Biomaterial Interfaces
Room 209 F W - Session BI2-MoM

Biomolecules and Biophysics at Interfaces

Moderators: Kenan Fears, U.S. Naval Research Laboratory, **Markus Valtiner**, Vienna University of Technology, Austria

10:30am **BI2-MoM-10 How Swelling Affects Microscale Wetting and Friction of Soft Interfaces**, ***Jonathan Pham***, University of Cincinnati **INVITED**

Soft materials are found in a host of applications, from adhesives and coatings to natural and synthetic biomaterials. Many of these materials comprise a lightly crosslinked polymer network, which can also be infused with a compatible liquid (i.e., swelling). Swelling offers additional functionality, like molecular transport, lubrication, and control over mechanical properties. However, understanding the behavior of soft and swollen interfaces is an ongoing challenge. For example, when crosslinked solids are sufficiently soft, or the characteristic size scale is small, they display liquid-like characteristics like capillarity, even without an infused liquid. When the networks are swollen, the swelling liquid itself provides true liquid behavior, creating multi-phase situations that are even more complex. Here we will leverage confocal microscopy to show how combinations of solid and liquid characteristics control the wetting on soft, swollen networks. In addition to network elasticity, we demonstrate that surface tension, liquid separation, and osmotic pressure are important considerations. We expand on our findings by developing a route to visualize dynamic contact lines of a dynamic, sliding drop. In addition to wetting, we exploit a combination of confocal microscopy and colloidal probe microscopy to study the effects of swelling on microscale friction. In this situation, creasing occurs, leading to solid-like stick-slip behavior. Creasing is mitigated by swelling, which appears to be a function of the swelling ratios.

11:00am **BI2-MoM-12 Stability of Semi-Conducting Oxides Under Photocatalytic and Hydrogen Evolving Conditions**, *Tatjana Ott, Ruri Lee,* ***Markus Valtiner,*** Technische Universität Wien, Austria

Transparent semiconducting oxides play a critical role in fields ranging from corrosion, electrocatalysis and biocatalysis to the development of artificial leaf systems for solar fuel generation. However, their long-term stability remains a significant challenge, with photocorrosion being a major factor limiting performance. I will demonstrate how we employ an electrochemical flow cell coupled with inductively coupled plasma mass spectrometry (ICP-MS) to enable in situ, time-resolved monitoring of zinc release from zinc oxide (ZnO) single crystals under UV irradiation. This approach provides direct insights into the degradation pathways of ZnO, a key material in photoelectrochemical systems, including those inspired by natural photosynthesis.

We investigate the dissolution behavior of ZnO with (0001) and (10$\bar{1}$0) crystal orientations across a range of acidic and alkaline pH levels, examining potential-dependent dissolution under both oxygen and hydrogen evolution conditions. Our results highlight the significant influence of UV light and electrolyte pH on stability, closely linked to the intrinsic surface chemistry of ZnO. Notably, the polar ZnO(0001) orientation demonstrates superior stability at low potentials and under hydrogen evolution conditions. In contrast, non-polar ZnO(10$\bar{1}$0) exhibits higher dissolution rates, limiting its suitability for long-term water splitting and biocatalytic processes. It also highligths its role in corrosive processes where hydrogen can penetrate into materials leading to embrittlement.[1]

These findings underscore the critical role of surface structure and chemical stabilization in enhancing the durability of semiconducting oxides for materials stable against hydrogen permeation and next-generation energy conversion technologies. By optimizing surface design and understanding fundamental degradation mechanisms, it is possible to develop more resilient electroactive materials. I will discuss how the approach can be extended to other materials.

Reference.

[1] Dworschak et al. in ACS Appl Mater Interfaces, 2020 Nov 9;12(46):51530–51536. doi: 10.1021/acsami.0c15508 [https://doi.org/10.1021/acsami.0c15508]

[2] Ott et al. submitted

11:15am **BI2-MoM-13 PFAS-Protein Interactions: Effects of Perfluorooctanoate on the Structure and Function of Cytochrome C**, ***William Maza,*** US Naval Research Laboratory

The unique chemical nature of perfluoroalkyl substances (PFAS) renders it resistant to common metabolic processes. Consequently, the resulting bioaccumulation of FPAS has been implicated in long-term health risks associated with liver, kidney, and thyroid disease, increased cholesterol (hypertension and heart disease), disruption of reproductive function, and disruption of the immune response to name a few. However, the cytotoxic effects of PFAS in human organs is still poorly understood. Recent evidence points to increased levels of reactive oxygen species (ROS) as a primary source of cytotoxicity. The cause of the observed increase in ROS has to be established. To better understand the potential disruption of cellular respiration by PFAS we examine the effect of PFAS on the structure and function of the heme-containing electron carrier cytochrome c (Cc). We observe that in the presence of perfluorooctanoate (PFOA) Cc undergoes significant structural changes up to 2mM PFOA. These PFAS-induced conformational change include disruption of the putative MET80-heme charge transfer absorption band and increase in the Trp59 fluorescence indicating disruption of the Cc tertiary structure and at least partial exposure of the active site to water. The disruption of the heme coordination and tertiary structure of the Cc induces a significant change in the electrochemical redox potential of the active-site heme group which likely results in short circuiting its function as an electron shuttle between cyctochrome C reductase and cytochrome C oxidase in the electron transfer pathway. This likely results in downstream disruption of respiratory process and buildup of ROS.

11:30am **BI2-MoM-14 Confirmation of Jarzynski's Equality Based on Single Molecular and Macroscopic Interaction Force Measurements**, ***Iago Peters***, *Markus Valtiner,* TU Wien, Austria

Knowledge about the free energy landscape of biomolecular reactions is necessary to understand how life works on the smallest scale. Unfortunately, obtaining experimental values of the free energy difference between two states like an unbound and a bound state of two molecules is rather difficult. [1] Jarzynski proposed an equality that connects the free energy difference between two states with the irreversible work that leads from one state to the other. Precisely, an average of all possible realizations of a process that moves the system from an equilibrium state to another state in equilibrium. Here, we test this hypothesis with experimental values. Using a simple model system, different nucleobase-pair interactions are measured using three different techniques that are able to measure the interactions force between two single molecules and up to 10^7 interactions in a single experiment run. Using the Atomic Force Microscope (AFM), Optical Tweezers and the Surface Force Apparatus allows us to additionally investigate the scaling of biological single molecule interactions. Together with molecular dynamics simulations a strong foundation is laid to confirm Jarzynski's equality and investigate the scaling of single-molecule interactions with a model system that is simplistic and biologically significant.

[1] 1. Gore J, Ritort F, Bustamante C. Bias and error in estimates of equilibrium free-energy differences from nonequilibrium measurements [Internet]. Vol. 100, Proceedings of the National Academy of Sciences. Proceedings of the National Academy of Sciences; 2003. p. 12564–9.

Corresponding/Presenting Author:Iago Peters, peters@iap.tuwien.ac.at

11:45am **BI2-MoM-15 Influence of Surface Structural and Electronic Properties on Antibacterial Action of Nano- and Microcrystalline Fe:ZnO**, ***Yuri M. Strzhemechny***, *John H. Brannon, Dustin A. Johnson, Tiffany Y. McHenry, Devansh Kalluholematham,* Texas Christian University*; Rachel E. Cuth,* Kutztown University*; Kevin Srun,* James Martin High School

Antibacterial action of nano- and microcrystalline ZnO has been well established, although the fundamental mechanisms driving such cytotoxicity is still debated. In our recent works we suggested a model for an antibacterial action of ZnO via surface defect-mediated dissolution. To further validate our model, we perform surface/subsurface modification of hydrothermally grown ZnO nano- and microparticles in order to modulate their antibacterial efficacy. It appears that the instability of the ZnO in antibacterial assays results from the defect-rich reconstruction of polar surfaces with strong intrinsic dipole moment within the wurtzite lattice. In theory, Fe doping of ZnO may suppress this dipole and stabilize the free surface while preserving the wurtzite lattice. Importantly, iron ions are beneficial species for bacteria and thus do not change the cytotoxicity of the assay. We modify the hydrothermal synthesis protocol to obtain Fe:ZnO micro- and nanoparticles with controllable doping concentrations. We

perform systematic optoelectronic and physicochemical characterization of our particles before and after their interaction with bacteria in different growth media to verify both the surface stability of our ZnO specimens and the effects on the antibacterial action.

12:00pm **BI2-MoM-16 Molecular Insights into the Influence of Tail Architecture on Self-Assembly of Peptide-Polymer Amphiphile***, **Sabila Kader Pinky,*** North Carolina State University*; Benjamin Allen, Abigail Knight,* University of North Carolina at Chapel Hill*; Yaroslava Yingling,* North Carolina State University

Peptide-polymer amphiphiles (PPAs) combine functional peptides with a hydrophobic tail that drives self-assembly in aqueous environment. Their ability to form well-defined nanostructures with tunable physical properties makes them ideal candidates for a wide range of applications. However, predicting and tuning these features remains challenging due to the complex interplay of molecular interactions. Here, we systematically investigated the self-assembly of a random coil peptide (XTEN2)-based PPAs by varying the side chains of alkyl acrylate tail (ethyl, n-butyl, tert-butyl, hexyl, and cyclohexyl). We used all-atom molecular dynamics (AMD) simulations to examine how molecular interactions influence the formation, structure, and stability of micellar assemblies. The simulations reveal the formation of a range of core morphologies, including worm-like, perforated, spherical, and multi-core structures. Our findings indicate that the balance between tail-to-tail versus tail-to-water non-bonded interactions primarily determines the micellar morphology. Additionally, the extent of core hydration also impacts the structural stability. Furthermore, the comparison between experimentally obtained particle sizes and simulation-obtained particle sizes supports the accuracy of our computational approach in replicating real particle sizes and indicates that the models accurately capture the size characteristics of these self-assembled structures. We anticipate that the insight from this study will collectively provide a comprehensive understanding of how molecular properties and interactions drive the self-assembly and structural diversity of PPAs, offering insights into designing nanostructures with tailored morphologies for specific applications.

Author Index

Bold page numbers indicate presenter