Modelling Aqueous Electrolyte with Molecular Density Functional Theory

Jeanmairet Guillaume;[A] **Belloni Luc**;[B] **Borgis Daniel**[C]

A)Sorbonne Université, CNRS, Physico-Chimie des Électrolytes et Nanosystèmes Interfaciaux, PHENIX, F-75005 Paris, France; B)LIONS, NIMBE, CEA, CNRS, Université Paris-Saclay, 91191 Gif-sur-Yvette, France; C)Maison de la Simulation, USR 3441 CNRS-CEA-Université Paris-Saclay, 91191 Gif-sur-Yvette, France et PASTEUR, Département de chimie, École normale supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris, France

guillaume.jeanmairet@sorbonne-universite.fr

Molecular Density Functional Theory (MDFT) is a flavor of classical DFT designed to study the solvation of chemically complexed solutes in a molecular solvent. The solvent is described by a density field. Due to the presence of the solute molecule, represented by an external potential acting on the solvent, this density is perturbed and become inhomogeneous. The DFT ansatz guarantee the existence of a functional of the solvent density that reaches its minimum for the equilibrium solvent density and that is equal to the solvation free energy at this minimum[1]. This theory has proved to be competitive with respect to state-of-the-art simulation techniques for the description of the solvation of a wide range of solutes into molecular solvent such as water and acetonitrile [2]. It is actually possible to generalize the theory to describe a mixture of liquid, each being described by its own density field. In this talk, I will show how this development can be used to describe the solvation of an electrolytic solution. I will start by the simplest model of electrolytic solution that is the primitive model where cation and anion are described by identical sphere of opposite unity charges while the solvent is modelled by a dielectric medium of homogeneous permittivity. A more evolved approach where the solvent is explicitly represented by a third density field will be presented afterwards.

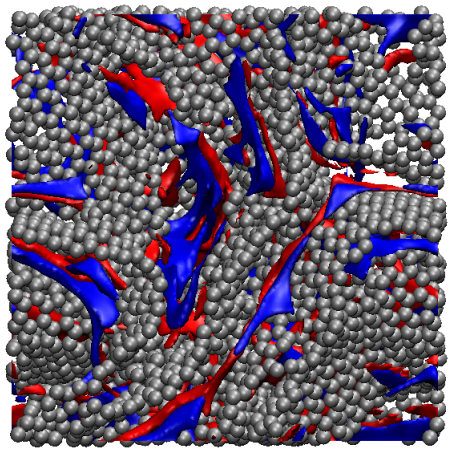

Figure 1. Density of sodium (red) and chloride (blue) into a carbide-derived carbon predicted with MDFT.

Keywords: classical DFT, electrolyte, statistical physics

[1]Robert Evans, The nature of the liquid-vapour interface and other topics in the statistical mechanics of non-uniform, classical fluids, Advances in Physics 28, 143 (1979).

[2]Guillaume Jeanmairet, Benjamin Rotenberg, Maximilien Levesque, Daniel Borgis, and Mathieu Salanne. A molecular density functional theory approach to electron transfer reactions. Chemical Science, 10(7) :2130–2143, 2019.