

数学与系统科学研究院

计算数学所学术报告

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报告题目:

Time-dependent density functional theory for ion diffusion in electrochemical systems

邀请人: 卢本卓 研究员

报告时间: 2014 年 5 月 15 日 (周四)

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报告地点: 科技综合楼三层 311

计算数学所报告厅

Abstract:

We introduce a generic form of time-dependent density functional theory (TDDFT) for describing ion diffusion in electrochemical systems to account for steric effects and electrostatic correlations neglected in the Poisson-Nernst-Planck equations. An efficient numerical algorithm is proposed to analyze the charging kinetics of electric double layers in model electrochemical systems that consist of spherical ions in a dielectric continuum confined between two planar electrodes. Firstly, we consider the aqueous electrolytes based electrochemical system. By comparing the theoretical predictions from TDDFT and conventional electrokinetic methods for constant-voltage charging of the model electrochemical cells, we demonstrate that thermodynamic non-ideality plays a pivotal role in electrodiffusion even at relatively low electrolyte concentrations and such effect cannot be captured by the lattice-gas model for the excluded volume effects. Secondly, the kinetics properties of ionic liquid based electrochemical system are also considered in this work. By examining the variations of the ionic density profiles and the surface charging density in response to a sudden increase of the electrode voltage, we observe that, at certain conditions, the energy density shows a rapid increase only at the initial stage of charging and decays as the system reaches equilibrium. The nonmonotonic charging behavior can be explained in terms of the long-range layering structure of ionic liquids and the oscillatory variation of the capacitance with the system geometry.

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