The Role of Energy Scales for the Structure of Electrochemical Double Layers in Ionic Liquids

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From non-equilibrium thermodynamics, we developed a transport theory for general liquid electrolytes [1] and applied it to carbonate-based electrolytes [2] as well as ionic liquid electrolytes [3]. We model intra-molecular repulsion in the free energy functional with an integral, which is quadratic in the molecular concentrations. Our approach agrees with AFM measurements of the multi-layer structure of electrochemical double layers (EDL) of ionic liquids [3]. Most importantly, it connects rigorously to molecular properties and the intra-molecular forces can be calculated with molecular dynamics simulations.

In this contribution, we perform a gradient expansion of the intra-molecular repulsion and calculate the EDL structure with asymptotic analysis. This justifies the phenomenological approach of Bazant et al.[4] We find that three energy scales describing electrostatic forces between ions, molecular repulsion, and thermal motion determine the shape and width of the long-ranging charged double layer (see Fig. 1). Depending upon the relative magnitude of the competing energy scales, the charge density of electrochemical double layers in ionic liquids either decays exponentially or oscillates continuously (see Fig. 2). Charge ordering occurs if the repulsion between molecules dominates over thermal energy and Coulomb interaction. Our rigorous analytic results reveal the full parameter dependence and will help to design interfacial behaviour.

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Keywords: ionic liquid electrolyte, electrochemical double layer, phase diagram

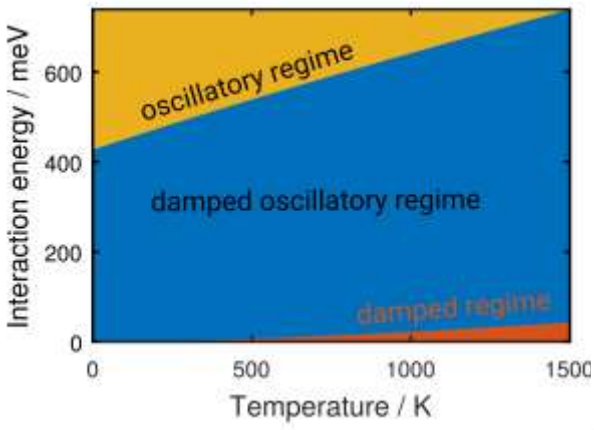

Figure 1: Phase diagram of electrochemical double layers.

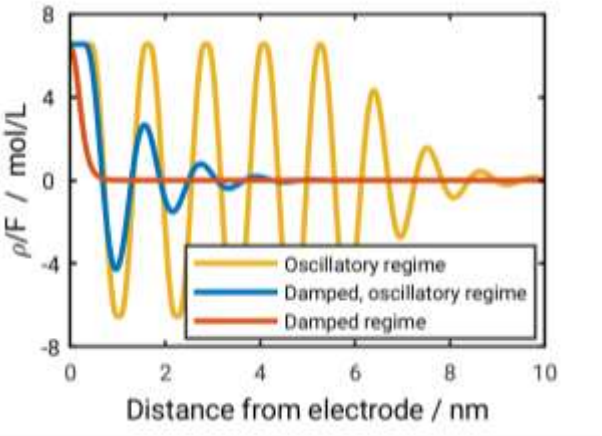

Figure 2: Charge density for binary ionic liquid.

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