THE ELECTROCHEMICAL INTERFACE AND STOCHASTIC FUNCTIONS: A DATA-DRIVEN APPROACH TO MODELING NON-IDEAL BEHAVIOR IN CONCENTRATED SYSTEMS

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Researchers in the ionics field make frequent use of the mass-action principle – or the assumption of ideal thermodynamic behavior – in its physical models. These models are relatively easy to work with, leading to many useful and convenient formulae. However, they are strictly correct only in the limit of infinite dilution, and over-reliance on mass-action models in concentrated systems can lead to models that are grossly incorrect when compared with experimental reality. Recent microscopic experimental results gathered at surfaces and interfaces of ionic and mixed ionic-electronic conductors provide a striking example: classical models utilizing mass-action assumptions routinely underpredict the thickness of defect accumulation zones by an order of magnitude. Although atomistic models can be employed for concentrated systems, their utility is limited to very small simulation domains: continuum models must be used to predict the behavior of devices.

A key issue in any continuum-level thermodynamic treatment is the intractability of the microscopic defect interaction problem: beyond the ideal case, very few closed form solutions for the free energy in terms of concentrations are available. This presentation will introduce a data-driven methodology for determining these functions using either experimental or theoretical datasets. The method utilizes Gaussian process stochastic functions to represent the unknown functional relationships between defect concentrations and free energy, and calibrates these functions to data using Bayesian methods for calibration and model selection.

A continuum model for the structure of electrochemical interfaces in concentrated systems is the ‘Poisson-Cahn’ theory, which incorporates defect interactions and, crucially, gradient effects in a model that has proven successful in the replication of both macroscopic and microscopic experimental results. The data-driven approach to model building will be demonstrated in the context of Poisson-Cahn variational approaches applied to microscopic experimental datasets for grain boundaries in calcium-doped ceria.