Modeling Aqueous Halide Salts at the Interface with Many-Body Molecular Dynamics

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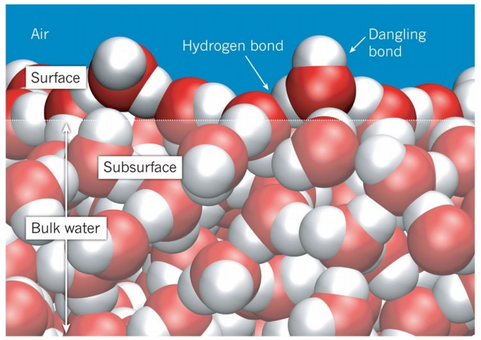
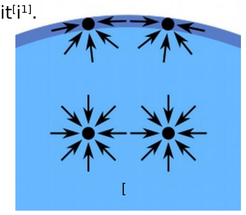
Introduction

- Scientists began studying liquid surfaces(interfaces) as early as the late 1800s. Today, the search for answers continues, as further elucidation of interfacial water properties would great contributions to many scientific fields.
- Ions near interfaces behave differently from ions in the bulk. The traditional view is that ions are depleted at the interface because it is energetically unfavorable for them to be there[1].
- However, recent work on inorganic salt solutions have found that cations are repelled from the surface, but certain halide anions are attracted to it[1].





- This means reevaluating the picture of the surface tension of solutions
- Surface tension is affected by hydrogen bonds and induced dipoles. Hydrogen bond strength is related to charge density, which decreases as the ion size and polarizability increase.

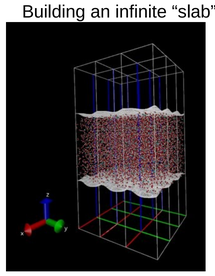
Method

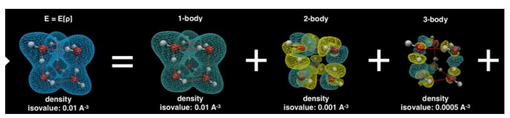
- **Many-Body Molecular Dynamics (MB-MD)** was used to model ions in a thin, flat, infinite "slab" of water
- (x,y,z) coordinates for each atom at every time step recorded
- NVT simulations for NaCl, NaBr and NaI in concentrations of 1.0M, 3.0M, and 5.0M at 298 K with 50% and 0% polarizability force fields
- Potential Energy Functionals ($F=-\nabla U(X_i)$) used:

—**MB-pol**[3]

- Used to model water.
- Calculates potentials with quantum approximations for up to 3 bodies

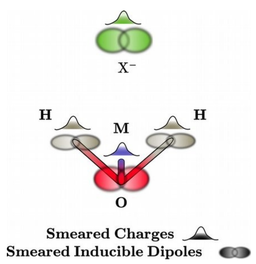
Building an infinite "slab"





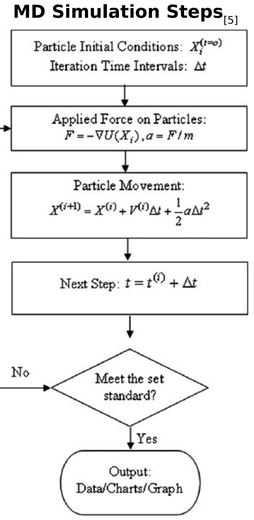
—**i-TTM**[4]

- Used to model ions
- Thole type model: accounts for inducible dipole effects
- Classical model, but compatible with MB-pol



Polarizable ion model for i-TTM[4]

MD Simulation Steps[5]



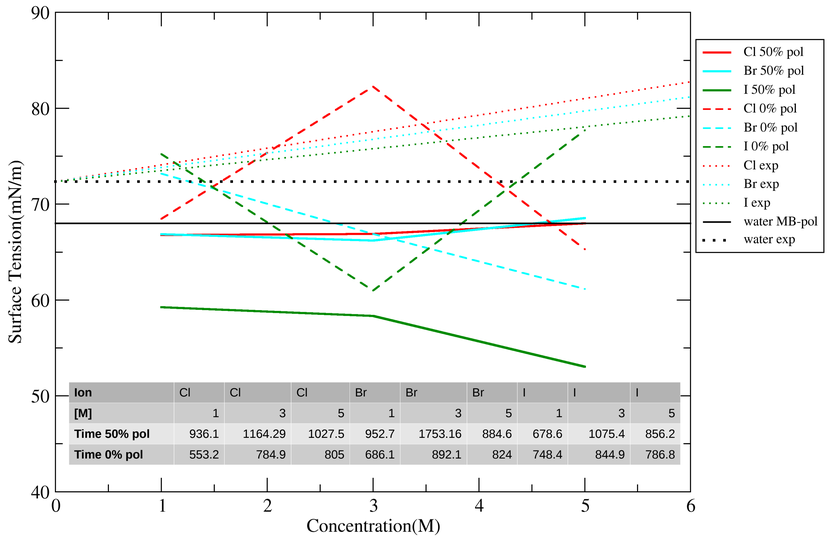
Data Analysis

- Surface tension found with:

$$\gamma=\frac{1}{2}L_z\left\langle P_{zz}-\frac{1}{2}(P_{xx}+P_{yy})\right\rangle$$

- Gaussian function used to normalize data and remove noise in density distribution functions

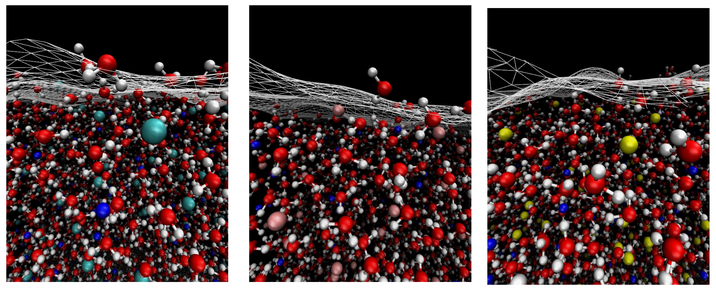
Surface Tension [2,3]

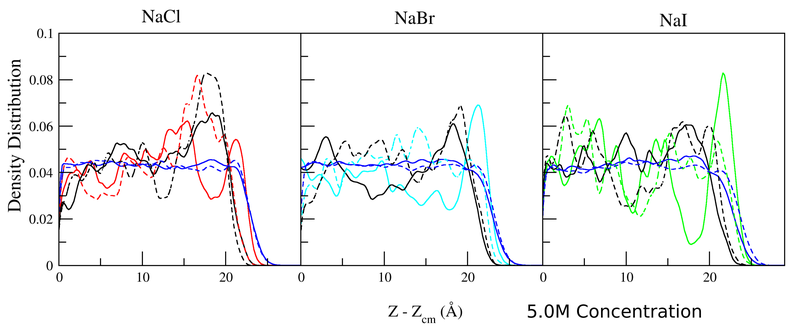


Ion	Cl	Cl	Cl	Br	Br	Br	I	I	I
[M]	1	3	5	1	3	5	1	3	5
Time 50% pol	936.1	1164.29	1027.5	952.7	1753.16	884.6	678.6	1075.4	856.2
Time 0% pol	553.2	784.9	805	686.1	892.1	824	748.4	844.9	786.8

- Increasing concentration of ion decreased surface tension
- Increase in surface tension decreases from Cl^- to I^-
- Data is not converged

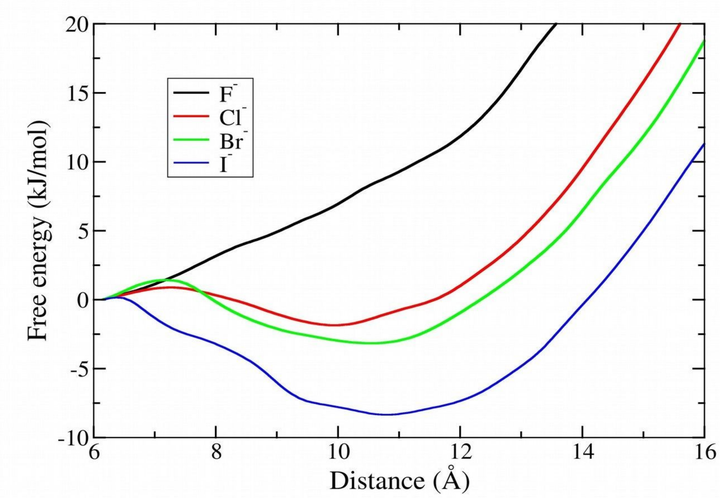
Density Distribution Functions





- Solid line is data with 50% polarizability. Dashed is 0%.
- Affinity for the surface increases with ion size and polarizability
- Flat line of water represents bulk; downward slope represents interface
- With anions closest to the surface, the region below is depleted of anions and filled with cations, forming alternating sublayers that disappear towards the bulk

Potential of Mean Force



- X axis = distance from center of mass
- Umbrella sampling used to get entire free energy profile
- From a separate slab simulation with an infinitely dilute solution(1 anion and water molecules only)
- PMF describes effect of entire system on one particle in the system

Summary and Outlook

- Higher polarizability and larger ion size cause higher surface affinity because it is energetically favorable for them to be there.
- Surface tension increases with ion concentration because the ion-water bonds are stronger than water-water bonds. Larger halides cause a lower increase in surface tension because the contribution from their weaker electrostatic interaction is greater than the contribution from their size and polarizability.
- Future work would involve continuing to run simulations and gather more data as well as comparing the simulations to future experiments

Acknowledgments

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