Force Fields Parametrization of Ion-Water Interactions via the Force Matching Algorithm

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Ion solvation constitutes a central topic in chemical physics and theoretical chemistry; up to now a huge quantity of classic Molecular Dynamics studies have been performed to look into different aspects of Ion solvation. One crucial point lies in the choice of parameters of the interaction model, the so-called force-field. In most refined approaches, they are usually found by fitting hundreds of points on the ab initio potential energy surface (PES) for relatively small clusters, (cf. Ref. 1). Although being accurate, the main drawback of this approach is that the PES explored is not the one for the condensed phase and some points included in the fit could be physically unimportant, while at the same time missing some points that are important. To overcome this problem, a new method has been recently introduced, which is based on a least-square fitting to forces obtained from ab initio calculations of the condensed phase of interest[2,3]. In this contribution the focus is on the parameters for the interaction between ions and water. To this end, Car Parrinello Molecular Dynamics simulations[4] have been used to compute the reference forces; then, we fitted ion-solvent interaction parameters in conjunction with the most widespread classical force fields for water. The ions studied include F^-, Cl^-,Br^-, I^-, Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+}. Fig. 1 shows some representative scatter plots of the ion-water force fields derived in combination with the SPC water model. The slope b of the fitted forces versus the ab initio forces is also included.

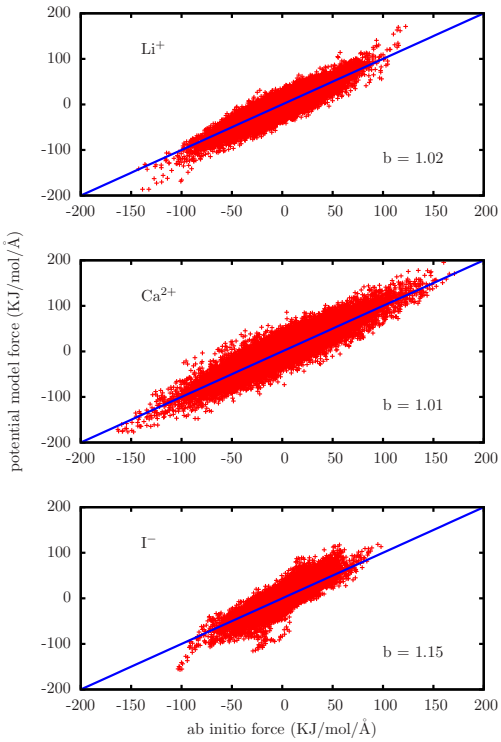

FIG. 1. Scatter plots of ion-water atomic forces: The potential model force vs. the ab initio Car-Parrinello force for the force fields derived in combination with the SPC water model. The line corresponds to a perfect match, i. e. $b = 1$. Top: Li^+, Medium: Ca^{2+}, Bottom: I^-

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