The double-layer has a life of its own

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The electric double layer is generally viewed as simply the boundary that interpolates between an electrolyte solution and a metal surface. Contrary to that view, molecular simulations show that the interface between ionic liquids and metallic electrodes can exhibit structures and fluctuations that are not simple reflections of surrounding bulk materials [1]. This rich behavior is absent from a mean-field picture that averages over intraplanar structure. The charge of the electrode is screened by the interfacial fluid and induces subtle changes in its structure, which cannot be captured by the conventional Gouy-Chapman theory.

In recent years, we have performed molecular dynamics simulations on a variety of electrochemical systems made of ionic liquids (either pure or mixed with acetonitrile), and electrodes of different geometries ranging from planar to nanoporous. A key aspect of our simulations is to use a realistic model for the electrodes, by allowing the local charges on the atoms to vary dynamically in response to the electrical potential caused by the ions and molecules in the electrolyte [2].

These simulations have allowed us to gain strong insight on the structure and dynamics of ionic liquids at electrified interfaces [3]. From the comparison between graphite and porous CDC electrodes, we have elucidated the molecular mechanism at the origin of the increase of the capacitance enhancement in nanoporous carbons [4]. The simulations also provide us the diffusion coefficients of the ions and the charging times for the full supercapacitor device [5].

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