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Monte Carlo simulation of electric double-layer capacitors in Gibbs ensemble

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Abstract

Supercapacitors deliver higher power than batteries, and find applications in grid integration and electric vehicles. Recent work by Chmiola et al. 2006[1] has revealed unexpected increase in the capacitance of porous carbon electrodes using ionic liquids as electrolytes. This is attributed to ions filling subnanometer pores enabled by deformation of their solvation shells under electric field. The work has generated curiosity among both experimentalists and theoreticians. We use molecular simulation to study the electric double-layer (EDLC) to understand this behaviour. The simulations are performed using a recently developed technique[2] for simulating supercapacitor system. In this technique, the two electrodes (containing electrolyte in slit pore) are simulated in two different boxes using the Gibbs ensemble methodology. This reduces the number of particles required and interfacial interactions which helps in reducing computational load. The method simulates an EDLC with macroscopic electrodes with much smaller system sizes. In addition, the charges on individual electrode atoms are allowed to vary in response to movement of electrolyte ions while ensuring these atoms are at the same electric potential. Our method is capable of simulating the effects of pore size distribution, pore topology, electrolyte ions, solvent effects, etc. towards the capacitance of the EDLC in a rigorous manner. We present the application of our technique on EDLCs with the electrodes modelled as slit pores and as complex three-dimensional pore networks for different electrolyte geometries.

References:

1. J. Chmiola, G. Yushin, Y. Gogotsi, P. Simon, L. Taberna, Anomalous increase in carbon capacitance at pore sizes less than 1 nm, Science., 313 (2006) 1760.
2. Sudeep N. Punnathanam, A Gibbs-ensemble based technique for Monte Carlo simulation of electric double-layer capacitors (EDLC) at constant voltage, The Journal of Chemical Physics 140 (2014) 174110.