Research Interests

1. **Characterization and engineering of self-assembly, dispersion, and emulsification**

The Nanostructural Materials and Process program is a consortium of faculty addressing problems of self-assembly, dispersion, and characterization at the nanometer scale in liquid and soft material systems. The program, then called the Surfactancy and Self-Assembly program, was pioneered by H. Ted Davis over 30 years ago with an NSF-funded Engineering Research Center called the Center for Interfacial Engineering. Self-assembly at the molecular level is crucial to the performance of many applied systems, including detergents and foams in personal care products, drug delivery in pharmaceuticals, and industrial applications such as adhesives, paints, sensors, catalysts and the creation of nanostructured materials. The processes of nanostructure development are central to the function of the system. Critical issues in such applications are to control both intra-molecular and inter-molecular forces that govern the structure and properties of the self-assembled materials, to elucidate into the mechanisms governing these processes, and to correlate the structure and performance of such materials. The overriding goal is to enable interfacial engineers to synthesize materials and control processes which perform optimally with specified constraints at the nanoscale. The researchers in the NMP program combine experiment, theory, and modeling to correlate molecular and their process parameters through synthesis of novel materials, investigation of phase behavior, and discovery of novel self-assembled molecular and colloidal systems.
Our group is active in several projects that capitalize on complementary microscopy techniques to understand the formation of micelles and nano-sized dispersions in surfactant systems. These projects typically involve collaboration with other faculty and with industrial collaborators who participate in a nonproprietary way through our NMP program. For instance, we have used cryogenic transmission and scanning electron microscopy (cryoTEM and cryoSEM) to explain the nanostructure formation process steps, and sensitivity to process variables, in the formation of certain nanoparticles and in the formation of long-lived nanoscale oil-in-water dispersions. Our goal is to develop principles for the engineering of systems that develop nanostructures.

### Molecular engineering of dispersant systems for oil spills

(with collaborators in the Consortium for Molecular Engineering of Dispersant Systems (CMEDS)- a multi-university consortium funded by the Gulf of Mexico Research Initiative www.gomri.org)

Spilling of crude oil into sea water due to accidents involving oil wells or tankers (such as the Deepwater Horizon incident in the Gulf of Mexico in 2010) can be a major problem to marine life, the aquatic and coastal environment, and to people living in coastal areas. The spilled oil forms a surface film or slick, which can spread and occupy a vast area. Remediation of this oil slick can involve many approaches, but the most common by far is termed “dispersion”. Here a material called a “dispersant” is introduced onto the oil slick. This causes the slick to disintegrate into small droplets, which are then carried away into the water column to a depth of several meters under the ocean surface. In the water column, many species of bacteria and other micro-organisms are present that can digest and degrade the oil in the droplets. Dispersant molecules are expected to coat the surfaces of the droplets and thereby prevent their re-agglomeration. The presence of the dispersant on the droplets should not prevent the bacteria from digesting the droplets. Also, the dispersant should not be toxic to the bacteria or to other aquatic life in the ocean.

Our group has used dynamic interfacial tension measurements in dispersion conditions to help distinguish "good" dispersants from "bad" ones. For example, the main components of currently stockpiled dispersants - such as Tween 80, DOSS, and Span 80 (sorbitan monooleate) - are all needed in an optimal formulation for oil dispersal, but it has been unclear what governs the optimum. Our work to date has shed light on why it is that a specific mix of surfactants is particularly effective. For example, for DOSS-Tween 80 mixtures, the maximum in effectiveness correlates roughly with a minimum in the initial interfacial tension, but the precise optimum is offset in the direction that is favored by the dynamics in the interfacial tension (not shown). Our first reports of such results and rationale for Corexit surfactant components has been well-cited as a methodology to emulate in future studies. We will continue to use this approach in our studies with other surfactant/solvent mixtures. Moreover, results to date suggest that microstructures (e.g., micelles, and possibly vesicles) can influence the dispersion process, both by stabilizing surfactants that would not otherwise penetrate the oil and also by influencing rates of transport to the newly-created surface during the dispersion process.

### UV Curing and property development of coatings

(description adapted from the Coating Process Fundamentals website, http://research.cems.umn.edu/cfpf/solidcoating.html) (with collaborators in the CPFP program, particularly Prof. Lorraine Francis and Dr. Greg Haugstad)

After successful deposition of a liquid on a substrate, coatings are solidified by drying, curing, cooling, or coalescence. During solidification, microstructure and properties develop. Solidification must be understood at a fundamental level in order to maximize the overall yield of a coating process, and to develop the desired microstructure and properties of the final coating. Diffusion and mass transport (drying), chemical reaction kinetics (curing), heat transfer (cooling), particle-particle interactions (coalescence) and often combinations of these are at the heart of solidification research.

Coupled with solidification is the development of stress, which along with adhesion and coating mechanical properties, determines the durability and likelihood of defects, such as curling, cracking, and delamination. Additionally, the microstructure and nanostructure of the coating is developed during solidification, and it is the microstructure that eventually impacts the properties and performance of the coating. The connections between the solidification process, the development of stress and microstructure, and the coating properties create a complex, but crucial, set of challenges for research.

Currently we are interested in the replication of surface microstructures in coatings with UV curing, i.e. UV-
micromolding. Widely used in electronics, optics and microfluidic systems, the UV-micromolding process is limited in rate of throughput. Understanding limitations caused by chemical conversion rates, and caused by defect formation from stress development, may lead to improvements in the throughput of UV-micromolding processes.

We are also currently engaged in the problem of optimal UV cure when one needs to balance durability against segmental mobility. This work has bearing for instance in the fabrication of lubricity coatings on arterial catheters.

Our research approach in the CPFP program combines experimental methods that are particularly geared to characterizing solid coating development as it happens: cryo-SEM captures microstructure of dispersions and coatings as they solidify, cantilever beam measurement monitors accumulation of stress, FTIR and Raman spectroscopies follow composition and structure change, and (with Greg Haugstad) scanning probe microscopy techniques to characterize surface features and mechanical properties.

I. Sustainable, distributed, small scale ammonia production enabled by high temperature solid absorbent systems

(with collaborators in the "Wind to Ammonia" team, especially Profs. Ed Cussler, Lanny Schmidt, Paul Dauenhauer, and Prodromos Daoutidis, and also Mike Reese of the West Central Research and Outreach Center in Morris MN https://wcroc.cfans.umn.edu/research-programs/renewable-energy)

Ammonia is one of the most important chemicals in our society. It is basic to chemical fertilizer and key to feeding a large percentage of the world’s population. Ammonia is usually made at large scale with the Haber-Bosch process, using natural gas and air. This process works well, the result of a century of careful optimization. It is a centerpiece of our modern industrial society and produces fertilizer for much of the world. At the same time, it requires major capital investment and a fossil fuel feedstock, and so may be hard to sustain in the centuries to come.

With Cussler and other collaborators in the Wind-to-Ammonia team, we are exploring the potential of a small-scale ammonia process with a novel design that uses a high temperature ammonia-selective absorbent at near-catalytic conditions to simplify the process. This absorbent captures and releases ammonia at temperatures and pressures like those used in conventional ammonia synthesis. With this development, we hope to assist synthesis of fertilizer at the farm and agricultural co-op level so that carbon footprint, transport limitations, and renewable energy sources can be addressed.

Selected Publications


