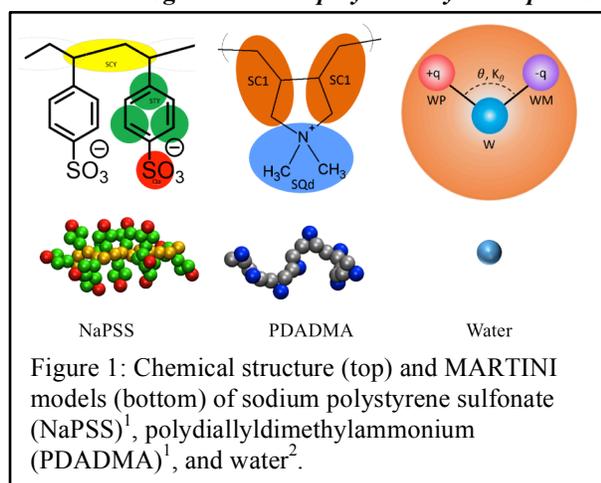
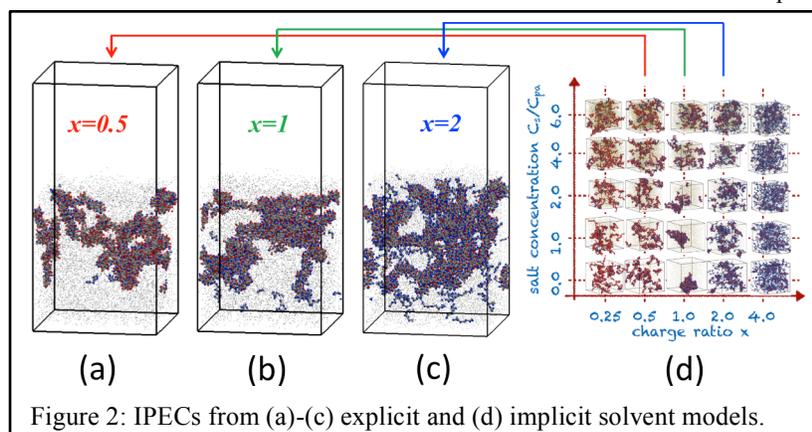


**Impact of the Research Funded by this PRF Grant:** This PRF grant has enabled the PI (Cheng) to venture into the field of ionic polymers and identify several research topics that will define the research portfolio of the PI's group in the coming years. In 2018, the PI has developed a CAREER proposal to NSF based on the research supported by this grant. Yanfei Tang, a graduate student from the PI's group supported by this grant at the 100% level in the past 2 years, has published 3 papers, has 1 paper currently under review, and will submit 1 more in a few weeks, which are all based on the research funded by this grant. He is scheduled to defend his PhD thesis on November 16, 2018. The grant is also used to provide summer support for one Hispanic student (Ralph Romero) who obtained a BS degree in May 2018 and is currently a physics graduate student at Virginia Tech (VT) under the PI's supervision, and one female student (Shreya Dayal) who is currently a physics junior at VT.

### Research Progress 1: *Inter-polyelectrolyte complexes (IPECs) with an explicit solvent model.*



We have adopted MARTINI models [Figure 1] of sodium polystyrene sulfonate (NaPSS)<sup>1</sup>, polydiallyldimethylammonium (PDADMA)<sup>1</sup>, and water<sup>2</sup> to study the complexation between polyanions (PAs) and polycations (PCs) in an aqueous solution with the solvent included explicitly, when the PC/PA charge ratio ( $x$ ) and the salt concentration ( $C_s$ ) are varied. In particular, we have adapted the water model in Ref. [2] to capture the polarizability and surface tension of water, which allow us to model both equilibrium aqueous solutions and nonequilibrium evaporating solutions. Mobile ions, including counterions and salts, are included explicitly in the model as well. The results on IPECs in equilibrium solutions are compared with those obtained with bead-spring (Kremer-Grest) chains containing charged beads in an implicit solvent, which were discussed in the 2017 Narrative Report of this grant. This comparison is shown

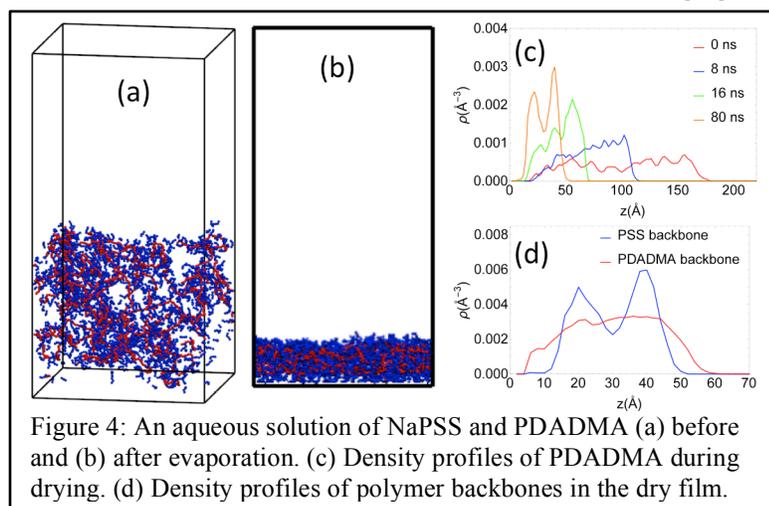
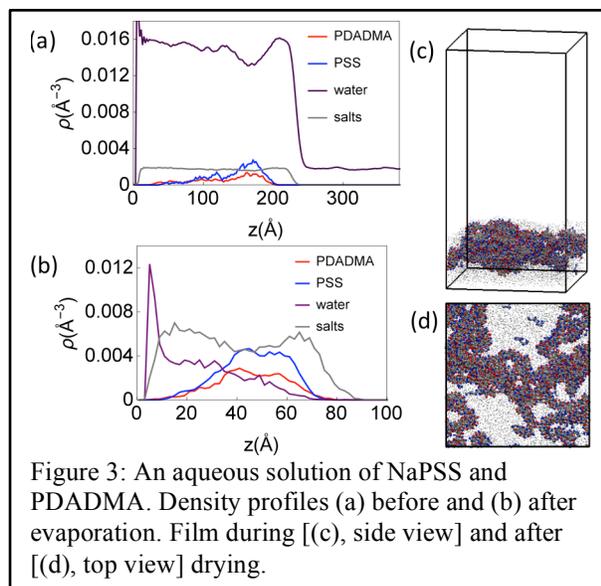


in Figure 2, which shows that IPECs with similar structures have been obtained with both implicit and explicit solvent models at the same  $x$  and  $C_s$ . For  $x=1$ , a large IPEC is formed [Figure 2(b)]. When  $x$  is different from 1, more clusters are observed [Figure 2(a) and 2(c)], consistent with the trend observed in the implicit solvent simulations [Figure 2(d)]. In the next stage, we will use the explicit solvent model to map out the full structural diagram of IPECs in the  $x$ - $C_s$  plane and compare it with the results from the implicit

solvent model [Figure 2(d)]. The available data show that IPECs show similar types of structures as those predicted by the mean-field theory of Zhang and Shklovskii<sup>3</sup>, but the structural diagram is qualitatively different from the theoretical prediction. We will further compare our simulation results with some recent theories<sup>4</sup>.

### Research Progress 2: *Evaporation of aqueous solutions of NaPSS and PDADMA.*

We have used the MARTINI models of NaPSS, PDADMA, and water shown in Figure 1 to simulate the evaporation of aqueous solutions of polyelectrolytes. Figure 3 shows the results for a solution of a mixture of 64-monomer PSS chains and 8-monomer PDADMA chains. Prior to evaporation, IPECs are formed in the solution [Figure 3(a)].



During evaporation, IPECs merge together to form a large cluster as the polymer concentration increases [Figure 3(c)]. However, after evaporation, the dry film shows a porous structure and the coverage of the substrate is incomplete [Figure 3(d)]. A layer of residual water is trapped below the polymer film [Figure 3(b) and 3(c)]. The main issue seems to be due to the fact that PAs and PCs bind strongly and form a complex in the initial solution. Even in a larger system with more PSS and PDADMA chains, a porous film is still formed after drying, though the coverage of the substrate is improved. To achieve a dry film with a more uniform structure in the plane of the film, we switch to dimeric PDADMA chains, which are expected to behave as multivalent ions. The degree of complexation is suppressed in the equilibrium solution [Figure 4(a)]. After drying, PSS chains are enriched and form a skin layer near the evaporating interface and eventually a stratified film of PSS is formed [Figure 4(b)-(d)], likely because of the bridging effect associated with multivalent ions. We are

currently exploring various strategies to uniformly disperse long PA and PC chains in a solution, e.g., by adding a sufficient amount of salt. Such solutions are expected to produce multilayered dry films of polyelectrolyte mixtures with alternating layers of PAs and PCs after evaporation, similar to those generated via the layer-by-layer deposition method. Rich physics has already been observed when electrostatics is combined with the nonequilibrium nature of drying, as shown in Figure 4. The ultimate goal is to demonstrate a one-pot drying protocol that can be used to produce stratified polyelectrolyte films quickly and efficiently via solvent evaporation.

### Research Progress 3: Drying-induced stratification of bidisperse nanoparticle suspensions.

Our work on modeling stratification in drying bidisperse nanoparticle suspensions is published in Langmuir<sup>5</sup>. Our results showed that existing theories of stratification based on the idea of diffusiophoresis that treat the solvent as a uniform viscous background tend to overestimate stratification, consistent with recent experimental evidence. The role of solvent thus needs to be taken into account explicitly to understand the physical mechanism of stratification. We recently developed a method to control stratification in such systems using thermophoresis and the paper is currently under review. Possible approaches to implement this method experimentally are proposed. We are currently also exploring other strategies to control stratification in drying polydisperse particle suspensions. In two recent papers<sup>6,7</sup>, we clarified the physical foundation of the moving interface method that can be used to model the drying of soft matter solutions without explicitly including the solvent. We are comparing results from explicit and implicit solvent models of drying polymer and colloidal solutions. Such comparison will reveal regimes where implicit solvent models can be used and where caution must be taken when results from implicit solvent simulations are interpreted.

**References:** [1] Vögele *et al.*, J. Chem. Phys. **143**, 243151 (2015). [2] Yesylevskyy *et al.*, PLoS Comput. Biol. **6**, e1000810 (2010). [3] Zhang, Shklovskii, Physica A **352**, 216 (2005). [4] Sing, Adv. Colloid Interface Sci. **239**, 2 (2017). [5] Tang, Grest, Cheng, Langmuir **34**, 7161 (2018). [6] Tang, Cheng, Phys. Rev. E **98**, 032802 (2018). [7] Tang, Cheng, J. Colloid Interface Sci. **533**, 401 (2019).