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Joint Density Functional Theory for the electrode/electrolyte interface: Benchmarking liquid structure with experiment and *ab initio* molecular dynamics KENDRA LETCHWORTH-WEAVER, Argonne National Laboratory, Cornell University, CHRISTINE UMBRIGHT, Cornell University, MARIA CHAN, PAUL FENTER, Argonne National Laboratory, T. A. ARIAS, Cornell University — Understanding the physics of the interface between a charged electrode surface and a fluid electrolyte would inform design of electrochemical energy storage and conversion devices. However, such studies require a simultaneously accurate yet inherently multi-scale theory. Joint density-functional theory (JDFT) bridges the relevant length-scales by joining a fully *ab initio* description of the electrode with a low computational cost, yet atomically detailed classical DFT description of the liquid electrolyte structure. Leveraging JDFT within our framework to treat charged systems in periodic boundary conditions, we can predict the voltage-dependent structure and energetics of solvated ions at the interface between graphitic and single-crystalline metallic electrodes and technologically relevant liquid electrolytes. First, we elucidate the physical origin of the experimentally measured voltage-dependent differential capacitance of an Ag(111) electrode in aqueous NaF electrolyte, examining the crucial role of ion de-solvation and physisorption onto the electrode surface. We go on to compare the JDFT-predicted interfacial liquid structure next to a graphitic electrode with results obtained from X-ray reflectivity measurements and *ab initio* molecular dynamics simulations.

Kendra Letchworth-Weaver
Argonne National Laboratory, Cornell University

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