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Addressing the complexity of electrochemical interfaces via machine-learning-accelerated molecular dynamics

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Declaration

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Electrochemical technologies are at the heart of a growing range of applications for sustainable energy conversion and storage, including electrolysers able to convert abundant species such as water and carbon dioxide into valuable products using renewable electricity. Despite their broad appeal, the applicability of many electrochemical technologies is still limited due to the low energy efficiency and poor control of the core electrochemical reactions. The control of the nanoscale processes occurring at electrochemical interfaces is subordinated to a more fundamental challenge: a comprehensive understanding of the physics governing these systems. Grasping the effects of the applied electric potential, surface charge and hydrogen bond network in aqueous electrolytes in contact with solid electrodes is an essential advancement in surface physics.
In this respect, molecular dynamics (MD) simulations at the *ab initio* level are one of the most common and comprehensive atomistic modelling approaches to directly access an accurate nanoscale picture of dynamical environments such as electrochemical interfaces. Nonetheless, the predictive capabilities of these approaches are often limited by their high computational cost and by the difficulty of accurately capturing all the key physical elements, including the screening action of the liquid solvent, the local surface/solvent molecule interactions and, above all, the effects of a constant applied potential while the surface charge is fluctuating.

In this thesis we address the challenge of simulating electrochemical interfaces, specifically metal/water interfaces, by developing *ab initio*-accurate machine learning interatomic potentials (MLIPs) to accelerate MD simulations of electrochemical systems. Even if MLIPs are promising, the requirements of a large amount of data computed at the Density Functional Theory (DFT) level to train the ML models can result in a high computational cost, particularly in electrochemical simulations. At present, studies employing MLIPs often generate the DFT dataset, opting for computationally feasible, yet not highly accurate schemes for representing the effects of the solvent and the applied potential.

Here, instead, MLIPs are developed not only to overcome the spatial and time limits of *ab initio* MD but also to enable more advanced and computationally expensive setups, including a fully explicit solvent approach, an accurate description of the structure of liquid water at the meta-GGA exchange-correlation functional level and, above all, a robust and rigorous electrification scheme for constant potential simulations. To address the problem of generating a dataset at this high level of accuracy, we propose TRECI (TRansfer learning for ElectroChemical Interfaces), a general and data-efficient workflow that allows for developing MLIPs for electrochemical interfaces with only a few hundred configurations computed at the DFT level, making the generation of a small but high-quality dataset affordable.
We show the potential of TRECI by developing MLIPs for a representative electrochemical interface, a copper/water system, at several values of reducing potential. By comparing low-index Cu surfaces in contact with water, we revisit these systems with a level of accuracy and resolution not achievable with standard *ab initio* approaches. We also describe key rate-limiting steps for the hydrogen evolution and the CO_2 electroreduction, correlating the activation of these reactions with the effects of the surface charge and the structuring phenomena of interfacial water.
The results presented in this thesis clearly demonstrate that TRECI enables an advanced atomistic characterisation of electrochemical interfaces. This capability will support progress in the development of increasingly accurate modelling techniques as well as advancements of fundamental and applied research in the physics of electrochemical interfaces.