

Molecular dynamics and reactive trajectory approaches to modeling of electrochemical reactions near the liquid/solid interface

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A reactive trajectory approach for the study of proton discharge at charged metal surfaces (here a simplistic model of a platinum surface is used) is discussed. The approach is based on an extension of a minimalistic empirical valence bond (EVB) model to study proton transfer in the bulk [1]. Extensive quantum mechanical density functional theory calculations were parametrized for the EVB force field. The model is used to investigate reactive (discharging) proton trajectories that were started in the bulk of a water film adsorbed on charged metal electrodes. The results indicate a transition between a reaction-dominated regime at moderate negative charges, where the rate constant increases exponentially, to a “transport limited” regime where the transfer rate is almost independent of the surface charge density (at more negative surface charge densities) [2, 3].

The results are critically analysed in view of the nature of the approximations and together with free energy calculations for quasi-stationary hydronium and Zundel ion species. Some recent results of extensions of the model which introduce background electrolytes with and without specific ion adsorption are also presented.

[1] Wilhelm, F., Schmickler, W., Nazmutdinov, R.R., Spohr, E. *J. Phys. Chem. C* 112 (2008) 10814–10826.

[2] Wilhelm, F., Schmickler, W., Spohr, E. *J. Phys.: Condens. Matter* 22 (2010) 175001.

[3] Wilhelm, F., Schmickler, W., Nazmutdinov, R.R., Spohr, E. *Electrochim. Acta* 56 (2011) 10632–10644.