Adaptive QM/MM: Modeling processes in complex diffusive systems

Rosa E. Bulo, A. Goetz, R. Walker

Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, The Netherlands

The coordination of Ca^{2+} to a carboxylate group is relevant in both biochemistry and in material sciences, where it occurs in the presence of water as a solvent and of bulky (bio)-catalytic compounds. Like many other chemical processes, it is difficult for simple classical force fields to describe, but including the large and complex environment in an electronic structure calculation is unfeasible. When applying a combined quantum mechanical / molecular mechanical (QM/MM) description to an aqueous system such as this, one has to account for the fact that water molecules can diffuse across the predefined QM/MM boundary. We use an adaptive QM/MM approach to describe the coordination of Ca^{2+} to an aspartate molecule dissolved in water, as a model system for the above process. We show that our method can describe water diffusion across the QM/MM boundary, but that the inhomogeneous nature of the multi-scale solvent does affect the diffusivity. If we ensure that the reaction coordinate for the process does not explicitly involve reactants crossing the QM/MM boundary, our adaptive QM/MM simulations yield reliable free energies for the dissociation of the calcium and aspartate ions.