MASTER DE CHIMIE DE PARIS CENTRE - M2S2
Proposition de stage 2020-2021
Internship Proposal 2020-2021

Parcours type(s) / *Specialty(ies) :*

x Chimie Analytique, Physique et Théorique / *Analytical, Physical and Theoretical Chemistry* :
□ Chimie Moléculaire / *Molecular Chemistry* :
□ Chimie et Sciences Du Vivant / *Chemistry and Life Sciences* :
x Chimie des Matériaux / *Materials Chemistry:*
□ Ingénierie Chimique / *Chemical Engineering:*

Laboratoire d'accueil / *Host Institution*
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E-mail : laurent.michot@sorbonne-universite.fr

Equipe d'accueil / *Hosting Team* : Electrochimie et Liquides Ioniques
Adresse / *Address* : Barre 42-43, campus Pierre et Marie Curie
Responsable équipe / *Team leader* : Anne-Laure Rollet et Mathieu Salanne
Site Web / *Web site :* http://www.phenix.cnrs.fr/spip.php?article20
Responsable du stage (encadrant) / *Direct Supervisor :* Mathieu Salanne et Kyle Reeves
Fonction / *Position :* Professeur
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Période de stage / *Internship period* * : 18/01 au 16/07

Applications of machine learning and molecular simulations to predict solvent influence on electrochemical potentials of redox-active molecules

Projet scientifique (1 page maximum) / *Scientific Project (maximum 1 page):*

1. Description du projet / *Description of the project*

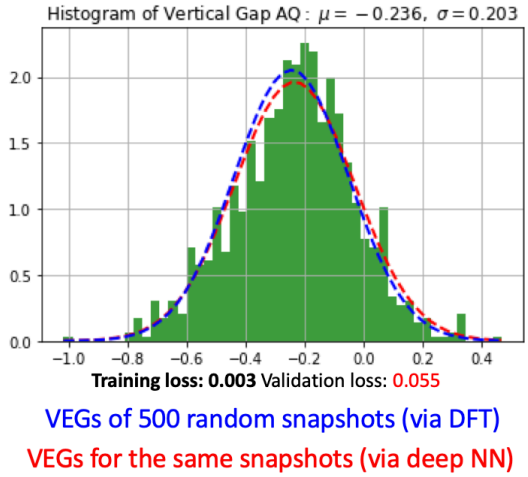
Supercapacitors are promising electrochemical energy storage in which the electricity is stored at the electrode/electrolyte interface [1]. Recently, it was proposed to increase their energy density by using redox-active ionic liquids [2]. This approach is very promising, yet it requires much further understanding of the mechanism of electron transfer and its coupling with the adsorption of molecules inside the electrodes.

Molecular simulations are often used to provide atomistic details into complex physical chemical problems on timescales and length-scales inaccessible by experimental approaches [3]. In the context of electrochemistry, the quantum nature of the electron requires an appropriate level of theory (e.g. density functional theory (DFT)) to compute accurate energies. Methods developed by Sprik *et al.* [4] have taken advantage of first-principles molecular dynamics simulations to compute electrochemical properties such

* min. 5 mois à partir du 18 janv 2021 / *min. 5 months not earlier than January, 18th 2021.*
Fin de stage au plus tard le 16/07/2021 ou le 30/09/2021 (dates de validation de diplôme). / *End of internship at the latest July 16, 2021 or Sept. 30, 2021 (dates of graduation).*

as redox free energies from vertical energy gaps. This approach, while rigorous, remains computationally expensive and thus limits its use.

In an approach to reduce the computational cost of these simulations, several alternative approaches can be imagined. First, assuming that a given forcefield generates an accurate structural representation of the system being investigated, it is feasible to imagine performing a classical molecular dynamics simulation from which structures would be sampled in order to compute the vertical energy gap using DFT. Second, deep neural networks represent a growing methodology to develop predictive models that relate sometimes non-intuitive input properties to one or several target properties. Thus, we can imagine using a range of sources of structure input to predict the vertical energy gap necessary to compute redox free energies. In addition to providing input data, however, hyperparameters that determine the network and how it is trained must also be carefully tested. Previous work in the PHENIX laboratory has demonstrated the use of a feed-forward artificial neural network (ANN) which accurately predicts the magnitude and distribution of vertical energy gaps of a solvated, electrochemically active small molecule (*right*).



We therefore propose for the master's intern to train and test the existing ANN model to relate structures and local environments computed by classical molecular dynamics simulations of a redox-active small molecule in different solvents to recover the so-called vertical energy gaps in each system. The free-energy curves will be constructed to compare the influence of solvent on the electrochemical properties of the small molecule, and compare these conclusions to experimental results.

2. Techniques ou méthodes utilisées / *Specific techniques or methods*

Classical molecular dynamics will be used to simulate the redox-active small molecule in three separate, pure solvent systems. Sampling from these structures, density functional theory will be used to compute the reference energies to be used as training data. The existing ANN (PyTorch library) will be used to immediately predict vertical energy gaps for each of the simulated systems. Depending on their background, the student may also explore further improving and extending the ANN (e.g. taking advantage of GPUs).

3. Références / *References*

[1] Salanne et al., Efficient storage mechanisms for building better supercapacitors, *Nature Energy* 1, 16070 (2016)
[2] Mourad et al., Biredox ionic liquids with solid-like redox density in the liquid state for high-energy supercapacitors, *Nature Materials* 16, 446 (2017)
[3] Merlet et al., On the molecular origin of supercapacitance in nanoporous carbon electrodes, *Nature Materials* 11, 306 (2012)
[4] VandeVondele, Lynden-Bell, Meijer and Michiel Sprik, Density Functional Theory Study of Tetrathiafulvalene and Thianthrene in Acetonitrile: Structure, Dynamics, and Redox Properties, *J. Phys. Chem. B* 110, 3614 (2006)