Ionic transport in soft subnanometric films

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In February 2022, the Intergovernmental Panel on Climate Change (IPCC) report [1] has been published by the UNO, which stated the critical situation and the environmental emergency to reduce greenhouse gases emission to keep the global warmth below 1.5° C. Thus, an effort has to be made to be able to harvest energy with a minimal CO₂ emission; nanofluidics appears to be one of the promising field to address this challenge.

Nanofluidics is a booming research field considering fluidic transport – such as hydrodynamic, electrical or thermal transport – in nanoconfined liquids. At such scales, the surface to volume ratio is extremely large and transport properties are mainly governed by interactions at interfaces.

Whereas macroscopic continuous models for electrostatics and hydrodynamics predict well ionic transport for 1-10 nm thick nanochannels, some anomalous properties have been reported in the regime of ultraconfinement, below 1 nm, where a continuous description fails, such as dielectric anomalies in confined water [2], anomalous ionic mobilities in angstrom-scale confined water [3] and other unexpected behaviors [4]. An effort has to be made to precisely understand such behaviors in ultraconfined system, with the ultimate goal to enhance the harvesting of energy in nanofluidic systems.

In the present work, this regime of ultraconfinement is investigated. For that, the conductance of water soft films that condense spontaneously from undersaturated vapor on hydrophilic silica surfaces (see figure below) is measured as a function of their thickness. This thickness is modulated by the relative humidity above the substrate. To our knowledge, this experiment is one of a kind to control continuously the confinement down subnanometric scales. Despite some aging effects, the measurements are very stable and reproducible. A regime of surface conductivity is recovered for large humidity, i.e. for thickness above 1 nm but fails below. A model based on a hindered diffusion layer close to the interface is developed to explain the measurements below the hydrodynamic limit (1 nm). These experimental results open the way to new transport descriptions in ultraconfinement.

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Water vapor Water film Pt electrode Pt electrode

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Figure 1: Schematic of the experimental setup
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