Swelling and Collapse of Polyelectrolyte Gels in Equilibrium with Monovalent and Divalent Electrolyte Solutions

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Polyelectrolyte (PE) gels exhibit a remarkable swelling capacity and a strong affinity to aqueous solvents; as such, PE gels have found widespread use in medical, agricultural, and environmental applications. Some PE gels have the ability to undergo reversible volume phase transitions that can be controlled by temperature, salinity of the environment, and exposure to light. Their study has served to explain physiological processes including muscle contraction and nerve excitation. Moreover, many biological networks, including chromosomes (*J. F. Marko Chromosome Research (2008) 16:469–497*), share several physical properties with PE gels, including their ability to swell and de-swell, and change volume with the addition of monovalent and divalent salt.

We explain the electrostatic driven hyper-condensation of PE gels in the presence of oppositely charged divalent ions by using a model that only includes purely repulsive soft-core potential among all components and Coulomb interactions. We demonstrate that the compaction of the PE gels in the presence of divalent counter-ions induce a disorder-percolated structure of dense connected regions rich in chain monomers and divalent counter-ions, separated by regions rich in monovalent co-ions.

The swelling of polyelectrolyte (PE) gels by 1:1 and 2:1 salts is studied via osmotic ensemble Monte Carlo simulations at constant osmotic pressure and electrolyte chemical potential of a reservoir phase in equilibrium with a model PE network. The swelling ratio of the gels decreases strongly in the presence of explicit divalent counter-ions and a percolated disordered structure of regions of collapsed gel and swollen gel is observed, as opposed to a homogeneously macroscopic segregated state (see Figure). This structure may exhibit increased functionality, given the large number of interfaces that are generated in the system.

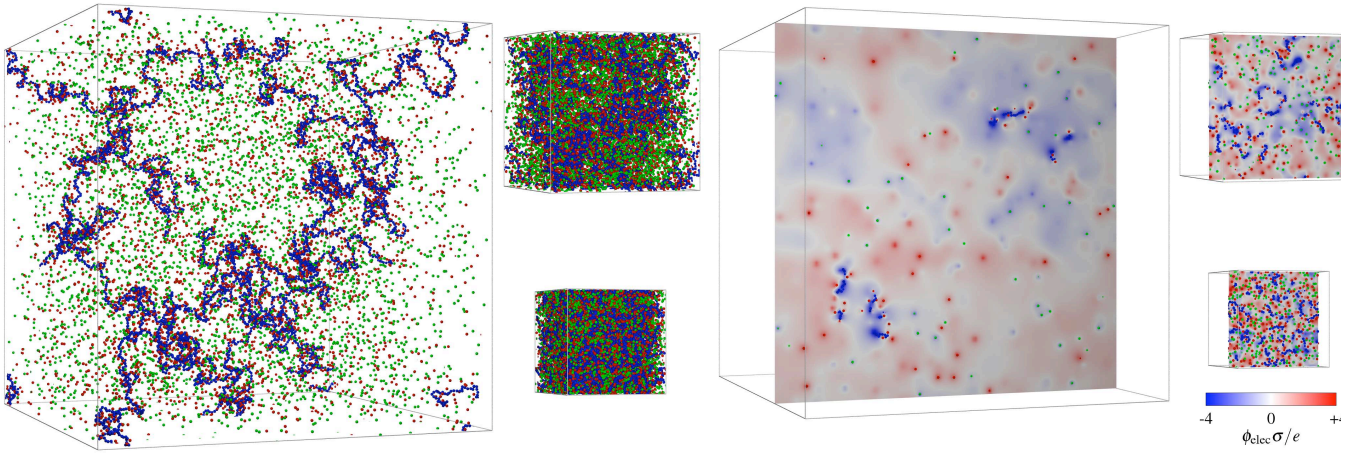

Figure Caption. Simulated 300-mer PE gels in equilibrium with 2:1 electrolyte reservoirs. (a) Left: swollen state, ϕ= 9:21 X10^{-4}; upper right: partially swollen state, ϕ= 1:37X10^{-2}; lower right: collapsed state, ϕ= 4:6X10^{-2} and (b) Two-dimensional cross-sectional color map of electrosatic potential for the same parameters. Blue: monomers; red: divalent counter-ions; green: monovalent co-ions. All three subfigures are rendered at the same scale.