

NIST CHAPTER OF SIGMA XI

23rd ANNUAL POSTDOC POSTER PRESENTATION

PROGRAM AND ABSTRACT BOOKLET

**Friday February 19th, 2016
NIST Gaithersburg Campus
Administration Building (101)
Front Hallway (formerly the Hall of Flags)
and Lecture Rooms A & B**

Morning Session (9:00 am to 12:00 pm)

Engineering	Page 2
Materials	Page 7
Physics	Page 18

Lunch (12:00 pm to 1:00 pm)

Afternoon Session (1:00 pm to 4:00 pm)

Biology	Page 24
Biotechnology	Page 30
Chemistry	Page 35
Polymers	Page 44
Materials 2	Page 49

**2016 AWARD CERMONY
Monday March 7th, 2016 at 2:30 pm
NIST Gaithersburg Campus
Administration Building (101)
Portrait Room**

SESSION I (9:00 am to 12:00 pm)

ENGINEERING CATEGORY

E1: Low Frequency vibration energy harvesting using diamagnetically stabilized magnet levitation

Position 14

Sri Vikram Palagummi and Fuh-Gwo Yuan

Over the last decade, vibration-based energy harvesting has provided a technology push on the possibility of self-powered portable small electronic devices and wireless sensor nodes. Vibration energy harvesters, in general, transduce energy by damping out the environmentally induced relative motion in a cantilever beam or an equivalent suspension mechanism by coupling them with either a piezoelectric, electrostatic, electromagnetic or magnetostrictive transduction mechanism. Two major challenges face the present harvesters in literature, one, they suffer from the unavoidable mechanical damping due to internal friction present in the mechanical systems, second, they cannot operate efficiently in the low frequency range (< 10 Hz), when most of the ambient vibrational energy is in this low frequency range. Two passive and friction free diamagnetically stabilized magnet levitation mechanisms are investigated in this work to address these challenges.

First, detailed theoretical modelling techniques are presented to validate the frequency response characteristics of the magnetic levitation setups. After this validation, key parametric studies on the different components of the mechanisms were carried out to quantify their influence on stability, size and frequency characteristics of the system. For vibration energy harvesting using these mechanisms, copper coil geometries for transduction and eddy current damping due to the conductivity of the diamagnetic material were critically discussed. Based on the analysis, efficient experimental systems were setup which showed up to an average system efficiency of 25.8% when base excited with a sinusoidal frequency of 1.9 Hz and a root mean square acceleration of 0.0546 m/s^2 . This is an improvement to the state of the art in the field when considering very low frequency (< 5 Hz) by an order of magnitude. Finally, a bi-stable magnetic levitation system is also investigated to take advantage of the broad bandwidth frequency response inherent in a bi-stable nonlinear system.

E2: High-Q plasmonic cup resonator at visible wavelengths

Position 19

Wenqi Zhu, Ting Xu, Amit Agrawal, and Henri J. Lezec

The detection limit of an optical sensor is determined by the Purcell factor which relates the quality factor (Q) of an optical cavity to its mode volume (V) through the ratio Q/V . Plasmonic sensors benefit from ultra-small mode volumes, owing to tight confinement of the electromagnetic field at a metal-dielectric interface. However, optical losses inherent in metals have limited the Q values in conventional plasmonic resonators to ≈ 10 . Here, we report a plasmonic cup resonator with Q values up to ≈ 231 at visible wavelengths. The high-Q plasmonic cup resonator consists of two vertical Ag sidewalls (thicknesses of 230 nm) placed orthogonal to a planar Ag film (thickness of 180 nm) to form a two-dimensional Fabry-Perot cavity. This structure is fabricated using the template-stripping method, which benefit the high Q-factors in two aspects: firstly, low propagation loss for propagating surface plasmons can be achieved on the ultra-smooth template-stripped Ag films; and secondly, up to $3 \mu\text{m}$ tall smooth Ag-sidewalls with tapering angles of less than 2° , enabled by the deep dry-etched silicon template, can be achieved. Such tall and vertical sidewalls provide high reflectivity for the propagating surface plasmons. To characterize the Q-values of the plasmonic resonance supported by these cavities, we mill an ultra-narrow slit (width of ≈ 20 nm, depth of ≈ 150 nm) from the bottom of the cup structure, and measure the transmission under white-light illumination. This coupling slit is not milled through the planar Ag film, such that the out-scattering of the surface plasmons resident in the cup is minimized but still detectable. For a cup resonator with width of $2 \mu\text{m}$, resonance linewidth of 2.9 nm is achieved at a wavelength of 670 nm, corresponding to a Q-factor of 231. To our knowledge, this is the largest Q-value achieved from a plasmonic structure in a transmission configuration. Finally, we demonstrate that the plasmonic cup resonator is able to detect thin Al_2O_3 layers (deposited using atomic layer deposition) with thickness down to 0.8 nm, corresponding to a refractive index sensitivity of 714 RIU-1 for the resonance at the wavelength of 670 nm. Considering the narrow linewidth of the resonance, a figure-of-merit (FOM, defined as the refractive index sensitivity over the resonance linewidth) of 246 is achieved for this optical index sensor. We believe that this plasmonic cup resonator could serve as an ultrasensitive and integration-friendly platform for single-particle/molecule detection for applications in biosensing.

E3: Model-based estimation and control of laser powder bed fusion processes

Position 25

Felipe Lopez, Paul Witherell, and Brandon Lane

The adoption of additive manufacturing (AM) is being hindered by the inadequate quality obtained in some applications. In the case of metals, the quality of an AM-produced component can be linked to its thermal history during the build. In spite of its importance, current systems do not control thermal history directly, but instead use constant pre-computed processing conditions. Such control systems lack robustness in the presence of thermal perturbations, which often appear as a result of overhanging structures, track-to-track and layer-to-layer interactions. Some of the reasons for the lack of advanced AM controllers are the need for open-architecture machines for development and testing, sensors for process monitoring, and models developed explicitly for process control. This work describes the development of a stochastic thermal model that relates processing conditions and thermal perturbations to melt pool geometry. In this work, it is hypothesized that by controlling melt pool geometry, thermal history is controlled indirectly and quality is improved. The proposed model is validated by comparison with experiments carried out for Inconel 625. Simulation results show that the proposed estimator is capable of detecting thermal perturbations resulting from building an overhanging structure. Future work includes the implementation of the estimator in an online monitoring system (currently under development), and the development of solidification controllers. In the long term, the real-time control system developed by NIST – constituted by an open-architecture testbed, a thermographic monitoring system, and a process model for estimation and control – will be made available for collaborators to test feedback control approaches and their effects in a wide range of materials and processing conditions.

E4: Data analytics and uncertainty quantification for energy prediction in manufacturing

Position 11

Ronay Ak and Raunak Bhinge

Many industries are applying various methods for optimizing energy use across the manufacturing life cycle. These methods are either physics-based or data-driven. Manufacturing systems generate a vast amount of data from operations and in simulations. Advances in data collection systems and data analytics (DA) tools have enabled the development of predictive analytics for energy prediction. Many of these prediction methods do not account for the uncertainty quantification-UQ (both in data and model). This work addresses the issue of uncertainty quantification in predictive analytics.

This work focuses on metal cutting processes and presents a Neural Network (NN) based regression model to predict the required energy consumption during the manufacturing of a part on a milling machine. The model accounts for the uncertainty associated with both the manufacturing processes parameters, and assumptions in building the prediction model. To achieve this, prediction intervals are estimated instead of point predictions. In order to increase the ability to generalize over new data sets, an ensemble model of neural networks (NNs) is used, and the k-nearest-neighbors (k-nn) approach is applied to identify similar patterns between training and test data sets to increase the accuracy of the results by using local information from the closest patterns of the training sets. Case study results demonstrate consistency and high prediction precision as compared to the individual NNs of the ensembles. Moreover, it is shown that with advanced data collection and processing techniques, one can construct a prediction model to predict the energy consumption of a machine tool for machining a part with multiple operations and process parameters.

E5: Pulsed laser interferometry with sub-picometer resolution using quadrature detection

Position 33

Lei Shao and Jason Gorman

Femtosecond pulsed laser interferometry has been used in a number of important applications. For example, to visualize the propagation of acoustic waves¹, a high-energy pump pulse is used to replicate an impulse to excite elastic waves induced by rapid thermal expansion and then a delay-time controlled low-energy probe pulse is used to measure the displacement by means of interferometry. By continuously varying the delay between the pump and probe, temporal-resolved displacements can be obtained. Other examples of pulsed laser interferometry include time-resolved imaging of surface ablation (e.g., laser cutting)², high-precision long distance ranging (e.g., distance between two satellites^{3,4}, and laser interferometric nondestructive inspection (e.g., electronic packaging)^{5,6}.

Despite of its wide applications, the performance of pulsed laser interferometry in terms of sensitivity and resolution has still not been investigated. More important, there is also huge interest in expanding the capabilities of pulsed laser interferometry for GHz vibrations in a number of important devices such as nanoelectromechanical (NEM) resonators^{7,8}. As a result, in this work, we examine the metrics (sensitivity, resolution, error, ect.) of a pulsed laser interferometer and how the broad and irregular optical spectrum of the pulse affects performance. This is accomplished by demonstrating two-beam interferometry which used both a femtosecond pulsed laser and a CW HeNe laser as the light source in separate occasions. The CW laser is used to align the optics and also functions as a standard baseline to compare the performance of the pulsed laser interferometer.

Here, we experimentally demonstrated pulsed laser interferometry by measuring displacement over micrometer range with triangular wave. We fitted the wavelength used to infer the displacement and found that the wavelength at the peak intensity of the broad optical spectrum of a pulse can be simply used to infer displacements measured by pulsed laser interferometry with high accuracy. Finally, we compared the displacement sensitivity and resolution of a pulsed laser interferometer with a CW laser interferometer and concluded that the difference in their displacement resolutions is only caused by their different optical wavelengths.

1. T. Tachizaki, T. Muroya, O. Matsuda, Y. Sugawara, D. H. Hurley, and O. B. Wright, "Scanning ultrafast Sagnac interferometry for imaging two-dimensional surface wave propagation," *Rev Sci Instrum* 77, 043713 (2006).
2. H. Furutani, H. Fukumura, and H. Masuhara, "Nanosecond time-resolved interferometric study on morphological dynamics of doped poly (methyl methacrylate) film upon laser ablation," *Appl Phys Lett* 65, 3413-3415 (1994).
3. J. Ye, "Absolute measurement of a long, arbitrary distance to less than an optical fringe," *Opt Lett* 29, 1153-1155 (2004).
4. K. N. Joo, Y. Kim, and S. W. Kim, "Distance measurements by combined method based on a femtosecond pulse laser," *Opt Express* 16, 19799-19806 (2008).
5. J. Gong, and I.C. Ume, "Nondestructive Evaluation of Poor-Wetted Lead-Free Solder Bumps in Ball Grid Array Packages Using Laser Ultrasound and Interferometric Technique," *IEEE Trans. Comp. Packag. Manufact. Technol.*, 3, 1301-1309 (2013).
6. C. Ume, J. Gong, R. Ahmad, and A. Valdes, "Laser ultrasonic inspection of solder bumps in flip-chip packages using virtual chip package as reference," *IEEE Trans. Comp. Packag. Manufact. Technol.*, 1, 1739-1746 (2011).
7. N. Liu, F. Giesen, M. Belov, J. Losby, J. Moroz, A. E. Fraser, G. McKinnon, T. J. Clement, V. Sauer, W. K. Hiebert, and M. R. Freeman, "Time-domain control of ultrahigh-frequency nanomechanical systems," *Nat Nanotechnol* 3, 715-719 (2008).
8. A. Bruchhausen, R. Gebs, F. Hudert, D. Isenmann, G. Klatt, A. Bartels, O. Schecker, R. Waitz, A. Erbe, E. Scheer, J. R. Huntzinger, A. Mlayah, and T. Dekorsy, "Subharmonic Resonant Optical Excitation of Confined Acoustic Modes in a Free-Standing Semiconductor Membrane at GHz Frequencies with a High-Repetition-Rate Femtosecond Laser," *Phys Rev Lett* 106, 077401 (2011).

E6: Reconstruction of in-plane vibration mode shapes in MEMS resonators using optical knife-edge and photoelastic measurements

Position 13

Vikrant J. Gokhale and Jason J. Gorman

Micromechanical resonators are commercially used as timing references, signal processing elements and sensors. Much of the success of such resonators stems from their ability to vibrate in a specific resonant mode, with a high mechanical quality factor and hence a sharp spectral linewidth. Contemporary design of micromechanical resonators is heavily reliant on analytical equations and finite element modeling of the device, followed by validation using comprehensive electrical testing. The drawback of purely electrical testing is that it presents only aggregate performance parameters (i.e. the capacitively induced current or the piezoelectrically induced voltage) at the output transduction port of the system, without providing spatially resolved measurements of the device dynamics. Methods such as laser Doppler vibrometry can work in limited scenarios, but are expensive to set up and are generally restricted to out-of-plane displacements. We present a combination of optical knife-edge and photoelastic measurements, both operated in the reflection mode, that allow us to measure dynamic displacement and strain at various points on the resonator respectively. Experimental results are acquired using both methods on a pure silicon bulk acoustic resonator (BAR) vibrating in-plane with a fundamental resonance frequency of 13.6 MHz. Preliminary data suggest that while there is some qualitative agreement between the expected and measured forced-motion mode shapes, there are enough differences to warrant further investigation. Insights into the real mode shape of such devices should lead to better designs. These measurement techniques could also quantitatively evaluate the energy lost through the tethers into the substrate and thus provide a way to optimize for low loss resonator performance. The optical techniques we use are less susceptible to noise than standard electrical characterization, allowing more accurate measurements at lower drive levels and at much higher frequencies.

E7: Preliminary safety analyses on the proposed NIST new reactor using ANL-PARET code

Position 54

Zeyun Wu, Robert Williams, and J. Michael Rowe

In anticipation of the eventual retirement of the research reactor (NBSR) at the National Institute of Standards and Technology (NIST), research efforts are ongoing at NIST Center for Neutron Research (NCNR) to design a new research reactor. The primary purpose of the new reactor is to optimize cold neutron production for scientific neutron scattering experiments. The new design will have at least two high quality cold neutron sources (CNS). The thermal power of the new reactor will be 20 MW and the operating cycle of the equilibrium core is set to be around 30 days. Low enrichment uranium (LEU) fuel - U_3Si_2/Al fuel – with U-235 % by mass less than 20% will be used to comply with nuclear non-proliferation agreements.

In this paper, the preliminary safety analyses are performed on the split core through a transient analysis on a couple of design basis accidents with the emphasis to investigate the thermal-hydraulics (T/H) safety characteristics of the new design during transients. In particular, the hypothetical reactivity insertion accident (RIA) and the loss-of-flow (LOF) accident are analyzed using the system safety analysis code PARET, which was developed by Argonne National Laboratory (ANL). The PARET code is intended primarily for safety analysis of research and test reactors that use plate-type fuel elements, or round fuel pins. It was initially written for nondestructive reactivity accident analyses, and was recently extended to provide an ability to follow a LOF transient with down flow initially, through flow reversal and finally through the establishment of natural convection cooling. All the features perfectly meet the requirements of the safety analysis on the split core. The active core is simplified as a two-channel model with kinetics and feedback parameters provided by neutronics calculations. The RIA and LOF transients are simulated with the real-time monitoring of the cladding temperature, power rate and mass flow rate. The T/H safety margins of the new design are verified by the minimum critical heat flux ratio and the peak cladding temperature.

E8: Simultaneous multimodal neutron and x-ray imaging for multiphase quantifications in engineering and material science

Position 41

Jacob LaManna, Dan Hussey, Eli Baltic, and David Jacobson

Neutrons and x-rays provide complimentary imaging data due to their differences in elemental sensitivity. X-ray attenuation increases with increasing atomic mass whereas neutrons have a random scattering in attenuation with high sensitivity to hydrogen and lithium among others but low sensitivity to most metals such as aluminum and steel. To utilize this complementarity, a system for simultaneous neutron and x-ray imaging has been developed at NIST and is available to users at the Center for Neutron Research. This system orients an x-ray source 90° to a neutron beam to facilitate simultaneous tomography with both imaging systems. Simultaneously imaging with both modes will improve data acquisition times and allow samples that are changing with time or with stochastic processes to be better characterized when compared to sequential imaging with neutrons and x-rays. Applications for this system include studies on the formation of detrimental mineral formation in curing concrete, understanding multiphase flow in hydraulic fracturing and oil recovery, and battery and fuel cell durability, among others.

MATERIALS CATEGORY

M1: Entropic control over nanoscale colloidal crystals

Position 38

Nathan Mahynski, Sanat Kumar, and Athanassios Panagiotopoulos

Globally ordered colloidal lattices have broad utility in a wide range of novel optical and catalytic devices, for example, as photonic bandgap materials. However, the self-assembly of stereospecific structures is often confounded by defects created by, for instance, polymorphism. Weak free energy differences and complex hierarchical length scales often characterize ensembles of these structures, making it difficult to produce a single morphology at will. Current techniques to handle this problem adopt one of two approaches: that of the “top-down”, or “bottom-up” methodology whereby structures are engineered starting from the largest, or smallest relevant length scales, respectively. The ubiquitous design strategy in such approaches is energy minimization; many colloids have been computationally engineered with anisotropic pairwise interactions to achieve morphological control in theory. However, the complexity of these designs often makes experimental realization difficult. I will show how extensive computer simulations reveal that the introduction of polymeric co-solutes into crystallizing colloidal suspensions can be used to intelligently direct the resulting nano- and mesoscale colloidal structures by relying upon the polymer's entropic interactions alone.¹⁻³ These entropic interactions result entirely from the interplay between the polymer's internal degrees of freedom and the void structure of a material. This represents a novel third design paradigm that has the potential to significantly simplify control over colloidal polymorphism. I will elaborate on how to rationally design the co-solute structure to thermodynamically stabilize a single desired polymorph in a binary mixture, and the consequences that thermal perturbations have on this effect.² I will also offer insights into how to design temperature-dependent co-solute “switches” that allow the stability of a polymorph to be controlled via experimentally accessible parameters.³ As a whole, this work represents a novel entropic route to polymorphic control that has not yet been explored.

1. Mahynski, Panagiotopoulos, Meng, and Kumar, Nature Communications 5, 4472 (2014).
2. Mahynski, Kumar, and Panagiotopoulos, Soft Matter 11, 280-289 (2015).
3. Mahynski, Kumar, and Panagiotopoulos, Soft Matter 11, 5146-5153 (2015).

M2: Elucidation of sequence-dependent structure/function relationships for monometallic and bimetallic nanoparticles: toward the establishment of bio-inspired rational design rules

Position 4

Nicholas Bedford

Peptide-enabled synthesis of inorganic nanostructures represents an emerging avenue to create materials with optimized properties. Peptide complexity and programmability allows for the development of rational synthesis strategies that are lacking in traditional ligands for catalytic nanomaterials. Unfortunately, there is limited information correlating peptide sequence to particle structure and properties, limiting the development of these materials to trial & error methods. In this presentation, sequence-dependent structural properties of peptide-enabled monometallic and bimetallic nanoparticles are elucidated using synchrotron X-ray characterization techniques and molecular dynamics (MD) simulations. High-energy X-ray diffraction (HE-XRD) coupled with atomic pair distribution function (PDF) analysis and extended X-ray absorption fine-structure spectroscopy (EXAFS) were used to uncover sequence-dependent differences in surface structural disorder and stoichiometry which assist in explaining catalytic properties. Nanoparticle configurations were then determined directly from experimental data using reverse Monte Carlo methods, followed by MD simulations to model peptide morphology onto the experimentally-derived structures. Sequence-dependent catalytic property differences were then elucidated through the atomic-scale identification of the biotic/abiotic interface. This hybrid methodology provides a clear route to determine peptide-dependent structure/function relationships, enabling the generation of guidelines for catalyst design through the rational tailoring of peptide sequences.

M3: Identifying the effects of size and shape on the physicochemical properties of cerium oxide nanoparticles

Position 27

Christopher M. Sims, Alline F. Myers, Justin M. Gorham, Igor Levin, Tae Joon Cho, Vincent A. Hackley, and Bryant C. Nelson

Recently, the use of cerium oxide (CeO₂, ceria) nanoparticles (NPs) has grown extensively due to their current and potential applications, spanning from automotive catalysts and UV filters to agricultural treatment agents and antioxidant therapeutics. While the physicochemical characteristics (e.g. size, shape, surface chemistry) of ceria NPs are known to highly influence their performance for a given application, the impact of these characteristics on their environmental and toxicological fates is not yet fully understood. Previous research designed to understand the potential environmental and toxicological effects of ceria NPs have yielded conflicting results, with ceria NPs found to be both toxic and non-toxic to cells and organisms. The mixed results of these studies reinforce the need to better understand the physicochemical characteristics of ceria NPs and how these characteristics affect their interaction with the environment and their potential mechanisms of toxicity.

Here, we utilize multiple analytical techniques, including powder X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), electron-energy loss spectroscopy (EELS), dynamic light scattering (DLS), and ultraviolet-visible spectroscopy (UV-Vis) to thoroughly characterize a suite of ceria NPs, both as dry powders and in environmentally relevant media. Preliminary data suggest the primary particle size has a large effect on the oxidation state of the ceria NPs, with smaller particles appearing to have increased Ce³⁺/Ce⁴⁺ ratios compared to their larger counterparts (Figure 1 and Figure 2), in agreement with previous research. Attempts to create stable aqueous suspensions of the studied ceria NPs were unsuccessful unless their surfaces were modified by various ligands (e.g. citrate, polyvinylpyrrolidone). Additional experiments suggest the identity and amount of surface coating on the ceria NPs highly impact their resultant dynamics in media. Imminent work will investigate the potential toxicity of ceria NPs as a function of their physicochemical characteristics and the resultant effects on uptake, distribution, and potential mechanisms of toxicity in the model organism, *C. elegans*.

M4: Enhanced light absorption and wavelength dependence due to coating and mixing states of black carbon

Position 3

Rian You, James Radney, Christopher Zangmeister, and Michael Zachariah

Black carbon (BC) can warm the atmosphere through absorption of solar radiation. Internal mixing of BC with other aerosol materials has been previously shown to enhance the magnitude of light absorption of BC and, therefore, amplify the particles' radiative heating potential. To investigate this effect we have measured the spectral dependence of BC particles mixed with both absorbing and non-absorbing materials. Black aqueous pigment particles are used as a surrogate for BC and ammonium sulfate and sodium chloride were used as non-absorbing coatings. The BC particles were also coated with brown carbon (BrC) to investigate the enhancement effect from a light absorbing coating. Aerosol absorption spectra were measured for particles with a ~10 % by mass ratio of BC, mimicking particles observed in the atmosphere. Data was collected using a photoacoustic spectrometer with a supercontinuum laser spanning $\lambda = 500$ nm to 840 nm. The size and the mass of particles were classified using differential mobility analyzer (DMA) and aerosol particle mass analyzer (APM), respectively. For clear coatings, the absorption of BC absorption cross-section is enhanced relative to non-coated particles. The enhancement is wavelength dependent, ranging from 20% to 60% and is the highest at the shortest wavelength. Mixed BC/BrC particles also showed enhancements and changes in spectral shape. Using the T-matrix method we calculated the absorption of coating aggregates and successfully mapped the mixing states of coated BC. The modelling data is also consistent with findings from transmission electron microscopy.

M5: Methane adsorption in model porous materials studied by small-angle neutron scattering

Position 31

Wei-Shan Chiang, Emiliano Fratini, Piero Baglioni, Daniel Georgi, Jinhong Chen, and Yun Liu

Over the past decade, shale gas production significantly increases in the United States. The adsorption properties of natural gas highly influence the gas transportation in shales and the estimation of total shale gas in place (GIP). These properties closely relate to the size and surface properties of shale nanopores. In this study, adsorption behavior of methane onto the surface of model mesoporous materials, SBA-15 and MCM-41, is investigated by small-angle neutron scattering (SANS). A new scattering model is developed to investigate the gas adsorption behaviors at a wide temperature range at ambient pressure. Detailed structure determination of gas adsorption is achieved by the model fitting. The adsorption layer thickness and the excess adsorption are extracted above capillary condensation temperature T_c . The liquid and solid methane density are determined using the SANS data at the temperature below T_c . The surface roughness is found to play a very important role for the gas adsorption. However, the proposed models of density profile for gas adsorbed on the solid matrix in literatures are insufficient to explain our scattering data. These results are important for us to eventually understand methane gas adsorption in nanometer-sized pores, which are abundant in shale rocks, at high temperatures and high pressures.

M6: Al₂O₃ as a suitable substrate and a dielectric layer for n-layer MoS₂

Position 9

Arunima K. Singh, Richard G. Hennig, Albert V. Davydov, and Francesca Tavazza

Sapphire (α -Al₂O₃) is a common substrate for the growth of single- to few-layer MoS₂ films, and amorphous aluminium oxide serves as a high- κ dielectric gate oxide for MoS₂ based transistors. Using density-functional theory calculations with a van der Waals functional, we investigate the structural, energetic, and electronic properties of n-layer MoS₂ ($n = 1$ and 3) on the α -Al₂O₃ (0001) surface. Our results show that the sapphire stabilizes single-layer and tri-layer MoS₂, while having a negligible effect on the structure, band gap, and electron effective masses of MoS₂. This combination of a strong energetic stabilization and weak perturbation of the electronic properties shows that α -Al₂O₃ can serve as an ideal substrate for depositing ultra-thin MoS₂ layers and can also serve as a passivation or gate-oxide layer for MoS₂ based devices.

M7: Development of μ RheoSANS at NIST

Position 49

Daniel Seeman, Javen Weston, Steve Hudson, and Katie Weigandt

There is a critical and unmet need for simultaneous measurements of rheology and structure of complex fluids at high shear rates. Neutrons are particularly useful, as they probe the appropriate length scales of many fluids, they penetrate easily the hard materials used to construct a viscometer, and the contrast is adjustable to selectively probe different aspects of structure within the fluid. Scattering techniques have been utilized to measure molecular shape and alignment in solutions of wormlike micelles at conditions of high shear.

M8: Deconvolution of μ RheoSANS scattering data: A comparison with traditional RheoSANS

Position 51

Javen Weston, Daniel Seeman, Katie Weigandt, and Steve Hudson

Work is underway at the NCNR to develop a microfluidic device for use in small-angle neutron scattering (SANS) experiments. This device and technique can then be used to characterize the structure of complex fluids at extremely high shear rates. However, the velocity profile present in the μ RheoSANS devices being developed changes non-linearly. Therefore, the microfluidic channel contains a convolution of different shear rates that vary throughout the channel as a function of depth; creating a convolution of different scattering patterns during a SANS experiment. Another complicating factor is that most, if not all, of the samples of interest for μ RheoSANS have complex, non-Newtonian rheology, making it much more difficult to understand how the shear-rate changes across the channel when compared to a parabolic Newtonian velocity profile. Our proposed method for analyzing the convoluted scattering data obtained from μ RheoSANS experiments will use the measured sample rheology and a rheological model to generate a flow profile for each flow rate at which scattering data was obtained. The calculated flow profile will then be discretized into a series of layers that are assumed to have a linear velocity gradient and constant shear rate throughout. Then, scattering data obtained at lower shear rates in central layers of the channel can be subtracted from the overall absolute scattering pattern in order to provide a scattering pattern that approximately corresponds only to the layer with the highest shear rate nearest to the wall of the channel. Scattering data from a model worm-like micelle solution was used to test the efficacy and accuracy of this approach.

M9: Degradation studies of CNT-polymer nanocomposites under hygrothermal conditions

Position 45

Ajay Krishnamurthy, Aaron Forster, Debbie Stanley, and Donald Hunston

Composites that are used for aerospace applications are often exposed to hygrothermal conditions that can deteriorate their structural properties over long term use. The use of nanomaterials such as CNTs enhance the mechanical properties of these composites at almost no significant increase in their net-weight, thereby proving to be a viable cost effective solution. However, the current increase in the use of MWCNT composites for structural applications makes it critical to study the effects of nanofiller addition on the composite properties when exposed to water at high temperatures. In this study, a multi-walled carbon nanotube forest is grown on alumina woven fiber mats and is infiltrated with a high-strength polymer (RTM6). The composites were exposed to hygrothermal conditions and their physical, chemical and microstructural properties are evaluated to better understand the role of MWCNTs in maintaining integrity of these composites over large time scales (~3 m).

M10: Total ion yields from U020a monodisperse particles deposited on graphite and silicon planchets with O^- , O_2^- , and O_2^+ primary ion beams

Position 30

Nicholas Sharp, Jack Fassett, and Dave Simons

Large geometry secondary ion mass spectrometers (LG-SIMS) play an important role in nuclear forensics through their ability to identify accurately and precisely isotopic ratios of particles obtained from inspectors. As the particle mass can be on the order of sub-picograms it is important to maximize the sample utilization efficiency of U^+ to make high quality measurements. The influence of primary ion beam species and polarity on U^+ sample utilization efficiency has been previously investigated by Ranebo et al. (2008). To further that work we have analyzed the influence of sample substrate as well as primary ion beams on U^+ sample utilization efficiency by analyzing mono-disperse U020a microspheres deposited onto graphite and silicon planchets. The particles were mapped using a scanning electron microscope with automated particle recognition and analysis and their coordinates were converted to the LG-SIMS coordinate system using fiducial marks. Results indicate higher U^+ sample utilization efficiencies when sputtering with O^- and O_2^- with graphite planchets, while O_2^+ gave slightly higher U^+ sample utilization efficiencies with silicon substrates. Overall the negative primary ion beams produced higher U^+ sample utilization efficiencies compared to positive primary ions. Additionally, during sputtering of uranium particles on silicon with O^- and O_2^- a sudden drop in U^+ signal intensity was observed which was not present during sputtering with O_2^+ or with particles on graphite. This drop in U^+ signal intensity occurred simultaneously with an increase in UO^+ and UO_2^+ signals, indicating a change in environment around the uranium particle that is unique to silicon compared to graphite.

M11: Design, synthesis, and characterization of mixed ionic/electronic conducting surface layers adsorbed on metal oxide particles

Position 44

Jeffrey Richards and Norman Wagner

Inexpensive grid-scale storage remains a major hurdle slowing the wide-scale adoption of renewable energy by public power utilities. Flow batteries have been proposed as one viable solution. Whereas, the capacity of a traditional battery is limited by its packaging, flow batteries pump redox active fluids from external storage tanks through a flow cell where electrical energy is extracted or stored via reversible redox reactions. In this way, the capacity of the battery becomes scalable independent of the specific redox chemistry and battery geometry. Semi-Solid flow batteries (SSFBS) use “flowable electrodes” for both the anode and cathode materials that consist of a mixture of lithiated metal oxide particles and carbon black particles. Carbon black is added to these dispersions to improve the utilization of lithium as the particles flow by the electrodes. Unfortunately, the presence of this percolated carbon black network leads to significant increases in viscosity, both at low and high shear rates. In this work, we outline the synthesis of a composite polyelectrolyte/conjugated polymer adsorbed surface layer on cationic silica particles. This layer is formed through the adsorption of poly(styrene sulfonate) onto oppositely charged metal oxide particles and subsequent polymerization of the surface polyelectrolyte with 3,4-ethylenedioxythiophene (EDOT) monomer. The PEDOT:PSS layer is characterized as a function of EDOT:SO4-2 loading using a combination of light scattering, neutron scattering and dielectric spectroscopy to understand the connection between the surface layer’s composition, nanostructure and electrical properties.

M12: Engineering functional magnetic properties through interfacial discontinuities

Position 18

Alexander Grutter, Brian Kirby, Arturas Vailionis, Julie Borchers, Charles Flint, Matthew Gray, Urusa Alaan, Elke Arenholz, Alpha N'Daiye, and Yuri Suzuki

In the search for materials with which to build next-generation spintronic devices, the discovery of unexpected electronic and magnetic behavior at atomically sharp perovskite oxide interfaces has generated considerable excitement. In these new low-dimensional materials the mismatch of bands, oxidation states, and interaction lengths at interfaces gives rise to emergent behavior not found in the bulk, such as the stabilization of ferromagnetism at the interface between CaRuO_3 , a paramagnetic metal, and CaMnO_3 , an antiferromagnetic insulator. Although the origins and underlying physics of these interfaces are not yet well understood, such effects suggest new methods of engineering functional interfaces by tuning the magnetic properties of these systems. In this poster we will demonstrate the emergence of interfacial magnetic states which are highly sensitive to changes in interfacial symmetry or the application of electric fields. We will show several unexpected mechanisms by which we may control the ferromagnetism at complex oxide interfaces, demonstrating the tunability which make this class of materials so desirable for integration into magnetic logic systems.

M13: Magnetic order in the mixed-spin triangular lattice antiferromagnets Na_xMnO_2

Position 15

Robin Chisnell, Dan Parshall, James Feng, Takehito Suzuki, Amber Larson, Efrain Rodriguez, Joseph Checkelsky, Xin Li, and Jeffrey Lynn

Na_xTMO_2 (TM = transition metal) materials consist of alternating layers of Na and TM ions with the TM ions arranged on a geometrically frustrated triangular lattice. Na can be easily and reversibly removed from these materials, making them of interest for application in rechargeable batteries and allowing for exploration of their rich phase diagrams as a function of Na concentration. Na ordering is an important factor in ground state selection, and is driven by electrostatic interactions in many Na_xTMO_2 systems. The TM = Mn series differs in that Na ordering is driven by a cooperative Jahn-Teller effect, due to the coexistence of Jahn-Teller active Mn^{3+} and inactive Mn^{4+} ions. This effect also results in an ordered arrangement of the Mn^{3+} and Mn^{4+} ions, and thus of spin-2 and spin-3/2 moments. For $x = 5/8$, we have recently shown the coexistence of charge and magnetic stripe orderings. Here, we present the results of neutron diffraction measurements performed on single crystal samples of Na_xMnO_2 and discuss the details of the magnetic structure in the magnetically ordered phase.

M14: Phase separation in a eptiaxially strained narrow bandgap manganites

Position 52

Steven Disseler, A. Grutter, E. Moon, and S. May

Thin films of complex oxides provide a rich phase diagram where charge, spin, and structural degrees of freedom may all be used to tune the magnetic and electronic properties. Perhaps the best example of this behavior is in the doped rare-earth manganites exhibiting colossal magnetoresistance which may play an important role in future technologies. In this work, we examine narrow bandgap manganite $\text{Eu}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films epitaxially deposited on various substrates thereby using the resultant biaxial strain to tune the magnetic properties. Using a variety of probes, including magnetometry, neutron diffraction, and muon-spin relaxation, we demonstrate evidence for magnetoelectric phase separation as well as strong dependence of the ground state magnetic structure on the resulting strain.

M15: Intensity ratio of resonant Raman modes for (n,m) enriched semiconducting carbon nanotubes

Position 34

Yanmei Piao, Jeffrey R. Simpson, Jason K. Streit, Geyou Ao, Ming Zheng, Jeffrey A. Fagan, and Angela R. Hight Walker

Relative intensities of resonant Raman spectral features, specifically the radial breathing mode (RBM) and G modes, of eleven, chirality-enriched, single-wall carbon nanotube (SWCNT) species were established under second-order optical transition excitation. The results demonstrate an under-recognized complexity in the evaluation of Raman spectra for the assignment of (n,m) population distributions in agreement with theory predicted by a symmetry-adapted nonorthogonal tight-binding model. Strong chiral angle and mod dependencies affect the intensity ratio of the RBM to G modes and can result in misleading interpretations. Furthermore, we report five additional values for chirality dependent G^+ and G^- Raman peak positions and intensity ratios extending the available data to cover more of the smaller diameter regime by including the first (5,4) second-order, resonance Raman spectra. Together, the Raman spectral library is demonstrated to be sufficient for decoupling multiple species via a spectral fitting process, and enables fundamental characterization even in mixed chiral population samples.

M16: Effects of solid-solid boundary anisotropy on directional solidification microstructures

Position 50

Supriyo Ghosh, Alain Karma, and Mathis Plapp

The microstructures arising from the solidification processing possess various types of boundaries: solid-liquid interfaces, grain boundaries (GB), interphase boundaries (IB). Whereas solid(S)-liquid(L) interfaces have been investigated extensively, relatively little attention has been paid to the solid(S)-solid(S) boundaries (GB and IB). Recently, it has been found that S-S boundary anisotropy can also have a significant influence, particularly on the overall orientation selection of the growing patterns. More specifically, the present poster investigates the effects of GB and IB anisotropy through phase-field simulations of solidification morphologies.

M17: Trijunction drag affects polycrystal topology

Position 12

Trevor Keller and Daniel Lewis

Experimental evidence demonstrates that triple junctions in metallic polycrystals migrate with finite velocity, counter to the assumptions of ideal grain growth. Phase field simulations were performed to study the influence of this "trijunction drag" on the process of grain growth. The topology of the polycrystal is affected. Details of the differences with alternative phase field models and mobility formulations are presented.

M18: Characterizing adsorbed surfactant and hydration layers around single wall carbon nanotubes using analytical ultracentrifugation

Position 6

Stephanie Lam, Ming Zheng, and J. A. Fagan

Over the past decade, numerous methods have emerged for the dispersion and liquid phase purification of single wall carbon nanotubes (SWCNTs). The success and efficiency of the dispersion and purification methods are believed to be strongly dependent on the characteristics of the bound layer of dispersant (such as small molecule surfactant(s) or DNA) both in the amount of bound dispersant as well as the specific structure it forms at the nanotube surface. However, only limited direct measurements of the differences in the bound layers on well-resolved SWCNT populations have been reported. Thus, it is important to elucidate the structure of the adsorbed surfactant and hydration shells around different single species SWCNTs and surfactant-SWCNT complexes, respectively, to quantitatively address the differences in structure that drive differential separation. To study the structure of the adsorbed surfactant layer, we utilize analytical ultracentrifugation (AUC) to resolve the density and radial distribution of bile salt surfactants on different species of SWCNTs at various solution conditions. AUC is a powerful technique which allows simultaneous sampling of the entire population distribution of a solute (e.g. proteins, DNA, particles). In our experiments, we use single wall carbon nanotubes which have been both chirality and length sorted, giving us a population of particles which not only have a narrow length and diameter distribution, but also unique optical transitions and unique interactions with surfactants. We characterize and compare the anhydrous and buoyant radii of (7,6) SWCNTs dispersed in aqueous solutions of sodium deoxycholate and provide direct measurements pertaining to the effect of electrolyte addition on the size of the counterion cloud around the nanotube-surfactant complex using AUC. Such results not only push the current limits of nanoscale metrology but also improve our understanding of contemporary nanotube separation and purification processes on a broader scale by contributing knowledge pertaining to interactions between SWCNTs of different electronic properties with various types of amphiphilic molecules.

M19: Materials project based testing of classical empirical potentials

Position 26

Kamal Choudhary, Faiçal Congo, and Fancesca Tavazza

Classical empirical potentials are in dire need of an organized dissemination and consistent testing. In this work, 3138 LAMMPS calculation were done using MPinterfaced code with crystal structures downloaded from materials project (MP) using REST API on empirical potentials obtained from interatomic potentials repository project and LAMMPS software. Cohesive energy, elastic constants and convex energy hull plot can be drawn and the data is presented on the web with an interactive periodic table format. Corresponding links for density functional theory (DFT) based cohesive energy, electronic properties and elastic constants were provided for comparison. Typically any force-field based calculation with density functional theory based energy above convex hull = 0 (stable structure) should have reasonable cohesive energy and non-negative elastic constants. The force-fields include EAM, EIM, MEAM, AIREBO, REAXFF, COMB, COMB3, TERSOFF and SW. The data is presented on web at (<http://www.ctcms.nist.gov/~knc6/periodic.html>).

M20: Individual observations of strain band behaviors of TWIP steels in uniaxial tension

Position 37

Brian Lin, Adam Creuziger, and Timothy Foecke

Twining induced plasticity (TWIP) steels are known for their high strength combined with an extremely high stretchability. While many other advanced high strength steels also feature high strengths, the elongations are usually low. TWIP steels have high elongation due to the formation of deformation twins in microstructure. The abundant formation of deformation twins in the microstructure produces unique stress-strain behaviors in TWIP in comparison to conventional steels. In a series of uniaxial tension experiments at quasi-static strain rates, the local strain behavior of 980TWIP was studied using digital image correlation. The formation of strain bands were observed when the true strain of the specimen was above a certain threshold. Several propagations of these strain bands were observed up until the specimen fractured. The individual behaviors of each localized strain band were examined, and the band width, the band velocity, and the degree of strain hardening were measured and compared. The characteristics of the localized strain band behaviors were compared to other more commonly known dynamic strain aging phenomena, like Portevin-Le Chatelier bands.

M21: The quest for new high- T_c superconductors: Combined neutron scattering and first-principles finite displacement approach

Position 5

Linda Hung and Taner Yildirim

The standard linear response theory has been successfully used to calculate electron-phonon coupling in systems with few atoms per unit cell. However, when the system size is large and/or magnetism and phonons are strongly coupled, the linear response approach may not be feasible. Hence, we use a finite-displacement method, combined with first-principles DFT calculations, such that both the phonon energies and electron-phonon coupling can be readily calculated for large systems with and without magnetism. In this poster, we report on the properties of several classes of superconductors: namely BKBO, alkali-doped solid picene, metal-doped few-layer graphene, and the very recently discovered hydrogen sulfide superconductor ($T_c \sim 200$ K under pressures ~ 200 GPa). We address the effects of doping, phonon anharmonicity, and the dimensionality of the material on electron-phonon coupling and the resulting superconductivity. Theoretical spectra for some systems are compared to inelastic neutron scattering spectra measured at the NIST Center for Neutron Research, and found to be in good agreement. We also explore the properties of potential new superconductors via structural and lattice dynamics calculations.

M22: Nanoscale measurement of carrier recombination using cathodoluminescence combined with transmission electron microscopy

Position 46

Wei-Chang D. Yang, Yohan Yoon, Benoit H. Gaury, Paul M. Haney, Nikolai Zhitenev, and Renu Sharma

Solar power is an attractive alternative to replace fossil fuels to meet the growing need for clean energy. Although the use of solar energy is increasing, the cost to produce electricity (price per watt) is one of the obstacles that limits its share of the total energy market. Thin-film solar cells minimize the use of expensive materials, and can be made using low-cost manufacturing methods. However, in many cases, poor power conversion efficiency is preventing solar power from being economically competitive. Improving solar cell efficiency requires a fundamental understanding of the mechanisms by which photovoltaic materials absorb sunlight and separate electron-hole pairs (free carriers) and thus generate power. The interaction of a focused electron beam with a photovoltaic material is similar to that of sunlight, i.e. electron-hole pairs can also be generated. These electron-hole pairs will emit photons if they recombine. The resulting cathodoluminescence (CL) signal provides spectroscopic information that can be used to infer important features of the electronic structure of the material and provide insight into the factors that may limit its conversion efficiency. CL spectroscopy has been employed routinely to characterize photovoltaic materials in the scanning electron microscope (SEM). Correlation of the CL spectra with the position of the electron beam is used to investigate free-carrier recombination and its relationship to the microstructure, chemistry and defect density in solar cells. In the SEM, the typical size of the interaction volume from which CL signals are collected is greater than ≈ 250 nm. This limits the resolution of the technique and obscures important nanoscale information. Here we utilize a transmission electron microscope (TEM) based CL spectroscopy system – developed at the CNST – that reduces interaction volume to ≈ 10 nm in diameter. We use a wedge-shaped lamella, prepared from a commercial polycrystalline CdTe solar panel, to collect the CL and energy-dispersive X-ray spectra in scanning transmission electron microscopy (STEM) mode and atomic-resolution images in TEM mode. This high-resolution information enables us to correlate the atomic structures and chemical compositions at grain interiors and grain boundaries to the free carrier recombination rate. The intensity of CdTe intra-grain luminescence at ≈ 1.51 eV, as determined by CL spectroscopy, is found to depend on sample thickness. This suggests that the thin regions of the lamella may induce high levels of non-radiative surface-recombination that reduces the radiative recombination signal. The thickness and beam current-dependence of the signal is analyzed with diffusion/recombination models to determine the surface recombination velocity. At CdTe grain boundaries, a redshift of emission energy and a decrease in CL intensity are observed. EDX spectra show that chlorine is present at the CdTe grain boundaries and may serve as a shallow donor giving rise to a free-carrier recombination process that is different from the one at the grain interior. The results presented here show that a TEM CL spectroscopy system is a powerful tool to elucidate various types of free-carrier recombination that can be related to the chemical compositions and atomic structures of grain interiors and grain boundaries. This technique can also be extended to measure the effect of other defect structures such as twins and dislocations that may be present in photovoltaic materials. Such information is essential in enabling improvements in solar cell efficiency.

M23: Novel sheet metal straining devices for *in-situ* neutron diffraction

Position 2

Justin Milner

Purpose built straining devices, octo-strain and shear device, is designed to enable deformation across a wide range of strain ratios. These devices are purpose built to be used with neutron diffraction to acquire lattice strains along the principle directions of the sheet sample during in-situ deformation. Shear device is a multi-directional shearing mechanism capable of producing simple shear, pure shear, and shear with tension/compression all while collection of diffraction data of the sample. To add to this, octo-strain is an independent multi-directional straining mechanism capable of producing uniaxial, balanced-biaxial, plane strain, and tension-compression of the sheet sample. Furthermore, octo-strain can be paired with an anti-buckling device to acquire hysteresis loading, such as balanced-biaxial tension-compression while maintaining the capability of collection diffraction data. Where neutron diffraction is known to be able to penetrate thick samples or devices. These devices had to be designed to work on a neutron beamline which includes: an open design for the beam path, rotation about sample center and size limitations to fit within the instrument. When complete these devices will aid in the measurement of the mechanical response of materials, not only at the macro level but also the micro or crystal level, during complex strain paths.

M24: Recent investigations on complex closo-borane materials as fast ionic-conductors

Position 36

Wan Si Tang, Motoaki Matsuo, Hui Wu, Vitalie Stavila, Wei Zhou, Alexei V. Soloninin, Roman V. Skoryunov, Oglia A. Babanova, Alexander V. Skripov, Atsushi Unemoto, Shin-ichi Orimo, and Terrence J. Udovic

The continuous research for better batteries have driven the investigation on solid electrolytes towards all solid-state battery application. Recently, superionic conductivity was observed for the extremely stable hydro-closo-boranes, $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{10}\text{H}_{10}$. These compounds exhibited sudden jumps to high-conductivity values of $\sim 0.1 \text{ S cm}^{-1}$ (at 540 K) for the former¹ and $\sim 0.01 \text{ S cm}^{-1}$ (at 380 K) for the latter², above their respective order-disorder transition temperatures of 529 K¹ and 370 K². This rapid surge in conductivity was closely linked to the entropy-driven phase transformations from ordered low-temperature structures to highly mobile, disordered high-temperature structures, due to a vacancy-rich cation sublattice and a concomitant onset of high reorientational mobility ($>10^{10}$ - 10^{11} reorientational jumps/s) for the large, quasi-spherical anions.^{2,3} Since the transition temperature greatly affects the usefulness of these materials as electrolytes in next-generation solid-state batteries, it is vital to study and fine-tune this property by various chemical and morphological modifications. Partial cationic substitutions of Na^+ into $\text{Li}_2\text{B}_{12}\text{H}_{12}$ in different concentrations have seen a reduction in its pristine phase transition temperature from 615 K to lower values.⁴ More recently, low phase transition temperatures were observed in a related family of hydro-closo-carborane materials, i.e., $[\text{CB}_{11}\text{H}_{12}]^-$, by replacement of one $\{\text{B-H}\}$ vertex for an isostructural $\{\text{C-H}\}$ group. Improved high-conductivity values were observed similarly above their phase transitions of 0.15 S cm^{-1} (at 403 K) for the Li^+ and 0.12 S cm^{-1} (at 383 K) for the Na^+ analogs.⁵ A combination of results from x-ray diffraction, neutron powder diffraction, differential scanning calorimetry, neutron vibrational spectroscopy, quasielastic neutron scattering, neutron magnetic resonance spin-lattice relaxation, and ionic conductivity experiments will be presented, pertaining to the structural and dynamical behaviors of these light-weight alkali-containing materials.

1. T. J. Udovic, M. Matsuo, A. Unemoto, N. Verdal, V. Stavila, A. V. Skripov, J. J. Rush, H. Takamura, and S. Orimo, Chem. Commun. 50 (2014) 3750–3752.
2. T. J. Udovic, M. Matsuo, W. S. Tang, H. Wu, V. Stavila, A. V. Soloninin, R. V. Skoryunov, O. A. Babanova, A. V. Skripov, J. J. Rush, A. Unemoto, H. Takamura, and S. Orimo, Adv. Mat. 26 (2014) 7622–7626.
3. N. Verdal, T. J. Udovic, V. Stavila, W. S. Tang, J. J. Rush, and A. V. Skripov, J. Phys. Chem, C 118 (2014) 17483–17489.
4. W. S. Tang, T. J. Udovic, and V. Stavila, J. Alloys and Comp. 645 (2015) S200–S204.
5. W. S. Tang, A. Unemoto, W. Zhou, V. Stavila, M. Matsuo, H. Wu, S. Orimo, T. J. Udovic, Energy Environ. Sci. 8 (2015) 3637–3645.

M25: Redox separation of double-wall carbon nanotubes

Position 48

Jason K. Streit, Yanmei Piao, Jeffery A. Fagan, Angela R. Hight Walker, and Ming Zheng

Charge-transfer reactions have been shown to alter the electronic structure of carbon nanotubes in a bandgap-dependent fashion. Such electronic modification holds great promise for isolating single nanotube structures from their heterogeneous synthetic mixtures. This study investigates the role of redox chemistry in the aqueous two-phase extraction of both single-wall carbon nanotubes (SWCNTs) and double-wall carbon nanotubes (DWCNTs). We demonstrate that redox-modulation can be applied to separate small diameter SWCNTs from DWCNTs, while also facilitating the enrichment of DWCNTs by outer-wall electronic type. We propose that electron transfer between redox molecules and the nanotubes induces reorganization of the surfactant coating layer, which in turn affects the partitioning of the nanotubes between the two different polymer phases. Redox-induced modulation of the dispersant coating is a generally observed phenomenon in many different nanotube sorting processes which can be further tuned to improve separation reproducibility and purity.

M26: High resolution holographic colloidal particle tracking for adsorption and flow measurements

Position 8

Paul Salipante

We use in-line holographic microscopy to track the 3-d position of micron sized colloidal particles with nanometer scale resolution. We investigate the effect of shape on reversible adsorption kinetics using colloidal polystyrene dimers near a solid glass surface as a model system. Each monomer has a double well interaction potential with the wall, which is produced by tuning electrostatic, depletion, and gravity forces. The measured transition probability distributions are used to determine the flux between adsorbed and desorbed states. The adsorption kinetics of dimers are compared to independent isolated monomers to determine the effects of shape. The results show that dimers produce slower adsorption and lower surface coverage compared monomers. We use the same setup to track the flow of particles in microfluidic channels using holographic microscopy. We use the measured flow profiles to determine flow rate as well as rheological information in non-Newtonian fluids.

M27: Effect of interlayer-coupling on bandgap and Raman spectra of SnS studied using first-principles calculations

Position 53

Sugata Chowdhury, Adam J. Biacchi, Jeffrey Simpson, and Angela R. Hight Walker

Tin (II) sulfide (SnS) is a layered mineral found in nature. In the frame work of density functional theoretical calculations, the electronic and lattice dynamical properties of few-layer SnS have been systematically investigated and analyzed using the plane wave pseudopotentials within local density approximation functional. We find that due to the interlayer van der Waals interactions, the low-frequency Ag mode and B2g mode can shift by as much as 40.1 cm^{-1} and 33.3 cm^{-1} , respectively, as the layer numbers increase from 1L to 5L. Furthermore our results indicate that, a typical characteristic for the experimentally observable B2g mode ($\sim 290 \text{ cm}^{-1}$ in bulk) is identified. Interestingly, this mode changes from coupled in-plane and out-of-plane vibrations in single layer to pure in-plane vibration in few layers and the corresponding frequencies vary by as much as 16 cm^{-1} . We also predict the band-gap is reducing with the increase of layer and density of states of all the systems. We concluded that Raman frequency variation might be used to experimentally characterize the thickness of this intriguing 2D layered material.

M28: Controlling magnetism by electric field moderated forced oxygen migration

Position 16

Dustin Gilbert, Alex Grutter, Elke Arenholz, Kai Liu, Brian J. Kirby, Julie Borchers, and Brian Maranville

Controlling the oxygen distribution in materials using electric fields offers the opportunity to directly tune their optical, thermal, electronic and magnetic properties. Ionic migration has so far been demonstrated in the modification of interfacial magnetic characteristics. We demonstrate magnetoelectric coupling moderated by voltage-driven oxygen migration beyond the interface, in relatively thick $\text{AlO}_x/\text{GdO}_x/\text{Co}$ (15 nm) films. Oxygen migration and its ramifications on the Co magnetization are quantitatively mapped with neutron reflectometry under (electro-)thermal conditioning. The depth-resolved profiles identify semi-reversible modifications of the interfacial and bulk magnetic and chemical characteristics. Magnetometry measurements show that conditioning changes the microstructure, resulting in an emergent magnetically soft phase. X-ray spectroscopy confirms changes in the Co oxidation state but not in the Gd, suggesting that the GdO_x transmits oxygen but does not source or sink it. These results provide crucial insights into controlling magnetism via magneto-ionic motion at interfaces and throughout the bulk of the film.

PHYSICS CATEGORY

P1: Thermalization of photons in strongly driven double quantum dot

Position 20

Michael Gullans

Embedding a double quantum dot (DQD) in a low loss microwave resonator results in a large electric dipole interaction between the charge states of the DQD and single microwave photons in the resonator. In the regime of a few electrons and photons, this system is reminiscent of well-known models of cavity quantum electrodynamics from atomic physics; however, there are important deviations due to the strong coupling of the DQD to the electronic reservoirs in the leads, as well as phonons in the lattice. In this talk we show that simply driving the DQD with a periodic voltage can lead to thermalization of the cavity photons into a state with a temperature given by the phonons and a chemical potential given by a harmonic of the drive frequency. Such a tunable chemical potential has utility for quantum simulation with photons. As an example, we show how several DQDs embedded in an array of microwave resonators can induce a phase transition to a Bose-Einstein condensate of light.

P2: Nanomechanical motion metrology using plasmonic NEMS

Position 1

Brian Roxworthy and Vladimir Aksyuk

With progress in nanoscience pushing engineered systems toward increasingly smaller sizes, there is a growing need for monitoring the physical parameters – mass, force, strain – of such systems with nanometer spatial precision. We present a conceptually new approach to this metrology problem that uses a unique architecture integrating plasmonic structures into nanomechanical resonators. This system achieves motion transduction with an imprecision that is 1.5 orders of magnitude better than the state of the art, from an area 150× smaller than the diffraction-limited focal spot. Moreover, the fabrication process enables parallel production of thousands of functioning devices per chip, with the flexibility to tune the plasmonic and mechanical parameters of an individual device. This work thereby represents not only a significant advance in plasmon-based motion transduction, but also serves as a launch pad for developing the nascent field of reconfigurable nanoplasmonics.

P3: Optical spintronics in organic-inorganic perovskite photovoltaic absorbers

Position 24

Junwen Li and Paul Haney

Organic-inorganic halide $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells have attracted enormous attention in recent years due to their remarkable power conversion efficiency. These materials should exhibit interesting spin-dependent properties as well, owing to the strong spin-orbit coupling and broken inversion symmetry. In this work, we consider the spin-dependent optical response of $\text{CH}_3\text{NH}_3\text{PbI}_3$. We first use density functional theory to compute the ballistic spin current generated by absorption of linearly polarized light. We then consider diffusive transport of photogenerated charge and spin for a thin $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer with a passivated surface and an Ohmic, non-selective back contact. The spin densities and spin currents are evaluated by solving the drift-diffusion equations for a simplified 3-dimensional Rashba model of the electronic structure of the valence and conduction bands. We comment on the applications of optically excited spin densities and spin currents in these materials.

P4: Probing surface recombination velocities in semiconductors using two-photon microscopy

Position 35

Benoit Gaury and Paul Haney

The determination of minority-carrier lifetimes and surface recombination velocities is essential for the development of semiconductor technologies such as solar cells. The recent development of two-photon time-resolved microscopy allows for better measurements of bulk and subsurface interfaces properties. Here we analyze the diffusion problem related to this optical technique. Our three-dimensional treatment enables us to separate lifetime (recombination) from transport effects (diffusion) in the photoluminescence intensity. It also allows us to consider surface recombination occurring at a variety of geometries: a single plane (representing an isolated exposed or buried interface), two parallel planes (representing two inequivalent interfaces), and a spherical surface (representing the enclosing surface of a grain boundary). We provide fully analytical results and scalings directly amenable to data fitting, and apply those to experimental data collected on heteroepitaxial CdTe/ZnTe/Si.

P5: Charge effects on surfactant bilayer dynamics

Position 42

Robert Bradbury and Michihiro Nagao

The mechanical properties of surfactant bilayer membranes have been measured over a range of surface charge densities using small-angle neutron scattering and neutron spin echo spectroscopy. An increase in the surface charge density leads to a stiffening of the membrane, which is consistent with classical theory of charge effects on membranes. The fluctuations in the membrane thickness, however, become slower with increasing charge density, which can be explained by an increase in the membrane viscosity as predicted by Bingham et al. We suggest that an increase in the repulsive interactions between the charged headgroups is responsible for this increased membrane viscosity. Furthermore, the amplitude of the thickness fluctuations is observed to remain almost constant with variation in surface charge density which suggests almost constant values for the total compressibility modulus of the bilayer and the optimum fluctuation wavelength. This indicates that the time scale and amplitude of membrane thickness fluctuations are controlled by different membrane effects. This work demonstrates that charge stabilization of lamellar bilayers is not merely affected by inter-membrane interactions but that intra-membrane dynamics also have a significant contribution.

P6: Heterodyne detection method for spin precession

Position 17

Seungha Yoon and Robert D. McMichael

Spin precession in ferromagnets (ferromagnetic resonance, FMR) is not only a powerful method for measuring magnetic materials properties but it also offers measurements of “spintronic” spin transfer torque effects. The ability to determine the precession phase offers additional information on the vector direction of an applied spin torque, and the direction is a key factor in discriminating between different theoretical models. Therefore the phase sensitive FMR detection is important for new developments in spintronics. In this presentation, we describe a new FMR measurement method using heterodyne detection to produce a strong FMR signal with lower phase uncertainties leading to the possibility of better spin torque analysis.

In general, FMR is observed in the GHz driving frequency range. For low-noise detection using conventional AC detection systems such as lock-in amplifiers, it is helpful to use additional signal modulation with an intermediate frequency, fIF. Here, we use the magneto-optical Kerr effect to measure the magnetic state using light that has been amplitude modulated at frequency fRF. The magnetization is driven at a slightly different frequency, fRF + fIF. The product of the Kerr rotation angle (fRF + fIF) with the light intensity (fRF) produces a lower frequency FMR signal at the intermediate frequency fIF. The phase of this signal is comprised of the precession phase and an additional phase due to propagation delays along the paths of the probe laser pulses and the microwave excitation. We will discuss this phase variation as a function of the optical delay and driving frequency. Compared to a single-frequency homodyne method, this detection method conveniently eliminates the need for field modulation coils and it also produces a stronger FMR signal. In addition, higher intermediate frequencies can be selected to avoid a 1/f noise floor.

P7: Calibration of BTBT models for III-V heterojunction tunnel-FET performance prediction

Position 22

Quentin Smets, Anne S. Verhulst, Salim El Kazzi, Devin Verreck, Koen Martens, Eddy Simoen, Han Chung Lin, Olivier Richard, Jean-Pierre Raskin, Rita Rooyackers, Clement Merckling, Maarten van de Put, Hugo Bender, Nadine Collaert, Anda Mocuta, Aaron Thean, and Marc M. Heyns

The Tunnel Field-Effect Transistor (TFET) is a promising candidate for future low-power logic applications because of its steep turn-on capabilities. However, there is still a large discrepancy between TFET simulations and experimental results. In this work, we experimentally determine three parameters crucial for TFET operation. First, we calibrate the band-to-band tunneling parameters used in Kane's formalism and the k.p formalism. We achieve this with p+/intrinsic/n+ diodes with different intrinsic region thicknesses, and by combining current-voltage, capacitance-voltage, and secondary ion mass spectrometry measurements. Secondly, we experimentally verify the effect of field-induced quantum confinement on band-to-band tunneling. We accomplish this by developing a method where line-TFET are modeled using highly doped MOS capacitors, and we demonstrate AC inversion by BTBT, which was so far unobserved. Thirdly, we measure the effective tunneling bandgap of the In_{0.53}Ga_{0.47}As/GaAs_{0.5}Sb_{0.5} heterojunction from a characteristic exponentially increasing band-to-band tunneling current with forward bias, caused by sharp energy filtering at cryogenic temperature. Combining these different findings allows us to make more accurate TFET performance predictions.

P8: Phase mask-based multimodal superresolution microscopy

Position 39

Ryan Beams, Jeremiah Woodcock, Jeffrey Gilman, and Stephan Stranick

We demonstrate a versatile superresolution microscopy technique that utilized phase engineered excitation in combination with spatially filtered detection. To illustrate the flexibility of this method, we acquired second harmonic images as well as two-photon fluorescent lifetime images of 80 nm gold particles mixed with fluorophores with 100 nm spatial resolution using 800 nm excitation. Since this method exclusively relies on engineering the excitation and collection volumes, it is applicable for a wide variety of linear and non-linear optical processes that are inaccessible with other superresolution techniques.

P9: Spin transport near spin-orbit coupled interface

Position 32

Kyoung-Whan Kim, Kyung-Jin Lee, Hyun-Woo Lee, and Mark Stiles

Many spin-related phenomena of recent interest, such as spin pumping, spin Hall effect, and spin-transfer torques, are measured in systems with ferromagnetic/normal metal interfaces. The use of heavy metals as the normal metal layer has attracted interest because their strong spin-orbit coupling allows efficient control of the magnetization by spin-orbit torques and advances the realization of spintronics devices. Spin-orbit torques arise from at least two different mechanisms, the bulk spin Hall effect and interfacial spin-orbit coupling. For all combinations of mechanisms, the spin dynamics near interfaces affects spin-related measurements and thus needs careful assessment. Unfortunately, existing theories do not take proper account of the spin dynamics near spin-orbit coupled interface. Theories of the bulk spin Hall effect often resort to the semi-classical drift-diffusion equation with boundary conditions that neglect spin-orbit coupling at the interface, and most theories of the interfacial spin-orbit coupling adopt two-dimensional descriptions. In this work, we develop a three-dimensional interfacial spin-orbit coupling model and discuss how current understanding changes for spin-orbit coupled interfaces.

P10: Nitrogen-vacancy magnetometry on patterned permalloy nanostructures

Position 21

Jason Liu and Robert McMichael

Patterned ferromagnetic nanostructures have attracted a great deal of attention recently due to their potential application as logic and random access memory devices. Information from the stray magnetic fields produced from these nanostructures can give insight into material parameters like resonant frequencies and anisotropy fields. Our work involves measuring these stray magnetic fields using nitrogen-vacancy (NV) center magnetometry. An NV center is a lattice defect in diamond with fluorescent properties that depend on its spin state. The Zeeman splitting of the $m_z = \pm 1$ state, combined with a spin coherence time that can approach 1 ms at room temperature, makes the NV center a sensitive, atom-sized magnetometer, which is ideal for measuring magnetic nanostructures. We studied Permalloy ($\text{Ni}_{80}\text{Fe}_{20}$) structures grown on top of a gold microstrip antenna and the measurements were conducted on a home-built confocal microscope. The microstrip antenna was used to simultaneously excite spins in the Permalloy structures and electron spin resonance in the NV center. Preliminary measurements show photoluminescence contrast around 15% and magnetic field detectivity on the order of $\mu\text{T}/\text{Hz}^{1/2}$. This allows for fine field mapping of stray magnetic fields produced by magnetic micro and nanostructures, which are typically a few milliteslas in magnitude.

P11: Viscosity modeling of fluids based on residual entropy scaling

Position 29

Ian Bell and Arno Laesecke

The accurate prediction of the viscosity of working fluids in thermal systems (heat pump, refrigeration, Organic Rankine Cycle, etc.) is of importance in a wide range of technical systems. A recently rediscovered method for modeling the viscosity of fluids is the use of the residual entropy scaling method. In this method, the reduced viscosity (the ratio of the viscosity of the fluid to the dilute-gas viscosity) is expressed as a function of the residual entropy. For many fluids, there is a nearly one-to-one relationship between reduced viscosity and residual entropy over the entire range in temperature and pressure for which experimental data are available. The goal is to be able to accurately model the viscosity of fluids using a simple methodology that has a solid foundation in theory. In future work, it is hoped to be able to arrive at a universal correlation for fluid viscosity that will allow for a reasonable estimation of viscosity for fluids with no experimental measurements.

P12: Strain-evaluation in two graphene-based systems via Raman spectroscopies

Position 43

Erin Wood, Yanfei Yang, Will Gannet, Gordon A. Shaw, Randolph E. Elmquist, Mark W. Keller, and Angela R. Hight Walter

Understanding local strain and deformation phenomena at the nanoscale is critical in designing robust high performing devices. While Raman spectroscopy is an indispensable, non-destructive tool in understanding chemical and structural information of materials, it is a diffraction limited technique which suffers from weak scattering. However, recent breakthroughs, such as the coupling of Raman spectroscopy with atomic force microscopy (AFM) have helped to increase both the spatial resolution and signal intensity of Raman maps. We employ these co-located techniques to enable characterization of strain induced through indentation methods in graphene-based systems. In this poster, we present efforts to detect strain in two different graphene-based systems; CVD-grown graphene on single-crystalline copper and epitaxial-grown graphene on silicon carbide, and compare and contrast confocal Raman and co-located Raman and AFM techniques.

P13: Metrology with correlated photon pairs

Position 7

Eric Zhu, C. Corbari, A.V. Gladyshev, P.G. Kazansky, and Li Qian

I will show experimentally how broadband correlated photon pairs can be used to measure the dispersion of a long spool of telecom-band optical fiber (Corning SMF28). The measurement is made possible by the unique properties of the photon pairs, including their time-correlated and frequency-conjugate natures.

The photon pairs used are generated through the process of spontaneous parametric downconversion (SPDC), a nonlinear optical process, from a specially-treated poled optical fiber. With the same long spool of fiber whose dispersion is previously characterized, a dispersion-based spectrometer is used to measure the spectrum of the photon pairs generated by the specialty fiber.

P14: Multi-direction spin transport at interfaces with spin-orbit coupling

Position 28

Vivek Amin and Mark Stiles

Electronic devices used in information processing (such as transistors) will soon reach a fundamental limit in which quantum effects prevent further miniaturization and greatly limit power efficiency. However, by reliably manipulating the spin of electrons in such devices one might overcome these limitations. Many spin-based electronic devices rely on manipulating the flow of spin across the interface between a magnetic and non-magnetic material. The spin-orbit interaction, which couples the spin and momentum of carriers, allows for such manipulation but remains poorly understood at material interfaces. While the important consequences of this interaction can be captured by a spin-dependent Boltzmann equation, currently they cannot be captured by drift-diffusion models, which are the primary tools used for analyzing experiments. Here we present boundary conditions suitable for drift-diffusion models that capture the phenomenology of the spin-orbit interaction at interfaces. We compare solutions of the drift-diffusion equations using these boundary conditions to solutions of the spin-dependent Boltzmann equation for a heavy metal/ferromagnet bilayer. We find that these drift-diffusion equations predict spin transport in quantitative agreement with the Boltzmann equation and allow for much simpler interpretation of the results. Our model enhances the understanding of spin dynamics at material interfaces, and potentially influences the optimization of future spin-based electronic devices.

P15: Improved and expanded near-IR oscillator strengths for Fe-group elements

Position 40

Michael Wood, Gillian Nave, and Chris Sneden

The use of modern experimental techniques, including LIF lifetime and FTS branching fraction measurements, has significantly increased the scope and reliability of laboratory atomic transition probabilities in the UV and visible. However, this combination of techniques is problematic in the IR, a region of increasing importance due to improved detector, spectrometer, and telescope technologies. The result is a significant gap between the capabilities to record new IR astronomical spectra and the data needed to sufficiently analyze them. To aid in closing this gap, we are incorporating new techniques, including reverse stellar analyses, to measure sets of oscillator strengths in the near-IR ($\lambda \approx 1\text{-}5 \mu\text{m}$), with a primary focus on the Fe-group elements. A description of the methods and their applicability will be presented, including recent results for Ti I.

P16: Double-electron capture by highly-ionized atoms isolated at very low energy

Position 47

Joan Dreiling, Shannon Hoogerheide, Arda Sahiner, and Joseph Tan

Charge exchange with background gasses, also known as electron capture, is important in the study of comets¹, controlled fusion energy², anti-matter atoms³, and proposed one-electron ions in Rydberg states⁴. However, few studies have been performed at very low energies (velocities less than 0.01 atomic units).

The electron beam ion trap (EBIT) at NIST is used to produce highly-charged ions, which can then be extracted as an ion bunch. A specific charge state in the ion bunch is separated and captured in a compact Penning trap⁵. Here, the isolated ions are held for varying lengths of time at thermal energies less than 10 eV. During their dwell time in the trap, the ions interact with controlled amounts of background gasses from which they can capture electrons. The ions are then ejected from the trap to a time-of-flight (TOF) detector, which allows determination of the population of each charge state.

A systematic study was performed on bare neon nuclei by injecting several different back-ground gasses into the Penning trap region at various pressures. By analyzing the signal measured by the TOF detector, the evolution of the ions' charge composition was determined, revealing the rates of the different loss mechanisms. In addition to trap loss and single-electron capture, direct evidence of double-electron capture has been observed.

We report on the experimental progress towards resonant charge exchange between bare neon nuclei and laser-excited rubidium atoms to make one-electron ions in high angular momentum states. These ions are suited for a different measurement of the Rydberg constant.

1. T.E. Cravens 2002 Science 296 1042
2. R.C. Isler 1994 Plasma Phys. Control. Fusion 36 171-208
3. C.H. Storry et al. 2004 Phys. Rev. Lett. 93 263401
4. U. Jentschura et al. 2008 Phys. Rev. Lett. 100 160404
5. J.N. Tan et al. 2012 Rev. Sci. Instrum. 83 023103

P17: Optoelectronic properties of a curved infrared focal plane array

Position 10

Kevin Tekaya, Karim Inal, Manuel Fendler, and Elisabeth Massoni

At the optoelectronics and optical systems conception boundary, focal plane arrays have a planar shape because of microelectronics technologies. Yet spherical focal plane arrays would simplify optical systems conception and reduce volume, weight and total cost. This shape is widespread in Nature - human concave eye, arthropods convex compound eyes, etc.

The advantages of the bio-inspired curved retina have been established in previous works, where a spherical infrared microbolometers array was manufactured.

During this thesis, the silicon-based devices curving process (e.g. bolometers) has been optimized thanks to a design of experiments and a finite element simulation including silicon anisotropy. Convex and concave shapes without defects (folds and flat part) have been demonstrated with square and rectangular chips due to their flexibility at small thicknesses.

Then, a new and different curving process for hybrid devices (flip-chip) was developed. Several curved CdHgTe focal plane arrays were obtained and fully functional. Concave and convex spherical shapes as well as concave cylindrical shapes have been successfully achieved despite a high CdHgTe fragility.

Optoelectronic measurements such as photonic current, responsivity, noise and dark current were performed with some adaptation for curved devices. High operabilities have been demonstrated (> 97%). In addition a finite element simulation of the process has been conducted with the CdHgTe anisotropy. Direct relations between induced stress and strain, and optoelectronic properties, have been proved in this II-VI semiconductor. Location and surfacing of slip lines as well as dislocations identification are discussed.

Finally, a compact infrared camera prototype with a curved CdHgTe focal plane array has been manufactured for the first time. It confirms that the device is fully functional and has a great potential for high value applications.

P18: Low temperature magneto-optical measurements of SL-TMDs: Breaking of valley degeneracy in MoSe₂ by magnetic field

Position 23

Colin Heikes

Using polarization-resolved photoluminescence spectroscopy, we investigate valley degeneracy breaking by out-of-plane magnetic field in back-gated monolayer MoSe₂ devices. We observe a linear splitting of -0.22 meV/T between luminescence peak energies in σ^+ and σ^- emission for both neutral and charged excitons. The optical selection rules of monolayer MoSe₂ couple photon handedness to the exciton valley degree of freedom, so this splitting demonstrates valley degeneracy breaking. In addition, we find that the luminescence handedness can be controlled with magnetic field, to a degree that depends on the back-gate voltage. An applied magnetic field therefore provides effective strategies for control over the valley degree of freedom.

SESSION II (1:00 pm to 4:00 pm)

BIOLOGY CATETORY

B1: Automated method for structural characterization of membrane proteins in bicelles using HDX-MS

Position 31

Kyle Anderson

The majority of pharmaceutical targets are membrane proteins. However, structural characterization of membrane proteins has been a consistent challenge for LC-MS analysis. Membrane lipids are deleterious to chromatography performance and cause ion suppression of peptide signal. Typically, LC-MS hydrogen deuterium exchange (HDX) studies solubilize membrane proteins by truncation or altered amino acid sequence in the membrane domain, which can induce erroneous structural changes and prevent the measurement of allosteric effects. Alternatively, membrane proteins may be solubilized with lipids prior to HDX and the lipids can be removed after HDX using manually performed methods, which introduces errors during short exchange rates in kinetic experiments. Our method enables fully-automated deuterium labeling, proteolysis, lipid removal, desalting, analytical separation, and MS acquisition. In addition to physiological relevance of measurements in membranes, our workflow enables studies for many membrane proteins that are not even available in a soluble variant for HDX-MS analysis and have yet to be studied. Furthermore, the effect of variations in glycosylation or modifications of protein therapeutics on the binding to membrane proteins can be studied with our method.

Bicelles were produced to solubilize membrane proteins using a mixture of long chain phospholipids, 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), and short chain phospholipids, 1,2-di-o-hexyl-sn-glycero-3-phosphocholine (DHPC). DOPC forms a bilayer around the hydrophobic transmembrane domain of the protein and the bilayer is capped by short chain DHPC. Deuterium labeling, proteolysis, lipid removal, desalting, and analytical separation were performed inline on a fully-automated HDX PAL robot coupled to a Thermo LTQ Velos Orbitrap Elite. DOPC/DHPC were removed inline using zirconium oxide beads, allowing lipid-free protein to continue to proteolysis and LC-MS analysis.

B2: Towards understanding the role of lipid diversity in tuning biomembrane dynamics

Position 49

Elizabeth Kelley, Michihiro Nagao, and Paul Butler

Lipid membranes undergo a wide array of dynamic transformations that are essential to cell function. These hierarchical dynamics span several decades in length and time scale, ranging from the rotation and diffusion of individual lipids to undulations of micron-sized patches of the membrane. Accessing the necessary length and time scales to study bilayer fluctuations can be experimentally challenging; however, over the past decade, neutron spin echo spectroscopy (NSE) has proven to be a unique tool for capturing the collective membrane dynamics on the nanometer and nanosecond scales. This work highlights new insights into the effects of lipid structure on membrane bending and thickness fluctuations gained from NSE. Specifically, subtle changes in lipid composition, such as simply mixing lipids with different tail lengths or incorporating an anionic headgroup, were found to have significant and unexpected effects on the membrane elastic properties. These results illustrate the importance of lipid structural diversity and composition in tuning the rich structure and dynamics of biological membranes.

B3: Association of model neurotransmitters with lipid bilayer membranes

Position 45

Brian Josey, Frank Heinrich, Mathias Lösche, and Robert Cantor

The conventional model of synaptic transmission between neurons is based on the specific binding of neurotransmitters to ligand-gated ion channels. Fast perfusion electrophysiological studies of receptor responses to neurotransmitters have revealed complex kinetic behavior that cannot be reproduced unless the standard model is expanded to include a number of additional conformational states. If one invokes neurotransmitter adsorption to the lipid membrane, the electrophysiological data may be reproduced with a simpler kinetic model that includes only the standard set of three conformational states¹. This putative indirect mechanism of influence of neurotransmitters on receptor conformational transitions is assumed to be nonspecific, i.e., a wide range of molecules, including neurotransmitters and anesthetics associate with the bilayer and affect receptor activity. Experimental verification of neurotransmitter-bilayer interactions has been difficult because of the low binding affinities of the neurotransmitters to a lipid bilayer membrane². We quantify this interaction with surface-sensitive techniques including surface plasmon resonance (SPR) spectroscopy and neutron reflectometry (NR) on artificial membranes. Sparsely-tethered bilayer lipid membranes (stBLMs) composed of zwitterionic (PC) and anionic (PS and PG) lipids were assembled and their interactions with serotonin and γ -aminobutyric acid (GABA) were studied as model systems. SPR shows a range of binding affinities for different neurotransmitters. Consistent with these results, NR shows that the ligand with the largest affinity (serotonin) penetrates the membrane deeply whereas GABA, for which the affinity is a tenth of serotonin, associates with the bilayer peripherally. Overall, we establish that some neurotransmitters interact non-specifically with the lipidic membrane matrix at physiologically relevant concentrations and that this interaction differs vastly for different neurotransmitters. These results could have a significant impact on our understanding of the molecular mechanism of synaptic transmission.

1. J.M. Sonner, R.S. Cantor, *Annu. Rev. Biophys.* 42, 143-167 (2013).
2. C. Wang, F. Ye, G.F. Valardez, G.H. Peters, P. Westh, *J. Phys. Chem. B.* 155, 196-203 (2011).

B4: New approach for detection of Lyme disease in human serum

Position 24

Crystal Cheung, Kyle Anderson, Mark J. Soloski, John Aucott, Karen Phinney, and Illarion Turko

Lyme disease, the most common tick-borne disease in the United States, is caused by the spirochete of *Borrelia burgdorferi*. Currently, the diagnosis of Lyme disease is primarily based on the clinical identification of the characteristic skin lesion called erythema migrans. Confirmatory laboratory testing relies on serological tests for the presence of antibodies that react to *Borrelia burgdorferi* antigens. Such an approach generally takes 3 weeks to 6 weeks before *Borrelia*-specific antibodies can be detected, and as a result, prompt treatment is often delayed. Untreated individuals with Lyme disease could develop neurological symptoms as well as severe rheumatic manifestations, leading to life-long disability.

The low abundance of bacterial proteins in human serum during infection imposes a challenge for early proteomic detection of Lyme disease. To address this challenge, we propose to detect membrane proteins in bacterial vesicles shed by *Borrelia burgdorferi*. These membrane proteins can be separated from the bulk of serum proteins by high-speed centrifugation, causing substantial sample enrichment prior to targeted protein quantification by multiple reaction monitoring-mass spectrometry (MRM-MS). A quantification concatamer (QconCAT) that comprises 25 unique signature peptides from seven *Borrelia burgdorferi* proteins (OspA, OspC, Flagellin, BmpA, p66, Aminopeptidase I, and DNA-binding Hu protein) was designed, expressed with 99% ¹⁵N isotope incorporation, and used as an internal standard in the MRM assay.

Serum samples (1 mL) were collected from three healthy individuals and three patients with undetected Lyme disease at the time of their initial medical visit. Lyme disease was later confirmed in these patients through standard serological tests. Using MRM-MS, Osp A (outer surface protein A) protein was detected in all the Lyme disease patient samples, but not in control patients, with concentrations ranging from 2.9 to 5.1 fmol ospA/mg of serum protein. These results suggest that membrane vesicles released from bacterial cells may be a source of membrane proteins indicative of bacterial infection.

In conclusion, targeting membrane proteins for quantification by mass spectrometry represents a novel approach to detect Lyme disease and may be applicable to detection of other bacterial infections in human serum.

B5: Hydrogen deuterium exchange mass spectrometry (HDX-MS) as a tool to map FcγRs interactions with specific mAb-glycoforms

Position 5

Ioannis Karageorgos, Kerry Bauer, Venkata Tayi, Michael Butler, and Jeffrey Hudgens

The family of Fc receptors (FcRs) for IgG (FcγRs) provides a prime example of how simultaneous triggering of activating and inhibitory signaling pathways sets thresholds for cell activation and thus generates a well-balanced immune response. Antibodies, in addition to their role in binding antigen, can regulate immune responses through interacting with Fc receptors. Analyzing antibody-FcR (mAb-FcR) interactions in vitro is essential to determine the effector mechanisms and binding characteristics. N-glycosylation is one of the critical quality attributes for the therapeutic monoclonal antibodies. Monoclonal antibodies (mAbs) are engineered proteins that undergo complicated folding and can exist in a number of low-energy structures, posing a challenge for traditional methods in structural biology. As their characterization has drawn considerable attention and urgency, we have investigated the effect of glycosylation in the mAb-FcR complex.

In this study we applied hydrogen deuterium exchange mass spectrometry (HDX-MS) to measure the structural effects that are derivative from the interaction between aIL8-hFc mAb in three different glycoforms [aIL8-hFc G0 (non-galactosylated), aIL8-hFc G2 (galactosylated) and aIL8-hFc SA (sialylated)], in combination with a soluble FcγR1a receptor. Peptic peptides of FcγR1a and aIL8-Fc were generated by passing 20 pmol of protein through an Enzymate pepsin column and identified using tandem on the Thermo LTQ Orbitrap Elite. For HDX-MS analyses, the FcγR1a and aIL8-Fc variant protein stocks were diluted in H₂O buffer. All samples were equilibrated at 1 °C. HDX was conducted on a HDX PAL robot. As a result of this study, we observed differences in dynamics of the Fcγ1Ra receptor that are distinct to each glycosylation pattern of aIL8-Fc mAb.

B6: Why do we have to measure DNA repair proteins? A close look to a ‘golden standard’ method.

Position 44

Erdem Coskun, Pawel Jaruga, Alex Tona, Mark S. Lowenthal, Prasad P. Reddy, and Miral Dizdaroglu

In aerobic organisms, intracellular metabolism and exogenous sources such as ionizing radiation and carcinogenic compounds generate reactive species including free radicals derived from either oxygen or nitrogen. Oxidative stress thereby generated may lead to increased genetic instability, proliferation, cell death, apoptosis and onset of inflammation; a hallmark of cancer. Oxidatively induced DNA damage is repaired in vivo by various mechanisms involving numerous DNA repair proteins. If not repaired, this may lead to mutagenesis, which is a fundamental part of the molecular basis of all cancers. In addition, use of repair protein inhibitors in chemotherapy as the novel treatment strategy increases the importance of our knowledge for expressions of those proteins in human tissues.

Our objective is to develop a reproducible and accurate quantitative method for positive identification and accurate quantification of repair proteins in human tissues which have important predictive and prognostic value for cancer development and therapy.

To achieve this goal, we used liquid chromatography-tandem mass spectrometry (LC-MS/MS) with isotope-dilution to identify and measure the amounts of the proteins. The use of ¹⁵N-labelled proteins as an internal standard is critical for accurate measurements of their levels. We, therefore, overexpressed and purified His-tagged and ¹⁵N-proteins from E.coli. Then, we hydrolyzed both labelled and unlabeled proteins with trypsin and used LC-MS/MS to separate and identify resulting tryptic peptides by their full-scan and product ion mass spectra. Finally, selected-reaction monitoring of the tryptic peptides were determined for positive quantification.

Here, we developed a methodology to positively identify and accurately measure some of the important repair proteins in human tissues using LC-MS/MS with isotope-dilution. Followed by the development of this novel method, we also measured levels of hAPE1 and hMTH1 in human normal and malignant breast tissues, and in four human cultured cell lines. We recorded extremely higher levels of hAPE1 and hMTH1 in MCF7 than in MCF10A, cancer and normal cell lines of the same origin, respectively. Supporting these results, highly significant differences between levels of hAPE1 and hMTH1 in normal and malignant tissues were observed. We also developed the methodology for other repair enzymes such as NEIL1, NTH1, OGG1, PARP1 and POL-β and moving forward to identify and measure them in cell lines and human tissues.

The novel approach described herein is expected to be applicable to the measurement of DNA repair proteins' expression levels in cancerous vs. normal tissues in patients. Our ultimate goal for the future is to evolve this novel approach to be as simple as a regular screening test, which will give us the expression levels of various DNA repair proteins in one pot. This would allow clinicians to develop treatment strategies and guide therapies instantly.

B7: Developing new physical, analytical, and documentary tools for biological applications of quantitative flow cytometry

Position 47

Peter McLean, Christina Smolke, and Marc Salit

Development of high-throughput technologies for biological applications has greatly accelerated our ability to design, modify, construct, and ultimately measure cellular activities. Flow cytometry is an example of a mature high-throughput technology that has been coopted for quantitative analysis of cellular gene expression. Despite its widespread adoption, however, appropriate controls and analytical methods are commonly neglected in the acquisition, processing, and subsequent publication of experimental results. A principle focus of the Synthetic Biology Standards Consortium's (SBSC) Flow Cytometry workgroup is to describe minimum information standards for flow cytometry that appropriately describe experimental and analytical conditions, and develop a reproducible reference protocol that can be used to validate conditions and facilitate experimental reproducibility. Laboratory support for these goals is focused on the development of 1) alternative analytical approaches for estimating gene expression from transiently transfected cell populations and 2) new biological reference constructs that accurately reflect in vivo gene expression and fluorescence. These products will support the ongoing efforts of NIST and the SBSC by improving the accuracy, precision, and reproducibility of quantitative measurements of gene expression acquired by flow cytometry.

B8: Rapid brain cancer diagnostics: Stratified blood serum analysis via ATR-FTIR spectroscopy

Position 17

James Hands, Graeme Clemens, Robert W. Lea, Katherine M. Ashton, Timothy Dawson, Michael D. Jenkinson, Andrew Brodbelt, Charles Davis, Carol Walker, and Matthew J. Baker

Gliomas are the most frequent primary brain tumours in adults, with these intracranial neoplasms accounting for 70% of adult malignant brain tumours (Wen & Kesari, 2008). The current diagnostic regime is to some extent subjective, invasive, and may require unnecessary surgery. Studies have shown the potential of ATR-FTIR spectroscopy for diagnostic applications when collecting spectral measurements of human serum to discriminate between healthy and diseased states; studies involve cardiology (Petrich et al, 2009), ovarian cancer (Owens et al. 2014; Gajjar et al. 2013) and our previous studies on brain cancer (Hands et al. 2013; Hands et al. 2014) to name but a few.

Previously (Hands et al. 2013; Hands et al. 2014), we used ATR-FTIR spectroscopy combined with a Radial Based Function Kernel Support Vector Machine (RBF-SVM) to diagnose high-grade gliomas (e.g. Glioblastoma multiforme), low grade gliomas (e.g. oligoendoglioma) and non-cancerous samples using serum volumes of 1 μ l. Optimum sensitivities and specificities of 93.75% and 96.53% respectively, were achieved when analysing whole (unfiltered) serum samples. We built upon our existing spectral dataset to construct 5 models; 1) cancer vs. non-cancer, 2) metastatic brain cancer vs. brain cancer vs. non-cancer, 3) organ of tumour origin, 4) high grade glioma vs. low grade glioma vs. meningioma, 5) subtype of brain cancer. In total, the latest research includes 433 patients demonstrating a rapid stratified serum diagnostic process using minimal sample.

Additionally, the power of each stratum through 525 iterations of the training and blind dataset were performed to understand the spectral variance inherent within this large biological sample set. In order to refine and identify the most salient features of the spectrum for each stratum analysed we show the use of Feature Extraction (FE) methodologies to enhance and tighten the range of sensitivities and specificities observed. Comparing an RBF-SVM performed on the full infrared fingerprint region and one performed on the top 130 performing features resulted in a smaller range of variance within the sensitivities and specificities observed. The full fingerprint region RBF-SVM resulted in a range of sensitivities and specificities of 81% to 97% and 51% to 95% respectively; in comparison, the FE-SVM performed on 130 spectral features resulted in 81% to 98% and 66% to 95% sensitivity and specificity respectively.

Presented is a rapid, robust and reproducible methodology that can be used to diagnose and distinguish between cancer, organ origin and tumour grade from non-cancer with a 1 μ L volume of human serum with high sensitivity and specificity.

B9: Using SANS to find easier ways to make nanodiscs

Position 13

Thomas Cleveland, Wei He, Matthew Coleman, and Paul Butler

Membrane proteins are essential to life, since they are the primary means through which all cells sense and interact with their environment. They are also disproportionately important in medicine; although only 20-30% of all proteins encoded in the genome are membrane proteins, more than half of all targets of existing drugs are membrane proteins. These proteins are more difficult to study than soluble proteins, however, because most biochemical assays require their removal from the membrane. Traditional methods of solubilizing membrane proteins, such as with detergents, often destroy their functional activity. Therefore, "nanodiscs" have been developed as a more native-like membrane environment for the solubilization and biochemical study of membrane proteins.

Nanodiscs, or nanolipoprotein particles (NLPs), are roughly 10 μm disc-shaped patches of membrane bilayer surrounded at the perimeter by a protein "belt," which packages the lipids and fixes the disc size. Membrane proteins are traditionally packaged into nanodiscs by mixing the isolated belt proteins, lipids, and purified membrane protein, all solubilized in detergent; removal of the detergent then causes the discs to form, capturing the membrane protein in the disc bilayer. These "packaged" membrane proteins then remain in solution and can be studied by traditional solution biochemical methods.

While the traditional disc packaging methods have been successful in many cases, the process of reconstitution is cumbersome, labor-intensive, and not easily amenable to high-throughput methods for the analysis of many membrane proteins at once. Therefore, packaging methods have been developed where the membrane protein and belt proteins are simultaneously co-expressed in the presence of lipid vesicles in a cell-free expression system. This causes discs to form, with enclosed membrane proteins, without the need for detergent solubilization or pre-purification of the membrane protein. Since the only starting material is the DNA for expression of the membrane protein, the method is highly amenable to high-throughput screens.

This cell-free method is, however, not as well-characterized as the traditional methods. Before wide adoption can be expected, it is necessary to show that the products of the cell-free method are equivalent to the traditional nanodisc preparations. Therefore, we have performed Small-Angle Neutron and X-Ray Scattering (SANS/SAXS) on nanodiscs produced via traditional methods, and by cell-free methods. These studies demonstrated unequivocally that discs with the same size and shape are produced by either method. Thus, it can be expected that cell-free nanodisc preparation methods will be appropriate for the study of membrane proteins, and will produce equivalent results to the traditional methods.

B10: Detection of structural variants using read clouds

Position 34

Noah Spies, Ziming Weng, Justin M Zook, Serafim Batzoglou, Arend Sidow, and Marc Salit

Structural variants are large changes in the DNA of a cell. Because of their size, structural variants typically have a substantial affect on cellular function and therefore often have a strong effect on cellular or even organismal fitness. Structural variants are much more complex than the common single-nucleotide variants, and are therefore much more difficult to accurately identify. In particular, whole-genome short-read sequencing is poorly-suited to identifying structural variants because the sequencing reads are typically several orders of magnitude shorter than the variants.

A recent innovation in sequencing involves breaking the genome into large fragments of DNA, each of which is sequenced by many short-reads with a single barcode. The barcodes allow reconstruction of the short reads into "read clouds" that represent the original large DNA fragments.

We are developing methods to use these read clouds to infer structural variants. We have used the 10X Genomics GemCode platform to produce read clouds for multiple tumor and normal samples from a single clinical sarcoma. We identified patterns of barcode overlaps in different genomic regions indicative of structural variation, and have developed a peak-finding approach to filter out false-positives and precisely identify the breakpoints. Because of the ~ 75 kb size of the read clouds, we are able to confidently identify breakpoints even in repetitive regions that cannot be analyzed by standard short-read sequencing. We are in the process of automating the process of calling structural variants from multiple samples simultaneously, allowing the comparison of matched tumor/normal samples in order to separate cancer-specific somatic mutations from germline mutations present in both samples. In addition, we have GemCode sequencing data for four normal Genome in a Bottle genomes (one individual and one family consisting of both parents and a son), which have also been sequenced using multiple orthogonal technologies, allowing us to identify false-positives and false-negatives. The methods we are developing should allow the efficient and accurate identification of structural variants from a single sequencing platform at a sequencing depth/cost reasonable for routine clinical or population-level studies.

B11: Microfluidic models of the microvasculature for red blood cell metrology in sickle cell disease

Position 54

Jordan Betz, Hans Ackerman, and David LaVan

The microvasculature plays an important role in the pathology of sickle cell disease. Sickle erythrocytes undergo changes in their mechanical and adhesive properties that lead to the obstruction of capillaries and postcapillary venules. In recent years, there have been several studies on the mechanical and adhesive properties of these cells, but the majority of these are done under static conditions- there is no fluid flow associated with the measurement. Researchers have tried to address this by using microfluidic devices, however the channels on the devices used are often much larger in diameter ($\geq 30 \mu\text{m}$) than human capillaries ($\leq 10 \mu\text{m}$). Our collaboration between NIST and the Sickle Cell Branch of the National Heart, Lung, and Blood Institute of the NIH has allowed us to design and fabricate microfluidic devices with the smallest channels matching the dimensions of human capillaries. We use high speed video microscopy to record and analyze the behavior of cells flowing through these devices at physiologically relevant speeds. We are using these devices to observe and measure obstruction of channels due to cellular jamming in the case of sickle cell disease. Furthermore, observing cells as they exit the constraints of our artificial capillaries provides insight into their deformability. Additional efforts are directed toward endothelialization of these devices, creating a more physiologically relevant model for investigating not only the effects of mechanical confinement on the obstruction of the channels, but also to measure the contributions of microvascular endothelial cells to the adhesion of infected or sickle cells.

BIOTECHNOLOGY CATEGORY

T1: Nanostructure fabrication by DNA and protein self-assembly

Position 28

Daniel Schiffels, Veronika Szalai, and J. Alexander Liddle

Self-assembly is a scalable method for the fabrication of nanostructures that does not require expensive instrumentation. In cells, proteins can self-assemble into stiff filaments (i.e. microtubules), virus capsids or even photosynthetic complexes. However, the experimental goals of modifying proteins for a custom application or designing novel, self-assembled protein structures currently suffer prohibitive challenges.

On the other hand, DNA can be “programmed” to self-assemble into custom nanoscale shapes using the “DNA origami” technique. DNA origami are exciting for applications such as drug delivery vehicles and controlling precise assemblies of plasmonic nanoparticles as well as for their potential to be integrated into top-down fabricated surfaces. However, many DNA origami applications are currently restricted by low yields and limitations in size.

Here we present a new strategy to combine protein and DNA self-assembly to create rationally designed nanoscale objects that can significantly exceed the size of traditional DNA origami and benefit from the high yield and low cost of protein self-assembly.

T2: Small-angle neutron scattering of therapeutic proteins

Position 33

Maria Monica Castellanos, Yun Liu, Susan Krueger, and Joseph E. Curtis

Advances in recombinant technology and the high specificity of monoclonal antibodies (mAbs) have positioned them as a rapidly growing class of biotherapeutics. Nonetheless, some challenges remain such as designing therapeutic proteins that remain structurally stable throughout the product lifecycle, and minimize their propensity to aggregate under different environments. Small-angle neutron scattering is a tool to study structure, protein-protein interactions and dynamics of mAbs in various liquid and solid phases. Aided by simulations and computational tools, the structure of these highly flexible molecules is analyzed, and these structural features are taken into account when estimating protein-protein interactions across different systems. The latter point is of particular relevance, since most protein models in the literature rely on rigid geometric shapes with uniform scattering density. Two model mAbs are presented: the IgG1 “NIST mAb” reference material, and an IgG2 provided by Amgen. Using Monte Carlo simulations, ensembles of structures are generated and the theoretical scattering profiles are directly compared to the experimental data in solution. Additionally freeze/thaw cycles were performed during the neutron scattering measurements, in order to investigate changes in the solution structure upon freezing. These results not only support the development of the “NIST mAb” reference material, but also provide insights on the structural stability of mAbs and guide future efforts for their development under different formulations.

T3: *In vivo* site-specific protein tagging using engineered sortase variants

Position 40

Jeff Glasgow, Marc Salit, and Jennifer Cochran

Protein conjugates are very important molecules for the treatment of many diseases. Chemical methods to attach new functionality to proteins can be very effective but often suffer from lack of specificity, instability, or harsh conjugation conditions. Chemoenzymatic modification of proteins is an attractive option to create highly specific conjugates in gentle, biological conditions; however, these methods often require expensive specialized substrates, bulky fusion tags, and extra purification steps to achieve the desired conjugate, sometimes in intractably low yield. *Staphylococcus aureus* sortase A and its engineered variants are used to attach oligoglycine derivatives to the C-terminus of proteins expressed with a minimal LPXTG tag. This strategy has been used extensively to make valuable conjugates *in vitro*, and to make protein-protein conjugates in living cells. Despite the simplicity of sortase-based labeling, several hurdles exist to limit the practicality of widespread use and scaling of sortase-based conjugation.

Here we demonstrate that by altering reaction conditions, engineered variants of this enzyme can have activity that allow proteins to be tagged using a diverse set of non-biological functional groups, including several adaptors for bioorthogonal “Click” labeling. We show this labeling works on several model proteins, including medically relevant antibody derivatives for imaging or therapeutic use. Importantly, this technique also works in living *Escherichia coli*, enabling simple, inexpensive production of chemically functionalized proteins with no additional purification steps.

T4: Chemical and biological imaging utilizing 4D structured illumination microscopy (4D-SIM)

Position 23

Jens Breffke, Garnett Bryant, and Stephan Stranick

Three-dimensional (3D) microscopy has been proven a valuable technique in both biological and chemical imaging using fluorescence. Taking the next step is to acquire also the emission lifetime which provides additional and complementary information about the probe's environment. We report a four-dimensional structured illumination microscope (4D-SIM) with multi band excitation, fluorescence lifetime capability and spatial resolution below the diffraction limitation.

T5: Rapid and sensitive DNA hybridization by isotachophoresis

Position 1

Crystal Han, Moran Bercovici, Supreet Bahga, Evaldas Katilius, and Juan Santiago

DNA hybridization is essential to a wide range of diagnostics and molecular biology techniques including genetic profiling, pathogen identification, and single-nucleotide polymorphism. However, slow second order hybridization kinetics at low concentration DNA targets, often the most interesting, results in long analysis time. This limits the applicability of state-of-the art techniques in point-of-care settings. The common methods to speed up DNA hybridization typically involve trade-offs between speed and specificity by varying concentration and type of cation or incubation temperature. This poster presents sequence-specific DNA quantitation method based on isotachophoresis (ITP) that significantly improves sensitivity and assay time through focusing of reactants. ITP is an electrokinetic technique, which enables greater than 10,000-fold preconcentration at its moving interface between heterogeneous electrolytes. We leverage a locally increased concentration to enhance hybridization rate either between suspended species or between suspended and immobilized species. We experimentally demonstrate ITP-based DNA hybridization with molecular beacon probes in free solution, which results in up to 14,000 fold reduction in reaction time. We have developed a model which captures the coupling of DNA hybridization kinetics with dynamics of ITP focusing. Our experimentally-validated model enables closed form solution for two-species hybridization under ITP, and reveals the key parameters which control the speed-up of reaction. We also demonstrate ITP-enhanced rapid (30 min) microarray assay where we enable quantitation of 20 target sequences over 4 orders of magnitude. We performed extensive quantitative experiments showing 2,300 fold speed up per spot, 30 fold speed up of hybridization for the entire array with 8.2 fold increase of signal.

T6: Toward structure determination of few-atom silver clusters stabilized by DNA: Explaining optical and antimicrobial activities.

Position 4

Danielle Schultz, Kira Gardner, Sumant S. R. Oemrawsingh, Nemanja Markešević, Kevin Olsson, Mark Debord, Dirk Bouwmeester, Elisabeth Gwinn, and Nancy Lin

Noble-metal clusters with sizes approaching their Fermi wavelengths (~0.5 nm for Ag and Au) display remarkable optical properties owing to the discretization of states. In recent years, efforts to stabilize few-atom clusters have seen success with the use of various ligands. Among these ligand-stabilized quantum-sized clusters, silver clusters stabilized by DNA (AgDNAs) stand out for their exceptional stabilities and tunability. By varying the sequence of the stabilizing strand, AgDNA cluster sizes can be tuned to produce fluorescence ranging from the blue to the near-infrared. The unique relationship between DNA sequence and cluster color makes AgDNAs exciting for a number of sensing schemes including detection of single base mutations and sequence identification. AgDNAs are further interesting for their potential as bio-degradable antimicrobials. The use of DNA as a ligand makes AgDNAs a greener alternative to conventional capped nanoparticles.

However, many applications involving AgDNAs remain limited by the lack of mechanistic understanding regarding their photo-physical and assembly pathways. This lack of understanding is largely due to challenges in obtaining structural information.

Here we aim to characterize the structure and antimicrobial activity of AgDNAs. We use reverse phased, high-performance liquid chromatography with in-line mass spectrometry as a first step toward AgDNA characterization, revealing their size-dependent optical properties, which can be rationalized by a rod-like structure. We further demonstrate their antimicrobial efficacy against the oral bacteria, *Streptococcus mutans* and propose the use of nuclear magnetic resonance (NMR) spectroscopy to elucidate the fine structural details of AgDNAs. Insights gained from determining AgDNA structure will not only help explain both their fascinating optical and antimicrobial properties, but will enable design strategies for targeted applications.

T7: Development of a digested yeast protein extract as a mass spectrometry reference material

Position 27

Candice Johnson, Ashley Beasley-Green, and Karen Phinney

The emergence of mass spectrometry (MS) based proteomic platforms as a prominent technology utilized in biomedical and clinical laboratories has increased the need for high quality MS measurements and optimal instrument performance. Reference Material (RM) 8323: Yeast Protein Extract, an intact yeast protein material, was previously designed to assess the pre-analytical and analytical variables that influence measurement quality in proteomics-based workflows. However, due to the overwhelming interest in a highly complex uniformly digested peptide material, we are developing RM 8313: Digested Yeast Protein Extract as a performance quality control material to benchmark the performance of MS-based instrumentation. *Saccharomyces cerevisiae* will be utilized as the protein source due to proteome complexity, extensive dynamic range and reduced production costs. To produce a cost effective large-scale digest, several grades of trypsin, such as sequencing grade and non-sequencing grade trypsin, will be evaluated. The digestion efficiency of each trypsin material will be assessed via the degree of protein sequence coverage of select yeast protein to determine the optimal trypsin digest conditions for RM 8313 production. In addition, the homogeneity of the digested material will be qualitatively examined using multiple LC-MS/MS platforms and the MS measurements will be quantitatively assessed via the NIST MS Quality Control (MSQC) performance metrics. By eliminating the variability in individual laboratory protein digestion protocols, RM 8313 will provide research and clinical laboratories with a complex and uniformly digested peptide material to benchmark and improve LC-MS/MS instrument performance and measurements.

T8: Forced degradation study of biopharmaceutical antibodies using electrochemistry

Position 16

Beijing Huang, Abigail Turner, Eunkyong Kim, Gregory Payne, and John Schiel

Forced degradation, the intentional application of stress conditions to artificially induce changes in product attribute, is a critical step in the evaluation of pharmaceutical antibodies. Information about changes that may occur to the antibody after exposure to stress conditions such as pH changes, heat or oxidation can be used to design production, processing and formulation that will decrease the likelihood of degradation. In this study, we demonstrate the use of electrochemistry for forced degradation of NISTmAb IgG1k reference material via oxidation. Using soluble small molecules called mediators that can be oxidized at different potentials (V), we apply increasingly positive V to a solution containing these mediators along with the NISTmAb to indirectly oxidize the antibody. Advantages of this system include the ability to easily detect and quantify the oxidation of NISTmAb in response to the mediators, and the ability to control the residues that are affected by tuning the oxidation potential. In parallel, we employ analytical techniques such as capillary electrophoresis and mass spectrometry to determine the specific modifications on the antibody caused by mediator oxidation. By coupling electrochemistry with analytical techniques, we are developing a quantitative and chemically controlled approach to evaluate biopharmaceutical integrity.

T9: Seeing the invisible: Exploiting crosstalk to measure genetic constructs

Position 2

Ariel Hecht, Drew Endy, Marc Salit, and Matthew S. Munson

The emerging bioeconomy is in need of a metrology infrastructure. One area where infrastructure is needed is the ability to measure the activity of genetic constructs that do not produce fluorescent proteins. This poster describes a measurement approach for genetic activity, based on developing a competitive assay in *Escherichia coli*. In cells, transcriptional and translational resources are limited, resulting in a limited capacity for protein expression. It has been shown that genetic constructs compete for resources, with expression of one construct coming at the expense of other constructs. We present experimental data showing that there is a regime where the competition between two constructs is linear. We exploit this linear resource competition to measure the expression of genetic constructs that produce spectroscopically invisible products. Spectroscopically invisible “test constructs,” can be benchmarked for activity against fluorescent reference constructs enabling relative quantification of test construct libraries. By measuring the decrease in expression from the reference construct, we infer the activity of the test construct. We have demonstrated proof-of-principle by characterizing a collection of constructs producing the fluorescent protein mRFP1. This serves as a mimic of an invisible test construct using a sfGFP producing reference. In addition, we have characterized a collection of constructs producing NanoLuc, an enzyme that is not spectroscopically detectable. These data show that the competitive assay can be used to measure the expression level of spectroscopically undetectable constructs, and can be a key tool in enabling forward engineering in synthetic biology.

T10: Synthetic biomineralization: Towards materials biomanufacturing

Position 6

Lukmaan A. Bawazer, Nikita Khlystov, Steven Hallam, Bob Chen, Jennifer Cochran, Tom Baer, Drew Endy, and Marc Salit

The production of high-performing hard materials occurs widely in biology, such as in the growth of bones, teeth, and seashells. My NIST NRC research seeks to harness the key genetic and biochemical features that control formation of these natural biomineralizing systems, ultimately to design new organisms that will enable genetic engineering and biomanufacturing of advanced materials. As a starting point, I am pursuing two approaches to install novel biomineralization functionality into laboratory *E. coli*. The first approach examines silica mineralization at *E. coli* surfaces, and the second approach explores metagenomic library screening as a method for developing new genetic toolkits for synthetic biomineralization.

To study silica mineralization, *E. coli* cells are reacted with liquid silica precursor tetraethylorthosilicate (TEOS) in the presence of a silica-labeling fluorophore. Reacted cells are then analyzed by flow cytometry, using light scattering to examine morphological features of cell-mineral composites and fluorescence to measure silica labeling and protein expression. A clustering algorithm known as SPADE (Spanning-tree Progression Analysis of Density-normalized Events) is used to analyze the multidimensional cytometry signals and thereby identify unique mineralization events. Initial results indicate that recombinant expression of a common outer membrane surface display scaffold, ice nucleation protein (INP), leads to enhanced silica mineralization relative to non-expressing control populations. Efforts are underway to quantify this differential mineralization behavior, and also to investigate mineralization performance from INP-displayed fusion constructs including proteins such as “silaffins”, biomineralizing domains identified from silica-mineralizing diatom algae.

To explore metagenomic screening, a high-throughput screening methods based on magnetic selection is used to select for heterologous genes that can endow *E. coli* with iron-oxide mineralizing activity. The metagenomic libraries, constructed by collaborator Steven Hallam’s laboratory at the University of British Columbia, are comprised of randomized gene cassettes isolated from bacterial consortia from diverse environmental niches, including salt marshes, oil sands, and mineral mines. Gene pools are transformed into *E. coli*, which are grown in the presence of iron sulfate metal salt (as a mineral precursor) within a micro-capillary array-based screening platform recently developed at Stanford which can accommodate growth of ~10⁵ bacterial cultures in parallel. For selection, the arrays are placed proximate to (within ~0.5 mm of) a magnetic surface to extract cells from exhibiting magnetic phenotypes. Initial work has identified 20 separate ~40 kb gene fragments, found by sequencing to originate from diverse proteobacteria and archaea species, that are currently being further investigated as sources of iron-oxide mineralizing behavior. This metagenomic approach represents a unique opportunity for “casting a wide net” across natural genetic diversity, and thereby efficiently prospecting for previously unidentified proteins and enzyme pathways that can be repurposed as material synthesis tool-kits.

Overall, this work is building towards a new generation of bioengineered, evolvable materials that can help enable solutions to pressing technological challenges that face our planet, including those in the areas of diagnostics, drug delivery, catalysis, energy production and storage, and ecological sustainability in our built environment.

T11: The effect of temperature, agitation, and solution environment on the mechanisms and rates of aggregation of an IgG1 monoclonal antibody

Position 37

Cavan Kalonia, Saba Ghazvini, Prajnaparamita Dhar, and David Volkin

Aggregation of therapeutic protein drugs can increase the risk of immunogenicity when a drug is administered to patients. In the pharmaceutical biotechnology literature, “protein aggregation” is used to describe a collection of mechanisms that produce non-native, net irreversible aggregate structures that are primarily composed of protein molecules. The work described in this poster is focused on developing quantitative tools and theoretical models to better understand how protein aggregation rates and mechanisms are affected by formulation conditions (e.g., solution pH, ionic strength, cosolutes) and applied stresses (e.g., temperature, agitation). The methods developed are then applied to obtain a comprehensive understanding of the aggregation pathways of a therapeutic IgG1 monoclonal antibody (mAb) in different solution environments.

Kinetic models describing protein aggregation in bulk solution were used to better understand how different solution environments and incubation temperatures can affect the rates of aggregate nucleation and growth for this mAb in bulk solution. Our preliminary results suggest that protein conformational stability affects both aggregate nucleation and growth for this mAb, whereas protein colloidal stability only affects the rate of aggregate growth. The theoretical basis of these observations are discussed within the context of the models developed in this study.

A Langmuir trough was used to apply a controlled compression-expansion stress to adsorbed proteins at the air-water interface. This study demonstrates that protein aggregates can form at the air-water interface when mAb solutions are exposed to mechanical agitation. We also demonstrate that aggregates produced at the interface can be released into the bulk solution when sufficient stress is applied. The results of this study help to elucidate the mechanism of protein aggregation induced by mechanical agitation and could be used to develop mechanistic and kinetic models.

CHEMISTRY CATEGORY

C1: Characterization and physiological application of zinc and copper metallic nanoparticles

Position 35

Yasmine C. Daniels, William A. MacCrehan, Oleg Pustovyy, Shin Muramoto, Gheorghe Stan, and Vitaly Vodyanoy

The unique physical, chemical and biological properties of nanomaterials have led to major advancements in modern technology and their increasing use in consumer products, energy, and medicine. Highly reactive nanoparticle surfaces, resulting from their large surface area to volume ratio, have contributed to their use in targeted drug delivery systems and in some cases, cancer cell treatment. Metal nanoparticles have been shown to cause degradation of cancer cells by inducing cancer cell apoptosis.¹ Zn and Cu metal nanoparticles in particular, measuring 1 nm to 2 nm in diameter, were determined to cause morphological changes in RG2, rat brain glioma cancer cells, including decreased cell adherence, shrinking/rounding, nuclear condensation and budding from cell bodies. These nanoparticles were lethal for the cells at the sub-nanomolar concentration.² Zn metal nanoparticles (1 nm to 2 nm) have also been found to enhance olfaction in rats.³ Olfactory enhancement is important to many U.S. agencies particularly in canine detection for illicit drugs and explosives (DHS and DARPA); the perfume and food industry (DOC); and health-related conditions such as Alzheimer's disease and anosmia (CDC and NIH). Although physiological data supports the enhancement of rat olfactory systems by Zn nanoparticles, chemical characterization of these nanoparticles is limited. The small size of these nanoparticles presents a great measurement challenge at the current state-of-the-art. We have used a number of approaches to estimate the physical and chemical properties of these nanoparticles including ultraviolet visible spectroscopy, atomic force microscopy, dynamic light scattering, electron microscopy and x-ray photoelectron spectroscopy. Both bare and modified nanoparticles are being characterized and their effects on physiological systems evaluated. This work has potential for the development of innovative technologies applicable to the advancement of canine detection, health and physical fitness sciences.

1. Jose, G.P., Santra, S., Mandal, S.K., Sengupta, T.K. Singlet oxygen mediated DNA degradation by copper nanoparticles: potential towards cytotoxic effect on cancer cells. *Journal of Nanobiotechnology*. 2011, 9:9.
2. Vodyanoy, V., Daniels, Y., Pustovyy, O., MacCrehan, W.A., Muramoto, S., and Stan, G. Engineered metal nanoparticles in the sub-nanomolar levels kill cancer cells *Nanomedicine: Nanotechnology, Biology and Medicine*, submitted, 2015.
3. Viswaprakash N., Dennis J.C., Globa L., Pustovyy, O., Josephson, E.M., Kanju, P., Morrison, E.E., Vodyanoy, V. Enhancement of odorant-induced responses in olfactory receptor neurons by zinc nanoparticles *Chem Senses* 2009, 34, 547-557.

C2: Liquid chromatographic retention behavior of polycyclic aromatic sulfur heterocycles and their alkyl-substituted derivatives

Position 51

Walter Wilson, Lane Sander, and Stephen Wise

Polycyclic aromatic compounds comprise a complex class of condensed multi-ring benzenoid compounds originating from a wide variety of natural and anthropogenic sources. The parent homocyclic species, which contain only carbon and hydrogen, are the familiar polycyclic aromatic hydrocarbons (PAHs). Along with PAHs, heterocyclic compounds containing at least one heteroatom such as polycyclic aromatic sulfur heterocycles (PASH) are largely present in petroleum products. The total number of possible isomeric structures for PASH is greatly increased compared with the corresponding PAH because both ring arrangement and position of the heteroatom substitution within the rings give rise to unique isomers. Similar to PAHs, alkylated-PASH isomers increase the sample complexity due to the increased number of structural isomers. Gas chromatography coupled to mass spectrometry (GC/MS) is the primary separation technique currently used for the determination of PASHs in complex samples. With the exception of a couple of publications, very limited data have been reported concerning liquid chromatographic (LC) retention characteristic of PASHs even though LC is a commonly used analytical technique for analyzing PAHs. In this study, the retention behavior of both PASHs and alkylated-PASHs on monomeric and polymeric C18 phases are reported. Molecular descriptors (length, breadth, thickness (T) and length-to-breadth (L/B) ratio) were calculated for all the compounds studied. Correlations for retention on both stationary phases and PASH geometry (L/B and T) ratios were investigated.

C3: Valence band dependent charge transport in bulk molecular electronic devices incorporating highly conjugated multi-[(porphinato)metal] oligomers

Position 22

Robert C. Bruce, Ruobing Wang, Jeff Rawson, Christina A. Hacker, Michael J. Therien, and Wei You

Molecular electronics offers the potential to control device functions through the fundamental electronic properties of individual molecules, but realization of such possibilities is typically frustrated when such specialized molecules are integrated into a larger area device. Here we utilize highly conjugated (porphinato)metal-based oligomers (PM [M = metal] structures) as molecular wire components of nanotransfer printed (nTP) molecular junctions; electrical characterization of these 'bulk' nTP devices highlights device resistances that depend on PM wire length. This length dependence parallels that evaluated previously in single molecule break junction measurements of identical molecules, underscoring that nanotransfer printing is a viable and reliable method for designing 'bulk' molecular electronics junctions with these molecular wires. Device resistance measurements, determined as a function of PMn molecular length, were utilized to evaluate the magnitude of a phenomenological β corresponding to the resistance decay parameter across the barrier; these data show that the magnitude of this β value is modulated via porphyrinmacrocycle central metal atom substitution [$\beta(\text{PZn}; 0.065 \text{ \AA}^{-1}) < \beta(\text{PCu}; 0.132 \text{ \AA}^{-1}) < \beta(\text{PNi}; 0.176 \text{ \AA}^{-1})$]. Cyclic voltammetric data, and ultraviolet photoelectron spectroscopic studies carried out at gold surfaces, demonstrate that these nTP device resistances track with the valence band energy levels of the PM wire, which were modulated via porphyrin macrocycle central metal atom substitution. This study demonstrates the ability to fabricate 'bulk' and scalable electronic devices in which function derives from the electronic properties of discrete single molecules, and underscores how a critical device function – wire resistance – may be straightforwardly engineered by PM molecular composition.

C4: A Bayesian prior probability algorithm to identify chemical compounds

Position 18

Tyler Zimmerman, Gary W. Mallard, Tytus D. Mak, Nirina R. Andriamaharavo, Dmitrii V. Tchekhovskoi, and Stephen E. Stein

Chemical identification through matching spectral properties to a spectral database is a common practice. One factor that is overlooked by many algorithms is the "prior probability" of finding the matched compound in the experiment. Mass spectral matching is not always accurate, therefore the combination of spectral matching with prior probability improves chemical identification. In this study, prior probability information is calculated from several chemical databases (including ChEBI, ChemExper, ChemSpider, HMDB, Jochem, KEGG, LIPID MAPS, MetaCyc, MolPort, NIST WebBook, PubChem, and UniChem) and is used to improve the compound identification from GC-MS spectra (gas chromatography-mass spectrometry) as searched against the NIST EI (electron-ionization) spectral library. In fact, a prior probability score was calculated from the above sources for all ~243,000 compounds in the NIST GC-MS library. A Bayesian prior probability algorithm was constructed that improves compound identification for two GC-MS datasets, essential oils and pediatric urine metabolites. The developed prior probability algorithms are generalizable to any type of spectral identification (including identifications based on mass spectrometry, infrared, Raman, and other spectroscopies).

C5: Ultramicroelectrode studies of self-terminated electrodeposition of nickel

Position 48

Nicole Ritzert and Thomas Moffat

Metal hydroxides, oxides, and related compounds, particularly those containing Ni and Fe, have received much attention for oxygen evolution reaction (OER) catalysts because they have produced some of the highest reported OER rates and are chemically stable in alkaline media. Electrocatalysts based on Ni and Fe are attractive because they exclude expensive precious metals, and thin films of these metals can be coupled with light-absorbing materials in photoelectrochemical energy conversion devices used in water electrolysis.

Our group has been investigating growth of thin metal films such as Pt and Ir through self-terminated reactions, i.e., wet atomic layer deposition. When coupled with controlled potential modulation, these reactions can be used to deposit films with precise thickness. Self-termination behavior has been recently uncovered for iron-group metals albeit through a different mechanism than that reported for Pt and Ir. Ni growth is quenched at the onset of water reduction while formation of a saturated H monolayer is responsible for termination of Pt and Ir deposition. Possible explanations for Ni growth termination include formation of a passivating surface-bound hydroxide species formed upon water reduction or cross reactions between the egress of hydroxide and the incoming Ni(II) species to form Ni(OH)₂ and related products.

Here, we employed ultramicroelectrodes (UME's) and scanning electrochemical microscopy (SECM) to further probe electrodeposition of thin metal films of Ni on Au electrodes and elucidate possible mechanisms for self-terminated deposition. Benefits of using UME's include minimized solution resistance and well-controlled mass transport. Voltammetry of Au UME's in electrolytes containing Ni(II) revealed a sharp, current spike at the onset of water reduction, demonstrating the first observed electrochemical signal of the quenching of the metal deposition reaction. The sharpness of this feature is reminiscent of nucleation process or the initiation of a catalytic reaction. Generation/collection SECM, where a second UME was used as the collector electrode, indicated that H₂ is generated during the process giving rise to this cathodic spike. One explanation is that a highly-active species for the hydrogen evolution reaction (HER) is generated upon water reduction in the presence of Ni(II), as it is well-known that hydroxy-nickel species form during Ni(II) reduction due to a rise in pH. Electrochemical results will be compared with optical characterization as well as SEM, EDX, and Raman spectroscopy to characterize electrodeposited films.

C6: Impact of structure on rate performance and durability of lithium ion battery electrodes

Position 43

Eleanor Gillette, Chanyuan Liu, Gary Rubloff, and Sang Bok Lee

Electrodes fabricated from the same active materials, but with different electrode structures may exhibit very different electrochemical behavior, as a result of ionic and electronic conductivities with the composite structure which are dictated not only by the composition of the material but also the interfaces, porosity and tortuosity. Shortcomings related to ionic or electronic conductivity can have direct consequences, particularly for rate performance and electrode durability. However, linking an individual structural feature to a subsequent loss in conductivity in randomly oriented, disordered material composites is challenging without predictable features for both the shape and size of individual components of the system as well as their orientation and interconnections within the electrode. As a result, systems which have been studied to date tend to be divided into either ordered systems, like aligned nanotube or nanowire arrays, or disordered systems, like carbon nanotube sponges. While the disordered systems generally rely on more scalable technologies, ordered systems do provide opportunities for understanding the consequences of structural changes to electrode design.

In order to understand the consequences of transitioning to less ordered, three-dimensional structures, we demonstrate anodized aluminum oxide template electrodes that can be modified to have increasing numbers of interconnected regions evenly spaced within the aligned nanopores. Atomic layer deposition (ALD) is used to conformally coat the template with V₂O₅ to produce electrodes with systematically modulated surface area and disorder. The rate performance of the interconnected structures is notably improved over their aligned counterparts, which can be attributed to electronic conductivity within the structures. Detailed analysis of cyclic voltammetry can be used to separate the contributions from faster surface charge storage mechanisms and slower bulk charging mechanisms, in order to understand the origin of rate performance increases. Additionally, the cycling performance of the two electrodes remains similar, despite the introduction of sharp corners and edges at the branch sites in the interconnected template.

C7: Nanoparticle photoacoustic enhancement through generation of nano-explosions

Position 41

Jimmy Radney

We present results on the apparent absorption enhancement of Nigrosin aerosol, a water soluble organic dye, and flame-generated soot with small water coatings. Measurements were made using a photoacoustic spectrometer using a continuous wave laser at high and low power and a supercontinuum laser with a pulse duration and repetition rate of 650 ps and 78 MHz. Water was deposited on the surface of these aerosols by increasing the relative humidity (RH) of the air in which they were suspended. While some absorption enhancement is expected as the water shell thickens, the measured enhancements are much larger than would be reasonably expected. In the case of Nigrosin, the measured enhancements are 20% larger at 70 % RH than predicted by Mie theory and are a function of RH, independent of the laser used. Above 70 % RH, the measured absorption decreases due to water evaporation. We attribute these observed enhancements to explosive vaporization of the water coating causing an increase in the photoacoustic response of the particles above what should be obtained from absorption alone. Above 70 % RH, the explosive vaporization still occurs, but a small residual water layer remains that is later slowly vaporized thereby removing energy from the photoacoustic response. In the case of soot, only a negligible amount of water is adsorbed to the surface as the change in mass is less than the resolution of our aerosol particle mass analyzer. Further, the measured enhancements are dependent upon the source used and decrease from the supercontinuum laser to the CW at low power to the CW at high power. We again attribute these trends to the generation of explosive vaporization of water vapor at the particle surface. We believe that for the short pulse case, only water on the illuminated side of the particle is explosively vaporized in a single pulse allowing for multiple explosions to occur. For the CW case thermal transfer inside the particle is capable of vaporizing water on the dark side thereby decreasing the observed enhancement relative to the short pulse case.

C8: NISTmAb: Structural variant analysis by capillary electrophoresis

Position 7

Abigail Turner, Trina Formolo, and John Schiel

The National Institute of Standards and Technology is developing a monoclonal antibody (mAb) standard reference material and accompanying characterization data whose purpose is to facilitate and harmonize analytical characterization of therapeutic mAbs. Therapeutic mAbs comprise the fastest-growing class of biologic drugs, including novel proteins as well as biosimilar and bio-better follow-on biologics. In particular, the growing market for biosimilars has inspired a call for improved analytical characterization of therapeutic mAbs which may reduce the burden of animal studies and clinical trials needed for regulatory approval. The NIST mAb is intended to fulfill the need for a highly characterized, well-defined reference protein to streamline and harmonize mAb characterization technologies and methods across industry. In the present work, we have optimized a set of microelectrophoretic methods for defining size and charge heterogeneity in the NIST mAb reference material. We present optimized methods for analysis of size variants by capillary SDS gel electrophoresis (cSDS) and of charge variants by capillary isoelectric focusing (cIEF) and capillary zone electrophoresis (CZE), focusing on resolution of known product variants produced under stressed conditions. This work is part of an ongoing effort to create a comprehensive analytical profile of NIST mAb purity and robustness which are essential to its utility as a reference material.

C9: Metabolomic serum profiling detection of early-stage high-grade serous ovarian cancer in a mouse model

Position 14

Christina Jones, María Eugenia Monge, Jaeyeon Kim, Martin M. Matzuk, and Facundo M. Fernández

Metabolomics is an emerging systems biology field focused on studying the biochemical processes associated with the metabolome. Metabolome changes occur as a result of modifications in the genome and proteome, and are, therefore, directly related to cellular phenotype. Thus, metabolomic analysis is capable of providing a snapshot of cellular physiology that has the potential to further the understanding of many diseases and provide detection of disease-related biomarkers. As such, the purpose of this investigation was to explore the feasibility of detecting early-stage high-grade serous (HGSC) ovarian cancer (OC) in a mouse model using metabolomic serum profiling.

OC is the fifth leading cause of cancer-related deaths for U.S. women, representing the highest mortality rate amongst gynecological cancers. Non-specific symptoms, combined with a lack of early detection methods, contribute to late diagnosis and low five-year survival rates. However, when detected and treated early in its progression, the five-year survival rate is ~90%. Specifically, HGSC is the most common and deadliest subtype that results in 90% of ovarian cancer deaths. To investigate metabolic patterns for early detection of this deadly ovarian cancer subtype, *Dicer-Pten* double knockout (DKO) mice that phenocopy many of the features of metastatic HGSC observed in women were studied. Using ultra performance liquid chromatography-mass spectrometry (UPLC-MS), serum samples from 14 early-stage tumor DKO mice and 11 controls were analyzed in depth to screen for metabolic signatures capable of differentiating early-stage HGSC from controls. Iterative multivariate classification selected 18 metabolites that, when considered as a panel for orthogonal projection to latent structures-discriminant analysis (oPLS-DA), yielded 100% cross-validated accuracy, sensitivity, and specificity for classification. Furthermore, principal component analysis using this 18-metabolite panel exhibited statistically significant class separation along the first principal component (unpaired *t*-test, $n = 25$, $p = 0.0055$). Altered metabolic pathways reflected in the panel included those of fatty acids, bile acids, glycerophospholipids, peptides, and some dietary phytochemicals. These alterations revealed impacts to cellular energy storage and membrane stability, as well as changes in defenses against oxidative stress, shedding new light on the metabolic alterations associated with early ovarian cancer stages. Future work to be performed under the guidance of John A. Bowden (NIST) includes utilizing a similar metabolomic workflow to explore metabolic alterations associated with endometrial cancer.

C10: Calculating photocatalytic conversion in bimetallic donor-acceptor systems

Position 30

Lisa Fredin and Petter Persson

The rapidly growing interest in photocatalytic systems for direct solar fuel production, such as hydrogen generation from water splitting through so-called artificial photosynthesis, is grounded in the unique opportunity to achieve charge separation in molecular systems provided by electron transfer processes. In general, both photoinduced and catalytic processes involve complicated dynamics that depend on both structural and electronic effects. Quantum chemical calculations provide detailed theoretical information concerning many key aspects of photoinduced electron and excitation transfer processes in supramolecular donor-acceptor systems, which are particularly relevant to better understand fundamental charge separation processes in emerging molecular approaches for solar energy conversion. In weakly bound systems, the interplay between structural and electronic factors involved can be constructed from the various mononuclear relaxed excited states.

The viability of photoinduced chemistry and catalysis by transition metal complexes hinges on a useable high-energy excited state and understanding the interplay of states during the decay of the initial photoexcitation. However, capturing the high excitation energies of such complexes is dependent on understanding the decay of this energy and its coupling it to a chemical or catalytic reaction. Here, supramolecular states of energy transfer and excitation transfer character have been constructed from constituent full density functional theory optimizations of multiple charge/spin states of each of the light harvester-catalyst pairs in terms of energy, structure, and electronic properties.

C11: Lyophilization phase separation: A pretreatment method for headspace sampling

Position 50

Christopher Gray and Thomas Bruno

Characterizing vapor in the headspace above recalcitrant matrices is a significant challenge. These substances contain compounds of differing volatility, polarity, availability, as well as other chemical characteristics. While this is a general problem, here we look at a specific application to a unique substance and substrate when sampling using the NIST developed Porous Layer Open Tubular cryoadsorption technique (PLOT-cryo). Since 2007, the FDA has become aware of increases in illnesses and deaths related to dog treats sourced from China. As part of a collaboration with the Center for Veterinary Medicine within the FDA, we have been asked to evaluate the vapor phase above dog jerky samples suspected to have caused ill effects or death in canines. To address these moist samples, (the dog treats), we used a combination of lyophilization and PLOT-cryo to measure the constituents within the dog jerky. We call the new method Lyophilization Phase Separation (LPS), which separates moist samples into 3 phases for subsequent characterization. In general terms, LPS produces three simplified or processed samples: the original dried solid sample, a liquid sample composed of medium volatility condensate, and a captured vapor sample composed of light volatile components. In this presentation I will review the preliminary findings from our approach to characterizing the vapor above this complicated substance.

C12: New carbonate standard reference materials for boron isotope geochemistry

Position 52

Joe Stewart, Steven J. Christopher, and Russell D. Day

The isotopic composition of boron ($\delta^{11}\text{B}$) in marine carbonates is well established as a proxy for past ocean pH. Yet, before palaeoceanographic interpretation can be made, rigorous assessment of analytical uncertainty of $\delta^{11}\text{B}$ data is required; particularly in light of recent interlaboratory comparison studies that reported significant measurement disagreement between laboratories.¹ Well characterised boron standard reference materials (SRMs) in a carbonate matrix are needed to assess the accuracy and precision of carbonate $\delta^{11}\text{B}$ measurements throughout the entire procedural chemistry; from sample cleaning, to ionic separation of boron from the carbonate matrix, and final $\delta^{11}\text{B}$ measurement by multi-collector inductively coupled plasma mass spectrometry. To date only two carbonate reference materials exist that have been value-assigned by the boron isotope measurement community²; JCp-1 (porites coral) and Jct-1 (Giant Clam)³. The National Institute of Standards and Technology (NIST) will supplement these existing standards with new solution based inorganic carbonate boron SRMs that replicate typical foraminiferal and coral B/Ca ratios and $\delta^{11}\text{B}$ values. These new SRMs will not only ensure quality control of full procedural chemistry between laboratories, but have the added benefits of being both in abundant supply and free from any restrictions associated with shipment of biogenic samples derived from protected species. Here we present in-house $\delta^{11}\text{B}$ measurements of these new boron carbonate SRM solutions. These preliminary data will feed into an interlaboratory comparison study to establish certified values for these new NIST SRMs.

C13: Evaluation of the vapor-time profiles of non-explosive PDMS canine training aids by automated training aid simulation using SPME (ATASS) and direct analysis in real time (DART)

Position 15

Mimmy Young, Michele M. Schantz, Edward Sisco, and William A. MacCrehan

Canine detection for explosives and illicit drugs and is well established worldwide and commonly used as a field technique for the forensic establishment of probable cause. However, canine detection is dependent on high-quality training materials and protocols. However, recently canine detection has faced challenges of its scientific validity. Current methods of training involve use of contraband materials as training materials which require care in storage and chain-of-custody. Alternative training aid materials contain the characteristic odors of the hazardous materials, but in a form that is safe to handle. Developing alternative training materials not only requires presenting the key characteristic odors, but also requires knowledge about the longevity of the odor release by the training aid. Volatile odor signatures of explosives are being used to develop and validate non-explosive, standardized training aids. Vapor-time metrology to characterize training aid materials and their time-dependent vapor behavior is performed using Automated Training Aid Simulation using Solid-Phase Microextraction (SPME), or ATASS technique, followed by gas chromatography/mass spectrometry (GC/MS) detection¹ using isotope-labeled externally sampled internal standards (ESIS)^{2,3}. This approach minimizes the irreproducibility of SPME and can be used to reliably evaluate the vapor-time profile of the prototype canine training aid materials.

Evaluation of alternative training aid materials was performed using 2-ethyl-1-hexanol and cyclohexanone, as signature canine odorants identified in the headspace of C-4 military explosives. Alternative training aids were prepared using a patent-pending odor capture-and-release technology based on polydimethylsiloxane (PDMS). The vapor profile of PDMS alternative training aids were based on the analyte/ESIS peak area ratio using the deuterated isomers, d17-2-ethyl-1-hexanol and d4-cyclohexanone, as the ESIS. This technique was also used to determine the vapor emission profile in an open system as a function of time. The effect of varying odor infusion times was studied using ATASS and Direct Analysis in Real Time (DART) coupled to MS. DART confirmed the absorption of the volatile odorants in the surface of the PDMS alternative training aid materials.

1. S. Moore, W. MacCrehan, M. Schantz. *Forensic Science International* (2011) 212, 90-95.
2. W. MacCrehan, S. Moore, M. Schantz. *Journal of Chromatography A* (2012) 1244, 28-36.
3. W. MacCrehan, S. Moore, M. Schantz. *Analytical Chemistry* (2011) 83, 8560-8565.

C14: Gas chromatographic retention behavior of polycyclic aromatic hydrocarbons (PAHs) and alkyl-substituted PAHs on two stationary phases of different selectivity

Position 10

Federica Nalin, Lane C. Sander, Walter B. Wilson, and Stephen A. Wise

Retention indices (RIs) for 45 polycyclic aromatic hydrocarbons (PAHs) and 63 methyl-substituted PAHs were determined by gas chromatography – mass spectrometry (GC-MS) using two different stationary phases: a 50% (mole fraction) phenyl-substituted methylpolysiloxane and a 50% (mole fraction) liquid crystalline polysiloxane. Retention data were obtained for 12 sets of methyl-PAHs (methylfluorenes, methylanthracenes, methylphenanthrenes, methylfluoranthenes, methylpyrenes, methylbenzo[a]anthracenes, methylbenzo[c]phenanthrenes, methylchrysenes, methyltriphenylenes, methylbenzo[a]pyrenes, methylperylene and methylpicenes) and for PAHs with a molecular mass ranging from 128 Da to 328 Da. Molecular descriptors such as thickness (T) and length-to-breadth ratio (L/B) were provided for all the compounds studied. Correlation between RIs and L/B ratio was evaluated for both stationary phases, with a better correlation determined for the 50% liquid crystalline phase (correlation coefficient ranging from 0.313 to 0.981).

C15: Novel solution chemistry routes to 2D tin chalcogenide nanoelectronic device components

Position 9

Adam J. Biacchi, Son T. Le, Joseph A. Hagmann, Sujitra J. Pookpanratana, Curt A. Richter, and Angela R. Hight Walker

2D nanostructures are an important class of materials that has seen an explosion of interest in recent years due to their unique electronic and optoelectronic properties, which lend themselves well for incorporation into nanoscale devices. Solution routes afford an economical and scalable means of making nanomaterials. In particular, solution synthesis has proven effective in producing size-, shape-, and composition-controlled 0D semiconductor nanoparticles. Thus far, however, the development of solution routes to 2D structures has lagged behind mechanical exfoliation and gas phase deposition techniques. Here we present novel syntheses of several nearly-monodisperse nanoscale tin chalcogenide 2D semiconductors using solution routes. The structure of these compounds is thoroughly characterized using electron microscopy, micro-Raman spectroscopy, and diffraction techniques. Further, we process these materials from solution to fabricate solid-state devices. Finally, we characterize the optoelectronic properties of these semiconductors as measured using spectroscopic and contact probe transport measurements. Our results suggest that these functional materials can find utility as integrated components of nanoscale electronic and optoelectronic devices relevant to energy applications.

C16: Applications of capillary electrophoresis for nanomaterials characterization

Position 29

Kathryn Riley, Daniel R. Schiffels, Hind El Hadri, Jiaojie Tan, Christopher M. Sims, Marlon L. Walker, and William A. MacCrehan

Nanomaterials are playing an increasingly significant role in applications as diverse as therapeutics and energy technologies, so the need for rapid materials characterization is growing. Capillary electrophoresis (CE) is a promising technique for the analysis of sub-micron and nanoscale materials, and as such, may be applicable to the development of methods for improved nanomaterials characterization. Three unique applications will be presented; namely, purification of DNA origami constructs, separation of functionalized gold nanomaterials, and evaluation of the interaction of nanomaterials with biomolecules. The analysis of protein-DNA origami constructs employs CE with laser-induced fluorescence (LIF) detection, whereby DNA origami is fluorescently labeled on-column using a non-covalent intercalating dye. CE fractionation of DNA origami is performed to isolate pure origami constructs from aggregated or poorly synthesized constructs and validated by transmission electron microscopy (TEM) of isolated fractions. CE separation of gold nanomaterials based on size, surface functionality, and geometry is also being explored, with particular emphasis on the separation of gold nanorods with different aspect ratios. These materials can pose a unique separation challenge for other methods (e.g. field flow fractionation, FFF, or single particle inductively coupled plasma mass spectrometry, spICP-MS) when similar diffusion coefficients and similar masses are observed, but CE has shown improved separation capabilities because it utilizes the nanorods' unique charge-to-size ratio as the basis for separation. Finally, CE is being used to evaluate the formation of protein coronas on either bare or surface PEGylated gold nanoparticles. Optimization of CE separation conditions is anticipated to allow for the determination of dissociation and rate constants for the interaction between the proteins and nanoparticles, which could be used as a measure of protein binding resistance.

C17: Evaluating the oxidative potential of indoor and outdoor particles with an EPR assay

Position 42

Shahana Khurshid, Steven Emmerich, and Andrew Persily

It is widely accepted that airborne particles have adverse effects on human health but the pathophysiological mechanisms for these effects haven't been established. Particulate matter (PM) are typically characterized by their physical and chemical properties, but there may be more physiologically relevant properties of PM that are better suited to characterize the ability of PM to induce cellular oxidative stress. The hydroxyl radical (OH) generating capacity of PM has been suggested as a way to assess the oxidative potential of particles. The hydroxyl radical generating capacity of outdoor PM has been measured in a few studies over the last decade. This study is the first to measure this metric indoors. Total suspended particle (TSP) samples were collected inside and outside an unoccupied, 15-year old research house in Gaithersburg, Maryland. Hydrogen peroxide and the spin trap, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), were added to PM suspensions prepared from the sampling filters. After a brief incubation period, the PM suspensions were analyzed in an electron paramagnetic resonance (EPR) spectrometer. The quantity of the DMPO-OH adducts was calculated by summing the area under the peaks in the characteristic 1:2:2:1 quartet in the spectra. In experiments to date, the quantity of DMPO-OH adducts in the indoor samples has been about 75% of the outdoor samples indicating that indoor particles have about three-fourth the OH generating capacity as outdoor PM on a sampling volume basis. On a mass basis, the OH generating capacity of indoor PM may equal or even exceed that of outdoor particles and experiments are underway to verify this. Indoor particles can have different oxidative potential than outdoor particles because a major fraction of indoor particles come from indoor homogeneous and heterogeneous chemical reactions. Measurements of indoor and outdoor particle concentrations, temperature, relative humidity and building air change rate are also being made in order to assess the role of these parameters on the oxidative potential of particles. This work highlights the importance of indoor pollutants for human exposure.

C18: Analysis of smoke residues from illicit drugs as a potential source of forensic evidence

Position 32

Julie Bitter and Matthew Staymates

Smoke aerosols and vapors, like those from cigarettes, deposit onto surfaces like clothing, countertops, tables, and chairs, in the form of residues which contaminate indoor environments. Studies have demonstrated that cigarette smoke residues and their decomposition products can be collected from various surfaces and identified in areas of habitual smoking. In this work, 500 µg samples of dried cocaine and methamphetamine solutions were volatilized at 200 °C to produce an illicit drug smoke that was left exposed to ambient conditions for up to four weeks. These residues were collected after discreet time intervals and analyzed by scanning electron microscopy, electrospray-ionization time of flight mass spectrometry, and secondary ion mass spectrometry. Chemical analyses of drug residues collected on various surfaces (plastic, laminate, artificial leather, etc.) indicated low recovery that decreased rapidly in the first 24 h, but was detectable out through four weeks. Decomposition products were also identified, which formed as a result of both volatilization and exposure to ambient laboratory conditions. Particles were collected by inertial impaction to examine the range of sizes produced by volatilization. Predominantly diameters less than 2 µm were seen, indicating particles of respirable sizes. The persistence and size data suggests that smoke residues could simultaneously be a useful form of forensic trace evidence and an environmental hazard to occupants where smoking takes place. Our most recent work has focused on creating realistic smoking scenarios using glass pipes to examine temperature effects and the chemical species that are generated. Additional new interest is of how adulterants and cutting agents impact product formation and sample recovery, with the goal of identifying limits of recovery and determining the usefulness of smoke residues as a viable source of forensic evidence. This work was funded in part by a National Research Council Fellowship.

POLYMERS CATEGORY

Y1: A rheological signature of frictional interactions in shear thickening suspension

Position 26

John Royer, Daniel Blair, and Steven Hudson

Understanding shear thickening (increased viscosity above a characteristic shear stress) presents a significant challenge in colloidal physics, because the macroscopic rheology is increasingly controlled by the microscopic details of short ranged particle interactions. Our measurements here of the first normal stress difference over a wide range of particle volume fraction elucidate the relative contributions from hydrodynamic lubrication and frictional contact forces, which have been debated. Hydrodynamic models predict $N_1 < 0$, while dilation ($N_1 > 0$) indicates friction. We find a transition between hydrodynamic and friction dominated behavior with increasing volume fraction. At concentrations near to this transition it is clear that both effects have significant contribution in the shear thickened state, because N_1 is negative at intermediate shear stress and positive at still higher stress. We introduce a simple modified particle interaction model to combine hydrodynamic and frictional forces, which accurately fits the measured viscosity over a wide range of particle volume fraction and shear stress.

Y2: Structure and self-assembly of oligocarbonate-fluorene end functionalized poly (ethylene glycol) ABA triblock polymer

Position 21

Guangmin Wei, Vivek Prabhu, Shrinivas Venkataraman, Yi Yan Yang, and James Hedrick

Hierarchical structures of oligocarbonate-fluorene end-functionalized poly(ethylene glycol) triblock copolymer (P(F-TMC)_m-PEG444-P(F-TMC)_m) were characterized by light scattering, atomic force microscopy, and Ultraviolet-visible spectroscopy in dilute regime in water, a poor solvent of F-TMC block. The evidence for pai-pai stacked of F-TMC block in self-assembled structure was provided. The self-assembly behavior is highly dependent on concentration and F-TMC block length, *m*. The presence of clusters dominates the population of scatterers once *m* is larger than 2, where there is no clear evidence of a separation of micelles and clusters. The molecular aggregation driven by F-TMC groups appears too strong to permit labile micelle-cluster dynamics as observed with *m* = 2 and 1.2. The non-mean field scaling of the aggregation number, when compared to models for triblock copolymers, highlights the need for a molecular-based model to predict the self-assembly at low end-group numbers. In our case, the end-groups are oligomers, so the comparison to Flory scaling may not be justified.

Y3: Novel phase behavior of a midblock sulfonated block copolymer

Position 36

Kenneth Mineart and Richard Spontak

Block copolymers constitute a versatile class of soft materials composed of different polymer chains that are covalently bonded together to form a single macromolecule. The dissimilar chains repel one another, but are unable to fully separate due to their covalent linkages. This combination of characteristics results in macromolecular self-assembly into a rich variety of nanostructural elements in bulk films. The specific geometry, or morphology, exhibited by a given copolymer at equilibrium typically depends on its composition (i.e., the relative size of its blocks) and the thermodynamic incompatibility between its blocks, with the degree of block segregation normally ranging from weak to strong. However, a number of recently developed materials exist in the superstrong segregation regime including sulfonated block copolymers, which have shown promise as fuel cell, desalination, and photovoltaic membranes due to their high hydrophilicity and ion exchange capabilities. Superstrong repulsion between the blocks (e.g. sulfonated and unsulfonated blocks) frequently yields nonequilibrium structures through kinetic entrapment. In this study, we experimentally investigate a number of different morphologies exhibited by a single midblock-sulfonated block copolymer highlighting that the final morphology is sensitive to the film deposition system utilized and that the formed morphology can be further tweaked using a phase-selective liquid penetrant, as well as various selective and non-selective vapor components. Ultimately, our results provide groundbreaking insight into the control of highly nonequilibrium structures existing in sulfonated block copolymers and help promote their further development for use in energy- and water-related technologies.

Y4: Diffusion of polyelectrolytes in polyelectrolyte gels

Position 39

Anand Rahalkar and Murugappan Muthukumar

Diffusion of polymers in hydrogels is an important process in many biological systems, filtration and membrane separations, as well as in controlled drug delivery applications. In this work, the dynamics of trapped polyelectrolytes in a polyelectrolyte gel is studied using dynamic light scattering technique. The effect of the crosslink density and the charge density of the gel, as well as of salt concentration is investigated. In light scattering experiments, two distinct diffusive modes (fast and slow) are observed, the fast mode corresponds to the gel elasticity and the slow mode corresponds to diffusion of the trapped polymer. The deduced diffusion coefficient of the trapped polymer obeys an exponential dependence on the volume fraction of the gel, in accordance with the presence of an entropic barrier for polymer diffusion.

Y5: Dynamic conformations of nucleosome arrays in solution from small-angle x-ray scattering

Position 11

Steven Howell, Joseph Curtis, and Xiangyun Qiu

Chromatin conformation and dynamics remains unsolved despite the critical role of the chromatin in fundamental genetic functions such as transcription, replication, and repair. At the molecular level, chromatin can be viewed as a linear array of nucleosomes, each consisting of 147 base pairs (bp) of double-stranded DNA (dsDNA) wrapped around a protein core and connected by 10 bp to 90 bp of linker dsDNA.

Using small-angle X-ray scattering (SAXS), we investigated how the conformations of model nucleosome arrays in solution are modulated by ionic condition as well as the effect of linker histone proteins. To facilitate ensemble modeling of these SAXS measurements, we developed a simulation method that treats coarse-grained DNA as a Markov chain, then explores possible DNA conformations using Metropolis Monte Carlo (MC) sampling. This algorithm extends the functionality of SASSIE, a program used to model intrinsically disordered biological molecules, adding to the previous methods for simulating protein, carbohydrates, and single-stranded DNA. Our SAXS measurements of various nucleosome arrays together with the MC generated models provide valuable solution structure information identifying specific differences from the structure of crystallized arrays.

Y6: Self-confinement and microscopic polymer motion in nanocomposites with dynamically asymmetric interphases

Position 8

Erkan Senses, Antonio Faraone, and Pinar Akcora

Dynamics within confined interphase region of matrix and nanoparticle-bound polymers is important to understand microscopic mechanisms controlling composite properties for advanced functionalities. We present neutron scattering investigations on model nanocomposite where nanoparticle-bound polymer and matrix chains are chemically different, yet miscible, and have a large difference in their glass-transition temperatures. Through selective isotope labeling of bound and matrix chains, we examine the role of dynamic asymmetry within the interphases on the segmental and reptation chain dynamics from sub-ns to 100 ns time range. Our results evidence that the local relaxation primarily depends on polymer-particle interaction and remains unaffected in weakly attractive composites. At larger scale, self-confinement of the chains is reduced with remarkable increase of reptation tube size when the bound polymer is vitrified. Recovery of the entanglements at elevated temperature underlines the importance of the softness of the adsorbed polymer on mechanical adaptivity of polymer-nanoparticle composites.

Y7: Probing polyethylene crystallization via simultaneous Raman spectroscopy and rheology

Position 27

Anthony P. Kotula, Kalman D. Migler, and Angela R. Hight Walker

The structure and rheology of polyolefins during crystallization is of critical importance to the polymer processing industry. Optical, thermal, and mechanical properties of polymer products are directly related to the amount of amorphous and crystalline material in the final product, which depends on the temperature and flow history during crystallization. Here we present simultaneous Raman scattering and rheological measurements on crystallizing high density polyethylenes during quiescent and slow flow conditions. Raman spectroscopic measurements during quiescent crystallization allow us to quantify and differentiate three mass fractions of chain conformers: an amorphous fraction, an orthorhombic crystalline fraction, and a fraction of chains that contain many consecutive trans bonds but are not part of the orthorhombic crystal. These non-crystalline consecutive trans (NCCT) conformers are generated as a precursor to crystallinity. Slow steady shear rates ($\sim 1 \text{ s}^{-1}$) applied during isothermal crystallization experiments dramatically increase the crystallization rate as well as the amount of NCCT conformers produced. Optical measurements of sheared samples during crystallization reveal the formation of fiber structures that compositionally contain more NCCT conformers than the surrounding melt. To correlate conformational changes with mechanical properties during crystallization we use a novel instrument for simultaneous optical, Raman, and rheological characterization of materials. The increase in the complex shear modulus commonly measured for crystallizing polyethylenes correlates with the growth of chain conformers and the appearance of spherulites within the melt.

Y8: Characterizing semiconducting polymer nanogratings with polarized resonant critical dimension small angle x-ray scattering

Position 12

Christopher Liman, Daniel F. Sunday, Hyun Wook Ro, Lee Richter, Adam F. Hannon, Thom Germer, and R. Joseph Kline

Critical dimension small angle X-ray scattering (CDSAXS) is a recently developed technique that enables the characterization of the three-dimensional shape of periodic patterns, in which scattering patterns are collected in transmission at variable angles. Information about the patterns is extracted by fitting simulated scattering patterns to the experimental ones using an inverse iterative algorithm. Conducting CDSAXS at resonant energies enhances the strength of the scattering and also causes it to be influenced by the preferential orientation of polymer chains. This technique has applications for next generation semiconductor lithography and for understanding the morphology of organic electronics.

In this work, we use capillary force lithography to pattern linear nanogratings of two semiconducting polymers with preferential orientation. We probe the shape and molecular orientation of the polymers using resonant CDSAXS at the carbon $1s\text{-}\pi^*$ transition energies, using two different linear polarizations of the incident X-rays. We discuss the ways in which the CDSAXS data need to be corrected and reduced to one-dimensional scattering patterns and how we use molecular orientation to generate simulated scattering. From this data we fit the cross-sectional periodic shape and molecular orientation of the nanogratings. Finally, we compare our CDSAXS results to those obtained by spectroscopic ellipsometry fitted by rigorous couple-wave analysis.

Y9: Water transport in highly crosslinked polyamide membranes

Position 3

Bradley Frieberg, Madhusudan Tyagi, Christopher Soles, Christopher Stafford, and Edwin Chan

Highly crosslinked polyamides for reverse osmosis are the state-of-the-art active material in membranes for desalination. The thin film composite membrane structure that is used commercially has been empirically designed to selectively allow the passage of water molecules and minimize the passage of solutes such as salt. However, due to the large roughness and variability of the polyamide layer, there is a limited understanding of the structure-property relationship for these materials as well as the transport mechanism. To better understand the water transport mechanism we measure the water and polymer dynamics of polyamide membranes using quasi-elastic neutron scattering (QENS). By hydrating the membrane with deuterated water, we are able to isolate the dynamics of the hydrogenated membrane on the pico- and nanosecond time scales. By subsequently hydrating the membranes with hydrogenated water, the QENS measurements on the same times scales reveal information about both the translational and rotational dynamics of water confined within the polyamide membrane. Further understanding of the water diffusion mechanism will establish design rules in which the performance of future membrane materials can be improved.

Y10: Bayesian calibration of transferable, coarse-grained force fields

Position 25

Thomas Rosch, Paul Patrone, and Frederick Phelan, Jr.

Generating and calibrating forces that are transferable across a range of state-points remains a challenging problem in coarse-grained (CG) molecular dynamics (MD). In this work, we present a Bayesian correction algorithm, inspired by ideas from uncertainty quantification and numerical analysis, for addressing this problem. The main idea behind our algorithm is to estimate functional derivatives (i.e. linear sensitivities) of CG simulations relative to small changes in the forces. Using these sensitivities, we construct a probabilistic update model in which we constrain the output of a CG method to yield target predictions to within statistical significance. Using density-temperature relationships as a running example, we demonstrate that this correction algorithm is robust to various choices the modeler can make when coarse-graining. Moreover, we show that our approach can speed up coarse-graining by reducing the number of atomistic simulations needed to construct initial estimates of CG forces.

Y11: Limits of single-molecule super-resolution microscopy in thin polymer films

Position 20

Muzhou Wang, Marcelo Davanco, James M. Marr, J. Alexander Liddle, and Jeffrey W. Gilman

Structural characterization by super-resolution microscopy has become increasingly widespread, particularly in the biological community. The technique is powerful because it can produce real-space images with resolutions of tens of nanometers, while sample preparation is relatively non-invasive. Previous studies have applied these techniques to important scientific problems in the life sciences, but relatively little work has explored the attainable limit of resolution using samples of known structure. In this work, we apply photo-activated localization microscopy (PALM) to polymer films that have been nanopatterned using electron-beam lithography. Trace amounts of a rhodamine spiroamide dye are dispersed into nanostructured poly(methyl methacrylate), and UV-induced switching of the fluorophores enables nanoscale localization of single molecules to generate a final composite super-resolution image. Features as small as 50 nm are clearly resolvable. To determine the ultimate resolution limit, we investigate sources of error in the system, particularly from systematic mislocalizations due to the effect of fluorophore orientation on the single-molecule point-spread function.

Y12: Alkane filled single-wall carbon nanotubes: Endohedral volume control for improved nanotube properties

Position 19

Jochen Campo, Yanmei Piao, Stephanie Lam, Christopher Stafford, Jason Streit, Jeffrey Simpson, Angela Walker, and Jeffrey Fagan

Liquid-phase processing of single-wall carbon nanotubes (SWCNTs) generally results in the exposure of their core to the environment (opening) due to the energy input necessary for purification and solubilization, and this often affects the SWCNT properties.¹⁻³ For instance, for aqueous processing, SWCNTs are routinely getting filled with water, which leads to significant redshifts to, and inhomogeneous broadening of, the electronic transitions of the SWCNTs, as well as a substantial decrease of their fluorescence quantum efficiency.¹ Selection of (remaining) empty (end-capped) SWCNTs to avoid these detrimental effects is possible by means of ultracentrifugation, but is a natively low yield process.⁴ In this work, adverse filling is prevented by intentionally prefilling the SWCNTs with alkanes, serving as a passive and highly homogeneous spacer. In contrast to water and other encountered fillants, the alkane core is of low dielectric nature and therefore only weakly affects the electronic structure of the SWCNTs, and hence effectively simulates empty core conditions. This yields highly resolved optical spectra with strongly shifted peak positions compared to water filled SWCNTs, and fluorescence efficiencies approaching those of empty SWCNTs. It is demonstrated that this can be realized using a wide variety of linear as well as cyclic alkanes, in combination with various SWCNT materials having very different diameter distributions.

1. Cambré, S.; Wenseleers, W. Separation and Diameter-Sorting of Empty (End-Capped) and Water-Filled (Open) Carbon Nanotubes by Density Gradient Ultracentrifugation. *Angew. Chem. Int. Ed.* 2011, 50, 2764–2768.
2. Cambré, S.; Santos, S. M.; Wenseleers, W.; Nugraha, A. R. T.; Saito, R.; Cognet, L.; Lounis, B. Luminescence Properties of Individual Empty and Water-Filled Single-Walled Carbon Nanotubes. *ACS Nano* 2012, 6, 2649.
3. Duque, J. G.; Oudjedi, L.; Crochet, J. J.; Tretiak, S.; Lounis, B.; Doorn, S. K.; Cognet, L. Mechanism of Electrolyte-Induced Brightening in Single-Wall Carbon Nanotubes. *J. Am. Chem. Soc.* 2013, 135 (9), 3379–3382.
4. Fagan, J.A.; Huh, J.Y.; Simpson, J.R.; Blackburn, J.L.; Holt, J.M.; Larsen, B.A.; Walker, A.R.H. Separation of Empty and Water-Filled Single-Wall Carbon Nanotubes. *ACS Nano* 2011, 5, 3943–3953.

Y13: DFT modeling of spiro lactam based mechanophores at polymer nanocomposite interphases

Position 53

Ketan S. Khare and Frederick R. Phelan Jr.

Mechanophores are molecules that contain a covalent bond that can be mechanically activated. In the Polymers and Complex Fluids group, the use of these molecules as probes for characterizing the mechanical behavior of polymeric systems is of tremendous interest. In polymer nanocomposites, the polymer matrix in the vicinity of the nano filler – the interphase, is known to show properties that are significantly different than those of the bulk polymer due to polymer-filler interfacial interactions. Carefully placed mechanophores can be used to quantify the role of the interphase in the load transfer between the matrix and the filler, which can be difficult to access by other techniques. In this work, we show the utility of DFT modeling of such mechanophores to calculate the energetics associated with the mechanical activation, which would be critical for analyzing experimental data obtain by our collaborators. Further, DFT can also be used to understand reaction mechanisms, which would be useful for improvements in experimental design.

MATERIALS 2 CATEGORY

M99: Matrix Effects and validation of single particle ICP-MS for measuring nanoparticle size and size distribution

Position 46

Antonio Montoro Bustos, Kavuri Purushotham, András Vladár, Karen Murphy, and Michael Winchester

Single particle inductively coupled plasma mass spectrometry (spICP-MS) is considered an emerging and promising analytical technique for the ultrasensitive detection and characterization of metal-containing nanoparticles (NPs). Particularly, spICP-MS offers exceptional potential for providing information about particle size and size distribution, agglomeration/aggregation state, and particle number concentration, at mass concentration levels down to ng L⁻¹. Ideally, under spICP-MS experimental conditions only one particle reaches the plasma during each reading period, producing a single signal pulse. Additionally, simultaneous detection of dissolved species, pristine NPs, and their agglomerates/aggregates can be carried out in a single analysis by using spICP-MS.

However, despite its highly valuable utility, some important limitations still remain, and spICP-MS cannot be considered a mature methodology. Validation of the technique for measuring NP size and size distribution is required before it can be properly applied for sizing and quantifying NPs. The main limitation to validation is the near total lack of NP test specimens having reliable reference information.

This communication explores the usefulness of high-resolution scanning electron microscopy (HR-SEM) as a reference technique for spICP-MS size validation. Test specimens include NIST reference materials RM 8012 and RM 8013, which are gold nanoparticles (AuNPs) with nominal diameters of 30 nm and 60 nm, respectively. Advantages of using these RMs include their chemical and colloidal stability and homogeneity and the fact that the mean particle sizes and particle size distributions have been thoroughly characterized by six different sizing techniques. This approach has also been applied for an extended and statistically significant size characterization of several coated commercial AuNPs (citrate, PVP, PEG and BPEI), whose mean size and size distribution information provided by the supplier is generally unreliable and typically is limited to the analysis of only 100 NPs. Comparisons of HR-SEM characterization results with the sizing and counting results obtained using spICP-MS for these four different coated AuNPs suspended in ultrapure water are presented.

Further, the capabilities of spICP-MS for the quantitative evaluation of the influence of different coatings on the stability of AuNPs are evaluated. It is expected that the information attainable by spICP-MS could offer a better understanding of the role of the coating in the behavior of AuNPs in suspension at environmentally relevant concentrations.

During the evaluation of the effect of different aqueous, environmental and biological conditions on the stability of the nanoparticulate species, an important matrix effect in the ionization and/or nebulization of the NPs in the plasma is observed, even though highly diluted NP samples are required for spICP-MS measurements. If the matrix interferes with the nebulization or ionization in the ICP-MS plasma, leading to suppression or enhancement of the analyte signal, an underestimation or overestimation of particle concentration and particle size would result.

The novel concept of “matrix-specific” transport efficiency will be presented to compensate the matrix influence on spICP-MS providing accurate particle size and particle concentration results and extending the validity of spICP-MS results to a large range of aqueous, environmental and biological conditions.