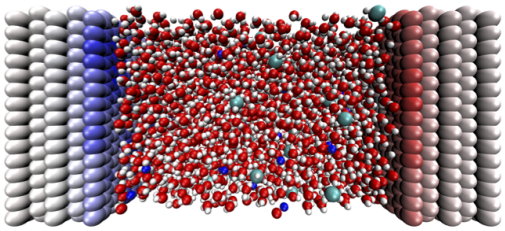
M2 internship in theoretical Physical Chemistry / Physics
from Jan/Feb to Jun/Jul 2020, with follow-up PhD opportunity

Ion adsorption at electrode/electrolyte interfaces : influence of the metallic character from classical molecular dynamics simulations

Context Solid-liquid interfaces play an important role in many contexts, including electrochemical interfaces and their applications for energy production and storage, fluids confined in porous materials or nanofluidic devices. Recent experiments emphasized the role of the electronic structure (more or less metallic) of confining materials on the properties of interfacial fluids [1]. In this context, the PHENIX laboratory develops classical molecular simulation tools to describe the interface between liquids and metals, taking into account the polarization of the latter by the former [2], and successfully applies them *e.g.* to electricity storage in supercapacitors or more recently the production of "blue energy" and water desalination [3].

Objectives This internship will investigate the role of the metallic nature of the solid on the adsorption of aqueous ions, which impacts the electrochemical properties or the transport of ions through nanopores/tubes [4]. We will evaluate the potential of mean force (PMF) for the adsorption of various ions, in the presence of solvent, for several surfaces including graphite. In this latter case, a recent publication proposed a study treating graphite as an insulator [5] and we will investigate the effect of such an approximation by taking its metallic character into account.



Methods This will be achieved using classical molecular dynamics with the Metalwalls code developed in PHENIX, which enables the description of metals by introducing additional degrees of freedom (the charge of electrode atoms), which fluctuate to enforce a constant-potential condition [6]. On-going developments also enable the simulation of imperfect metals based on the Thomas-Fermi model to account for screening within the solid. From the methodological point of view, another innovative aspect of the project is the coupling of this classical molecular simulation of electrodes with the thermodynamic integration method for the computation of PMFs for the adsorption of ions in the presence of solvent, thanks to recent developments of Metalwalls, enabling its interfacing with Python scripts.

PhD opportunity This study is part of broader project on understanding "electrical noise" in electrolytes (see *e.g.* [7] for ionic transport through nanotubes) and could be followed by a PhD (funding available).

Location PHENIX laboratory (Physicochimie des électrolytes et nanosystèmes interfaciaux), located in the Pierre et Marie Curie campus of Sorbonne Université, in the center of Paris (métro Jussieu).

Contact Candidates with a background in theoretical Physical Chemistry or Physics, ideally with some experience with simulation, can contact Benjamin Rotenberg (benjamin.rotenberg@sorbonne-universite.fr).

References Refs. [2,3] are from the PHENIX laboratory

[1] Comtet *et al. Nature Materials* 16, 634 (2017) ; Secchi *et al. Nature* 537, 210 (2016)
[2] Merlet *et al. J. Phys. Chem. Lett.* 4, 264 (2013) ; Limmer *et al. Phys. Rev. Lett.* 111, 106102 (2013)
[3] Merlet *et al. Nature Materials* 11, 306 (2012) ; Simoncelli *et al. Phys. Rev. X* 8, 021024 (2018)
[4] Limmer *et al. Chem. Phys. Lett.* 620, 144 (2015) ; Grosjean *et al. Nature Commun.* 10, 1656 (2019)
[5] Loche *et al. J. Phys. Chem. Lett.* 9, 6463 (2018)
[6] Siepmann *et al. J. Chem. Phys.* 102, 511 (1995) ; Reed *et al. J. Chem. Phys.* 126, 084704 (2007)
[7] Secchi *et al. Phys. Rev. Lett.* 116, 154501 (2016)