody>
<tr>
<td>Quantum X + H</td>
<td>—</td>
<td>-10.0256</td>
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<tr>
<td>TINKER X + H</td>
<td>—</td>
<td>-9.7898</td>
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<tr>
<td>Experiments solvation free energy</td>
<td>-61.66</td>
<td>-67.64</td>
</tr>
<tr>
<td>TINKER solvation free energy</td>
<td>-58.5</td>
<td>-69.2</td>
</tr>
</tbody>
</table>

a. An appropriate basis set for Cesium to be found.
b. TATB assumption — incorrect.

IODIDE
## Parametrization of Iodide

### Parametrization of I

<table>
<thead>
<tr>
<th></th>
<th>vdw Radius ($r$)</th>
<th>Depth of Energy Well ($\varepsilon$)</th>
<th>Polarizability ($\alpha$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>4.66</td>
<td>0.52</td>
<td>7.25</td>
</tr>
<tr>
<td>Increment</td>
<td>0.03</td>
<td>0.005</td>
<td>0.1</td>
</tr>
<tr>
<td>min</td>
<td>3.16</td>
<td>0.27</td>
<td>2.25</td>
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<tr>
<td>max</td>
<td>6.16</td>
<td>0.77</td>
<td>12.25</td>
</tr>
</tbody>
</table>

### Intermolecular Energy

![3D Diagram of Intermolecular Energy](image)
Screening: TINKER ANALYZE

Radius: ↑ — Energy: obviously less.
Epsilon: ↑ — Energy: less.
Alpha: ↑ — Energy: slightly more.
Q: How to choose parameters from these graphs?
A: Ask quantum. w/ BSSE: -10.0256, w/o BSSE: -11.6659 kcal/mol

Arbitrarily choose a small range: -10.02 ~ -10.12 kcal/mol

\{(r, \varepsilon, \alpha) \mid U(r, \varepsilon, \alpha) \in (-10.12, -10.02]\}
Screening

Within the range of -10.02 ~ -10.12: red; otherwise: blue.
## Results

### Simulation Results

<table>
<thead>
<tr>
<th>α</th>
<th>items</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.27</td>
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<tr>
<td>r</td>
<td></td>
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</tr>
<tr>
<td>2.25</td>
<td>ΔG</td>
<td>-82.0 +/- 0.2</td>
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<tr>
<td>D</td>
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<td>2.0023</td>
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<tr>
<td>r</td>
<td></td>
<td>4.51</td>
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<td>7.25</td>
<td>ΔG</td>
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<tr>
<td>r</td>
<td></td>
<td>4.645</td>
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<tr>
<td>12.25</td>
<td>ΔG</td>
<td>-79.0 +/- 0.7</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>1.3069*</td>
</tr>
</tbody>
</table>

* predicted by less data or no data reported due to the unexpected situations in cluster
Conclusion

- No idea for Cesium.
- Iodide: original parameters — intermolecular energy close to MP2/6-311G result.
- Iodide: (maybe) smaller polarizability?
Further More

• The range of intermolecular energy is arbitrary. What if …

• How does everything change with radius?

• A wild guess: the polarizability of Cesium cation is too large?

• …
The End