

A Molecular Dynamics Study of the Interfacial Structure of Calcite-Water Using Different Force-Fields

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We examined the structure of water near a calcite surface using different force fields to describe the interaction between water and calcite. While the majority of potentials used to model water-calcite interactions in atomistic simulations have been derived from dedicated fitting investigations aiming to match experimental properties of water in contact with surface [1, 2], our goal was to formulate a more general technique based on "same-atom" Lennard-Jones or exponential-six form potentials. Our potential-fitting procedure was based on potential splitting due to Weeks-Chandler-Andersen approach [3], with Barker-Henderson integration [4] employed to estimate the effective hard-sphere diameter. This procedure keeps the partial charges unchanged, and utilizes standard combination rules to determine the values of temperature-dependent hard-sphere diameter, well depth, and area under the curve to be matched by the cross-term potentials. The ultimate goal of this approach is to apply this methodology to molecular dynamic simulations of aqueous water systems to generate cross terms for solute species in cases where no pre-existing interaction potentials are available either from matching experimental results or *ab initio* studies. To validate the fitting procedure, we compared water structuring in an interfacial system composed of water and a slab of calcite measuring roughly 45Åx40Åx50Å. Tested force fields included those obtained from fitting Buckingham same-atom water and calcite as calculated in [5], water-calcite potential directly due to [6], and TIP4P-Ew water [7] – calcite cross terms of [1]. The location and the relative height of water density peaks in the vicinity of calcite agreed very well in case of parameters derived from fitting procedure and the force-field due to [5, 6], thus being closer to its experimental position of 2.5 Å in [8]. The structure of double-layered adsorbed water combined distinctive features of hydrated calcite surfaces in Gale et al [9] and Perry et al [10].

References

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