



2018 APS/CNM
USERS MEETING

GENERAL SESSION ABSTRACTS

APS PLENARY**The APS Upgrade Accelerator Design and Performance****Glenn Decker, APS-U**

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The APS Upgrade project will involve a complete replacement of the APS storage ring and will result in unprecedented brightness and coherence for a hard x-ray storage ring light source as a consequence of reducing the effective emittance by a factor of more than 70 from 3260 pm-rad at a 7 GeV operating energy to 42 pm-rad at a 6-GeV operating energy. In addition, the total stored beam current will increase from 100 to 200 mA, providing an overall brightness increase of more than two orders of magnitude at hard x-ray energies. The project has completed the R&D and preliminary design and is embarking upon the final design and early procurement phase. A full complement of insertion devices are planned, optimized for the 6 GeV beam energy and specific beamline requirements. This talk will give an overview of the machine design and performance parameters, including brightness, operation modes, and beam stability.

APS PLENARY**Characterizing Disordered Protein Ensembles Using Small-angle Scattering****Joshua A. Riback¹, Micayla A. Bowman², Adam Zmyslowski³, Catherine R. Knoverek², John M. Jumper^{3,4}, James Hinshaw⁴, Emily B. Kaye², Karl F. Freed⁴, Patricia L. Clark², and Tobin R. Sosnick^{3,5}**¹ Graduate Program in Biophysical Sciences, University of Chicago, Chicago, IL 60637² Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556³ Department of Biochemistry and Molecular Biology, University of Chicago, Chicago, IL 60637⁴ Department of Chemistry, University of Chicago, Chicago, IL 60637⁵ Institute for Biophysical Dynamics, University of Chicago, Chicago, IL 60637

A significant fraction of the proteome is intrinsically disordered, and even well-folded proteins adopt non-native geometries during their synthesis, folding, transport, and turnover. The characterization of intrinsically disordered proteins (IDPs) is challenging, in part due to the lack of accurate physical models and difficulties interpreting results from experimental techniques including small-angle x-ray scattering (SAXS) and Förster resonance energy transfer (FRET). We have developed a general method to extract the dimensions of IDPs and their self-interactions (solvent quality) from a single SAXS measurement. We apply this procedure to a variety of IDPs, finding that even those IDPs with relatively low net charge

and high hydrophobicity are highly expanded in water, contrary to general expectation that such sequences are collapsed in water. Our results suggest that the unfolded state of most foldable sequences is expanded; a property we conjecture was selected by evolution to minimize misfolding and aggregation.

APS PLENARY**Mapping the Brain with X-ray Microtomography****Eva Dyer**

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Methods for resolving the three-dimensional (3D) microstructure of the brain typically start by thinly slicing and staining the brain, followed by imaging numerous individual sections with visible light photons or electrons. In contrast, x-rays can be used to image thick samples, providing a rapid approach for producing large 3D brain maps without sectioning. In this talk, I will describe my lab's efforts in developing computational methods to create mesoscale maps of the brain with synchrotron x-ray microtomography (μ CT). Our results demonstrate that x-ray tomography achieves rapid quantification of large brain volumes, complementing other brain mapping and connectomics efforts.

APS PLENARY**Polymer-induced Structural Changes in Suspensions of Gold Nanorods****Ryan Poling-Skutvik, Ramanan Krishnamoorti, and Jacinta C. Conrad**

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Open, porous materials with controlled nanoscale structures can exhibit substantially improved mechanical and electrical properties while remaining lightweight. Production of these materials, however, is usually challenging and costly. Here, we use polymer-induced depletion interactions to assemble gold nanorods (AuNRs) in a bulk solution process into fractal structures with controllable interparticle spacing and fractal dimension. Depletion attractions arise in solutions because dissolved polymer chains are entropically excluded from a layer near the nanorod surface. To increase the free volume available to the polymer chains, the colloids aggregate to overlap their depletion layers. Although depletion forces are well understood for large spherical colloidal particles, how they drive the assembly of anisotropic particles in the "protein limit" where the particles are small in comparison to the polymer coils is poorly understood. Dispersing AuNRs grafted with polymer chains in solutions of high molecular weight poly(ethylene oxide) (PEO), we elucidate

the physics underlying depletion interactions in the “protein limit” and exploit these physics to generate fractal structures with controlled nanoscale structures. Using small-angle x-ray scattering, we quantify the changes in aggregate morphology as a function of depletant size and concentration. The depletion force increases monotonically with PEO concentration to compress the grafted layers and drive the gold nanorods closer. Surprisingly, however, the fractal dimension and number of nearest neighbors in the aggregates change non-monotonically with PEO concentration, exhibiting maximums at intermediate PEO concentrations. These structural changes suggest that the aggregation process is reaction limited (RLA) at low PEO concentration and diffusion limited (DLA) at high PEO concentration. In contrast to the depletion-induced aggregation of large colloids, the transition between RLA and DLA for the AuNRs is independent of polymer molecular weight and bulk solution viscosity, which we attribute to the small size of the AuNRs. This independent control between aggregate morphology and solution properties as well as the bulk solution process opens the door to cheap, facile synthesis of materials with controlled and tunable nanoscale properties.

APS PLENARY

Probing the Valence State of Fe in Mantle Mg-silicate Perovskite with Synchrotron X-ray

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Iron is the most abundant transition metal ion in the Earth’s mantle. Although the lower mantle has reducing conditions close to the equilibrium of $2\text{FeO} = 2\text{Fe} + \text{O}_2$, studies have shown that Fe has a mixed valence (+2: +3 = 50:50) in the most abundant mineral (bridgmanite, in orthorhombic perovskite structure) in the region. Such observations have been explained by the charge disproportionation of Fe, 3Fe^{2+} (bridgmanite) = 2Fe^{3+} (bridgmanite) + Fe^0 (metal), which does not require oxidizing conditions but is likely

driven by pressure effects. The charge disproportionation has many important implications, such as possible existence of Fe metal and the redox reactions in the lower mantle. However, most experiments have been conducted at lower pressures and the existing high-pressure data do not agree with each other. We have conducted a series of measurements on the valence state of Fe in bridgmanite at high pressures by combining laser-heated diamond-anvil cell with Mossbauer spectroscopy (sector 3) and x-ray diffraction (sectors 13 and 16). While our experiment found that 50% of Fe in bridgmanite is Fe^{3+} as found previously, Fe becomes dominantly Fe^{2+} in bridgmanite synthesized at 40–70 GPa and 2,000 K. Little Fe^{3+} in bridgmanite combined with the strong partitioning of Fe^{2+} into ferropericlase will alter the Fe content for these minerals at 1100- to 1700-km depths in the mid mantle. Our experiments support no significant changes in bulk composition for most of the mantle, but possible changes in physical properties and processes (such as viscosity and mantle flow patterns) in the mid mantle where some important structural changes have been proposed in seismic imaging studies in recent years.

CNM PLENARY

Quantum Materials: Insights from Infrared Nano-optics

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Light trapped at the nanoscale, deep below the optical wavelength, exhibits an increase in the associated electric-field strength, which results in enhanced light-matter interaction. This leads to strong nonlinearities, large photonic forces, and enhanced emission/absorption probabilities. Thus, compact nano-scale light offers outsized opportunities for exploring, controlling and creating novel physical phenomena [1]. I will discuss recent developments in infrared nano-optics of two classes of quantum materials: transition metal oxides and graphene. The nano-scale inquiry into the correlated oxides revealed rich nano-textures of coexisting metallic and insulating regions in the vicinity of the first-order insulator to metal transition [2]. Nano-infrared images of plasmon polaritonic waves [3,4] in graphene have uncovered novel aspects of electronic interactions in the Dirac electronic liquid.

[1] D.N. Basov, R.D. Averitt, and D. Hsieh (2017). “Towards properties on demand in quantum materials.” *Nature Materials* **16**: 1077.

[2] A.S. McLeod, E. van Heumen, J.G. Ramirez, S. Wang, T. Saerbeck, S. Guenon, M. Goldflam, L. Anderegg, P. Kelly, A. Mueller, M. Liu, Ivan K. Schuller, and D.N. Basov (2017). “Nanotextured phase coexistence in the correlated insulator V_2O_3 .” *Nature Physics* **13**: 80.

[3] D.N. Basov, M.M. Fogler, and F.J. Garcia de Abajo (2016). “Polaritons in van der Waals materials.” *Science* **354**: 195.

- [4] G.X. Ni, A.S. McLeod, Z. Sun, L. Wang, L. Xiong, K.W. Post, S.S. Sunku, B.-Y. Jiang, J. Hone, C.R. Dean, M.M. Fogler, and D.N. Basov (2018). "Fundamental limits to graphene plasmonics." *Nature* (in press).

CNM PLENARY

Active and Selective Designer Catalysts from First-principles

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Using a combination of first-principles calculations, microkinetic modeling, and reactivity experiments, we establish a rigorous framework for developing a fundamental mechanistic understanding of chemical reactions catalyzed by heterogeneous catalysts. First, and through an iterative process between these three components of our research, we demonstrate unique insights derived on the nature of the active site. Then, based on that understanding, and insights derived for the importance of atomic-scale structure sensitivity, we show how we can provide guidance to inorganic synthesis for preparing alloys, which are predicted to hold promise for improved activity and selectivity for the reactions of interest.

CNM PLENARY

Self-assembled van der Waals Heterostructures of 2D Materials and Organic Molecules

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Hybrid van der Waals (vdW) heterostructures composed of two-dimensional (2D) layered materials and self-assembled organic molecules are promising systems for electronic and optoelectronic applications with enhanced properties and performance. Control of molecular assembly is therefore paramount to fundamentally understand the nucleation, ordering, alignment, and electronic interaction of organic molecules with 2D materials. In this presentation, the self-assembly of organic molecules on the surfaces of 2D graphene and WSe_2 and their characterization by scanning tunneling microscopy (STM) are described. These systems are governed by a balance of adsorbate-adsorbate and adsorbate-substrate interactions. On the surface of epitaxial graphene, planar polycyclic aromatic molecules form well-ordered monolayers with geometries that depend on the number and orientation of hydrogen bonds between neighboring molecules. On the surface of WSe_2 , highly ordered monolayers of C60 molecules have a periodic 2×2 superstructure where the molecules exhibit four distinct molecular appearances. Using vdW-corrected *ab initio* density functional theory (DFT) simulations,

we determine the interplay of vdW and Coulomb interactions that govern the rotational arrangements of C60 molecules in the superstructure and identify the charge redistribution that links the molecule units in a long-range network. These results show the pathway towards engineering aligned hybrid vdW heterostructures with 2D layered materials.

CNM PLENARY

Material Dimensionality Effects on Electron Transfer Rates between $CsPbBr_3$ and CdSe Nanoparticles

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Recent advances in nanoparticle synthesis present opportunities to select not just the size and composition of a nanoparticle in a given application, but also the morphology and dimensionality. However, while extensive studies have led to an understanding of how electron transfer rates scale with nanoparticle size, analogous studies relating rates of electron transfer to nanoparticle dimensionality are lacking. In this work, we study electronic interactions between $CsPbBr_3$ and CdSe nanoparticles as a function of material dimensionality using broadband transient absorption and streak camera-detected transient photoluminescence, both available at the CNM. Films containing mixtures of zero- and/or two-dimensional nanostructures (quantum dots and/or nanoplatelets) with constant driving force and nanoparticle separation, achieved via the use of isoenergetic nanoparticles and identical capping ligands, were prepared in order to isolate the impact of dimensionality on electronic interactions. Electron transfer from $CsPbBr_3$ to CdSe was observed in all of the mixtures, regardless of particle dimensionality, and characterized via static and time-resolved photoluminescence and transient absorption spectroscopies. Rates of electron transfer for different combinations of dimensionalities in dilute and concentrated films reveal that dimensionality does, in fact, impact rates of electron transfer. This novel insight into how dimensionality affects exciton dynamics has implications in the design of photocatalysts and optoelectronic or photovoltaic devices, as the appropriate selection of nanoparticle dimension can potentially boost device efficiencies.