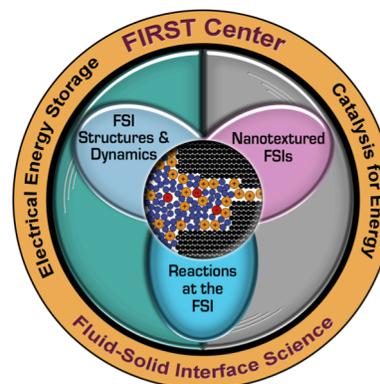


FIRST Center Research Perspective:

Development and application of static and dynamic classical density functional theory for capacitive energy storage

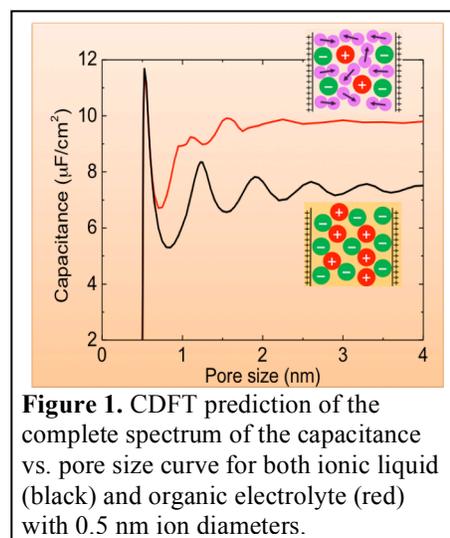
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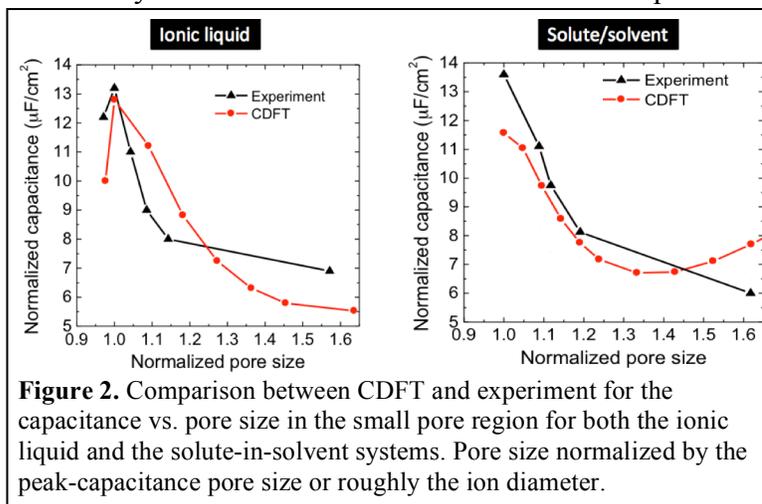


Research Summary: We have developed and applied static and dynamic classical density functional theory (CDFT) to charging of model electrochemical devices with model electrolytes, in an effort to understand capacitive energy storage. As a statistical mechanical tool and an alternative to molecular dynamics or Monte Carlo simulation methods, CDFT offers a powerful and efficient mathematical framework to describe the equilibrium and dynamic properties of many-body systems in terms of the one-body density profiles. It allows one to precisely tune the parameters such as ion diameter, solvent dipole, and pore size over a large range and to focus on the most important physical problems to be addressed, using a computationally efficient coarse-grained approach to model real fluids. Through CDFT, we have found novel behaviors of electrolytes inside nanopores, such as capacitance oscillation, optimal dipole moment, and wave-like charging. Further development of CDFT for complex pore structures and charging kinetics would allow us to directly predict power density and energy density for supercapacitors.

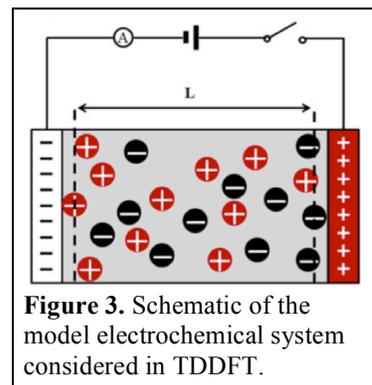
Technical Details: Within the context of using CDFT to model an electric double-layer (EDL) capacitor, the Helmholtz energy is expressed as a functional of the molecular densities. A primitive model is used for electrolytes: charged hard spheres for ions; connected hard-sphere dimers for the polar solvent. External interaction between electrolyte and electrode is electrostatic only. For the electrolyte itself, the excluded-volume effect is derived from modified fundamental measure theory, electrostatic correlation from a quadratic Taylor expansion of the excess Helmholtz energy functional, and chain connectivity for the polar solvent from an extension of thermodynamic perturbation theory for inhomogeneous polymer systems. Given an external potential on the electrodes and the pore width, one minimizes the Helmholtz energy functional against molecular densities of the electrolyte self-consistently, resulting in converged ionic and solvent density profiles which yield the surface charge density (Q). Integral capacitance is then derived by $C=Q/V$, where V is the applied potential. **Figure 1** shows the complete spectrum of the capacitance vs. pore size curve for ionic liquid and polar solvent electrolytes, in this example, the ion diameters in both types of electrolytes are fixed at 0.5 nm, and the polar solvent parameters are similar to that of acetonitrile. In the case of the ionic liquid, the capacitance shows a damped oscillatory pattern.



We found that this oscillation is due to the layered structures of cations and anions against the two charged walls of the slit pore and their interference. In the case of the polar solvent electrolyte, the capacitance varies only slightly when the pore size is beyond 1.0 nm (or two times the ion diameter) and becomes essentially flat after 2.0 nm. We attributed this capacitance invariance to the similar EDL structure at the larger pore sizes, and the EDL structure features an important participation of the aligned dipoles together with the counterions. Moreover, **Figure 2** shows that excellent agreement with the experiment has been achieved for both ionic liquid and organic electrolytes in the small-pore region: The capacitance does rise significantly when the pore size shrinks to the ion size.

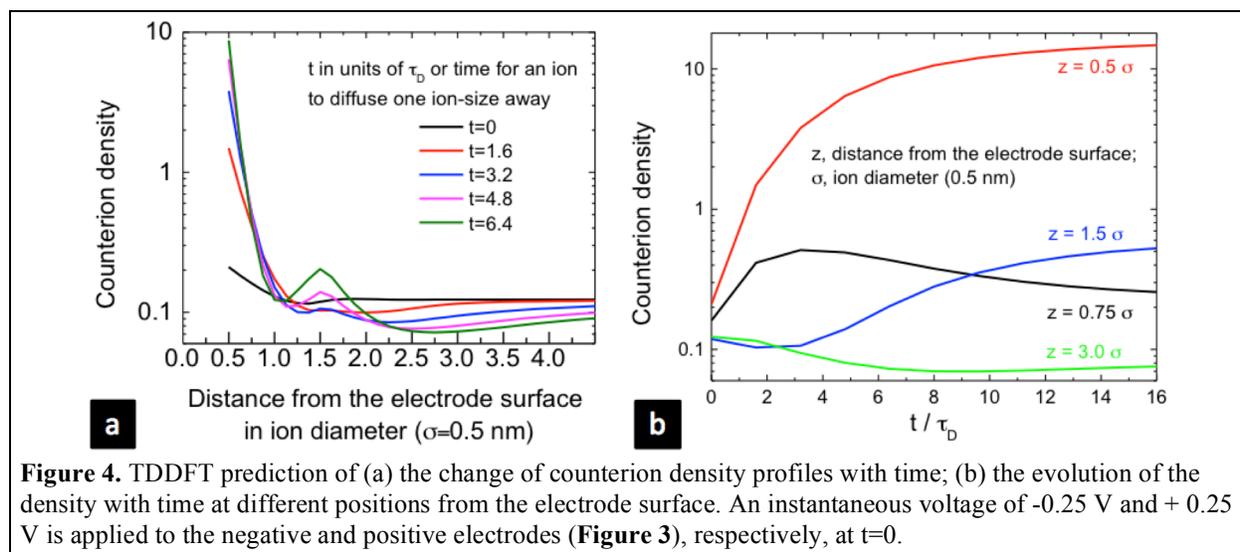


Theoretical analyses of ion transport in small pores are mostly based on conventional electrokinetic theories established for describing macroscopic electrochemical phenomena. To understand the microscopic charging process, we developed a generic form of time-dependent classical density functional theory (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 algorithm was implemented to analyze the charging kinetics of electric double layers in a model electrochemical system consisting of spherical ions in a dielectric continuum confined between two planar electrodes (**Figure 3**). We found that thermodynamic non-ideality plays a pivotal role in electrodiffusion and such effect cannot be captured by the lattice-gas model for the excluded volume effects. In particular, TDDFT predicts “wave-like” variation of the ionic density profiles (**Figure 4**) that has not been identified in previous investigations. For example, near the electrode surface ($z=0.5 \sigma$ in **Figure 4b**), counterion density rises quickly with time; at $z=0.75 \sigma$, counterion density first increases, and then decreases with time; at $z=1.5 \sigma$, counterion density first decreases, then increases with time. This kind of non-monotonic variation in density is very intriguing and calls for experimental confirmation.



Significant Impacts on Science and Technology: For the first time, a complete spectrum of the capacitance versus pore size relationship (bridging micro to mesopores) for an electric double-layer capacitance has been achieved through classical density functional theory for both ionic liquid and solute-in-polar-solvent electrolytes. Not only is a good agreement with the experiments achieved for the very small pore sizes, but a microscopic understanding has also been realized through analyses of density profiles of ions and solvents. The most significant implication of this CDFT study for technological development is the role of the polar solvent and the matching of the pore size with the ion size. Conversely, the success of the CDFT method in

modeling electric double-layer capacitors prompts further development of CDFT to address more complex issues in materials design, including predicting power and energy densities for real EDLC devices employing typical non-aqueous electrolytes.



Publications and Manuscripts:

- Jiang, D. E.; Wu, J. Z. "Unusual effects of solvent polarity on capacitance for organic electrolytes in a nanoporous electrode", *Nanoscale*, accepted.
- Jiang, J.; Cao, D. P.; Jiang, D. E.; Wu, J. Z. "Time-dependent density functional theory for ion diffusion in electrochemical systems", *J. Phys. Condens. Matter*, in press. ("Interfaces of Ionic Liquids" Special Issue, invited paper).
- Jiang, D. E.; Wu, J. Z. "Microscopic Insights into the Electrochemical Behavior of Non-aqueous Electrolytes in Electric Double-layer Capacitors", *J. Phys. Chem. Lett.*, 4, 1260-1267 (2013). (Invited perspective). <http://pubs.acs.org/doi/abs/10.1021/jz4002967>
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