Current and Past Research Accomplishments

My current postdoctoral training at Caltech focuses on understanding a) the ability of polyelectrolytes to prevent $CaCO_3$ mineralization, and b) the ability of surfactants to improve CO_2 bubble nucleation in polymer foams.

Prior to Caltech, my research activities involved c) modeling and designing gemini surfactant molecules to direct their self-assembly in water into bi-continuous cubic morphologies (such as the gyroid phase), d) studying the structure and dynamic properties of water confined in different self-assembled morphologies of gemini surfactants, e) examining the effect of polymer chain dispersity on the micellization of diblock copolymers in a selective solvent, and f) investigating the dynamics of diblock copolymer self-assembly.

I employed a variety of computational tools and theoretical models to investigate the physical principles underlying each of the research objectives mentioned above. These tools ranged from all-atom and coarse-grained particle-based simulations to study molecular properties of the system, to enhanced sampling approaches such as umbrella sampling, metadynamics, replica exchange molecular simulations, and the transition-state path-finding approach called the string method for modeling rare events in chemistry. Additionally, I utilized equation of state (EoS) approaches like perturbed chain statistical associating fluid theory (PC-SAFT), as well as field-theory-based approaches such as self-consistent field theory (SCFT), classical density functional theory (cDFT), and dynamic density functional theory (DDFT) for the mesoscopic characterization of system properties. Recently, in collaboration with Prof. Wang's group and the scientists at Dow Chemical Company, I have been exploring a synergistic approach to combine physics-based molecular models with the machines learning tools to advance the boundaries of computational materials science research.

In the following paragraphs, I will briefly summarize the objectives, major findings, and techniques I used to study the projects listed above.

Research at Caltech (Advisor: Prof. Zhen-Gang Wang):

I am currently affiliated with the Dow-Caltech University Partnership Initiative (UPI) to design negatively charged polyelectrolytes that can prevent $CaCO_3$ mineralization. My primary research activity is to develop novel computational techniques to investigate the antiscalant mechanism and support experimental scientists at Dow Inc. in synthesizing polyelectrolytes with better antiscalant activity.

I have developed enhanced sampling simulation tools to investigate the Ca^{2+}-mediated association between like-charged polyelectrolytes. Using Hamiltonian replica exchange molecular dynamics coupled with metadynamics, I quantified the free energy surface of Ca^{2+}-mediated polyelectrolyte association. By combining these enhanced sampling approaches with an Autoencoder framework, we identified the important electrostatic screening caused by Ca^{2+} bridging between the polyelectrolyte chains and the subsequent chain conformational transition leading to polyelectrolyte aggregation.[1].

Furthermore, I have built free energy perturbation protocols to investigate the site-specific mechanism of Ca^{2+} binding to the polyelectrolyte chain. This work has established positiondependent binding strengths for ion binding events[2]. Using these tools I have designed copolymer variants that could mitigate $CaCO_3$ mineralization with enhanced activity[3].

Prior to the current collaboration with Dow Inc., I was associated with another Dow-Caltech UPI that focused on the stability of polymer foams. I developed a molecule-specific cDFT and coupled it with the transition-state path-finding algorithm called the string method to study the effect of surfactants on CO_2 bubble nucleation in polymers. I discovered a new surfactant-mediated minimum free-energy pathway for CO_2 bubble nucleation in polymers. My observations clarified an important concept that enables surfactants to produce polymer foams with improved microstructural features and insulating properties[4].

Additionally, I authored successful two research proposals that secured major funding for Prof. Wang's lab.

Research at the Institute für Physik, JGU-Mainz, Germany (Advisor: Prof. Friederike Schmid):

Polymer self-assembly into desired morphologies is an active research area. However, two topics that are often neglected in any related modeling study are a) the effect of statistically distributed polymer sizes (polydispersity) on their self-assembly, and b) the dynamics of the self-assembly process itself. Addressing these was the focus of my research activities in Germany.

I built a numerical model called SCFT and discovered that polydisperse block copolymers lead to micellar aggregates of uniform size, while monodisperse polymers stabilize micellar aggregates of varied sizes. The associated energetics suggest that polydispersity raises free energies for micelle formation and dissolution, thereby reducing the size fluctuation in micelles[5].

To characterize the dynamics of the self-assembly process itself, I developed another numerical model called DDFT. My approach captures both the global dynamics and the relaxation due to local rearrangements of the chain at the relevant length scales. I applied this method to investigate the dynamics associated with the formation of a lamellar structure in diblock copolymer melts[6].

My research on the aggregation of polydisperse polymer chains was highlighted as a Physical Review Editors' Suggestion, and the work on the DDFT was highlighted in Advances in Engineering Magazine.

Graduate research at the University of Wisconsin, Madison (Advisor: Prof. Arun Yethiraj):

Experimental investigations suggest that the gemini architecture of anionic surfactants (i.e., twin-tailed surfactants connected by a linker) when self-assembled in an aqueous solution favor gyroid morphology, a bi-continuous cubic phase. These bicontinuous morphologies are desirable for membrane applications due to interpenetrating aqueous and hydrophobic domains. Understanding a) the molecular principles that stabilize the gyroid morphology over wide gemini surfactant concentration windows, and b) factors that effect water dynamics through the gyroid nano channels were the objectives of my graduate research work.

I employed molecular dynamics simulations to model gemini dicarboxylate surfactants and studied their aqueous lyotropic liquid crystal assemblies. My studies suggest that the long-range electrostatic repulsion between the surfactant head groups and subsequent differences in their linker-linker packing, lead to a linker length dependent self-assembly behavior of gemini surfactant molecules in an aqueous solution. Specifically, gemini surfactants with an odd number of carbon atoms in the linker stabilized the gyroid morphology over wider surfactant concentration window than the gemini surfactant molecules with even number of carbon atoms in the linker[7].

My investigations note that for a given counterion, the translational diffusion and rotational relaxation of water confined in the nano channels of gemini surfactant LLCs were predominantly a function of hydration level and the confinement length scale. While the surface functionality and the curvature are largely secondary[8-9]. Intriguingly though, the counterion significantly influenced self-diffusion of water in the nano channels of gemini surfactant LLCs. My studies note that at high hydration, water self-diffusion is in the order $D_{\mathrm{TMA}}<D_{\mathrm{Na}}<D_{\mathrm{K}}$, where TMA, Na and K refer to tetramethyl ammonium, sodium and potassium counter ions, respectively. At low hydrations, however, the order is different, that is $D_{Na}<D_{TMA}<D_{K}$. My simulations suggest that the excluded volume affect was the largest with TMA^{+}, and the electrostatic correlation was the strongest with Na^{+}. The observed trend in counterion dependent water diffusion was a result of the dominant of the two affects at a given surfactant to water ratio[10-11].

My modeling results were corroborated by the experimental studies conducted by Prof. Mahesh Mahanthappa's research group.

Publication References:

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