

## Interpolation scheme for accurate predictions of PMFs and dielectric constants of electrolyte solutions. The use in implicit solvent simulations

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We developed an interpolation method (i-PMF) for fast and accurate predictions of potentials of mean force (PMF) between univalent spherical ions interacting in explicit water [1]. The speed-up, compared to molecular dynamics simulations, is  $10^5$ -fold. i-PMF can be used to estimate, for example, the strengths of salt bridges and the effects of bridging waters in simulations of biomolecules. We demonstrate that the method works for a variety of commonly employed water models, as well as for pairs of charged-uncharged and two uncharged solutes. In addition, we present similar interpolation strategy, called the i-EPS, for predicting the dielectric constant in aqueous electrolyte solutions as a function of ion size and solution concentration. i-EPS allows to predict accurate values that can be used in implicit simulations before needing explicit or experimental results.

We combine i-PMF and i-EPS to probe the association behavior of implicit ion simulations to model explicit electrolyte solutions. Cluster fingerprinting is explored in light of collective concentration dependent effects. Such approach is beneficial for studying large systems and to speed-up sampling: one needs accurate simulations of charged particles with the solvent averaged into the interactions between particles. The concentration dependence of the static permittivity for electrolyte solutions affects how particles interact and cluster, and we investigate what controls this dependency. We highlight the asymmetry of response with cation/anion particle size. The increased precessional freedom keeps the static permittivity somewhat higher about solvated anions than about solvated cations.

[1] M. Lukšič, C.J. Fennell and K.A. Dill, *J. Phys. Chem. B* **2014**, *118*, 8017.