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Towards a Modeling Framework for Thermodynamics and Transport Coefficients in Polyelectrolyte Assemblies RONALD LARSON, ALI SALEHI, University of Michigan — A continuum description of polyelectrolyte (PE) equilibrium gelation, and the kinetics of assembly is developed, accounting for PE chain diffusion, complexation, network relaxation is reported here. Using a combination of Flory-Huggins and Flory-Rehner free energy model, an upper-convected Maxwell model to describe polyelectrolyte gel stress and relaxation, and a Poisson equation for the electrostatic potential profiles, we develop a model that can account for both equilibrium properties of PE gels and for transport of PE's and ions during layer-by-layer assembly. As PE chains diffuse, counterions readjust themselves to minimize the net local charge, but fail to do so completely as they would have to pay a significant entropic penalty. Diffusion of PE chains predominantly driven by the electrostatic field induced by the entropy of counterions is characterized by pulse-like PE composition profiles. Even without considering chain complexation, we demonstrate that it is possible to at least qualitatively explain the non-monotonic variation of PEM growth kinetics versus salt concentration, observed experimentally.

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