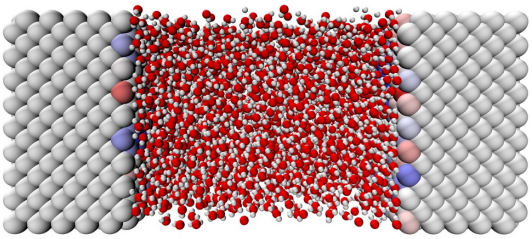
PHD

Modelling electrical fluctuations next to an electrode to probe the properties of interfacial electrolytes

The fluctuations of physical quantities are often considered as noise that should be minimized with respect to a signal. However, these fluctuations reflect the microscopic properties of the considered system and could in principle be a source of information, if only one could interpret them. This PhD will be part of a broader project which aims at exploiting the idea, well known in condensed matter physics, that « the noise is the signal » [1] to provide an integrated understanding of electrical fluctuations in bulk, interfacial and confined ionic fluids, and to interpret various experiments reflecting different facets of the same underlying dynamics of ions.

In this context, the PhD student will investigate the link between solvent polarization fluctuations around a solute near an electrode and electron transfer kinetics (see Marcus theory [2]), and how these fluctuations are reflected in the charge fluctuation of the electrode. We will consider in particular the effect of the Thomas-Fermi screening length within the electrode, which quantifies the metallic character of the latter. The project will involve molecular simulations and classical Density Functional Theory (see below) and the possibility to extract microscopic information on electron transfer kinetics from the electrode charge fluctuations will be tested in collaboration with an experimental electrochemistry group.



Snapshot of a gold/water nanocapacitor
The colors on electrode atoms indicate their instantaneous charge, which reflects the microscopic configuration of the interfacial liquid.

Specific techniques or methods

- Classical molecular dynamics simulations accounting for the polarisation of the metal, maintained at constant potential, by the interfacial electrolyte [3,4]. This approach allowed *e.g.* the study of complex systems related to energy storage in supercapacitors or more recently the harvesting of blue energy and desalination [5]. It offers a way to study the electrode charge fluctuations on the atomic scale and to make the link with interfacial properties such as the capacitance, or the structure of water and ions near the electrode [6]. It has also recently been extended to capture the Thomas-Fermi screening length within the electrode [7].
- Classical Density Functional Theory, which provides a simplified description of the system hence a much faster computation of the structural and thermodynamic properties of the interfaces, including some directly related to the kinetics of charge transfer to/from a solute [8].

References (4 to 8 are from the PHENIX laboratory)

[1] Landauer, *Nature* **392**, 658 (1998)
[2] Marcus, *J. Chem. Phys.* **24**, 979 (1956) ; *Ann. Rev. Phys. Chem.* **15**, 155 (1964)
[3] Siepmann *et al. J. Chem. Phys.* **102**, 511 (1995) ; Reed *et al. J. Chem. Phys.* **126**, 084704 (2007)
[4] Scalfi *et al. Ann. Rev. Phys. Chem.* **72**, 189 (2021)
[5] Merlet *et al. Nature Materials* **11**, 306 (2012) ; Simoncelli *et al. Phys. Rev. X* **8**, 021024 (2018)
[6] Limmer *et al. Phys. Rev. Lett.* **111**, 106102 (2013) ; Scalfi *et al. PCCP* **22**, 10480 (2020)
[7] Scalfi *et al. J. Chem. Phys.* **153**, 174704 (2020) ; *PNAS* **118**, e2108769118 (2021)
[8] Jeanmairet *et al. J. Chem. Phys.* **151**, 124111 (2019) ; *Chem. Sci.* **10**, 2130 (2019)

Candidates should hold a Master's degree in Physics or Physical Chemistry by the starting date of the PhD. Experience with molecular/mesoscopic simulation as well as good knowledge of the associated theoretical tools (Statistical Physics of liquids...; programming such as Python, Fortran, C++...) will be particularly appreciated. Knowledge of the French language is not necessary.

Practical information: Starting date no later than Oct. 1st, 2022. The PhD will take place in the PHENIX laboratory, located on the Pierre et Marie Curie campus of Sorbonne Université in Paris, France.

Funding: The PhD student will be hired by CNRS for the 3 years of the PhD project (monthly gross salary: 2135€), within the framework of the ERC project SENSES (https://benrotenberg.github.io/erc-senses/).

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Sorbonne University is a world-class, research-intensive university bringing together a broad range of arts, humanities, social sciences, natural sciences, engineering and medicine. The scientific Pierre and Marie Curie campus was completely refurbished in 2016.

PHENIX is a laboratory at the interface between Chemistry, Physics and Materials Science with a long-standing expertise of colloidal systems, electrolytes and fluids under confinement. Its strength lies in a combination of experimental and modelling activities (numerical simulations). Several international projects and networks are in place in PHENIX, providing a rich and multinational environment.