Effect of ion-ion correlations on polyelectrolyte gel collapse and reentrant swelling

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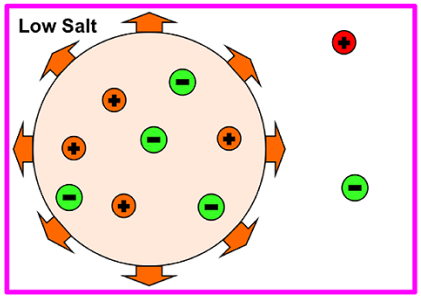
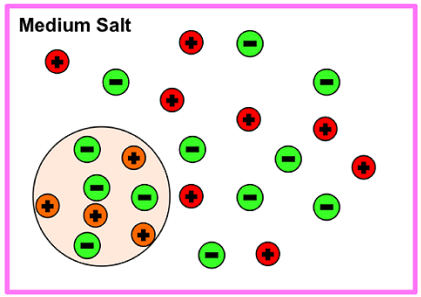
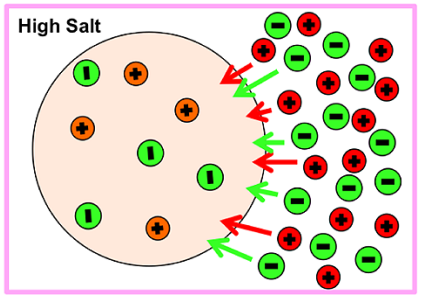
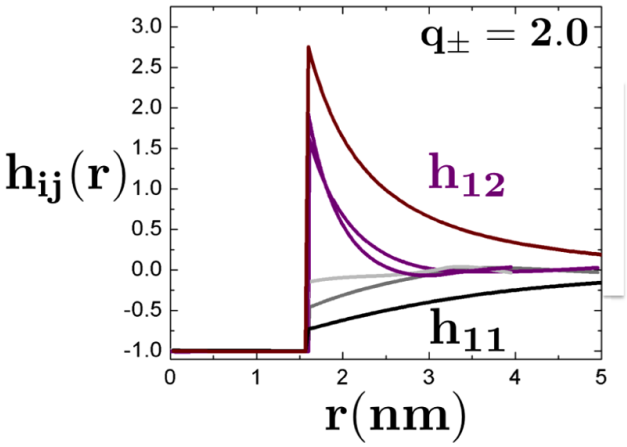
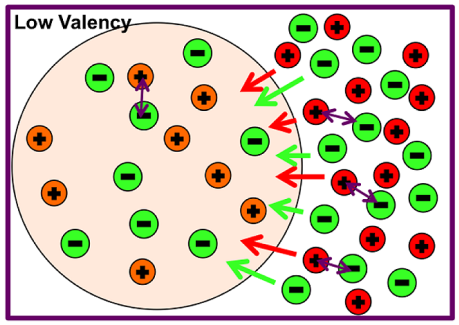
Polyelectrolyte gels are known to exhibit strong response to changes in salt concentration, an effect attributed to osmotic effects. Traditional theories are insufficient to describe all the properties observed in experiments; namely, reentrant swelling effects at high salt concentrations and complete polyelectrolyte collapse at high salt valencies. We incorporate liquid-state integral equation theories to account for the many-body correlations between finite-sized ions in a strongly charged polyelectrolyte gel. This represents a theory for such systems that goes well beyond well-known Debye-Huckel (DH) and Poisson-Boltzmann (PB) theories. We demonstrate that charge correlations give rise to enhanced gel deswelling, a first-order collapse to a highly correlated state at large valencies, and counterion size-dependent reentrant swelling. Such ion-specific effects provide routes for practical control of stimuli-responsive polymeric materials based on polyelectrolyte gels, and deeper understanding of biological systems.

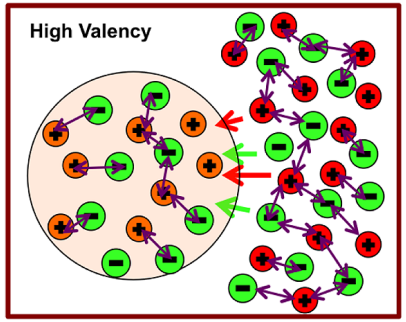












We demonstrate that osmotic reversals (top) can occur at high salt concentrations, and these can complement Coulombic cohesion effects (bottom) to reveal an array of ion-specific swelling behaviors involving reentrant transitions, discrete gel collapse, and enhanced deswelling. These arise from local ion correlation structure, which is calculated using liquid state theory (top right).

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