Resolution Effects on NaCl Potentials of Mean Force

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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.

In our study, we investigate the differences between bulk water and molecules nearby the ions, and how these characteristics change at different solvation shell thicknesses. We compare the ion-dipole potentials of mean force (PMF) and the contact ion pair (CIP) potentials of mean force with various methods and functional families, and assess their impact on the solvation shell thickness.

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.

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.

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 undersaturated in the first solvation shell, and then slightly overstructured in the interstitial region between shells.

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.

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].

REFERENCES


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.

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.