Mesoscale Modeling of Stimuli-Responsive Composite Colloids at Oil-Water Interfaces
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The broad goals of the project are (1) to deepen the understanding of interfacial dynamics and self-assembly behavior of pH-responsive polyelectrolyte-grafted nanoparticles (PGNPs) at the water–water interface and (2) to provide a theoretical framework that links nanoparticle properties to the possibility of controlling stabilization and destabilization of Pickering emulsions by external triggers. During this reporting period, one of our primary objectives was to establish a critical understanding of the microstructure and dynamics of PGNP monolayers at the fluid interface, with emphasis on the manipulation of monolayer properties through pH change. As part of this goal, we sought to discover the structural response of particle monolayer to different ionization states of the grafted polyelectrolytes, which is triggered by pH variation. In addition, we sought to establish the structure-dynamics relationship for PGNP monolayers, focusing on individual particle dynamics and cooperative behavior of the particle ensemble. We also sought to discover how interface adsorbed PGNPs can enable pH control over emulsion stability through direct simulations of droplet collision and coalescence.

The electrostatic dissipative particle dynamics (DPD) method developed in Year 1 was used to model the self-assembly of PGNP monolayers at the water–oil interface and the forced interaction between droplets covered by PGNPs. In order to probe collective dynamics of large-scale monolayers having sufficient particles and elucidate the deformation of particle-covered droplets during collision, we have improved the computational efficiency of the electrostatic DPD by parallelizing the finite difference Poisson solver.
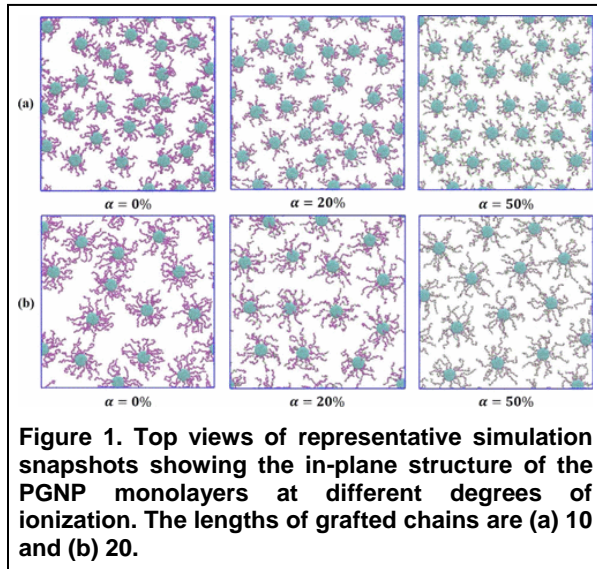

Figure 1. Top views of representative simulation snapshots showing the in-plane structure of the PGNP monolayers at different degrees of ionization. The lengths of grafted chains are (a) 10 and (b) 20.

The electrostatic DPD simulation allows us to directly visualize the individual particle morphology and the out-of-plane and in-plane structures of the entire monolayer. as the degree of ionization increases. As the degree of ionization increases we observe a phase transition in low density monolayers from a liquid state to a crystalline state with non-close-packed hexagonal order (see Figure 1). Quantitative characterization of the structural change shows long-range electrostatic repulsions as the driving forces, which enables the phase transition even at low particle surface coverage. The introduction of salt ions can effectively screen electrostatic interactions, which leads to a reverse order-to-disorder transition.
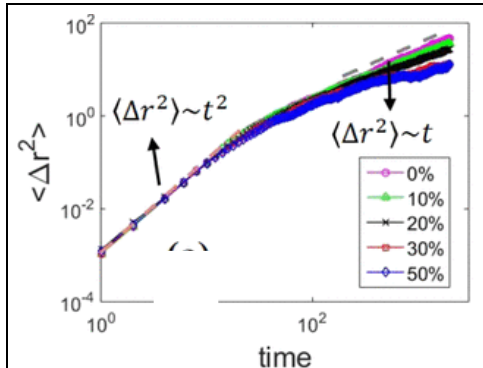

Figure 2. Log–log plot of MSDs $\langle \Delta r^2 \rangle$ as functions of simulation time at α = 0, 10, 20, 30, and 50%.

More importantly, the structural transition due to the long-range electrostatic interactions also affects the dynamics of PGNPs. The 2D mean square displacement shown in Figure 2 demonstrates a short-time ballistic motion and a transition to normal diffusive regime in long times. We find that the diffusion of individual particles is significantly inhibited as the monolayer develops the hexagonal pattern. The particle trajectories reveal that the motion is hindered by the cages formed by neighboring particles in the ordered state. Despite a clear decrease as the degree of ionization increases, the self-diffusion coefficient of particles is still greater than zero. The nonzero diffusivity at the fully crystalline state is attributed to collective dynamics of the

entire monolayer in a long-time period. In addition, a crossover to an anomalous subdiffusive regime is observed, which is caused by the caging effect as a result of the long-range ordering. Theses findings provide important insight into the self-assembly behavior of PGNP monolayers for compelling applications.

To directly explore the emulsion stablity using PGNPs as stabilizer, we conducted a mechanistic study of droplet interaction. A steered molecular dynamics approach imposes a forced collision between two oil-in-water droplets covered by PGNPs. The resistance to coalsecence as a function of the droplet center of mass distance was simulataneously characterized during the collision, which reflects the emulsion stability. Droplets stablized by 0% ionized (uncharged) and 50% ionized PGNPs were simulated to reveal the effect of degree of ionization. The snapshots in Figure 3 clearly demonstrate more pronounced deformation during droplet collision when the particles are highly charged. The resistance force also confirms that coalescence is delayed and requires larger driving forces in the system with 50% ionized particles. The resistance force to coalscence increases at higher degrees of ionzation and particle surface coverage. The simulations elucidate a synergistic effect of long-range direct electrostatic interactions between polyeletrolytes, image charge effects, and steric hindrance of extended polymers for inhibiting coalscence and stablizing the emulsion droplets.

The computational modeling in the past year has been carried out by PhD student Shiyi Qin. Shiyi is developing expertise in colloidal assembly, interfacial phenomena, low Reynolds number fluid dynamics, mesoscale simulation, and parallel computing. At the conclusion of his degree, we expect he will have a strong background in soft
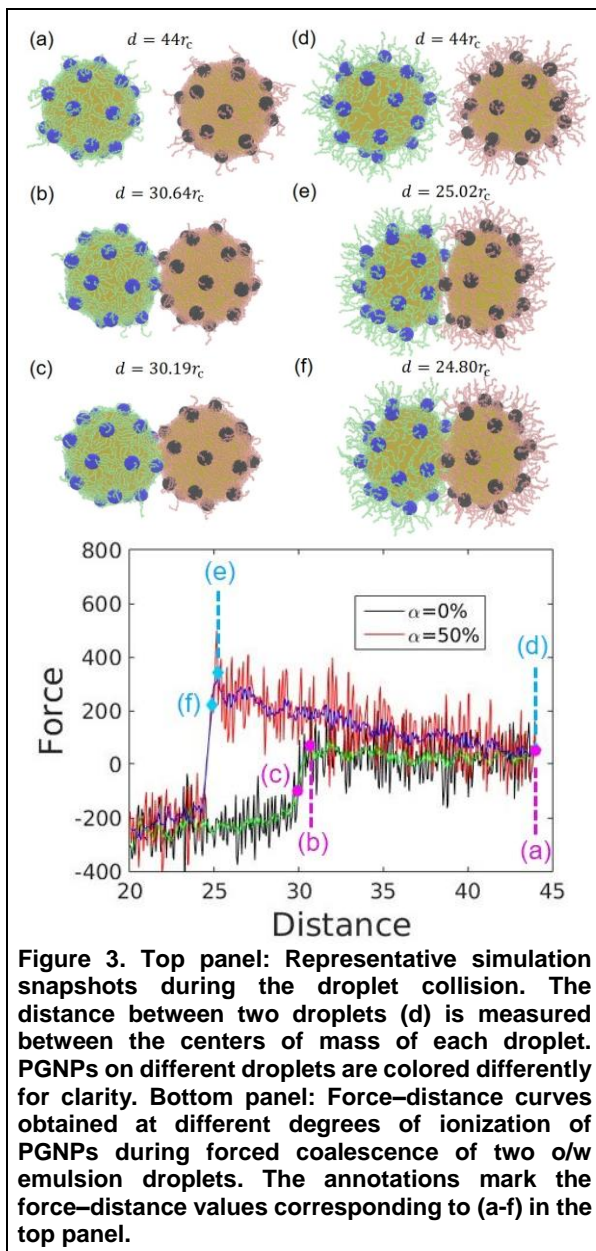

Figure 3. Top panel: Representative simulation snapshots during the droplet collision. The distance between two droplets (d) is measured between the centers of mass of each droplet. PGNPs on different droplets are colored differently for clarity. Bottom panel: Force–distance curves obtained at different degrees of ionization of PGNPs during forced coalescence of two o/w emulsion droplets. The annotations mark the force–distance values corresponding to (a-f) in the top panel.

matter and interfacial science and will possess a unique skill set for modeling complex fluid systems. Undergraduate student Junhyuk Kang participated in this research and contributed significantly to the monolayer simulations. By conducting simulations and drafting reports and manuscripts, he developed skills in particle simulations, fluid mechanics, scientific writing, and communications. These skills are essential as they pursue careers in mechanical engineering. The work on the PGNP monolayers was published in the journal Langmuir, which is a leading journal on research related to interfaical science. Two presentations were made at the APS March Meeting 2018 and 256th ACS National Meeting. Over the past year, this project has also fostered an extramural collaboration between PI and Dr. Shan Jiang at Iowa State, which leads to the submission of an NSF proposal. PI has also leveraged the results from this funded project to successfully request computational time of over half million CPU hours at the computating facility of Brookhaven National Laborartory.