

Grand canonical density functional theory for simulations of charged solid-liquid interfaces

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ABSTRACT

Charged solid-liquid interfaces occur frequently in many practical situations such as in electrochemical devices for energy conversion and storage. Transfer of charge carriers across electrochemical interfaces is a key process which can be controlled by an electric potential difference. A description of such interfaces in terms of the electronic structure and electrolyte ions requires a formulation in the grand canonical ensemble. To describe this phenomenon at the atomic scale, we have developed a method for performing density functional theory (DFT) calculations under potential control [1]. The charge developed on the electrode is neutralized by a build-up of counter charge in the electrolyte, which is represented via Poisson-Boltzmann theory in a grand canonical ensemble [2]. This model has been implemented in the ONETEP DFT program, which has linear-scaling cost with the system size [3] and works in both fully periodic as well as open boundary conditions [4]. The model parameters are calibrated against standard electrochemical reference electrodes and electrolytes. The model has been applied to study differential capacitance of graphene-based electrodes in supercapacitor applications, and lithium nucleation on graphite anode in Li-ion batteries [5]. We are able to predict critical voltage for Li nucleation, surface coverage and dendrite growth on graphite anode under electrochemical conditions. The predictions from the model agree well with experiments.

References

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