Nanometer-size Patterned Materials From Self-Assembled Monolayers

Non-polymeric organic thin films prepared by self-assembled monolayers, and Langmuir-Blodgett monolayers find various potential applications including protein crystallization and separation, immunosensing, and friction and lubrication control. One of the most attractive characteristic of these highly-ordered 2D domains is that the organic molecules that make up the assembled layer can be easily engineered to incorporate functionalities into specified groups, thus allowing for controlled tuning of the surface properties of the thin film. Recent advances in experimental techniques, and the advent of new simulation approaches allied with fast and inexpensive computers has allowed the investigation of the correlation between macro- and microscopic film properties with changes in molecular architecture of the adsorbate. My research explores such correlations along the following directions: 1. Long-range 2D order is required for many of the potential applications envisioned for self-assembled monolayers. Surface patterning in 2D can be accomplished in the nanometer-scale size based on phase separation or the formation of aggregates of adsorbed amphiphiles, in analogy to 3D systems. Our experimental and computer simulation research program investigates the fundamental issues controlling the assembly of several component monolayers, more specifically, the formation of thermodynamically-stable, nanometer-sized 2D patterns. 2. SAMs can grow from solution, vapor, or deposited by beam epitaxy. Traditionally, thiols or alklytrichlorosilanes are deposited onto substrates from hexane or ethanol. Compared to gas phase deposition, SAMs from organic solvents are simpler and less expensive. Liquid and supercritical CO₂ (lscCO₂) is an inexpensive and an environmentally friendly solvent, which is non-regulated by the FDA. It allows for an easy solvent-free product recovery step upon depressurization. We investigate the SAMs of functionalized thiols deposited from lscCO₂. Structural information of the monolayer such as molecular orientation and chain defects, and layer thickness and coverage can be determined by FTIR and ellipsometry. Direct imaging of the monolayer structure can be obtained by AFM. Relevant structural and dynamical information of the SAMs are investigated by atomistic molecular dynamics (MD) computer simulations. Functionalization of the monolayer associated with the fact that metal nanocrystals can be stabilized in lscCO₂ with certain ligands (possibly also functionalized), can provide for a single step deposition process of nanocrystals onto an organized self-assembled array, based on a molecular recognition process.

Vesicles and Bilayers with Naturally Occurring and Synthetic Surfactants

Enhancing thermal and mechanical stability of the relatively frail existing vesicular/bilayer systems has the potential to foster its use in fields including drug-delivery, biosensing, and protein crystallization. The nature of the amphiphile(s) has a profound effect on the self-assembled structure and its microenvironment. It has, therefore, a direct relationship with layer stability and its interaction with foreign compounds such as surfactants and DNA molecules. The incorporation of membrane proteins into lipid monolayer structures can lead to the formation of well-defined two-dimensional crystals suitable for structural studies by electron microscopy. The relationship between amphiphilic architecture, and layer structure and stability is investigated by MD simulations. Immediate goals include the systematic investigation of the effect of varying the lipid tail and head-group chemical functionalities on vesicular properties. Relevant, readily accessible experimental information include Π vs. Δ isotherms, UV-vis and IR spectroscopy, interfacial tension, cryoTEM, and dynamic light scattering. MD offers a means of investigating the interaction between membrane components and additives at the molecular level, such as surfactants, and DNA – lipid complexes (lipoplexes) with applications in gene therapy, thus complementing the results from the experimental techniques mentioned above.

Interfacial Phenomena at the CO₂–Water Interface

The nontoxic and nonflammable fluids water and CO₂ are the two most abundant and inexpensive solvents on earth. Recently discovered water-in-CO₂ and CO₂-in-water microemulsions and emulsions offer new possibilities in waste minimization by replacing organic solvents in separations, reactions, and material formation processes. In many ways water-in-CO₂ microemulsions resemble conventional reverse microemulsions. However, limited success has been attained in forming and stabilizing such systems. My research group addresses these issues by measuring the strength of interaction between microemulsion droplets dispersed in CO₂, using well-established light scattering techniques for different surfactant systems. In parallel to such experiments, we use interfacial tension measurements to guide the selection of surfactants and additives. Atomistic computer simulations are also used to probe information at the molecular level. One very promising application of reverse micellar systems is enzymatic catalysis. Technologies based on lscCO₂ holds promises given its ‘green’ nature, and ease of product separation and recovery.