# Schedule for the 19<sup>th</sup> MASM: The Mid-Atlantic Soft Matter Workshop The University of Maryland, College Park, MD

February 2, 2018

#### 8:45 am

**Opening Remarks** 

#### 8:50 am

Kristi Kiick (University of Delaware): Biopolymer Conjugates for the Production of Responsive Biomaterials

#### 9:30 am

Soundbite Session I

### 10:30 am

Coffee Break

# 10:50 am

Peter Basser (NIH): Cartilage as a composite medium

#### 11:30 am

Soundbite Session II

#### 12:20 pm

Lunch

#### 1:30 pm

Soundbite Session III

# 2:20 pm

Coffee Break

#### 2:40 pm

Robert Carpick (University of Pennsylvania): Applying Novel Nano-Rheology Methods to Understand Hydrogel Contact Mechanics

#### 3:20 pm

Soundbite Session IV

#### 4:10 pm

Coffee Break

#### 4:25 pm

Chris Li (Drexel University): Interface-directed crystallization and nonclassical crystallography

# 5:05 pm

Liangbing Hu (University of Maryland): Nanocellulose for Nanotechnologies

# 5:45 pm

End of Meeting

Peter Basser, National Institutes of Health

Cartilage as a composite medium

TBA

#### Robert Carpick, The University of Pennsylvania

Applying Novel Nano-Rheology Methods to Understand Hydrogel Contact Mechanics

Measuring the mechanical and tribological (i.e., contact, friction, adhesion, and wear) properties of soft materials at small scales presents unique challenges due to the large deformations and complex mechanical response that soft materials often exhibit. We developed a set of magnetic force-based direct drive modulation atomic force microscopy (AFM)-based methods to measure local nano-rheological properties of soft material across a broad frequency range (10 Hz - 2 kHz) [1,2,3]. The direct drive approach enables artefact-free measurements over several decades of excitation frequency in either torsional or flexural (normal) deformation modes, and eliminates hydrodynamic drag effects that otherwise inhibit dynamic mechanical measurements conducted in liquid environments which are often desired for soft material studies. The bandwidth can be further expanded to lower effective frequencies (0.1 Hz 10 Hz) by acquiring conventional force-displacement (FD) curves.

We then apply this approach to study polyacrylamide hydrogels [3]. Polymeric hydrogels are one of the most widely used soft materials in biomedical devices, sensing platforms, and cartilage tribology, among other applications. The optimum functionality of a hydrogel in a specific application strongly depends on appropriate mechanical, rheological, and tribological properties. Using colloid-attached atomic force microscope (AFM) probes in liquid, we observe that slow FD measurements showed a recoverable but highly hysteretic response to mechanical contact. Furthermore, the contact mechanical behavior depended on the loading approach curves showed non-adhesive Hertzian behavior, direction: while retraction curves fit the Johnson-Kendall Roberts (JKR) adhesive contact mechanics model well into the tensile regime, after which multiple stochastic detachment instabilities occurred. Using small amplitude direct drive modulation to explore higher strain rates, the load dependence of the storage stiffness transitioned from Hertzian to a dynamic punch-type (constant contact area) model, indicating significant influence of material dissipation coupled with adhesion. The results suggest a transition in the contact mechanical behavior for hydrogels, especially when the applied strain rates and the material relaxation rates become comparable.

- 1 Gosvami, N.N., Nalam, P.C., Exarhos, A.L., Tam, Q.Z., Kikkawa, J.M. and Carpick, R.W. Direct Torsional Actuation of Microcantilevers Using Magnetic Excitation. Appl. Phys. Lett. 105, 093101 (2014).
- 2 Krass, M.-D., Gosvami, N.N., Carpick, R.W., Mser, M.H. and Bennewitz, R. Dynamic Shear Force Microscopy of Viscosity in Nanometer-Confined Hexadecane Layers. J. Phys., Condens. Matter. 28, 134004 (2016).
- 3 Nalam, P. C., N. N. Gosvami, M. A. Caporizzo, R. J. Composto and R. W. Carpick (2015), Nano-Rheology of Hydrogels Using Direct Drive Force Modulation Atomic Force Microscopy, Soft Matter 11, 8165 (2015)

## Liangbing Hi, University of Maryland Nanocellulose for Nanotechnologies

One dimensional (1D) nanocellulose (NC) biopolymers provide the backbone of a large portion of the natural world. Produced by plants and bacteria, NC is the most available renewable nanomaterial on earth and one of the least expensive to access and utilize. Plant photosynthesis produces NC, with  $\sim 30-40$  wt.% of as ordered cellulose nanofibers (CNF) or nanocrystals (CNC, the crystalline part of CNF). The strong intra- and inter-chain hydrogen bonding leads to outstanding mechanical properties including a high Youngs modulus ( $\sim 200$  GPa) and tensile strength (3-6 GPa) in cellulose nanofibers that exceeds steel wires, multi-walled carbon nanotubes and synthetic Kevlar fibers. Due to these exceptional properties, wood-based cellulose nanofibers have attracted tremendous interest as a sustainable nanomaterial. If utilized efficiently, the global shortage of petroleum-based raw materials could be resolved. I will discuss assembly and functionalization strategies aimed at specific properties, with an eve toward high impact applications including energy, electronics, building materials and water treatment.

(1) Nanomanufacturing and light management in transparent nanopaper for optoelectronics (as a replacement of plastics);

(2) Thermal, optical and mechanical properties of nanostructured wood for building efficiency (transparent wood as a replacement of glass, thermal insulating nanowood);

(3) Mechanical properties of densely packed nanocellulose for lightweight structural materials (replacement of steel);

(4) Fluidicsand nanofluidics of aligned cellulose nanofiber framework for water treatment, ionic thermoelectrics and energy conversion devices;

(5) Artificial tree for high-performance water desalination and solar steam generations;

(6) Mesoporous, three-dimensional carbon derived from wood for advanced batteries (replacement of metal current collectors for beyond Li-ion batteries).

# **Kristi Kiick** , University of Delaware Biopolymer Conjugates for the Production of Responsive Biomaterials

Macromolecular structures that are capable of selectively and efficiently engaging cellular targets offer important approaches for mediating biological events and in the development of hybrid materials. We have employed a combination of biosynthetic tools, bioconjugation strategies, and biomimetic assembly in the design of multiple types of biopolymer conjugates. PEG-biopolymer conjugates have been used in the formation of hydrogels by covalent click-based chemistries that are selectively degradable under pathological conditions. These materials can be designed to control the release of both small-molecule and macromolecular cargo with tuned release profiles, and materials with select mechanical properties have demonstrated promise for healing vascular graft materials in vivo. The incorporation of (poly)peptides affords materials that not only show controllable micro- and nanoscale morphologies, but that also have promise for targeting drug delivery to damaged tissue.

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# **Christopher Li**, Drexel University Interface-directed crystallization and nonclassical crystallography

Crystallization is ubiquitous in nature and semicrystalline polymers are of crucial importance in our daily life. Compared with small molecules, polymers crystallize via a more complex pathway because of their long chain nature and various metastable states associated with polymer crystals. In this talk, I will show that this complex conformational change of polymer chains upon crystallization can be employed to design and fabricate functional nanomaterials. We will focus on crystallization directed by liquid/liquid interface. Not only can this type of dynamic interface direct the crystallization pathway, it can also alter chain packing in the final crystals, leading to intriguing macroscopic properties. In particular, curved interface, which is incommensurate with the classical translation symmetry, frustrates chain packing, and induced defect formation, a topic that will be discussed in the context of recently reported spherical crystallography.