Biomaterial Interfaces
Room 117 - Session BI1-MoM

Biomolecules and Biophysics at Interfaces

Moderators: Christopher So, Naval Research Laboratory, **Markus Valtiner**, Vienna University of Technology, Austria

8:15am **BI1-MoM-1 Molecular Modeling of Peptide and Protein-Based Materials: Role of Surface and Interface on Structure and Function***, **Yaroslava Yingling**,* North Carolina State University **INVITED**

Borrowing the structure and function of proteins to design novel multifunctional materials offers a potential solution for pressing technological needs and various applications. However, integration of proteins or peptides with synthetic materials requires a deeper understanding of properties and processes at the bio-material interfaces. We use molecular modeling for the detailed examination of proteins or peptides as they interact with material surfaces or interfaces revealing critical insights into binding dynamics, structural changes, orientation shifts, and conformational alterations. These molecular interactions are key to engineering materials that are not only stable and biocompatible but also capable of retaining specific biological functions. We specifically examine the interaction of proteins and peptides with heterogeneous material interfaces, such as graphene oxide and silica, elucidating how these interactions impact the protein structure. We also incorporated functional peptides into supramolecular structures, such as micelles, that would mimic protein functions from natural metalloproteins and phosphate-binding functionalities and explore the role of core-corona interface by altering the chemical nature of the core on the retention of protein function and structure, the influence of molecular tails on properties and secondary structures, and the adsorption behaviors of phosphate and zinc ions. Overall, we show that atomic-level understanding of the properties and processes at the protein-material interface is crucial for designing advanced materials that enhance functionality and performance across diverse applications.

8:45am **BI1-MoM-3 Crowding Accelerates Molecular Aging in Protein Droplets***, M. Brzezinski, P. Argudo, J. Michels,* Max Planck Institute for Polymer Research, Germany*; **Sapun Parekh**,* University of Texas at Austin

Protein liquid-liquid phase separation (LLPS) is a process in which a homogeneous mixture of proteins in a solvent self-assembles, upon certain stimuli, into a protein-rich and protein-depleted phase. In a simple two-component system, the protein-rich phase is called a protein condensate or droplet phase, and the protein-depleted phase is the continuous phase. Recent work has shown that many intrinsically disordered proteins (IDPs) undergo two-component phase separation in vitro due to a myriad of weak interactions. LLPS can be further enhanced by crowding agents. Crowders help to tune effective volume fractions to more “convenient” ratios, which results in a broader window of suitable parameters for obtaining phase separation. Moreover, with use of crowding agents, LLPS has been shown to occur not only for IDPs, but also for folded proteins. So, how do crowding agents affect LLPS of proteins? Depending on the affinity of the crowder for the protein, segregative and associative phase separation can be distinguished. In the following work, we present a systematic approach to quantifying LLPS influenced by crowding agents for an IDP and folded protein. We use fluorescence recovery after photobleaching (FRAP) to quantify material properties and coherent anti-Stokes Raman spectroscopy (CARS) to quantify molecular composition and secondary structure, and theory to demonstrate molecular aging in crowded condensates. We find that crowding accelerates aging in condensates and that folded proteins can phase separate and show molecular aging as well. These results have implication for studying transitions from condensates to fibrils over time.

9:00am **BI1-MoM-4 Self-Healing Nanotubes Consisting of Cyclic Peptides Conjugated by Azobenzene Derivatives***, **Olufolasade Atoyebi**, M. Beasley, W. Maza, M. Thum, C. Pyles, S. Tuck, A. Dunkelberger, M. Kolel-Veetil, K. Fears,* US Naval Research Laboratory

Cyclic peptides are capable of self-assembling into supramolecular peptide nanotube structures, via hydrogen bonding along the backbone of the peptide rings. Research from our lab has improved upon the synthesis of the self-assembled peptide nanotubes by covalently linking the cyclic peptides into a linear polymer chain that transitions from the unfolded structure to the peptide nanotube by varying the pH of the solution. Here we present an alternate way to control the self-assembly from the linear polymer chain to the rigid peptide nanotube via photo-isomerization. We capitalize on azobenzene’s photo-actuable nature using a di-carboxylic acid azobenzene to covalently crosslink the cyclic peptide rings (KVVKVV) via the two primary amines displayed by each ring. When the azobenzene crosslinker is in its thermally-relaxed, *trans* conformation, the cyclic peptide polymer adopts a rigid, nanotube conformation. When excited by UV light (320 nm), the *trans* to *cis* transition of the azobenzene crosslinker disrupts hydrogen bonding between adjacent rings, causing the polymer to unfold. Atomic force microscopy (AFM) shows that the polymer chain re-fold into rigid nanotube when the azobenzene crosslinkers return to the trans conformation, either by stimulation by visible light (420 nm) or thermal relaxation. This work introduces a novel class of intrinsically self-healing nanomaterials that can be used as reinforcement agents for a wide variety of industrial and biological materials.

9:15am **BI1-MoM-5 Anti-Biofouling Polymer Coatings with Statistical Amphiphilicity and Improved Environmental Sustainability***, **Rong Yang**[1],* Cornell University **INVITED**

Biofouling caused by bacterial biofilms is found in nearly every ecosystem on earth, ranging from ship hulls to membranes for separations and to bioimplants and live tissues (e.g., auditory bullae). It drives up energy consumption and causes dangerous infections. The need for economical, safe, and environmentally sustainable anti-biofouling coatings has motivated our recent investigations into a new class of copolymers with statistical amphiphilicity, demonstrating exceptional biofouling deterrence. Such amphiphilic copolymers simultaneously present hydrophilic and hydrophobic moieties mixed at a molecular level. As such, they are uniquely positioned to reduce biofouling at the air-liquid-solid three-phase interface, where bacterial biofilms are rampant via facile side-chain reorientation. However, their synthesis has challenged common solution-based techniques due to the need for a common solvent for the precursors that present disparate solubility. To overcome that challenge, my group has leveraged an all-dry polymer synthesis technique, namely initiated Chemical Vapor Deposition (iCVD), which has led to several synthesis pathways toward anti-biofouling coatings with statistical amphiphilicity. Our recent effort has focused on improving the environmental sustainability of this class of polymers by replacing the fluorine-bearing hydrophobic side chains with siloxanes or antimicrobial enzymes, which led to improved fouling deterrence. The iCVD method enables polymer synthesis and coating formation in a single step and on virtually any substrate. It has been scaled up to produce functional polymer coatings in a roll-to-roll configuration, pointing to rapid translation of the amphiphilic coatings to reduce the environmental and economic impact of biofouling.

9:45am **BI1-MoM-7 Aqueous Underwater Adhesives Made from Multiple Agricultural Proteins***, **Zachary Lamberty**, C. So,* U.S. Naval Research Laboratory

Underwater adhesion, *i.e.* binding to wet surfaces, is a major challenge for medical adhesives, marine repair, and for the durability of shoreside structures. The majority of industrial and academic solutions utilize hydrophobic solvents or polymers to exclude water from the bond area with the goal of obtaining a dry-like contact.However, many organisms have evolved methods of adhering in adverse underwater environments using water-borne protein adhesives. Not only are aqueous adhesives generally less toxic than their organic counterparts, but the water-soluble precursor components are believed capable of diffusing through interfacial water layers, vastly increasing the true contact area of the bond. Inspired by the tenaciously sticky barnacle, we have designed an aqueous two-part adhesive from common agricultural byproduct proteins. Upon mixing, the protein will denature and aggregate, forming a hydrogel. Overtime these proteins rearrange into β-sheet rich amyloid fibers, lending the material strength and allowing it to remain water-insoluble for long periods. We have previously demonstrated this adhesive system using Bovine Serum Albumin (BSA) proteins, with underwater-deposited bond strengths of 0.6 – 0.8 MPa on metal oxide or polymer substrates. Here I will demonstrate that similar principles can be applied to make underwater adhesives from bovine α-lactalbumin (αLa), an abundant milk protein. αLa adhesives can be deposited underwater like BSA adhesives, with bond strengths of 0.52 - 0.09 MPa on polycarbonate after 1 week aging in artificial sea water. Interestingly, unfolded αLa proteins are stabilized by the denaturant urea, remaining liquid for hours in air but rapidly solidifying when deposited in solution as the denaturant diffuses away. This offers unique advantages, including greatly reduced sag and the ability to densify the material to improve cohesive strength. By understanding and controlling the aggregation and densification process we aim to develop tunable, easily

[1] **BID Early Career Researchers Award**

deployable underwater adhesives made from non-toxic, domestically sourced agricultural proteins.

10:00am **BI1-MoM-8 How Is the Hydrophobic Force Modified by an Oscillation Frequency in Saline Conditions?**, *C. Wagner, P. Stöcher, M. Valtiner,* ***Laura Mears,*** Vienna University of Technology, Austria

Hydrophobic interactions can occur in many biorelevant systems, including hydrophobic side chains as part of many amino acids, drug molecules and surfaces used to support and control the adhesion of cells. Several of Stephanie Allen's works involve such hydrophobic amino acids [1] or surfaces [2] and their characterisation with atomic force microscopy (AFM). In this contribution we set our work on the hydrophobic force in the context of biointerfaces. There have been many investigations over the years regarding the mechanism behind the hydrophobic force and over how long a range it can be felt [3]. We present a detailed set of AFM force measurements of hydrophobic SAM modified surfaces, with varying salt concentration and oscillation frequency (0-2kHz). We observe dynamic changes in the force curve characteristics with both salt concentration and oscillation frequency. The changes lead to a reduction of the average force with increasing applied frequency, while multiple distinct characteristic curves are present and enhanced by certain conditions. We also notice changes in the range of the force away from the surface. Altogether, the results we will present bring new insight into the mechanism of hydrophobic interactions. Further they open the opportunity for discussion of how the addition of oscillations could, perhaps, be used in biorelevant applications to modify the hydrophobic forces directly.

[1] L. Niu, Xi. Chen, S. Allen, and S. J. B. Tendler, *Langmuir*, **2007**, 23, 14, 7443–7446.[2] S. Allen, S.D.A. Connell, X. Chen, J. Davies, M.C. Davies, A.C. Dawkes, C.J. Roberts, S.J.B. Tendler, P.M. Williams, *Journal of Colloid and Interface Science*, **2001**, 242, 2, 470-476.[3] W. A. Ducker and D. Mastropietro, Current Opinion in Colloid & Interface Science, **2016**, 22, 51–58.

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