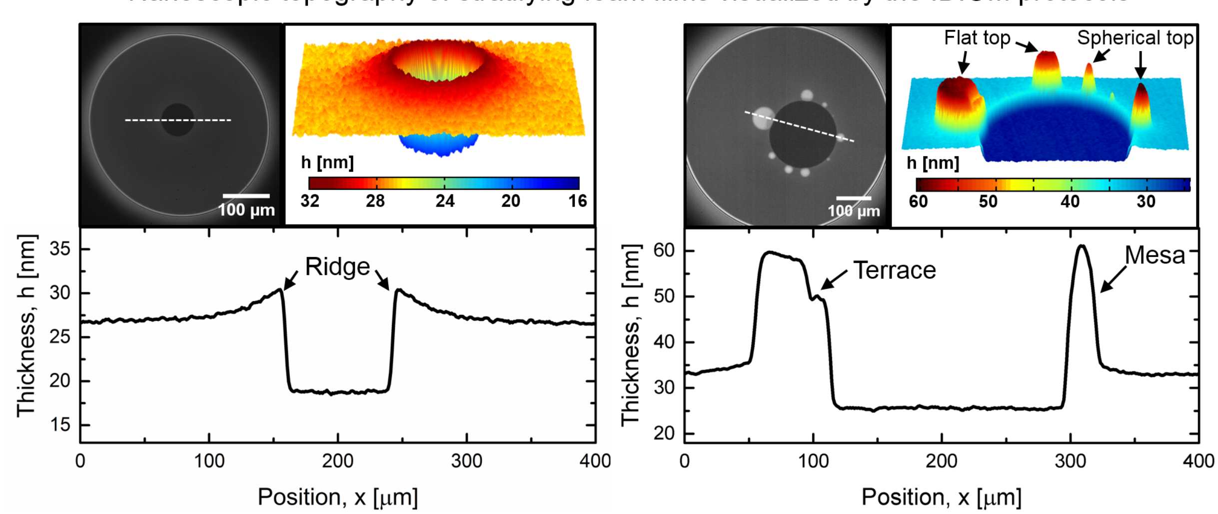
Surface Forces and Stratification in Micellar Foam Films

Vivek Sharma
Chemical Engineering, University of Illinois at Chicago, IL.

Ultrathin films of soft matter containing supramolecular structures like micelles, nanoparticles, smectic liquid crystals, lipid bilayers, and polyelectrolytes undergo drainage via stratification, manifested as step-wise thinning in interferometry-based measurements of average thickness. In this study, we focus exclusively on stratification in micellar foam films formed with aqueous solution of sodium dodecyl sulfate (SDS) above the critical micelle concentration (CMC). Foam films typically consist of fluid sandwiched between two surfactant-laden surfaces that are ~ 5 nm - 10 microns apart, and the drainage in films occurs under the influence of viscous, interfacial and intermolecular forces, including disjoining pressure. In reflected light microscopy, stratifying films (thickness < 100 nm) display regions with distinct shades of grey implying that domains and nanostructures with varied thickness coexist in the thinning film. Understanding and analyzing such nanoscopic thickness transitions and variations have been long-standing experimental challenge due to the lack of technique with the requisite spatio-temporal resolution, and theoretical challenge due to the absence of models for describing hydrodynamics and thermodynamics in stratified thin films. Using IDIOM (interferometry digital imaging optical microscopy) protocols we developed recently, we show that the nanoscopic thickness variations in stratifying films can be visualized and analyzed with an unprecedented spatial (thickness ~ 1 nm, lateral ~500 nm) and temporal resolution (< 1 ms). Stratification proceeds by formation of thinner domains that grow at the expense of surrounding films. Using the exquisite thickness maps created using IDIOM protocols, we provide the first visualization of nanoridges as well as mesas that form at the moving front around expanding domains. We contrast the step size measured in stratification studies with intermicellar distance obtained from scattering measurements, and explicitly measure the non-DLVO supramolecular oscillatory surface force contribution to disjoining pressure. Most significantly, we develop a self-consistent theoretical framework, a nonlinear thin film equation model that explicitly accounts for the influence of supramolecular oscillatory surface forces (using expressions we developed as a part of this study), as well as the physicochemical properties of surfactants including CMC, micellar size and interactions, Debye length, and surface tension. We show the complex spatio-temporal evolution of domains, nanoridges, nanoridge-to-mesa instability and mesas in stratifying foam films can be modeled quantitatively, and we elucidate how surfactant type and concentration can be manipulated and controlled for molecular engineering of micellar foams.

Nanoscopic topography of stratifying foam films visualized by the IDIOM protocols



Biography

Dr. Vivek Sharma is an Associate Professor of Chemical Engineering at the University of Illinois Chicago. Dr. Sharma's Soft Matter ODES-lab (optics, dynamics, elasticity and self-assembly laboratory) focuses on molecular science and engineering of flow behavior, stability, and processability of complex fluids. His group develops distinctive experiments and theory for investigating interfacial flows, surface forces, optics, and nonlinear viscoelasticity of industrial and biological soft matter. Before joining UIC in November 2012, Dr. Sharma worked as a post-doctoral researcher in Mechanical Engineering at Massachusetts Institute of Technology. He received his Ph. D. (Polymers/MSE, 2008) and M. S. (Chemical Engineering, 2006) from Georgia Tech., an M. S. (Polymer Science, 2003) from the University of Akron, and a bachelor's degree from IIT Delhi. Dr. Sharma was selected as the Distinguished Young Rheologist by TA Instruments in 2015, won the 2017 College of Engineering Teaching Award at UIC, and was awarded the 3M Non-Tenured Faculty Award in 2019.