283j Molecular Dynamics Simulation of Discontinuous Volume Phase Transitions in Permanently Crosslinked Polyelectrolyte Networks

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Polyelectrolyte networks are known to exhibit discontinuous volume phase transitions. The thermodynamic forces that drive these transitions in polyelectrolyte networks have not yet been completely elucidated. We have conducted molecular dynamics simulations of permanently crosslinked polyelectrolyte networks with explicit counterions, taking into consideration effects such as counterion valency, solvent quality, backbone chain length, and the addition of salts and other polyelectrolytic solutes. The simulation results show that the volumetric properties of polyelectrolyte networks depend considerably on these factors. In particular, discontinuous swelling-collapse transitions in the networks, which manifest as unstable loops along isotherms, can be realized with increases or enhancements in the strength of electrostatic interactions between charged sites, the charge density on the network backbone, the valency of the counterions, the degradation of the monomer-solvent interactions, the crosslinking density of the network, and the concentration of added salts. Based on our analysis of simulated data, we present a reevaluation of leading theories on the swelling and collapse of polyelectrolyte networks and identify the energetic and entropic effects whose interplay appears to be responsible for the discontinuous volume phase transitions in polyelectrolyte networks. We also relate these results to applications such as the diffusion, migration, and partitioning of absorbed solutes in polyelectrolyte networks.