Resolution Effects on NaCl Potentials of Mean Force

A. Wills[1] and M. Fernández-Serra[1,2]

[1]Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY, 11794, USA

[2]Institute for Advanced Computational Science, Stony Brook University, Stony Brook, NY 11794, USA

U.S. DEPARTMENT OF ENERGY

Office of Science

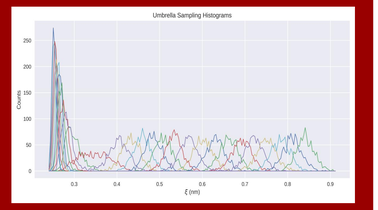
Stony Brook University

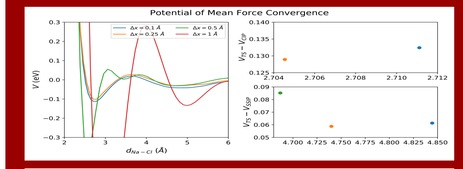
iACS INSTITUTE FOR ADVANCED COMPUTATIONAL SCIENCE

Introduction

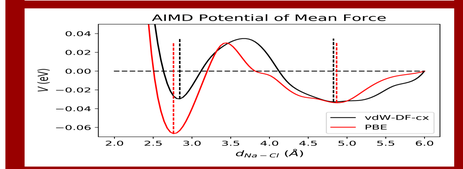
Potentials of mean force allow us to characterize the energetics of a process, such as ion solvation, along particular reaction coordinates [1]. But the modeling of pure water with DFT is still a matter of debate, and choice of how the bulk is simulated invariably affects the results. In contrast with single simulation results (e.g., distribution functions), reconstructing a PMF along a reaction coordinate requires multiple lengthy simulations, causing a quickly ballooning simulation expense for the potential along even a single coordinate to be well converged, requiring on the order of dozens of significantly long simulations. As a result, it becomes critically important to maximize efficiency without losing much accuracy in the converged results.

Umbrella sampling can be used to reconstruct a PMF by utilizing the Weighted Histogram Analysis (WHAM) method [2]. But this method requires long simulation times to accurately converge a histogram for a given region of constraint.



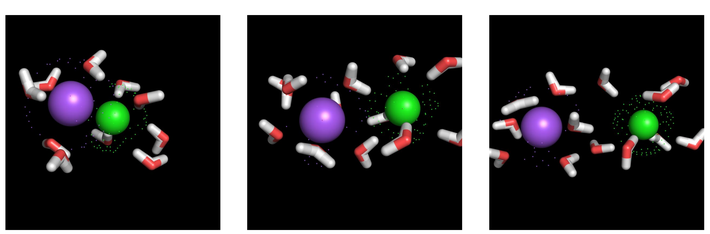


Imposing rigid constraints on the ion distance and instead directly integrating the average force gives a more controlled method of convergence – the mesh of ion distances.



	CIP, Depth	SSIP, Depth
PBE [3]	2.62 Å, 33 meV	4.76 Å, 44 meV
PBE	2.76 Å, 96 meV	4.86 Å, 63 meV
ωB97X-V	2.82 Å, 77 meV	4.44 Å, 46 meV
vdW-DF-cx	2.84 Å, 64 meV	4.82 Å, 67 meV

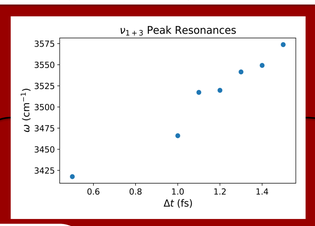
The energy landscape of solvated ionic interactions has structural information as well. A stable, intermediate solvent-separated state (SSIP) exists between bound and dissociated ion pairs, caused by solvation shell coordination. This is the second minimum in the PMF, while the first is the contact ion pair (CIP).



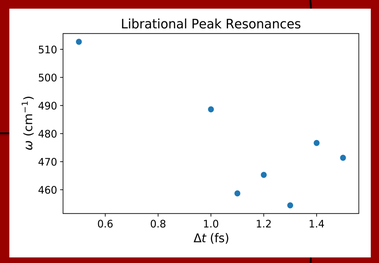
CIP SSIP Dissociated

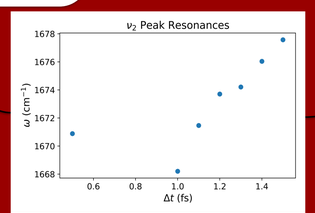
Time Step Resolution Effects

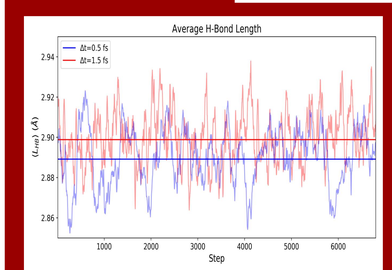
Sufficiently small time steps are required to accurately capture high frequency phenomena in simulations, and for this reason 1 fs steps are standard in AIMD. In particular, recent research used a 1.5 fs step in their solvated salt AIMD simulations [3] . We find that this significantly affects the resonant modes of water vibrations. Dynamic structural changes in water are indicative of changes in hydrogen bond network changes, thus changing the barrier strength separating the CIP from the SSIP.



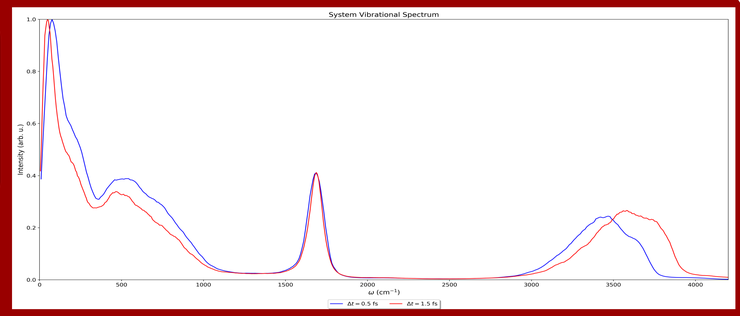
Blueshifting of stretching mode resonances is seen with increasing simulation time step, and a redshift in librational modes. These changes are consistent with an increased rigidity in the intramolecular bonding and a weaker hydrogen bond network [4, 5].



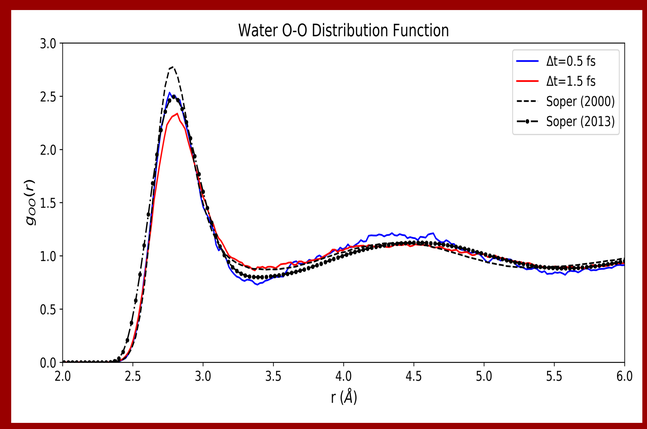




The weakened hydrogen bond strength is evident by the increased average distance between hydrogen bonded pairs. A weaker network through which to separate the ions would indicate a weaker CIP pair.



The effects on hydrogen bonding are further evident in the distribution functions of the simulated water. In an NVE ensemble, the 0.5 fs time step simulation reproduces experimental parametrizations of pure water. The 1.5 fs time step is slightly understructured in the first solvation shell, and then slightly overstructured in the interstitial region between shells.



Conclusions

There are many possible avenues along which simulations might be made more efficient, but at the cost of accuracy. In exploring the effect of time step length in ab initio simulations, we find that the dynamic characteristics of water are significantly affected, and thus results obtained will likely not accurately reflect reality.

Further Work

- Run simulations at different densities to see how the density of solvent will affect the solvation process and the CIP/SSIP relative stability.
- Investigate the differences between bulk water and molecules nearby the ions, and how these characteristics change at different ion separation distances.

REFERENCES: [1] J.G. Kirkwood, "Statistical mechanics of fluid mixtures," *J. Chem. Phys.* **3**, 300-313 (1935). [2] J. Hub, B. de Groot, D. van der Spoel. "g wham - A Free Weighted Histogram Analysis Implementation Including Robust Error and Autocorrelation Estimates". In: J. Chem. Theory Comput. 6.12 (Nov. 2010), pp. 3713–3720. [3] Y. Yao, Y. Kanai. "Free Energy Profile of NaCl in Water: First-Principles Molecular Dynamics with SCAN and ωB97X-V Exchange-Correlation Functionals". In: J. Chem. Theory and Computation 14 (2018), pp. 884–893. [4] M. Praprotnik, D. Janec. "Molecular dynamics integration and molecular vibrational theory. III. The infrared spectrum of water". In: J. Chem. Phys. 122 (Apr. 2005). [5] M. Allesch et al. "A first principles simulation of rigid water". In: J. Chem. Phys. 120.11 (2004).