Effective computational model of the electrochemical double-layer

Simone Pezzotti[a] and **Christopher J. Stein**[b]

[a] Lehrstuhl für Physikalische Chemie II, Ruhr–Universität Bochum 44780 Bochum, Germany; Univ. Paris-Saclay, Univ. Evry, CNRS, LAMBE UMR8586, Evry-Courcouronnes 91025, France

[b] Theoretical Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, 47048 Duisburg, Germany

Electrolyte solvation is omnipresent in biological systems and technical applications such as electrocatalysis and batteries. To model such processes, efficient yet accurate solvation models need to be devised that can describe the behavior of the electrolyte solution for varying ionic strengths. The Poisson–Boltzmann model is a numerical realization of the phenomenological Gouy–Chapman–Stern model and a suitable implicit solvation approach for quantum-chemical investigations. We implemented such a solvation model with correction terms for the Stern-layer thickness and different ion sizes in the Q-Chem electronic-structure package.[1]

Such implicit solvation models do not incorporate subtle changes in the water network structure at metal-electrolyte interfaces. In a joint experimental-theoretical study, we therefore investigated the properties of a sodium chloride electrolyte solution at a gold electrode at low bias potentials with THz spectroscopy, electrochemical analyses, molecular-dynamics simulations and quantum-chemical calculations.[2] In this contribution we show how the preferred hydration modes of the two ions in combination with the interfacial water network lead to an asymmetric behavior close to the interface, elucidating the structure of the electrochemical double-layer in such systems. We will demsonstrate how we incorporate these findings into an effective model of the EDL at metal-electrolyte interfaces.

[1] C. J. Stein, J. M. Herbert, M. Head-Gordon, *J. Chem. Phys.* (**2019**), *151*, 224111.
[2] S. R. Alfarano, S. Pezzotti, C. J. Stein, Z. Lin, F. Sebastiani, S. Funke, C. Hoberg, I. Kolling, C. Y. Ma, K. Mauelshagen, T. Ockelmann, G. Schwaab, L. Fu, J.-B. Brubach, P. Roy, M./Head-Gordon, K. Tschulik, M.-P. Gaigeot, M. Havenith, *Proc. Natl. Acad. Sci. U.S.A.* (**2021**), 118, *e2108568118*.