A host of interesting phenomena, both biological and technological, involve the complexation of charged polymers: these may be long polymers with well-defined secondary structure, such as proteins, linear polyelectrolytes, or multi-branched species. A particularly interesting phenomenon within polyelectrolyte solutions is coacervation, a liquid–liquid phase separation where polymer-enriched liquid droplets are formed within a dilute phase. Coacervation is a puzzling process where two primarily aqueous phases become immiscible. Aggregates (coacervates) formed in mixtures of oppositely charged polyelectrolytes are known as complex coacervates. Coacervates occur in many natural systems and have found application in microencapsulation and extraction processes, as their ultra-low surface tension allows them to readily assimilate nanoparticles or drug payloads within aqueous suspension. Coacervation is intimately related to the process of layer-by-layer deposition, where films up to micrometers in thickness are built by iterative surface adsorption of polyelectrolytes. These films are of interest as solid electrolytes in lightweight batteries, protective coatings, and drug micro-encapsulation. Solvation and electrostatic forces bind the layers, with hydrodynamics relevant to the histories of the nonequilibrium layers. Coacervation is further related to the phase separation of charged colloidal mixtures and molecular ionic liquids—organic salts whose balance of hydrophobic and electrostatic interactions renders them liquid near room temperature. As these systems exhibit common thermodynamic features, a primary goal of this research is the development of a unified theoretical and modeling framework capable of representing each system with arbitrary detail from continuum phase separation to the molecular conformations.

This topic inspires two REU projects involving characterization of coacervates through molecular dynamics simulation. In each, there will be a focus on utilizing coarse-grained modeling to understand the phase diagram of complex coacervates, as well as the structure and dynamics of coacervate phases. While some recent work has shown mean-field and PRISM theories capture the primary features of coacervate phases, limited simulation and structural characterization data exist. Thus, precise description of the phase remains elusive. In the first project, a student will utilize an open-source simulation package, such as LAMMPS, to characterize the structure of coacervates formed by oppositely charged linear polyelectrolytes at varying compositions of added salt. Salt acts as an artificial temperature in these systems, weakening electrostatic interactions between the chains and disrupting the coacervate phase. As such, a combination of salt and temperature variation will enable precise tuning of the strength of polyelectrolyte complexation for engineering applications. In the second project, the student will examine the intriguing limit of polyelectrolyte solutions with highly-valent polyoxometalate ions. Molecular simulations here will provide important information about the phase diagram, internal structure, and relaxation dynamics important for material applications.

It is preferable (but not required) for students interested in this project to have prior experience with writing computer code (C++ preferred) and with scripting languages to facilitate running computations on the Whitmer group cluster and CRC machines.

References


REU Project Proposal
Complex Coacervation

Jonathan K. Whitmer


