CSC-RUB PhD Project Proposal

Title: Electrified interfaces at the nanoscale using electronic structure -based molecular dynamics

Sector of research: PhD

Degree awarded: PhD in Physics

Keywords: molecular dynamics simulations, interfaces, electric field, ions, water structure and dynamics, nanofluids, ion channels, nanotubes.

Supervisor of PhD project: Prof. Dr. Marialore Sulpizi, department of Physics, e-mail: marialore.sulpizi@rub.de

Research focus of supervisor: Electrified solid/liquid interfaces

The group has a long-standing experience in the simulations of different aspects of solid/liquid interfaces, including structure, dynamics and vibrational spectroscopy.

Publications: 75 publications; h-index 37

1. The nanoscale structure of the Pt-water double layer under bias revealed; R Khatib, A Kumar, S Sanvito, M Sulpizi, CS Cucinotta, *Electrochimica Acta* 391, 138875; (2021)
4. From gold nanoseeds to nanorods: The microscopic origin of the anisotropic growth; SK Meena, M Sulpizi, *Angewandte Chemie* 128 (39), 12139-12143 (2016);

Second Supervisor of PhD project

Prof. Dr. Sebastian Kruss (Ruhr-Universität Bochum Physical Chemistry II)

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<th>Summary of research plan</th>
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<td><strong>Background:</strong> Nanometer-scale water confinement and transport occur in a vast range of natural phenomena (including ion channels, lubrication) as well as in artificial fluidic devices. In particular, recent experimental and theoretical investigation of fluids at the nanoscale have unveiled unexpected water- and ion-transport phenomena (Mouterde 2019) due to molecular aspects, such as the direct interactions between the channel walls and the hydration shells of the ions. Interestingly, in both the natural channels and artificial devices, transport mostly occurs under non-equilibrium conditions, e.g. in the presence of net electric fields.</td>
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<td><strong>Study objective:</strong> This project aims to investigate properties of electrolytes in confinement using non-equilibrium ab initio molecular dynamics where the interplay between liquid and confining walls, including the local chemistry is taken explicitly into account in the presence of an external electric field. Objectives:</td>
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<td>(i) Assess to what extend the current classical model can reproduce results from NE-AIMD for different field intensity.</td>
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<td>(ii) Results from NE-AIMD will be used to obtain an improved force field, including e.g. anharmonicity effects of bonds etc. This will be obtained combining state of the art deep learning algorithms and the force matching approach.</td>
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<td>(iii) Comparison to experiments: Surface Force Apparatus (SFA) in the group of S. Perkin and AFM experiments in the group of L. Bocquet.</td>
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<td><strong>Expected Results:</strong> NE-AIMD will permit to investigate the fluid dynamics in nano-confinement in both slit and pore geometry, explicitly including electronic aspect suggested by the experiments. The simulations are expected to unveil the interplay between local dielectric and diffusivity as</td>
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function of the ionic strength. Moreover, they are expected to elucidate the role of metallicity, local charges, and local protonation/deprotonation.

**Methods:** Simulations with an atomistic resolution play therefore a crucial role in complementing the experiments to understand the molecular origin of dynamics at the nanoscale and the influence of the confining chemistry. We plan to use ab initio molecular dynamics, which will permit to include the electronic structure for solid and liquid in a consistent way. Moreover electric field will be also applied, according to the Berry phase approach to ground-state NE-AIMD in external electric fields under periodic boundary conditions (Umari 2002), also applied to different studies, including e.g. the in silico version of the “Miller experiments” (Saitta 2014). NE-AIMD in both static and oscillating (time-dependent) external electric fields has been also applied to liquid water showing a range of field-induced effects on structural and dynamical properties, including diffusivities and hydrogen-bond kinetics (Futera 2017).

More recently an extended Hamiltonian approach where constant dielectric conditions are enforced has been also proposed and applied to ab initio simulations (Stengel 2009, Dufils 2019).

**References**


**Candidate Requirements:** Master in Physics or chemistry; experience with computational methods (e.g., molecular dynamics or electronic structure methods or Monte Carlo methods; some scripting programming ability) Good English language skills.

**For the iGSS:**
- You hold an A-grade (“very good”) qualifying degree at either the level of Master or Diploma to enter the iGSS’s Track I or an A-Grade (3 yr. or, preferably, 4 yr.) Bachelor to enter the iGSS’s Track II; degrees in chemistry, physics, biochemistry, engineering, or a related discipline will be accepted.
- You are fascinated by the interdisciplinary research field Solvation Science.
- You have very good English language skills (equal to B2, oral and writing).

**Motivation for CSC application** (max 250 words): The project will be hosted by the group on theory and simulations of solid/liquid interfaces, led by Prof. Marialore Sulpizi, in the physics department of the Ruhr Universität Bochum The group has a long-standing experience in the simulations of different aspects of solid/liquid interfaces, including structure, dynamics and vibrational spectroscopy. We offer a training in state-of-the-art atomistic simulation approach to the modelling of electrified interface, which play a key role in all the simulation of material for new energy production and storage. We also offer the possibility to collaborate with experimental groups, which, has led in the past, to successful joint theoretical and experimental studies. M. Sulpizi has hosted in the past (in Mainz) a Chinese student, Gang Huang, supported by the CSC who has successfully defended his PhD thesis.

**For the iGSS:**
- You will be embedded in a high-profile research environment.
- You are integrated in the International Faculty Solvation Science and will gain international work experience during a 2 – 3 months internship abroad.
- You will benefit from personal development possibilities, the entrepreneurial attitude within RESOLV and a broad spectrum of lectures as well as transferable skills courses.
- You will develop your science communication skills by presenting your research to the public.
- You are provided with funding for visiting international conferences.