

NIST CHAPTER OF SIGMA XI
24TH ANNUAL POSTDOCTORAL POSTER PRESENTATION
PROGRAM AND ABSTRACT BOOKLET

Wednesday February 15th 2017

9:00 AM to 4:00 PM

Administration Building Front Hall, Lecture Rooms A & B

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Awards Reception

4:30 PM

West Square

Organizing Committee

Jonathan Seppala	Robert Berg
M. Lorna De Leoz	Katya Delak
Magdalena Navarro	Aaron Forster
Lindsay Elliott	Amanda Forster
Sara Orski	Eric Shirley

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

AM SESSION (9:00 AM TO 12:00 PM)

BIOLOGY

Machine learning strategies to identify high confidence structural variants in human genome reference materials

Position 14B

Lesley Chapman, Justin Zook, Noah Spies, and Marc Salit

Next generation sequencing (NGS) technologies to measure DNA sequence are rapidly evolving. Clinical decision making has advanced as a result of NGS diagnostic tools. Yet, discordance exists amongst structural variant calls as a result of variance between NGS sequencing and analysis pipelines. Improvements in the accuracy of calling these difficult structural variants is needed to enable confidence in clinical decision making. The central aim of the current study is to use machine learning to integrate data from multiple sequencing technologies and generate a high confidence list of structural variants within NIST human genome Reference Materials that can be used as a benchmark. Sequence information from an Ashkenazim Jewish mother-father-son trio (NIST RM 8392) was assessed. Data was collected from 30 different informatics pipelines and 5 different sequencing technologies to describe over 300000 candidate structural variants within the human genome. For the following study, a sample of 1000 sites within the human genome was analyzed for each member of the trio. Unsupervised machine learning methods were used to classify genotypes of each candidate from each technology. These data will be used for the second part of the study which will involve using semi-supervised machine learning to assign discordant data points genotypes and their likelihoods. We are continuing to develop these machine learning strategies to assign a genotype and its confidence for each structural variant site within the human genome.

Association of model neurotransmitters with lipid bilayer membranes

Position 16B

Brian Josey, Frank Heinrich, Mathais Lösche, and Robert S. 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 kinetic model is expanded to include additional conformational states. However, if one invokes neurotransmitter adsorption to the lipid membrane, the electrophysiological data can be reproduced with a simpler kinetic model that includes only the standard set of three conformational states.¹ This indirect mechanism of influence neurotransmitters have on receptor conformational transitions is assumed to be nonspecific. Unlike anesthetics, experimental verification has been difficult because of the low binding affinities of neurotransmitters to lipid bilayer.² We quantify this interaction through the use of surface plasmon resonance (SPR) spectroscopy to measure the equilibrium dissociation constant of neurotransmitter association, and on and off rates under flow. Neutron reflectometry (NR) on artificial membranes is then used to characterize the association of the neurotransmitters to the 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 associates with the bilayer peripherally. Overall, we establish that some neurotransmitters interact non-specifically with the lipid membrane matrix at physiologically relevant concentration 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. Sonner and Cantor, *Annu. Rev. Biophys.* 42, 143 (2013).

2. Wang, et al., *J. Phys. Chem. B.* 155, 196 (2011).

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Detecting metastasis: The regulation of epithelial-mesenchymal transition and breast cancer metastasis by mechanistic interplay of TGF- β , P-bodies, SYK, and autophagy

Position 28B

Shana Hardy, Aparna Shinde, Wen-Horng Wang, Michael K. Wendt, and Robert L. Geahlen

Breast cancer is a clinically complex disease. The primary cause of breast cancer mortality is the development of distant metastases. Breast cancer metastasis occurs when breast cancer cells undergo an epithelial-mesenchymal transition (EMT) to leave the site of a primary tumor and travel to ectopic sites, where they undergo a mesenchymal-epithelial transition (MET) to establish macrometastases. SYK, a protein-tyrosine kinase and important mediator of receptor signaling in the immune system, also is found in many cancer cells of epithelial morphology. SYK is typically absent from invasive cells of mesenchymal phenotype and its inhibition or down-regulation in epithelial-like tumor cells can promote EMT. We show in this study that SYK associates with P-bodies, ribonucleoprotein complexes involved in mRNA repression and degradation, and promotes their clearance from cells through autophagy. P-bodies assemble in mammary epithelial cells in response to treatment with TGF- β as cells undergo EMT and are cleared through autophagy as cells undergo MET in response to removal of the growth factor. Inhibitors of autophagy block P-body clearance and attenuate MET. In contrast, activators of autophagy promote P-body clearance and block EMT. Blockage of P-body formation by disruption of the gene for DDX6, a protein essential for P-body assembly, blocks EMT and prevents tumor cell metastasis in vivo. These studies establish critical roles for P-body formation and clearance and autophagy in transitions of cancer cells between epithelial and mesenchymal phenotypes and help explain how both autophagy and SYK can function differentially as tumor suppressors or tumor promoters during different stages of tumorigenesis.

Conformational changes in active and inactive states of human PP2C α characterized by hydrogen-deuterium exchange mass spectrometry

Position 30B

Kyle Anderson, Sharlyn J. Mazur, Elyssia S. Gallagher, Subrata Debnath, Stewart R. Durell, Lisa M. Miller Jenkins, Ettore Appella, and Jeffrey W. Hudgens

PPM serine/threonine protein phosphatases function in signaling pathways and require millimolar concentrations of Mn²⁺ or Mg²⁺ ions for activity. Whereas the crystal structure of human PP2C α displayed two tightly bound Mn²⁺ ions in the active site, recent investigations of PPM phosphatases have characterized the binding of a third, catalytically essential metal ion. Hydrogen-deuterium exchange mass spectrometry was used to characterize conformational changes in PP2C α between the active and inactive states. In presence of high Mg²⁺ concentrations, metal-coordinating residues in PP2C α active site are maintained in a rigid state over catalytically relevant time scale of 30 s to 300 s. Low Mg²⁺ concentration or introduction of D146A mutation increased conformational mobility across the catalytic domain; these changes demonstrate conformational linkage between metal coordinating residues, the flap domain, and buttressing alpha helices. This linkage is critical for organization of the active site and enzyme activity.

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Effect of cholesterol on the elastic and viscous properties of dimyristoylphosphatidylcholine bilayers

Position 43B

Robert Bradbury and Michihiro Nagao

The dynamics of biological membranes have attracted significant experimental, computational and theoretical attention as they are critical to a large number of biological functions. Cholesterol is an essential component of animal cell membranes, helping to maintain membrane structural integrity and fluidity, as well as being considered to be a main component of raft domains, where saturated lipid and cholesterol segregate from unsaturated lipids. The raft domain hypothesis is still under great debate in biophysics, and the key feature in understanding the formation of these raft domains is characterizing the dynamics of the bilayers and domains. We have used neutron spin echo spectroscopy (NSE) to measure the internal membrane dynamics of a saturated lipid, dimyristoylphosphatidylcholine (DMPC) as a function of temperature at a fixed lipid - cholesterol ratio (20 mol % cholesterol). NSE measures collective membrane dynamics such as undulation and thickness fluctuations on both a nanometre and nanosecond scale. Cholesterol-rich raft domains are considered as liquid ordered phase, which is less mobile than the liquid disordered phase, but more mobile than solid gel or crystalline phases. We observed values for the undulation fluctuations - characterized by the bending modulus - for cholesterol incorporated DMPC bilayers that are in between those of the pure gel and fluid phase DMPC bilayers, suggesting that at 20 mol % cholesterol there exists a liquid ordered phase. However, the temperature dependence is much greater when cholesterol is incorporated to DMPC bilayers. Also, the thickness fluctuations, characterized by the membrane bending modulus and viscosity, produced larger membrane viscosity values for the mixed DMPC cholesterol bilayers.

Using the fluorescence lifetime to distinguish between metabolic states of *Streptococcus mutans*

Position 47B

Brynna Jones, Joy Dunkers, Ryan Beams, and Stephan Stranick

The oral bacteria *Streptococcus mutans* is an archetypical biofilm-forming species implicated in plaque formation and tooth decay. Like many bacteria in biofilms, it is able to enter a dormant state (low metabolic functionality) when nutrient-deprived. Distinguishing between dead and dormant bacteria is a difficult yet necessary task in testing oral disease mediation. Fluorescence lifetime imaging microscopy (FLIM) is used here on clusters of dead and dormant *Streptococcus mutans* suspended in saline solution. There are distinct differences between the lifetimes of dead and dormant bacteria that could enable non-fatal detection of the metabolic state of an individual bacterium in a biofilm.

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Molt-related metabolomic and transcriptomic analyses of the blue crab, *Callinectes sapidus*

Position 50B

Elena Legrand, Tracey Schock, and J. Sook Chung

Arthropod growth includes molting that is regulated by the interaction of multiple hormones. The peak of hemolymph ecdysteroid (molting hormone) that is produced and released by the Y-organ of decapod crustaceans precedes prior to molting. However, the exact mechanism by which the animals increase the production of ecdysteroid by Y-organ is still largely unknown. The blue crab, *Callinectes sapidus* inhabiting the Chesapeake Bay is considered to be a sentinel species, due to its economical, ecological importance in this region. This project aims to better understand the molting process by studying on the Y-organ activity of *C. sapidus* using metabolomics and transcriptomic analyses. Specifically, the ecdysteroidogenesis pathway are being investigated.

The animals: The females at pre-pubertal stage which experienced the last juvenile molt are used for the study. These animals were produced in the blue crab hatchery and raised in the Aquaculture Research Center, (ARC, IMET, Baltimore, MD).

Metabolomic method development: To optimize hemolymph sample collection/preparation for metabolomics analysis using Nuclear Magnetic Resonance (NMR), neat hemolymph was sampled, immediately frozen and then pooled. Three types of metabolite extractions were tested in triplicate and assessed using principal component analysis (PCA) and visual inspection of the NMR spectra. NMR sample stability was also assessed. A hemolymph collection volume (250 uL) and a 2:1 methanol:water extraction method was deemed appropriate for experimental metabolomic analysis.

Transcriptomic analysis of Y-organ Next Generation Sequencing (NGS) data: Y-organs obtained from 7 days after ablation were used for the sequencing. The whole assembly provide 362,308 sequences using Trinity. A differential expression analysis was realized using RSEM. 138,868 transcripts were expressed the Y-organ. The 2000 most abundant transcripts are initially screened and candidate genes potentially involved in the cholesterol metabolism and ecdysteroidogenesis are then selected for further functional analysis: cholesterol -7 desaturase "Neverland" and, CYP 450 "spook", respectively. Expression analysis of these candidate genes in the Y-organs at different molt stages is in progress.

DNA supercoiling for tuning transcription initiation in engineered biological systems

Position 51B

Jayan Rammohan and David Ross

Synthetic biology offers great promise across all sectors of industry including but not limited to manufacturing, medicine, and energy. Perhaps the biggest bottleneck to predictable engineering of biological systems is that performance of genetic parts is extremely sensitive to context. Therefore, predictive engineering of biology will require characterization of the influence of contextual parameters that may influence part performance, so that conditions can be defined under which systems will reliably behave. One of the most common measurements of genetic part performance is the flux of transcription through a promoter, which arises from the kinetics of transcription initiation by RNA polymerase. Thus far, measurements of transcription initiation in engineered systems are either qualitative, indirectly inferred from reporter proteins, or fail outside a range of conditions. Quantitative metrology for genetic part performance requires a comprehensive exploration of contextual influence on transcription initiation kinetics. Establishing an envelope of conditions under which measurements of transcription flux are reliable will enable reproducibility between groups and empower rational forward design of custom systems. To this point, several aspects of context have been explored including bacterial species and strain, culture medium (composition, temperature, pH, volume), as well as DNA sequence, length and organization. However, in many studies, the DNA template itself is largely treated as a passive object which serves primarily as a substrate for binding of factors and as a template for transcription. In vivo, however, plasmid DNA is negatively supercoiled and topologically dynamic: RNA polymerase generates positive supercoils downstream and negative supercoils upstream during transcription. Furthermore, factors such as DNA gyrase, DNA topoisomerase and HU control supercoiling within the cell. Supercoiling fundamentally and globally affects the flux of transcription initiation by changing the energetics of promoter unwinding by RNA polymerase. In this work, we will examine the dependence of genetic part performance on supercoiling using a range of orthogonal techniques. In-vitro characterization will be performed using high-throughput single-molecule magnetic tweezers, which can be used for real-time observation of promoter unwinding by RNA polymerase on supercoiled DNA tethers. In-vivo characterization will be performed using emerging microscopy techniques that enable tracking of single RNA transcripts in fixed and in live cells. This work will directly measure the dependence of parts performance on DNA topology, which will in turn empower engineers to (1) define the topological conditions under which part performance will hold, and (2) utilize supercoiling as a tunable parameter of genetic performance. This will in turn enable the inclusion of DNA topology in comprehensive models of information flow in biological systems, both for understanding natural genetic regulation and for rational design of engineered biological systems.

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Genome-wide reconstruction of complex structural variants using read clouds

Position 52B

Noah Spies, Ziming Weng, Alex Bishara, Jennifer McDaniel, David Catoe, Justin M. Zook, Marc Salit, Robert B. West, Serafim Batzoglou, and Arend Sidow

Recently developed methods that utilize partitioning of long genomic DNA fragments, and barcoding of shorter fragments derived from them, have succeeded in retaining long-range information in short sequencing reads. These so-called read cloud approaches represent a powerful, accurate, and cost-effective alternative to single-molecule long-read sequencing. We developed software, GROC-SVs, that takes advantage of read clouds for structural variant detection and assembly. We apply the method to two 10x Genomics data sets, one chromothriptic sarcoma with several spatially separated samples, and one breast cancer cell line, all Illumina-sequenced to high coverage. Comparison to short-fragment data from the same samples, and validation by mate-pair data from a subset of the sarcoma samples, demonstrate substantial improvement in specificity of breakpoint detection compared to short-fragment sequencing, at comparable sensitivity, and vice versa. The embedded long-range information also facilitates sequence assembly of a large fraction of the breakpoints; importantly, consecutive breakpoints that are closer than the average length of the input DNA molecules can be assembled together and their order and arrangement reconstructed, with some events exhibiting remarkable complexity. These features facilitated an analysis of the structural evolution of the sarcoma. In the chromothripsis, rearrangements occurred before copy number amplifications, and using the phylogenetic tree built from point mutation data we show that single nucleotide variants and structural variants are not correlated. We predict significant future advances in structural variant science using 10x data analyzed with GROC-SVs and other read cloud-specific methods.

Measurements of Translation Initiation from all 64 Codons in *E. coli*

Position 55B

Jeff Glasgow, Ariel Hecht, Paul Jaschke, Lukmaan Bawazer, Matt Munson, Marc Salit, Jennifer Cochran, and Drew Endy

Translation initiation is a fundamental piece of the central dogma of biology. In this process ribosomal components search mRNA for appropriate initiation sites and undergo a series of binding events leading to amino acid incorporation and protein synthesis. Early studies deciphering the genetic code suggested AUG and to a lesser extent GUG and UUG act as the primary “start” codons throughout all living organisms. This rule has proven largely true over the past five decades of biological research, with only a handful of genes annotated with non-canonical initiation codons (not AUG, GUG, or UUG) in bacteria. With the advent of more sensitive and higher throughput measurement techniques, significant effort has gone into characterizing the effects of mRNA structure, ribosome binding sites, 5'- and 3'-untranslated regions, codon usage, and other regulatory elements on gene expression level; however, surprisingly little research has been done to examine the effect of initiation fidelity on protein expression. We hypothesized that, like most biological processes, initiation of protein synthesis could exist on a continuum of optimal sites (i.e. canonical initiation codons, ideal RBS) to non-optimal initiation sites using other codons.

Here we show that a significant number of non-canonical initiation codons can lead to protein synthesis in *Escherichia coli*. We tested all 64 codons at the 5' end of green fluorescent protein and found that 46 led to measurable expression (0.01-2% of ATG). This trend was observable under multiple promoter/gene combinations, including single-copy bacterial artificial chromosomes with natural *E. coli* promoters. We believe this expression will prove relevant to both natural genes where expression varies over 5 orders of magnitude and engineered systems where precise control of expression is crucial to device performance.

BIOTECHNOLOGY

Fingerprinting prebiotic oligosaccharides in NIST human milk reference material (SRM 1953) by HILIC-ESI mass spectrometry

Position 1Bt

Connie Remoroza, M. Lorna A. De Leoz, and Stephen E. Stein

Human milk is regarded as the gold standard for infant feeding. According to the United Nations Children's Fund (UNICEF), very low percentage of mothers around the world practice exclusive breastfeeding during the first six months of their newborn infants. The low breastfeeding rate is the driving force for the infant formula manufacturers to produce formulas that simulate human milk as closely as possible. Human milk contains bioactive oligosaccharides known as prebiotics, fucosylated and sialylated, able to support baby's developing growth and immune system.¹ Recently, Center for Disease Control (CDC) and NIST crafted a project, a certified free from organic contaminants human milk standard reference material (SRM 1953) derived from one hundred breast-feeding mothers in the United States of America. However, the information on highly polar and complex mixtures of prebiotic oligosaccharides in SRM 1953 is limited. The workflow featured the sample preparation² and an in-depth characterization of oligosaccharides from SRM 1953 using the Hydrophilic Interaction Liquid Chromatography coupled with Electrospray Ionization Mass Spectrometry and SimGlycan analyses. This study focuses on the identification and molecular structure elucidation of prebiotic oligosaccharides derived from NIST SRM 1953.

The results showed an excellent separation of complex mixture of oligosaccharides on BEH amide column based on degree of polymerization, charge and isomeric structures. Neutral and acidic isomers of DP 5 have different retention times that makes the identification more robust. Moreover, a wide collection of high mass accuracy and high quality spectral data from an orbitrap based mass spectrometer, enabled the elucidation of known and unknown structure of fucosylated, sialylated and heteroglycan oligosaccharides. The mass spectral data will then be used for the initial development of structure library of annotated prebiotic oligosaccharides at NIST and for the fingerprinting of bioactive oligosaccharides from commercial infant formula and other domestic animal milk.

1. Mantovani, V. et al. (2016). Recent advances on separation and characterization of human milk oligosaccharides. *Electrophoresis* 37, 1514-1524.
2. Wu, S. et al. (2010). Development of an annotated library of neutral human milk oligosaccharides. *Journal of Proteome Research* 9, 4138-4151

Characterization of the NIST mAb reference material using small-angle scattering

Position 3Bt

Maria Monica Castellanos, David T. Gallagher, Kevin Mattison, Susan Krueger, and Joseph E. Curtis

Both conformation and colloidal stability of therapeutic proteins, such as monoclonal antibodies, must be closely monitored and thoroughly investigated to assess the long-term viability of a drug product. Small-angle scattering can provide unique information about tertiary structure and interactions of antibodies under a range of experimental conditions. In this poster, I will present small-angle x-ray and neutron scattering experiments to characterize the molecular structure and protein-protein interactions on the IgG1 NIST mAb reference material, a biological reference material available to evaluate method performance and serve as a representative test molecule for therapeutic protein characterization. After building a starting structure of the intact NIST mAb from the crystallographic coordinates of the Fc and Fab regions, molecular dynamics and Monte Carlo simulations are performed to explore the configurational space sampled by the Fabs with respect to the Fc. From these simulations, a set of atomistic structures that agree with experimental scattering data are obtained. In addition, small-angle neutron scattering profiles at high concentrations are used to study the colloidal stability of the NIST mAb. The strength of protein-protein interactions upon the addition of sodium chloride is evaluated using the effective structure factor and its consequent effect on the solution viscosity is described. Finally, I describe the conformational stability of the NIST mAb upon freezing samples in-situ while collecting small-angle neutron scattering data. Overall, this study provides new sets of experimental conditions, computational models and instrumentation used to characterize the NIST mAb under dilute and high concentrations, and after freezing/thawing cycles.

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Large field of view, live cell imaging for quantitative evaluation of stem cell heterogeneity

Position 8Bt

Edward Kwee, Alexander Peterson, Michael Halter, George Muschler, and John Elliott

Stem and progenitor cells are heterogeneous populations comprising of cells with varying biological states. Cells of the relevant biological state must be identified among the heterogeneous population of cells prior to use as a cell therapy. Current methods involve trained observers manually scanning across a culture vessel to identify cells of interest, but they are non-quantitative and subjective. Here we present two methods for large field of view, live cell imaging to characterize bone derived connective tissue progenitor cells and induced pluripotent stem cells to identify cells of interest.

First, conventional Zernike phase contrast and fluorescence microscopy were used to track colony formation of freshly isolated bone derived stem and progenitor cells. Image analysis enabled cell and colony segmentation. Tracking with time lapse imaging also enabled identification of the colony founding cell and characterization for cell surface marker expression. Second, quantitative phase imaging was used to image induced pluripotent stem cells that can be differentiated into other cell types. Prototype reference material prepared from beads were used to calibrate the optical pathlength difference of the cells in the culture media. The preliminary results indicate that the calibrated quantitative phase imaging technique can image iPSC colonies and maybe useful to study morphological transitions that occur as these cells convert to another cell type.

Conventional Zernike phase contrast and quantitative phase imaging are non-invasive, label-free methods that can provide objective, quantitative evaluation of cell cultures that may be critical in the biomanufacturing of cell therapies. These measurements could be suitable for quality control in the production of cell therapies and be used ensure cells of the appropriate identity are produced.

Evaluation of heat treatment for pre-analytical stabilization of the lipidome

Position 12Bt

Christina Jones, Jeremy P. Koelmel, Tracey B. Schock, Candice Z. Ulmer, and John A. Bowden

Over the last decade, lipidomics has emerged as an established strategy for monitoring health and disease, for both environmental and human applications. While each element of the lipidomics workflow is critical for reliable results, pre-analytical factors, specifically those decisions made regarding how samples are handled and treated prior to analysis, can greatly influence the resultant lipid profile. Thus, the impact of these pre-analytical factors must be reduced for lipid-based biomarkers to be determined and validated. In an effort to lessen the effect of these factors on lipid measurement and to stabilize the lipidome, a state-of-the-art heat treatment technique was employed to curtail enzymatic degradation of lipid species. This rapid-heat treatment technique was used for immediate euthanization of three environmental health sentinel invertebrates: common house crickets (*Acheta domestica*), earthworms (*Eisenia fetida*), and ghost shrimp (*Palaemonetes paludosus*). More than 1,000 lipids covering 23 lipid types were detected using ultra-high performance liquid chromatography-tandem high-resolution mass spectrometry. Notably, 11 lipid classes were significantly altered between heat-treated invertebrates and invertebrates euthanized via the current gold standard for sample preservation, i.e., flash-freezing. Specifically, decreased glycerophospholipid levels and increased lyso-glycerophospholipid levels were observed in invertebrates that did not undergo heat treatment compared to their heat-treated counterparts, suggesting that heat treatment inhibited phospholipase A activity. Moreover, increased diglyceride concentrations and the formation of phosphatidylmethanol in samples that were not heat treated suggests phospholipase D inhibition. Based on these results, rapid heat treatment using state-of-the-art technology warrants a closer examination for improving the robustness of lipid measurement.

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Adsorption behaviors of surfactant molecules and proteins on hydrophobic surfaces

Position 19Bt

Zhenhuan Zhang, Dan Zarraga, Guangcui Yuan, Brian Maranville, and Norm J. Wagner

Monoclonal antibodies (mAbs) have become increasingly popular for commercial pharmaceutical products development. And proper buffer solvent containing saccharides, surfactants, salts is typically used to increase the protein stability during the storage and drug delivery. But irreversible protein aggregates are still found in some products. One of important routes is believed due to protein adsorption on liquid-solid interfaces of product containers or syringes that are usually coated with hydrophobic oil layer to lubricate the injection process. The presence of surfactant molecules can also strongly affect the protein aggregations at the hydrophobic interfaces. However, the mechanisms of surface adsorption behaviors by surfactant molecules and proteins remain elusive. In this work, we used neutron reflectometers to investigate surface adsorption behaviors of both polysorbate 20 and protein complex. Polystyrene-water surface was used as a model surface to mimic possible hydrophobic surface exposure conditions which may occur during protein manufacturing and administrations. By analyzing the reflectivity data, adsorption behaviors and competition between polysorbate 20 and proteins, such as lysozyme and mAbs, were obtained.

Considerations for digital droplet PCR to quantitatively measure miRNA using a two-step method

Position 20Bt

Erica Stein, Hua-Jun He, Kenneth D. Cole, and Lili Wang

Digital Droplet PCR (ddPCR) is being advocated as a reference method to measure rare genomic targets. It has consistently been proven to be more sensitive and direct at discerning copy numbers of DNA than other quantitative methods. However, additional studies are needed to fully validate, standardize, and optimize its use in RNA and microRNA copy number quantification. For example, in detection of RNA, a through investigator would apply the minimum information for publication of quantitative digital PCR experimental guidelines (MIQE), but even these document standards recognize the need for additional studies to ensure reliable RNA measurements using ddPCR. Here we focus on the quantitation of microRNA. One of the largest obstacles to measuring microRNA using ddPCR is that reverse transcription efficiency can depend upon the target, meaning small RNA nucleotide composition directly effects primer specificity in a manner that prevents traditional MIQE strategies. Additionally, the use of reagents that are optimized for microRNA measurements using quantitative real-time PCR (qRT-PCR) appear to either cause false positive or false negative detection of certain targets when used with ddPCR quantification methods. False readings are often related to using inadequate enzymes, primers and probes. Given that two-step microRNA quantification using ddPCR relies solely on reverse transcription and, almost exclusively on proprietary reagents previously optimized only for qRT-PCR, these barriers are substantial. Therefore, here we have outlined essential controls, optimization techniques, and an efficacy model to improve the quality of ddPCR microRNA measurements. We have applied two-step principles used for microRNA qRT-PCR measurements and leveraged the use of synthetic microRNA targets to evaluate ddPCR following cDNA synthesis with four different commercial kits. We have discovered inefficiencies and limitations as well as proposed ways to attempt to circumvent the identified obstacles. Lastly, we have shown that we can apply these criteria to a model system in order to confidently quantify microRNA copy number or concentration. We hope that these criteria are helpful for implementing necessary controls, and only then, standard assays can be performed to accurately quantify microRNA in clinical and research experiments.

Capillary electrophoresis assays for characterization and quality control of the NISTmAb reference material

Position 34Bt

Abigail Turner and John E Schiel

The National Institute of Standards and Technology (NIST) has recently developed the NISTmAb Reference Material (RM 8671), an IgG1 κ class-representative monoclonal antibody. The NISTmAb is intended to serve as a platform for harmonization and open innovation in the biopharmaceutical analysis community. It is a widely and longitudinally available test material that will support novel technology and method development, serve as an external system suitability control, and provide a medium for open access information sharing. Here, we describe a series of capillary electrophoresis-based assays for quality monitoring and characterization of the NISTmAb material, including CE-SDS, cIEF, CZE, and CE-ESI-MS2. We demonstrate comprehensive electrophoretic characterization of the NISTmAb and discuss its utility as a reference standard in CE assay development.

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Next generation sequencing of CHO cells

Position 38Bt

Michael Muchow, Jamie Almeida, Kenneth D. Cole, Krista Evans, and Ronald Schoner

This project is to study the genomic stability of Chinese hamster ovary (CHO) cell lines during large-scale production of biopharmaceuticals. The goals of the project are measure the changes in the genomes of CHO cells that occur during prolonged passaging in culture that may led to changes in the expression of recombinant proteins. Next Generation Sequencing (NGS) methods will be developed to detect genomic changes to accurately monitor changes during production of therapeutic proteins. CHO cells were transfected with expression vectors for four different recombinant proteins, respectively, subjected to low and high passage (0 and 50 population doubling levels; PDL). A rough reference draft of the CHO-K1 genome is available. CHO DNA was extracted from cell pellets and sequenced using the Illumina HiSeq X 10 platform at 30X coverage with paired-end reads. FASTQC was used to check the quality of the reads. Bam files were generated using BWA and Bowtie2 aligners. FreeBayes was used to generate VCF files that show the differences between the CHO samples and the CHO-K1 reference genome. Expression vector insertion sites will be localized by identifying discordant paired-ends reads-one read matching the reference sequence and the other read matching the insert sequence.

Image attributes related to particle size and count using nanoparticle tracking analysis

Position 39Bt

Adrian Defante, Wyatt N. Vreeland, Kurt D. Benkstein, and Dean C. Ripple

Accurately measuring the size and count of particles in the sub-micrometer range is relevant to the manufacture and regulatory approval of products in the pharmaceutical industry. Nanoparticle tracking analysis (NTA) offers the capability to measure both of these critical attributes, by identifying and tracking particles through a series of micrographs. The accuracy of NTA measurements is dependent on particle illumination determined from recommended guidelines provided by the instrument manufacturer and user experience. We map out the image quality settings (camera gain and shutter) that control the image acquisition for the analysis of ideal polymer spherical systems. We quantify these image attributes and observe a region of interest that accurately measures particle size and count. Understanding these attributes will enable the proper measurement of more complex systems that have different optical, morphological, properties and vary in size distributions compared to well-defined particles.

Optofluidic devices: Measuring microflows and microparticles

Position 49Bt

James Hands and Gregory A. Cooksey

Aim: We aim to develop accurate and reproducible measurements of flow in microfluidic systems which are necessary for determining mass transfer or shear force through sensitive chemical and biological assays, such as in drug delivery, cell-based systems, and disease monitoring.

Approach: We are investigating an easy-to-fabricate optofluidic flowmeter that measures changes in light transmission across two integrated optical waveguides along a microfluidic channel. This proposed configuration allows measurement of the speed of a moving interface or characterization of microparticles having significant light absorption, scatter, or change in refractive index. Two waveguides were separated by 5 mm along a microfluidic channel (cross sections of $82 \mu\text{m} \pm 1 \mu\text{m}$ and $93 \mu\text{m} \pm 6 \mu\text{m}$). Light from optical fibers inserted into the waveguide channel were guided to the flow channel through total-internal reflection in a high index of refraction liquid ($n=1.54$, NOA 88, Norland Products). The addition of a curved lens at the end of the waveguide, to focus the light into the microchannel, increased light transmission significantly by almost a factor of 10.

We have found repeatability of measuring the speed of the air/water interface driven by syringe pump to be within 3% coefficient of variation. We are in the process of determining the absolute uncertainty compared to gravimetric calibration of the pump. The current configuration is capable of tracking beads as small as $3 \mu\text{m}$ diameter. Larger beads ($20 \mu\text{m}$, Coulter CC Size Standard L20, Beckman Coulter) were tracked at speeds of 0.32 m/s ($100 \mu\text{l}/\text{min}$) through the system.

Future Direction: Future work involves using the optical signals to characterize particle size and position within the channel, which will aid the rapid, in-line measurement of microparticles and cells. This project sets the framework for building high-throughput cell measurement capabilities. Our goal is to be able to rapidly process samples containing rare cells, like blood containing circulating tumor cells, for pre-symptomatic disease detection and monitoring of disease progression during treatment

CHEMISTRY

Performance and aging of graphene oxide/polyurethane nanocomposites

Position 7C

David Goodwin, Coralie Bernard, Deborah Stanley, Tinh Nguyen, and Lipiin Sung

Graphene oxide (GO) can be used to enhance the properties and extend the service life of polymer nanocomposites (PNCs). However, GO/PNC degradation can potentially impact material durability and environmental health and safety, especially if GO release occurs. Therefore, this research describes the performance properties and degradation behavior of GO/PNCs to assess the benefits and limitations of GO nanofillers, with a focus on their use in coatings to prevent corrosion. In particular, GO was incorporated into water-borne polyurethane (WBPU) coatings at different GO loadings and characterized with laser scanning confocal microscopy (LSCM), atomic force microscopy (AFM), and scanning electron microscopy (SEM). Relative to unfilled WBPU, GO/WBPU nanocomposites were shown to have superior performance properties such as decreased oxygen permeability and increased thermal stability and mechanical strength; the exception was an increased water uptake at high humidity.

Simulated sunlight aging of GO/PNCs was achieved by GO/PNC exposure to a highly collimated, uniform flux of ultraviolet (UV) light under controlled temperature and humidity conditions (NIST SPHERE). Mass loss and accumulation of a large GO concentration at the nanocomposite surface was observed with increased aging time. In terms of environmental health and safety, this indicates that exposure of GO at the material surface occurs and can potentially lead to GO release from the WBPU matrix with unknown effects on the surrounding environment. Loss of GO via release could also have a negative impact on the service life of the GO/PNC nanocomposite. Thus, released materials were collected from the surface using simulated rain and analyzed with UV-Visible spectroscopy, Raman spectroscopy, and thermal techniques. For the first time, insight into the concentration of released graphene-family nanomaterials from aged PNCs will be described along with the challenges associated with these measurements. Specifically, the interference of released polymer fragments, which are also carbonaceous materials, will be discussed.

NIST Lipidomics interlaboratory study: Highlighting the pitfalls and limitations in lipidomic measurement

Position 11C

Candice Ulmer, John Bowden, Christina Jones, Alan Heckert, and Jeremy Koelmel

Lipidomics, an emerging sub-field of metabolomics, is the comprehensive measurement of lipid species in a biological system. Advances in chromatography, ambient ionization, mass spectrometric techniques, and lipidomics application diversity have led to a substantial expansion in the number of lipid species detected. Measuring shifts in lipid profiles in connection to a disease or condition has promising potential in personalized medicine applications, biomarker discovery, and disease etiology elucidation. However, current pre-analytical sample handling/preparation protocols, data processing software, and tandem MS databases have not advanced at the same level to handle the complexity in these lipidomics datasets.

While the role of NIST in the omics community is to identify measurement issues, our role is also to optimize, promote, and standardize strategies for better measurement within the community. We have innovatively conducted a lipidomics interlaboratory study that encompassed the participation of over 30 laboratories to highlight many of the limitations and pitfalls in lipid measurement. Participating labs quantitated levels of lipid species in triplicate (nmol/mL) for each lipid class measured in the following samples: SRM 1950 (Metabolites in Frozen Human Plasma), SRM 2378 series 1-3 (Fatty Acids in Frozen Human Serum), and Avanti Bovine Liver Extract. In addition, labs were asked to answer questions regarding their (1) lab profile, (2) sample extraction, (3) sample introduction, (4) instrument and data processing details. Results from the lipidomics Interlaboratory study highlighted a broad range of diversity in the methodologies employed amongst the participating labs. This work will show the breadth of this diversity within each step of the lipidomics workflow. In an effort to promote SRM 1950 as a potential QC material for lipidomics studies, quantified lipid species with a low uncertainty and variance by more than 5 labs were further analyzed and compared to the SRM 1950 results reported in the Journal of Lipid Research. This work will also highlight two lipidomics data tools, LipidPioneer and LipidMatch, that were developed to address issues with exact mass libraries and lipid identification.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

Determination of polycyclic aromatic hydrocarbons in standard reference material 1597a via normal-phase liquid chromatography and gas chromatography/mass spectrometry

Position 15C

Walter Wilson, Hugh V. Hayes, Lane C. Sander, Andres D. Campiglia, and Stephen A. Wise

Standard reference materials (SRMs) are complex natural matrix samples certified at the National Institute of Standard and Technology for the evaluation and validation of analytical methods for the determination of polycyclic aromatic compounds (PACs) in complex mixtures. PACs 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). In this study, an analytical method was developed for the separation and identification of PAHs in SRM 1597a, which is a combustion-related mixture of PAHs isolated from a coal tar sample and dissolved in toluene. Due to the complexity of the sample matrix, the analytical method described requires a fractionation step using normal-phase liquid chromatography (NPLC) on an aminopropyl (NH₂) stationary phase. SRM 1597a was characterized before and after fractionation by gas chromatography/mass spectrometry (GC/MS) using a 50% phenyl stationary phase. The NPLC-GC/MS method presented here allowed for the identification of 75 PAHs and 54 methyl-substituted PAHs.

Enhanced metrology of short-lived isotopes with chopped-beam PGAA

Position 17C

Danyal Turkoglu, Heather Chen-Mayer, and Rolf Zeisler

Prompt gamma-ray activation analysis (PGAA) nondestructively determines elemental composition by measuring prompt gamma radiation emitted by samples during neutron irradiation. Decay gamma-ray emissions by activation products are also measured, but have relatively weak signals in most cases. To enable investigations of time-dependent processes following neutron capture, a fast shutter was installed for cyclically blocking the incident neutron beam upstream of the cold-neutron (CN)PGAA instrument at the NIST Center for Neutron Research. With prompt gamma radiation from the sample eliminated when the shutter is closed, the detection limits for decay gamma rays improve since the noise baseline is drastically decreased, allowing the previously-buried decay peaks to emerge. The ability to program the linear motor to run any cycle, a feature not available in traditional rotating disk choppers, allows for tuning irradiation and decay lengths for maximum signal from a nuclide with a particular half life. The fast shutter transitions between irradiation and decay in 10 ms, enabling measurement of short-lived isomers and fission products. The prompt and decay spectra are separated by gating on whether shutter is closed; acquisition of time-stamped list-mode data allows further selectivity for reconstructing spectra in specific time windows. The chopped-beam capability fills the gap of very short-lived nuclide measurements that are previously difficult, if not impossible, to measure with instrumental neutron activation analysis, and improves measurement of Standard Reference Materials as well as enables new applications such as active interrogation of fissile materials.

Characterization of fluorinated self-assembled monolayers with controllable surface dipoles

Position 22C

Robert Bruce and Christina A. Hacker

Interfacial modification of surfaces with organic monolayers is a powerful tool to create dramatic effects in device setting. Various self-assembled monolayers have been shown to impact surface characteristics such as wettability¹ as well as critical device characteristics such as charge and spin transport.² In particular, monolayers with selective fluorination have been shown to produce strong interfacial effects. Recent synthetic work has shown the ability to selectively generate thiol-terminated monolayers with fluorine atoms along an alkane backbone.³ The consequence of this selective fluorination is the generation of surface dipoles with controllable orientation and magnitude. In this work we study the properties of several of these alkane-based, thiol terminated self-assembled monolayers with selective fluorination. Spectroscopic analysis (XPS, ellipsometry, IR) shows that, when prepared on gold surfaces, these fluorinated molecules behave similarly as self-assembled monolayers to the typically well-packed and ordered alkane-based monolayers, exhibiting the negligible impact of fluorine molecules on monolayer quality. Meanwhile, UPS measurements present shifted work functions in the gold metal surface with different fluorinated monolayers attached. The work function shift is shown to depend on the selective fluorination of the monolayer, thereby demonstrating the presence of the permanent dipoles from selective monolayer fluorination and the ability to impact materials that they come into contact with. Further electrical characterization of the monolayers using a eutectic-gallium indium (EGaIn) top contact probes the effects of the fluorination on transport properties of the monolayers.

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Using surface enhanced infrared spectroscopy to track the formic acid oxidation reaction on ultra-thin platinum films

Position 25C

Eleanor Gillette and Thomas Moffat

Monolayer Pt catalysts are of broad interest in the field of electrocatalysis for the potential advantages of maximizing activity while minimizing the Pt content. Self-terminated electrodeposition of platinum group metals has been demonstrated as a strategy for producing ultra-thin films on a variety of substrates. Along with demonstrating excellent catalytic activity, these self-terminated films provide an easily controllable model surface for studying the underlying chemistry of the reactions taking place. Here we will describe our current efforts to use surface enhanced infrared spectroscopy to explore the formic acid oxidation reaction on ultra-thin Pt films. Infrared adsorption of adsorbed CO, an intermediate in the formic acid oxidation reaction, as well as signal from water and sulfate adsorbed at the surface provide distinct signatures for Pt films of various thickness, providing insight into the origin of improved catalytic activity, as well as insight into sources of instability or degradation at the surface.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

Controlled doping of two-dimensional (2d) materials with molecular reductants and oxidants

Position 32C

Siyuan Zhang, Christina Hacker, and Sujitra J. Pookpanratana

Controlled doping of 2D materials such as graphene and transition-metal dichalcogenides (TMDC) can provide a powerful tool for modifying their electrical and optical properties. For n-type dopants, the ability to reduce a variety of materials, formation of stable relatively immobile ions, and air stability are desirable properties. We have designed and synthesized a series of new benzimidazole-based dimeric dopants. This presentation will focus on the doping studies of 2D materials using these dimeric dopants. The doping behavior has been extensively characterized in both solution and films. Different doping mechanisms were found for different dimeric dopants. By applying the dopants, the work function of CVD graphene can be tuned from ca. 3 eV to 5 eV, and the sheet resistance of monolayer graphene can be reduced by more than 90%. Organic field-effect transistors and solar cells devices with doped graphene electrodes were fabricated, the performance of which is comparable to, or even better than, that of similar devices with metal or metal-oxide electrodes. Doping studies of two TMDCs, molybdenum disulfide (MoS₂) and tungsten diselenide (WSe₂), will be discussed; these materials were characterized by electrical measurements, ultraviolet- and X-ray-photoelectron spectroscopy (UPS and XPS), and Raman spectroscopy.

Identifying emerging designer drugs with the NIST mass spectra library: an assessment of search algorithms

Position 35C

Arun S. Moorthy, Anthony J. Kearsley, Stephen E. Stein, and William E. Wallace

The identification of structural analogs to illicit compounds, so-called ‘designer drugs’, is a major issue in the forensics community. Many of the emerging compounds have never been seen before and are not in any mass spectral library. Methods that can identify such compounds are urgently needed by law enforcement laboratories. We explore the capabilities and limitations of two mass spectra based search algorithms as tools for identifying these illicit compounds. In particular, we assess the NIST MS Search implementation of the “Simple Similarity Search (SSS)” and new “Hybrid Similarity Search (HSS)” algorithms in clustering fentanyl-type (e.g. analog, modification, precursor, etc.) compounds with similar compounds. Preliminary results demonstrate that the hit list generated from searching any fentanyl-type compound using the HSS contains significantly more fentanyl-type compounds than a hit list generated using the SSS, suggesting that the HSS might be a useful tool in identifying emerging designer drugs given that similar analogs are contained in the NIST MS Libraries. Further testing with other classes of illicit compounds is underway.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

Matrix-specific transport efficiency to compensate matrix effects on single particle ICP-MS nanoparticles sizing and counting capabilities

Position 40C

Antonio R. Montoro Bustos, Karen E. Murphy, and Michael R. 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. Ideally, within a 10 ms read time, only one particle reaches the plasma and is detected 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 due to its simplicity, speed and ability to obtain a particle number size distribution, some important limitations still remain, and spICP-MS cannot be considered a mature methodology.

In spICP-MS, samples are introduced into the instrument as an aqueous suspension. Only a small percentage of the sample solution is transported into the plasma. The ratio of the amount of sample entering the plasma to the amount of sample introduced into the instrument is called the transport efficiency. The most widely used calibration strategy for spICP-MS is based on the measurement of a reference NP standard followed by calibration of the instrument response with ionic standard solution calibrants, both combined to obtain the transport efficiency.

Although samples often have to be diluted to a large extent to fit into the dynamic range of spICP-MS, matrix components can affect the accuracy of nanoparticle sizing and counting capabilities of spICP-MS impacting the transport efficiency determination. So, if the matrix interferes with the nebulization or ionization in the plasma, leading to suppression or enhancement of the analyte signal, an underestimation or overestimation of particle concentration and particle size would result, respectively.

We propose to overcome this limitation, with the novel concept of “matrix-specific” transport efficiency. In this approach, matrix matched ionic standard solutions and nanoparticle suspensions are used to compensate for the influence of matrix on spICP-MS in order to improve the accuracy of particle size and particle concentration results. The approach also has the possibility to expand the applicability of spICP-MS to a wide range of aqueous, environmental and biological conditions.

The proof of concept of this “matrix-specific” transport efficiency will be presented for the spICP-MS analysis of NIST gold nanoparticles RM8012 and RM8013, with nominal diameters of 30 nm and 60 nm, respectively. Results include three concentration levels of different matrices, such as phosphate buffered saline, methanol and sodium dodecyl sulfate.

New statistical tool for automated data processing of single particle ICP-MS for the size determination and quantification of gold nanoparticles

Position 41C

Monique E. Johnson, Bryan Calderon-Jimenez, Sara Stoudt, Gabriel Samanho, Antonio R. Montoro Bustos, and Karen E. Murphy

Advances in the synthesis, stabilization, and production of nanoparticles (NPs) have fostered a new generation of commercial products and intensified scientific investigation of these materials. Recently, single particle inductively coupled plasma-mass spectrometry (spICP-MS) has emerged as a highly valuable analytical technique for the characterization of aqueous NP suspensions. The capability of spICP-MS to simultaneously measure nanoparticle size, size distribution, and particle number concentration at very low NP number concentration, makes this measurement technique extremely useful from a metrological and analytical point of view. However, single particle ICP-MS datasets are large. For measurements on the millisecond scale a typical sample measurement contains tens of thousands of data points and for measurements on the microsecond scale, millions of data points are acquired, making data processing complex and laborious. In recent years, some data analysis tools such as spreadsheets¹, custom programs², and ICP-MS vendor software programs have been developed. However, a lack of sophistication and transparency in the algorithms used, restrictions due to software licenses, and in some cases, the need for extensive knowledge in programming can limit the applicability of these spICP-MS data analysis tools.

This study describes the development of a new spICP-MS data processing tool capable of computing size, size distribution and number concentration as well as providing graphical display and statistical analysis of the data. At present, the tool can be used for applications involving inert NPs and has been used to characterize gold nanoparticle (AuNP) suspensions measured using millisecond-scale data acquisition. The tool was developed to work with Shiny by RStudio which provides a user-friendly interface. Raw data files in csv format from any ICP-MS instrument vendor can be processed and results rapidly generated without sophisticated knowledge of R-studio programming. Sample data are processed simultaneously rather than sequentially reducing data analysis times from days to minutes.

This tool uses the criterion of limit of detection based on a Poisson-normal approximation³ to separate the instrument and reagent background signal from particle signals. An extreme outlier correction approach was proposed as a strategy to deal with systematic error due to particle agglomeration and/or particle coincidence. Different parametric and robust algorithms are included in the tool to provide versatility in the estimation of the central tendency of the particle size distribution. Particularly, Huber's algorithm⁴ provides an excellent alternative to the arithmetic mean in order to mitigate the effect of mild outliers on the computed particle size. Additional programs outputs include the critical value, limit of detection, transport efficiency by the particle size method, and transport efficiency by the frequency method. Efforts are currently under way to develop this software for application to all types of NPs measurable by spICP-MS analysis.

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Designing microelectrodes for electrochemical sensing applications

Position 42C

Pengfei Niu

I want to present our two novel designs to make microelectrodes for electrochemical sensing applications. On the one side, we have overcome the limitation of weak interfacial adhesion between carbon films and Silicon substrate, by the material design, and yield robust carbon based thin films which can pass through the harsh lithographically patterning process. The resulting carbon thin film electrodes be used repeatedly in various experimental conditions as electrochemical sensors. On the other side, we develop a new approach to measure the volumetric flow rate of liquid fluid in micro-channel by measuring the channel geometry variation.

ELECTRONIC AND MAGNETIC MATERIALS

Designing cobaltites by controlling oxygen distributions

Position 4EM

Dustin Gilbert, Peyton Murray, Aleksey Lonin, Steven R. Spurgeon, Rajesh Chopdekar, Brian J. Kirby, Brian B. Maranville, Julie A. Borchers, A. T. N'Diaye, Kai Liu, Elke Arenholz, Yayoi Takamura, and Alexander J. Grutter

Magneto-ionic control of magnetism has been recently demonstrated as a powerful tool with potential applications to ultra-low power data storage and logic devices. Perovskites (ABO_3) have shown particular promise for magneto-ionic technologies due to their huge oxygen mobility, and high sensitivity of the magnetic ordering on oxygen stoichiometry. In this work, we demonstrate complete control of magnetism throughout the thickness of a 35 nm film of $(La,Sr)CoO_3$ by using a oxygen-leaching Gd capping film. The as-grown strained LSCO film is shown to be a high-anisotropy ferromagnet, with a coercivity of more than 1 T at 100 K. Depositing a Gd capping layer caused an increase in the out-of-plane lattice parameter, and eventual formation of a Brownmillerite ordering. STEM and polarized neutron reflectometry (PNR) directly map the decrease in oxygen content throughout the film, resulting from the high oxygen mobility. These results also independently identify a depth-dependent transition in the oxygen profile, particularly near the interface. PNR also showed that commensurate with the reduction in oxygen content, the magnetization was controllably suppressed, and eventually extinguished, with increasing Gd thickness. Interestingly, while we observe changes both in stoichiometry, and lattice structure, magnetoresistance measurements indicate little change in the coercivity, suggesting only small changes in the magnetic anisotropy. This work both explores redox driven magneto-ionic control of magnetism in unprecedented detail, but also, for the first time, demonstrates complete control of magnetism in thick films.

Effective control of magnetization rotation as a function of applied electric field in FeGa/NiFe multilayers on PMN-PT

Position 6EM

Michelle Jamer, C.R. Rementer, T. Barra, Q. Xu, P. Nordeen, G. Carman, Y. Wang, D.B. Gopman, A.J. Grutter, J. Borchers, B.J. Kirby, and J.P. Chang

There is a growing interest in developing magnetostrictive compounds for micro actuators and novel microwave magnetic devices to replace Terfenol-D, as it is difficult to fabricate and contains rare earth materials. Galfenol, Fe_xGa ($x = 75-85$), is the most prominent possible alternative due to its large magnetostriction (>200 ppm), high piezomagnetic coefficient (3 ppm/Oe), and high stiffness (70 GPa). In previous research, Fe_xGa and NiFe were deposited in a multilayer heterostructure in order to exchange couple the two layers, thereby improving the properties of the galfenol layer while maintaining the magnetostrictive integrity.

In this work, multilayer laminates were fabricated with $Fe_{86}Ga_{14}$ and $Ni_{81}Fe_{19}$ on piezoelectric PMN-PT [011] in order to explore voltage control of the magnetization. Using SQUID magnetometry with in situ poling, we find that straining the substrate with 400 V in remnant magnetic field strains the multilayer enough to induce a significant change in anisotropy. To understand how this effect varies with proximity to the piezoelectric substrate, we have used polarized neutron reflectometry to determine the depth profiles of the structure and in-plane vector magnetization as functions of applied magnetic field and voltage. We find that we are insensitive to any structural changes with voltage, but we do observe pronounced magnetic changes. Application of 400 V results in an enormous increase in spin-flip scattering, unambiguously demonstrating a substantial rotation of the magnetization perpendicular to the applied magnetic field direction. Model fitting of the data suggests that the $Fe_{86}Ga_{14}$ and $Ni_{81}Fe_{19}$ layers rotated coherently. Results for a series of multilayers with different layer thicknesses will be discussed. These measurements thus provide direct evidence of a voltage-induced rotation of the both the NiFe and FeGa magnetization as well as a means to separate the response of the magnetostrictive and soft layer components. Magneto-optic imaging film (MOIF) apparatus will be used to explore the domain formation and field dependence.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

The pulse laser deposition of nitrogen doped TiO₂ thin films for photoelectrochemical measurements

Position 9EM

Nacole King, Nam Nguyen, and Winnie Wong-Ng

Research on metal oxynitrides has increased significantly over the last decade in the area of photocatalysis. The introduction of nitrogen into a metal-oxide compound has been used to modify and tune the band gap of ultraviolet light active photocatalyst. In this investigation, thin films of TiO₂-xN_x were deposited using pulse laser deposition under various conditions (i.e., TiN and TiO₂ target, deposition temperature, O₂/N₂ pressure, and post annealing technique). The thin films were annealed in a flowing O₂/N₂ atmosphere in order to crystallize the amorphous phase that is produced upon deposition. The crystallinity and surface chemistry of the thin films were analyzed using X-ray diffraction and X-ray photoelectron spectroscopy. Further, the particle morphology was characterized using electron microscope techniques. Mott-Schottky calculations photoelectrochemical measurements of the nitrogen doped TiO₂ thin films will be evaluated under standard solar irradiation conditions.

Synthesis and properties of superlattices of BiFeO₃ and La-doped BiFeO₃

Position 13EM

Colin Heikes, Julia Mundy, Ramamoorthy Ramesh, Darrell Schlom, and William Ratcliff

We report the growth of BiFeO₃/La_xBi_{1-x}FeO₃ superlattices as well as the results of neutron diffraction and reflectometry measurements of the magnetic structure of these films. We have synthesized these superlattice films using reactive oxygen molecular beam epitaxy (MBE) with a variety of La-doping concentrations in the La-doped BiFeO₃ layers. We have made a range of films of the structure y*[n(BiFeO₃)/m(La_xBi_{1-x}FeO₃)]/substrate where n is the number of unit cells of BiFeO₃, m is the number of unit cells of La_xBi_{1-x}FeO₃, x is the La doping concentration, y is the number of superlattice repeats, and our substrate is either Nb:SrTiO₃ (100), SrTiO₃(100), or TbScO₃(110). X-ray diffraction and TEM measurements illustrate the high crystal quality of these films with this growth technique. We have performed both diffraction and reflectometry measurements at the NCNR at NIST and report initial results of these studies.

Effects of anharmonicity and doping on high-pressure superconductive hydrogen sulfide and other related materials

Position 24EM

Linda Hung and Taner Yildirim

Following initial theoretical predictions of high-temperature superconductivity in high-pressure Im-3m hydrogen sulfide, experiments have demonstrated superconductivity with critical temperatures (T_c) ~200 K at pressures ~150 GPa. In this work we use first-principles calculations to explore the role of anharmonicity and the effect of doping on T_c in H₃S and H₃Se with Im-3m symmetry. A finite-displacement / frozen-phonon approach is validated by comparison to density-functional perturbation theory. The anharmonic contributions, accessible through the frozen-phonon framework, are used to examine the isotope effect in these materials and to test the validity of the harmonic approximation. We simulate hole and electron doping of the materials by substitution of S and Se with the Groups VA and VIIA elements, but find they do not increase the superconducting temperature. The pressure dependence of pure and doped H₃S and H₃Se is also studied.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

Remote control electrodeposition: Metal patterning on substrates without direct electrical connections

Position 29EM

Trevor Braun and Daniel Schwartz

Bipolar electrochemistry can overcome a key limitation in traditional electrochemistry, the need to electrically connect to the substrate. Wiring to a substrate is especially difficult for micro/nano-manufactured systems or complex three-dimensional geometries. Bipolar electrochemistry involves spatially segregated, equal and opposite reduction and oxidation on an electrically floating substrate. We show that spatial and temporal control of bipolar electrochemical couples enables patterned electrodeposition (or etching) by "remote control" without wiring to the substrate. This requires more intricate electrolyte design, through the addition of an electron donating species that can undergo oxidation on the substrate concomitantly with metal reduction. We characterize local bipolar electrodeposition beneath the tip of a rastering microjet anode configuration we call a scanning bipolar cell (SBC). The fundamental interactions of thermodynamics, kinetics, and ionic transport in the SBC are explored using a range of metal reduction reactions of varying nobility and kinetic stability. Selection of the counter bipolar oxidation couple is dependent on the kinetic reversibility and thermodynamics of the accompanying metal reduction chemistry. This technology provides a platform for additive manufacturing in micro/nano-scale devices such as integrated circuits and printed circuit boards.

Towards wearable electronics and sensors: structure and tensile properties of cross-linked Pluronic-diacrylate copolymers/ethylammonium nitrate iono-elastomers

Position 31EM

Ru Chen, Carlos R. López-Barrón, Norman J. Wagner, and Paul D. Butler

Wearable electronics and sensors to be incorporated into clothing, uniforms, and sporting equipment require flexible, robust soft materials with high conductivity and high extensibility- so called "stretchable electronics". Applications include stretchable batteries, wearable sensors and integrated circuits. Fabrication of such materials usually requires the use of hybrid technology that mixes metals, polymers and conductive materials, to tie the system together electronically. Current strategies include composite materials with "wavy" or fractal designs, micro- or nano-structured metal embedded in elastomeric matrices, biphasic solid-liquid metal thin films embedded in elastomeric substrates, composite films of carbon nanotubes or graphene and metals and polymeric materials doped with dispersions of carbon nanotubes in ionic liquids (bucky gels) which are subsequently coated with elastomeric substrates. Manufacturing of these materials involve sophisticated and complex integration of elastomeric substrates with micro- or nano-structured organic or inorganic electronic materials via multi-step and often costly processes. We have demonstrated a simplified manufacturing process to create stretchable conductor materials applicable for stretchable electronic technologies by self-assembly of concentrated solutions of end-functionalized commercially available, in-expensive triblock copolymer Pluronic F127 in a protic ionic liquid ethylammonium nitrate, followed by micelle corona crosslinking to generate elastomeric ion gels (iono-elastomers) under UV-curing initiator. We found that these morphologies remain unchanged upon crosslinking the solutions in presence of a UV-curing initiator. The resulted materials exhibit an unprecedented combination of high stretchability, high ionic conductivity and mechano-electrical response. Importantly, the materials conductivity increases with extension, a unique and non-trivial material response.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

Quality preservation of epitaxial graphene devices by amorphous boron nitride encapsulation

Position 53EM

Albert F. Rigosi, Chieh-I Liu, Nicholas R. Glavin, Yanfei Yang, Heather M. Hill, Jiuning Hu, Angela R. Hight Walker, Curt A. Richter, Randolph E. Elmquist, and David B. Newell

Homogeneous monolayer epitaxial graphene (EG) is an ideal candidate for the development of a quantum Hall resistance (QHR) standard. A clean fabrication process was used to produce EG-based quantum Hall devices with n-type doping level of order 10^{12} cm^{-2} . Generally, electrical properties of EG, such as longitudinal resistivity and carrier density, remain unstable when devices are exposed to air due to adsorption of molecular dopants, whose presence shifts the carrier density close to the Dirac point ($<10^{10} \text{ cm}^{-2}$) or into the p-type regime. Here we report experimental results on the use of amorphous boron nitride (aBN) as an encapsulation layer, whereby EG can maintain some of its electrical properties under ambient laboratory conditions for at least a few days. Furthermore, we exposed one dozen devices to controllable temperatures up to 85 °C and relative humidities up to 85% and report that a 15 nm to 20 nm aBN encapsulation thickness is sufficient to preserve longitudinal resistivity to within 10% of its previously-measured value. We monitored the electronic properties of our encapsulated and unprotected EG samples by room temperature magnetotransport measurements using a neodymium iron boron (NIB) magnet. Our results have essential importance in the mass production of millimeter-scale graphene devices with stable electrical properties.

Resonance Raman spectroscopy of layered niobium diselenide

Position 54EM

Heather M. Hill, Albert V. Davydov, and Angela R. Hight Walker

Transition metal dichalcogenides (TMDs) are a popular set of materials that can be isolated into atomically-thin, 2D layers. Much recent research has focused on semiconducting TMDs, but TMDs can also be insulating, metallic, and superconducting. Niobium diselenide (NbSe₂) is a metallic, superconducting TMD that exhibits a charge density wave phase below 33.5 K in bulk. In our work, we investigate the laser energy dependence of the Raman modes of NbSe₂; i.e. resonance Raman spectroscopy, and compare our results with reflectance contrast spectroscopy. We analyze Raman intensity, shift, and FWHM as a function of polarization and excitation energy in the range from 1.6 eV to 2.7 eV. An increasing intensity of one Raman mode, A_{1g}, with decreasing energy in the visible range is observed, while the opposite behavior is seen for the other dominant Raman mode, E_{2g}. We use the absorption peaks in the reflectance contrast of NbSe₂ to relate the resonance Raman spectrum to the band structure. Finally, we compare our results with the existing literature on the resonance Raman spectroscopy on molybdenum disulfide, a semiconducting TMD with surprising band structure similarities.

ENGINEERING

Benchmarking surface conduction measurements to quantify soot deposition

Position 2E

Amy Mensch and Thomas Cleary

The ability to measure soot deposition on surfaces in fire environments in real-time would advance forensic fire studies and fire model predictions. Conductometric measurements of deposited soot have been developed into sensor designs to monitor diesel exhaust emissions.^{1,2} A sensor that could provide accurate, time-resolved measurement of soot deposition in full-scale fire experiments would help explain the formation of fire patterns typically interpreted in forensic fire analysis, and improve fire modeling capabilities by validating smoke deposition sub-routines. We have studied the feasibility of a conductometric measurement to determine the time resolved soot deposition. Laminar flow through a thin rectangular channel with a transverse temperature gradient is used to generate repeatable deposition exposures on a target surface. The channel orientation, channel flow rate and overall temperature difference are each varied between two conditions. The flow and temperature conditions expected in the experiment are predicted through computational fluid dynamics (CFD) modeling. Fully developed flow and temperature profiles are predicted to be established by at least the midpoint of the channel for higher channel flow rate. The linear temperature gradient between channel walls causes thermophoretic deposition of soot particles on the cold wall of the channel. As the particles deposit, the conductance on the interdigitated electrodes on the target surface increases, as measured intermittently by a pico ammeter with an applied voltage. The mass loading of soot deposited at the end of the exposure is determined by two separate measurement methods, a gravimetric method and a light transmission method. The light transmission method tends to under-predict the soot deposits. The relationship between the amount of deposition and the conductometric response is evaluated for each mass loading measurement and compared to the mass loading predicted from thermophoretic deposition theory assuming a constant soot particle size. It appears that a conductometric gauge could provide reasonably accurate measurement of deposited soot. Development of a high-temperature gauge and full-scale testing is planned.

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Assessing fuel lubricity with inductive micro-flash desorption

Position 5E

Kimberly Urness and Thomas Bruno

Liquid fuels for high-performance aircraft currently serve as the propellant, the heat sink for regenerative cooling, and the hydraulic fluid. The fuels themselves have now reached their thermal capacity for effective cooling, resulting in unfavorable thermal stress and restricting performance gains. A proposed method to improve the performance of these aircraft and increase efficiency is to eliminate the entire lubricant system, requiring that the fuel also serve as the lubricant. To enable this transition, it is necessary to identify the important characteristics of fuel lubricity to design appropriate fuel blends. Here we present a solvent-free extraction technique called Inductive Micro-Flash Desorption to rapidly characterize the molecular species in complex mixtures, such as fuels, that are involved in boundary lubrication. The technique identifies surface-active species in a fluid by thermally desorbing the interacting species from a substrate into a heated vapor slipstream with induction heating. The desorbed species are then detected by suitable analytic techniques such as gas chromatography with mass spectrometry.

Effect of microencapsulated ammonium polyphosphate on flame retardancy and mechanical properties of wood flour/polypropylene composites

Position 10E

Wen Wang and Jianzhang, Li

Microencapsulated ammonium polyphosphate (MCAPP) was prepared by using melamine-formaldehyde (MF) resin via polymerization in situ. The product was characterized

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by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, energy dispersive spectroscopy, water solubility tests, water contact angle, and thermogravimetric analysis. The tests indicate that ammonium phosphate (APP) was successfully coated by the MF resin, and MCAPP with lower water solubility and higher water resistance outperformed APP. After modification by MCAPP, the flammability of wood-plastic composites (WPCs) was investigated by limiting oxygen index (LOI) and cone calorimetry. The results showed that MCAPP/WPC had higher LOI value, lower heat release rate, and more char residual at the end of cone calorimetry than APP/WPC, indicating that the WPC used MCAPP as flame retardant performed better flame retardancy than the WPC mixed with unmodified APP. Moreover, all measured mechanical properties of MCAPP/WPC were distinctly better than APP/WPC.

Time-resolved imaging of electrically excited GHz micromechanical resonators by asynchronous femtosecond laser interferometry

Position 18E

Lei Shao

Time-resolved imaging of electrically excited GHz micromechanical resonators by asynchronous femtosecond laser interferometry 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 laser pulse is used to replicate an impulse to excite elastic waves induced by rapid thermal expansion and then a synchronized low-energy probe laser pulse is used to measure the displacement by means of interferometry. By continuously varying the delay between the pump and probe and scanning the position of the probe laser pulse, spatiotemporal-resolved displacements can be obtained. In some other examples, the device or material under test is excited electrically by converting the pump laser pulse to a short electrical pulse using a high-speed photodetector and a pulser.^{2,3}

Despite of its wide applications, all these prior works are limited by the facts that the excitation is an impulse train and also needs to be synchronized with the probing. This restricts its usage in a lot of more practical imaging applications such as resonators and acoustic wave filters, in which the excitation is usually continuous and the resonance frequency can be arbitrary depending on a particular design and the fabrication tolerance as well.

In this work, we experimentally demonstrate time-resolved imaging of GHz micromechanical resonators using asynchronous pulsed laser interferometry where the electrical excitation does not need to be synchronized with the laser probing. This is achieved using laser heterodyne technique by carefully preparing the lock-in reference by directly mixing the excitation signal and the laser pulse train, along with other simple signal processing methods such as filtering and amplification. In this way, we can retrieve the amplitude and phase of the resonance by a spatiotemporal scanning. Several silicon bulk acoustic resonators are fabricated using standard nanofabrication process and successfully imaged using this novel technique.

1. Tachizaki, T., Muroya, T., Matsuda, O., Sugawara, Y., Hurley, D.H. and Wright, O.B., 2006. Scanning ultrafast Sagnac interferometry for imaging two-dimensional surface wave propagation. *Review of scientific instruments*, 77(4), p.043713.
2. Liu, N., Giesen, F., Belov, M., Losby, J., Moroz, J., Fraser, A.E., McKinnon, G., Clement, T.J., Sauer, V., Hiebert, W.K. and Freeman, M.R., 2008. Time-domain control of ultrahigh-frequency nanomechanical systems. *Nature nanotechnology*, 3(12), pp.715-719.
3. Fujikura, T., Matsuda, O., Profunser, D.M., Wright, O.B., Masson, J. and Ballandras, S., 2008. Real-time imaging of acoustic waves on a bulk acoustic resonator. *Applied Physics Letters*, 93(26), p.261101.

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An optomechanical accelerometer with a high-finesse hemispherical optical cavity

Position 21E

Yiliang Bao, Feng Zhou, Thomas W. LeBrun, and Jason J. Gorman

Accelerometers with high accuracy and resolution are critical for numerous applications involving vibration analysis, navigation, seismology, gravimetry, and acoustic sensing. The key component to achieve micro-g resolution ($1\text{ g} = 9.81\text{ m/s}^2$) is a displacement sensor with sub-angstrom resolution. Fabry-Pérot interferometry is a displacement measurement approach with high sensitivity and low uncertainty, making it a compelling candidate for use in accelerometers.

This poster will report on the design, fabrication, and preliminary testing of an optomechanical accelerometer that uses Fabry-Pérot interferometry to transduce acceleration. The accelerometer consists of two silicon chips, one with a microscale hemispherical mirror and the other with a suspended proof mass. Compared with previous developed MEMS accelerometers that use Fabry-Pérot interferometry, the sensor presented in this paper utilized a hemispherical cavity, which is more stable than existing plane parallel cavities. Our design can achieve high optical finesse, which provides greater acceleration sensitivity. In addition, the two-chip system is designed to assemble by direct silicon wafer bonding for excellent thermal stability. Based on calculations, the accelerometer is expected to achieve a resolution better than $1\text{ }\mu\text{g/rt-Hz}$ for a wide range of sensor resonant frequencies, making it highly competitive compared to conventional MEMS accelerometers.

The hemispherical mirror is etched using a silicon nitride hard mask in a slow isotropic wet etch (HNA) solution to achieve low surface roughness and a high radius of curvature. The mask aperture diameter and etching time have been optimized to maximize the ratio between the radius of curvature and the depth, resulting in a highly stable cavity. The surface quality is better than $\lambda/25$ and the surface roughness is approximately 1 nm RMS, making it an exceptional mirror for interferometry. The proof mass is designed to be suspended on both top and bottom. As a result, the first rocking mode frequencies are at least ten times higher than the fundamental. A variety of sensors have been fabricated with square proof masses with a side length ranging from 1 mm to 5 mm. We also developed a fiber-optic mount with customized fiber-aspheric lens assembly, which allowed us to optimize mode matching into the cavity and achieve fiber coupled portable accelerometer packaging.

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Characterization of a lab based CD-SAXS tool

Position 23E

William Thompson, R. Joseph Kline, and Osman Sorkhabi

In accordance with Moore's Law, the reduction of critical dimensions (CDs) and increased densities of semiconductor devices continue to push the limits of current nanofabrication methods. Novel techniques for overcoming the limitations of standard 193 nm immersion lithography include multiple patterning techniques such as self-aligned double patterning (SADP) and self-aligned quadruple patterning (SAQP). These multiple patterning techniques can achieve CDs and pitches far below that of standard optical lithography, but are subject to compounding detrimental effects, such as pitch walk. Metrology techniques for monitoring the CDs and pitches of future technology nodes would be limited by current techniques such as optical scatterometry (OCD), which is reaching its fundamental limits, and CD scanning electron microscopy (CD-SEM), which only samples small areas and has difficulty producing detailed 3D information. Three dimensional structural information attained through destructive cross sectioning transmission electron microscopy (TEM) and SEM methods, are not practical for in-line metrology. A non-destructive, relatively large area, 3D metrology technique that shows promise for meeting future metrology needs is the CD small angle x-ray scattering (CD-SAXS) technique.¹ The technique has previously been shown to be capable of resolving CD, pitch, and pitch walk with sub-nanometer precision.² Previous reports on the results of the CD-SAXS technique have been generated from measurements performed at large synchrotron x-ray sources, but newly developed compact high brightness x-ray sources have made the development of viable lab based tools possible. A lab based CD-SAXS tool capable of providing the quality of information previously demonstrated by the CD-SAXS technique would be invaluable for satisfying the future metrology needs of the semiconductor industry.

In this work we report on the results of continued efforts to calibrate and characterize a lab based CD-SAXS tool. For the CD-SAXS technique it is desirable to maximize the x-ray flux through the sample area, while minimizing the x-ray beam spot size at the sample and the divergence of the x-ray beam. Optimizing each of these properties is nontrivial and it is necessary to understand how each might be varied, as well as any interdependencies that may exist between them. A liquid metal jet x-ray source³ was used in this work, operated using indium K α x-rays at 24.2 keV. X-rays were generated using a variety of electron beam sizes, accelerating voltages, and powers. The CD-SAXS system is also equipped with two sets of horizontal and vertical variable aperture GaAs scatterless slits. The resulting x-ray beam divergences, intensities, and spot sizes at the sample were examined for a variety of electron beam settings and aperture configurations. These data allow for maximizing the x-ray flux through the target during the CD-SAXS measurement, when there are constraints presented by a limited sample target area.

In conclusion, significant progress is being made in characterizing a lab based CD-SAXS tool and is providing information that will aid in optimizing future CD-SAXS measurements on semiconductor samples. Examples of how these results aided in performing CD-SAXS measurements on silicon gratings will be presented. In addition, results of preliminary CD-SAXS measurements on silicon gratings using the lab based tool will be compared to measurements taken using a synchrotron source.

1. Jones, R. L.; Hu, T.; Lin, E. K.; Wu, W.-L.; Kolb, R.; Casa, D. M.; Bolton, P. J.; Barclay, G. G. Small Angle X-Ray Scattering for Sub-100 Nm Pattern Characterization. *Appl. Phys. Lett.* 2003, 83, 4059.

2. Sunday, D. F.; List, S.; Chawla, J. S.; Kline, R. J. Determining the shape and periodicity of nanostructures using small-angle X-ray scattering. *J. Appl. Cryst.* 2015, 48, 1

3. Hemberg, O.; Otendal, M.; Hertz, H. M. Liquid-Metal-Jet Anode Electron-Impact X-Ray Source. *Appl. Phys. Lett.* 2003, 83, 1483.

Octo-strain: A novel multiaxial loading device for in-situ stress measurements via neutron diffraction

Position 26E

Justin Milner

This work reports on the design and first results from a novel mechanical loading device that was conceived specifically for measuring the applied stresses using neutron diffraction. The purpose of this device is to obtain multiaxial yield stresses of sheet metal samples at large magnitudes of strain. The full strain field is determined using a dedicated digital image correlation system (DIC); thus, the macroscopic plastic strain tensor is known precisely in the neutron gauge volume. The device is an eight-arm device called Octo-Strain that was designed for a variety of planar straining scenarios and large magnitudes of strain as compared to cruciform testing. Now possible strain paths are a plane strain expansion followed by another plane strain expansion at a 45-degree angle to the major strain axis. The ability of 360-degree rotation allows measurements for any in-plane orientation of the scattering vector for the determination of the stress tensor.

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Physics and safety analyses on a conceptual reactor for advanced neutron source

Position 27E

Zeyun Wu, Robert E. Williams, and J. Michael Rowe

The reactor physics and thermal-hydraulics safety analyses for a conceptually designed LEU-fueled research reactor are performed at NIST. The main goal of the research reactor is to provide advanced neutron sources for scientific experiments with a particular emphasis for high quality cold neutron sources. In order to maximize the yield of the thermal flux trap in the reflector area, a tank-in-pool type reactor with a horizontally split compact was developed. To develop a cost-effective scientific research facility, the reactor was designed with 20 MW thermal power and 30 days operating cycle. For non-proliferation purpose, the LEU fuel (U_3Si_2-Al) with enrichment 19.75 wt.% was used. The core performance characteristics of an equilibrium cycle with several representative burnup states including startup (SU) and end of cycle (EOC) was obtained using the Monte-Carlo code MCNP6. The estimated maximum thermal flux of the core is $\sim 5 \times 10^{14}$ n/cm²-s. The surface current at the exit of the cold neutron source achieves a gain factor ~ 3 compared to the cold neutron performance of the existing NIST reactor. The evaluated reactivity coefficients offer negative feedbacks. The reactivity control assessment confirms sufficient control worth and shutdown margins of the control system. Thermal-hydraulics (T/H) safety studies of the reactor was performed using multi-channel safety analysis code PARET/ANL. Steady-state analysis results showed that the peak cladding temperature (PCT) and minimum critical heat flux ratio (MCHFR) were less than design limits with sufficient margins. Detailed transient analyses for postulated maximum reactivity insertion accident and fast loss of flow accident showed that no fuel damage or cladding failure would occur with the protection of reactor scram.

Direct measurement of dissipation in phononic crystal and straight tethers for MEMS resonators

Position 33E

Vikrant Gokhale, Vikrant J. Gokhale, and Jason J. Gorman

We present the first direct measurements of dynamic mechanical strain profiles along the tethers of MEMS resonators oscillating at high frequencies, using photoelastic modulation of a He-Ne laser probe. Such measurements allow for the quantification of tether dissipation and fair comparison between various tether designs. Our experiments present the first systematic comparison between the best-performing conventional straight-beam tethers with 1-D phononic crystal (PnC) tethers for silicon bulk acoustic wave resonators (SiBARs), and demonstrate an improvement in Q by a factor of two to three when the PnC tethers are used. The spatial decay rate of mechanical strain along the tethers correlates with the measured Q. This work is also the first to demonstrate PnC tethers for electrostatic SiBARs, which can be used as pristine, single-material test platforms to better understand intrinsic material loss mechanisms, as well as for ultra-high Q optomechanical resonators. We characterize the frequency-quality factor (f-Q) product for SiBARs ranging from 169 MHz to 286 MHz, and show that appropriately designed PnC tethers always outperform conventional tethers. The use of low loss PnC tethers enables operation of the SiBAR in phonon-scattering dominated loss regimes, with measured f-Q products greater than 10^{13} Hz. We demonstrate that the photoelastic modulation technique can also be used to obtain high-resolution scans of dynamic surface strain on the resonators, enabling precise characterization of strain mode shapes at high frequencies.

Flash calculations of (almost) guaranteed reliability

Position 36E

Ian Bell and Bradley Alpert

Flash calculations (most especially the calculation of the density given the temperature and pressure) from complex thermodynamic equations of state like those in REFPROP is a calculation fraught with numerous challenges. These calculation routines are quite fragile for mixtures, requiring a level of accuracy in guess values that is often difficult or impossible to achieve in practice. Furthermore, the state-of-the-art in flash calculations only returns one of the density roots, while the ability to obtain all roots at once is extremely beneficial.

In this work we describe a means of approximating the full equation of state with Chebyshev expansions. This Chebyshev expansion allows for ALL density solutions to be obtained explicitly, and without iteration, for a given temperature and pressure. This calculation is the underpinning of most other calculations done with mixture equations of state, and its reliability is of paramount importance. The reformulation of the mixture model in terms of Chebyshev expansions makes highly-accurate equations of state as useful in practice as cubic equations of state.

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Chemical and nanomechanical depth profiling on degradation of photovoltaic laminates

Position 37E

Yadong Lyu, Xiaohong Gu, and Jae Hyun Kim

Polymeric packaging materials, including encapsulant and backsheet (BS), play a critical role to protect the photovoltaic (PV) modules to survive the harsh operating environments. Due to the complicated multilayer and multicomponent construction of PV modules, it is challenging to quantify the structural and property degradation of individual component during their service lifetime. Current approach for characterization of bulk property of packaging materials is deficient for understanding the common failure modes such as yellowing and delamination in the laminates. Hence, the purpose of the present study is (1) to identify the origin and mechanism of the yellowing and delamination; (2) further to quantify the depth-profile of degradation products and (3) to assess the correlation between degradation products distribution and property changes. In the present study, a model PV laminate, glass/ethylene vinyl acetate (EVA) encapsulant/polymeric backsheet (BS) laminate, was selected and exposed to UV on the NIST SPHERE (Simulated Photodegradation via High Energy Radiant Exposure). Our previous results showed that the polymeric BS was mainly composed of seven layers of EVA outer layer, EVA middle layer, EVA inner layer, polyester terephthalate (PET) core layer, PET outer layer, and two adhesive layers between PET outer and core layers, and PET core and EVA inner layers. Multiple complementary depth-profiling techniques were then utilized to characterize the chemical structure, fluorescence, nanomechanical property and color changes of EVA encapsulant/BS along the thickness direction, including micro-FTIR, laser scanning confocal fluorescence microscopy (LSCFM), AFM and micro-UV-Vis. Fluorescence and micro-UV-Vis results show that yellowing is mainly from the EVA encapsulant. Obvious modulus decrease and deacetylation of EVA encapsulant were found principally in its top 300 μm layer (total thickness 1 mm), which is well related with fluorescence products distribution. Severe degradation of two adhesive layers was also observed, implying the potential risk of delamination in these areas. In summary, cross-sectional analysis combining all these techniques is a powerful method to evaluate the spatially heterogeneous degradation of complicated multilayer system at different size scales.

Electromechanical resonance tuning and phonon lasing of individual optical meta-molecules

Position 44E

Brian Roxworthy and Vladimir Aksyuk

We demonstrate reconfigurable optical meta-molecules produced by integrating individual plasmonic antennas into electrically and thermally tunable nanomechanical resonators. The meta-molecules, comprising a subwavelength-sized (350×150) nm^2 gold cuboids embedded within a silicon nitride cantilevers, have optical resonances that sensitivity depend on the motion of the overall device. Taking advantage of this strong optomechanical coupling, we use electrical actuation to tune individual meta-molecule resonances by more than 120% of their native linewidth with up to 50% optical intensity modulation in the far-field. Furthermore, by exploiting thermomechanical coupling of the system, we demonstrate nanomechanical phonon lasing seeded by individual meta-molecule absorption and driven by a thermal bimorph effect. Our results pave the way toward building dynamically tunable optical metasurfaces for applications to tunable flat optical components and ultra-fast spatial light modulators, as well as extreme miniaturization of mechanical oscillators for sensitive detection of mass and force and studying nonlinear dynamics on the nanoscale.

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The nanolithography toolbox

Position 45E

Christopher Wallin, Krishna C. Balram, Daron A. Westly, Marcelo Davanco, Karen E. Grutter, Qing Li, Thomas Michels, Christopher H. Ray, Liya Yu, Richard J. Kasica, Ian J. Gilbert, Brian A. Bryce, Gregory Simelgor, Juraj Topolancik, Nicolae Lobontiu, Yuxiang Liu, Pavel Neuz

Various lithographic processes enable patterning of structures with nanometer-scale lateral dimensions. Lithographic nanostructures are overlaid on one another many times to fabricate the complex integrated circuit (IC) devices that make up modern semiconductor electronics. The first step in any lithographic process consists of device design. There are a number of available software packages for device design that output semiconductor-standard graphic database system II (GDSII) files, which is a binary format representing planar geometric shapes. The predominance of IC devices in manufacturing has led to the development of software packages that are ideal for designing and laying out integrated circuits, which typically have rectilinear geometries. As a result, many of these software packages are not ideal for designing curved geometries with aggressively-scaled dimensions for nanophotonic, nanoplasmonic, nanofluidic, and nanomechanical devices. To solve this problem, the Center for Nanoscale Science and Technology (CNST) at the National Institute of Standards and Technology (NIST) has developed the Nanolithography Toolbox to help users of the CNST NanoFab design devices with complex curves and aggressive critical dimensions. The Nanolithography Toolbox is a platform-independent software package for scripted lithography pattern layout generation. Using parameterized shapes as building blocks, the Nanolithography Toolbox allows users to rapidly design and layout nanoscale devices of arbitrary complexity through scripting and programming. The Toolbox offers many parameterized shapes including structure libraries for micro- and nanoelectromechanical systems and nanophotonic devices. Furthermore, the Toolbox allows users to precisely define the number of vertices for each shape or create vectorized shapes using Bezier curves. The Nanolithography Toolbox is applicable to a broad range of design tasks in the fabrication of microscale and nanoscale devices.

Fabrication and application of complex films and slits with subnanometer surface topography

Position 46E

Kuo-Tang Liao, Joshua Schumacher, Henri J. Lezec, Samuel M. Stavis

The relationship between structure and function is fundamental to nanotechnologies of all dimensionalities, including complex surfaces, films, and slits with nanoscale vertical dimensions and microscale lateral dimensions. We quantitatively investigate the use of a focused ion beam to mill such nanostructures into bulk silicon and thin films of silicon dioxide and silicon nitride. In particular, we explore the unknown limits of dimensional control of these three materials, which are essential to many device technologies. We find that this nanofabrication process can resolve vertical features across the nanoscale and into the atomic scale, with lateral features extending across the microscale and into the macroscale. These results are unprecedented, establishing new limits of dimensional control. Moreover, this nanofabrication process is highly efficient, enabling rapid prototyping of complex surfaces for practical applications. To demonstrate the utility of such nanostructures, we introduce optical films and fluidic slits with subnanometer surface topography. Optical films, milled in silicon dioxide and silicon nitride, show structural colors as an engineered function with future applications in metrology of device dimensions and integration of spectroscopic optics. Nanofluidic slits, milled in silicon dioxide and sealed with a soft layer of silicone resin, separate nanoparticles by size exclusion with subnanometer resolution. In this size separation process, an array of nanofluidic slits simultaneously functions as a reference material, allowing characterization of nanoparticles by particle tracking and reference to device dimensions. These applications emphasize subnanometer control over vertical dimensions and demonstrate the potential utility of complex surfaces, films, and slits with subnanometer topography. Finally, we transfer these structures with subnanometer surface topography to silicone to form replica structures with high fidelity. Silicone devices are biocompatible and disposable for the manipulation and measurement of nanobioparticles.

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Photovoltaic module backsheet degradation and differential exposure conditions due to site design

Position 48E

Andrew Fairbrother, Julien Avenent, Yadong Liu, Matt Boyd, Brian Dougherty, and Xiaohong Gu

Outdoor exposure can be incredibly harsh on electronic devices, which is why backsheets hold a critical role in a photovoltaic (PV) module by acting as both a barrier to weathering and as electrical insulation for the solar cells. Backsheets are typically polymer laminates composed of an outer, core, and inner layer, each serving a unique function. For decades the PV industry has been dominated by fluoropolymer-based backsheets, but continued pressure to reduce costs has led to the development of non-fluoropolymer-based backsheets, such as those based on polyester, polyamide, or polypropylene materials. However, these newer backsheets often lack extensive field testing which would provide insight into their useful service life. At the NIST Gaithersburg site there is a 1152 module ground-mounted PV array which utilizes one of these newer backsheet materials (polyester-based). The array was put into service in August 2012, and as such provides one of the first extensive field studies of non-fluoropolymer-based backsheets. Degradation was documented by visual inspection, Fourier-transform infrared spectroscopy, color, and gloss measurements, and significant differences between modules were observed, depending on its position within the array. The magnitude of the difference is extremely significant, with yellow index values ranging from 9-21, and gloss (60°) ranging from 10-120 Gloss Units. Modules up to 5 meters from the edge of the array and those at the top experienced the greatest change in properties, while those near the bottom and middle of the array experienced less. These changes were compared and correlated to the exposure conditions (irradiance, temperature) at the site. The most significant differential exposure condition was found to be irradiance, especially of ultraviolet light, due to differences in ground albedo and the orientation of array structures themselves.

The degradation patterns observed at the NIST PV array highlight serious implications for site design, which could lead to a wide range of service lifetimes within a single array. Detail on polyester-based backsheet degradation and potential means to mitigate or minimize it will be presented.

PM SESSION (1:00 PM TO 4:00 PM)

COMPUTER MODELING AND SIMULATION

Self-assembly of multi-flavored two-dimensional colloidal crystals

Position 2CS

Nathan Mahynski, Hasan Zerze, Jeetain Mittal, and Vincent K. Shen

DNA-functionalized nanoparticles are now routinely used to assemble complex multicomponent nanoscale crystals.¹ Current techniques operate by grafting one sequence of single stranded DNA (ssDNA) onto the surface of one type of colloid, while the strand's complement is grafted onto another type; the resulting Watson-Crick base-pairing confers highly specific interactions between the two colloidal species. One consequence of these approaches is that, for a given type of colloid, its self interactions cannot be decoupled from its cross interactions with other species. However, recently it has been suggested that by introducing multiple ssDNA sequences (and their complements) onto the colloids, the self and cross interactions in a binary mixture of two distinct types of colloids can be independently tuned.^{2,3} This “multi-flavoring” motif could potentially open new avenues for engineering nanoscale materials, though the thermodynamic behavior of such systems remains largely unexplored. We have developed a computational model to investigate the consequences of independently tuning the pairwise interactions between all species in a binary mixture of colloids on the types of self-assembled structures which form in two-dimensional space. We used a combination of Monte Carlo simulations, stochastic global optimization procedures, and free energy methods to examine the relative stability of an array of different possible structures, which range from low symmetry morphologies such as strings, to various crystal lattices with either 4- or 6-fold symmetry. In the absence of multi-flavoring the relative stability of different structures can generally be predicted by considering the balance of cohesive and adhesive energies between species present in each candidate morphology; however, in multi-flavored systems we find that this simplified description fails to capture the emergence of distinct lattices with similar symmetries even when the binary system is size-symmetric. In the zero-temperature limit, we identify a phase space which provides a semi-universal description of the regimes in which different symmetries are found. We further investigate the effects of size asymmetry and find that the phase space defining the most stable morphologies in the ground state undergoes a seemingly continuous transformation as the colloids become more asymmetric, rather than displaying any discontinuous emergence of new structures.

1. Macfarlane, et al., Science 334, 204 (2011)
2. Scarlett, et al., Soft Matter 7, 1912 (2011)
3. Casey, et al., Nat. Commun 3, 1209 (2012)

Effect of entropic and enthalpic driving forces on morphology in polymer grafted particle filled nanocomposites: Integral equation theory and molecular simulations

Position 1ICS

Tyler Martin and Arthi Jayaraman

Controlling polymer nanocomposite (PNC) morphology is an essential step towards designing PNCs with target macroscopic properties for specific applications. One strategy to control PNC morphology is to modify the surface of the nanoscale filler (nanoparticles) with polymer chains. By tailoring the properties of the grafted and matrix polymers, the effective filler-filler interactions and the PNC morphology can be tuned. In my Ph.D. thesis work, we studied homopolymer grafted particles in chemically-identical matrix homopolymer. Specifically, we examined how polydispersity and flexibility of graft and matrix polymers affect the mixing of the graft and matrix chains, and in turn the dispersion and aggregation of the grafted particles in the matrix. We found that increasing graft length polydispersity or decreasing graft and matrix flexibility increases the mixing of the graft and matrix chains (i.e. grafted layer wetting) and stabilizes the dispersed morphology of the composites. Finally, we showed that for composites where the graft and matrix chains are chemically-dissimilar, the wetting-dewetting and dispersion-aggregation transitions are distinct transitions, unlike what is generally assumed for the chemically identical case. Using temperature, graft-matrix χ , or polymer composition, the degree of wetting of the grafted layer by matrix chains is tuned in the dispersed state. The ability to tune wetting in the dispersed state is not present for chemically-identical composites and reveals the possibility of greater macroscopic property control in composites where the graft and matrix chains are chemically-dissimilar than chemically-identical.

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High-throughput identification and characterization of two-dimensional materials using density functional theory

Position 13CS

Kamal Choudhary and Francesca Tavazza

Two-dimensional (2D) Van der Waals (vdW) heterostructures have recently emerged as a new family of materials, due to their great potential for atomically thin opto-electronic and photovoltaic applications. However, among all the 3D bulk materials only a subset can be exfoliated as 2D single-layer materials. In this work, we introduce a simple criterion to identify 2D materials based on the comparison between experimental lattice constant and lattice constant obtained from density functional theory (DFT) calculations. Specifically, if the relative difference between the two lattice constants for a specific material is more than 5%, we predict them to be good candidates for 2D materials. For all the systems satisfying our criteria, we manually create a single layer system and calculate their energetics, structural, electronic, and elastic properties for both the bulk and the single layer cases. To validate our criterion, we calculated the exfoliation energy of the suggested layered materials, and we found that in 91% of the cases the currently accepted criterion for exfoliation was satisfied. At present, we have 341 bulk and 200 single layer materials in our database but many more calculations are currently underway. The data is publicly available at the website <http://www.ctcms.nist.gov/~knc6/JVASP.html>

On the primary spacing and microsegregation of cellular dendrites in laser deposited Ni-Nb alloys

Position 15CS

Supriyo Ghosh, William J. Boettinger, Li Ma, Nana Ofori-Opoku, Jonathan E. Guyer

In this study, an alloy phase-field model is used to simulate the solidification microstructures at different locations within a solidified molten pool. A macroscopic heat transfer finite element model is used to assess the local solidification conditions appropriate for additive manufacturing. The effect of laser beam speed and the location within the melt pool on the primary arm spacing and on the extent of Nb partitioning at the cell tips are investigated. Simulated primary spacings are compared with power law and geometrical models. Cell tip compositions are compared to a dendrite growth model. The extent of non-equilibrium interface partitioning of the phase-field model is investigated.

Thermodynamic re-assessment of the Co-Al-W system

Position 17CS

Peisheng Wang, Wei Xiong, Ursula R. Kattner, Carelyn E. Campbell, Eric A. Lass, and Gregory B. Olson

The Co-Al-W system and its binary sub-systems Al-Co, Al-W and Co-W were critically reviewed. The thermodynamic description of the Co-Al-W system including all three binaries was developed considering thermodynamic and constitutional data of the systems. Results from density functional theory (DFT) calculations were employed to improve reliability of the descriptions. The Gibbs energy for the thermal vacancy in the Bcc_A2 phase is discussed. $G_V = 30 \text{ T-J/(mol-K)}$ is suggested for the Gibbs energy of the pure vacancy end-member. Large positive values were used for the interaction parameters between the elements, Al, Co and W, and this vacancy. The descriptions obtained for the Al-W and Co-W systems describe the thermodynamic and phase equilibrium data well. Earlier description of the Al-Co and Al-W systems result in the formation of inverse miscibility gaps below 5000 K. In the present work, the inverse miscibility gaps were successfully eliminated for temperatures below 6000 K while describing the phase equilibria and thermodynamic data well. The ordered γ' (Fcc_L12) phase of the Co-Al-W system is described as a metastable phase in the entire temperature range. The calculated Gibbs energy of the γ' is only slightly above that of the equilibrium state, which indicates that there is a great possibility of stabilizing the γ' phase with the addition of γ' -stabilizing elements, such as Ti, Ta and Hf.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

Development of diffusion mobility descriptions for additive manufactured Ti-6Al-4V

Position 20CS

Greta Lindwall, Kil-Won Moon, Michael Mengason, Maureen Williams, and Carelyn Campbell

Essential for the success of additive manufacturing using electron beam melting (EBM) is control of the microstructure evolution during post-processing of the as-built part, e.g. during hot isostatic pressing (HIP). In this work, we study the role of diffusion during HIP of an EBM manufactured Ti-6Al-4V alloy. A CALPHAD-diffusion mobility description for diffusion in the α and β phase in the Ti-Al-V system is developed using information obtained from diffusion-couple experiments. The accuracy of the description is discussed based on comparison with experimental investigations of the microstructure evolution.

Localization and hyperuniformity in polymer-grafted nanoparticles

Position 22CS

Alexandros Chremos and Jack Douglas

Polymer-grafted nanoparticles (GNPs) have been observed in both experiments and simulations to associate into dynamic clusters in both solution and in polymer melts- forming string-like and sheet-like aggregates as molecular parameters are varied. The association into large scale clusters can cause significant property changes in the material, making these materials very promising if the clustering can be controlled. However, there are no known governing principles that serve in the rational design of these hierarchically organized materials. We use molecular dynamics simulation to investigate how the molecular characteristics a liquid composed of GNPs, which exhibit a reversible self-assembly into dynamic polymeric GNP structures below a temperature threshold (liquid-gel transition), influence the GNPs' effective interactions and nanoparticle self-assembly. Materials having significantly suppressed density fluctuations on large length scales, while at the same time being disordered at intermediate length scales, are of particular interest to the material science community and are termed "disordered hyperuniform". It has been suggested that such materials would have the ability to transmit light with the efficiency of a crystal, while still retaining the deformability of a liquid. We construct structural maps that track the degree of the self-assembly in GNP materials with variation of temperature and the size of the nanoparticle core and we also determine relevant spatial and temporal correlations. We find a transition to a gel-like state in this material that is accompanied by the emergence of an effectively hyperuniform state under a wide range of conditions. These materials are then promising for the fabrication of materials having novel and tunable optical and elastic properties.

Using molecular dynamics to investigate the effect of intra- and inter-strand hydrogen bonding on sequence-chirality specific adsorption of single-stranded DNA (ssDNA) onto single-walled carbon nanotubes (SWCNTs)

Position 23CS

Kevin R. Hinkle and Frederick R. Phelan

The unique structural, optical, and electronic properties of single-walled carbon nanotubes (SWCNTs) lend themselves to a breadth of potential applications. However, a difficulty in realizing widespread use of these materials is the polydispersity of samples in terms of size, chirality, and handedness due to the uncontrolled nature of current synthesis techniques. Numerous separation techniques with related protocols have been developed for use on SWCNTs. Most protocols involve adding surfactants to suspend the tubes in an aqueous media before using techniques such as ion-exchange chromatography (IEX) or aqueous two phase extraction (ATPE) to separate the SWCNTs based on their physiochemical properties. Single-stranded DNA (ssDNA) has proven to be an effective dispersant that exhibits sequence-chirality specific binding behavior. Experimental work has displayed the ability to exploit this specificity to tune the separation for particular nanotube chiralities. However, the mechanism that leads to optimal ssDNA-sequence/ SWCNT-chirality pairs is not understood and the search for further successful pairs requires lengthy trial and error studies. In this study, we are using replica exchange molecular dynamics (REMD) simulations to compare the adsorption of experimentally determined optimal and unfavorable sequence-chirality pairings as a means to determine the factors that lead to optimal binding. Our studies show that all ssDNA sequences adsorb on the SWCNT surface and form a network of intra- and inter-strand hydrogen bonds. However, the nature of the binding network that forms is unique for different pairings and can be roughly cast into the categories of stabilizing, non-stabilizing, and destabilizing. Current work is focused on developing quantitative measures that describe the binding process to clearly identify these categories. These investigations work towards our ultimate goal of providing better insight into the sequence-chirality specific binding mechanism, and eventually developing a model that allows for the prediction of other pairs leading to the efficient sorting of a desired nanotube chirality.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

Considerations for atomistic modeling of small-angle scattering data

Position 24CS

Steven Howell, Maria Monica Castellanos, and Joseph Curtis

Developing atomistic models from small-angle scattering (SAS) experiments depends on low resolution experimental results to make detailed conclusions about molecular structures. To identify atomistic models that describe this low resolution data involves several data processing steps that must be performed with care to avoid statistically misrepresenting the experimental measurement. Often those performing this type of analysis have expertise specific to the system studied and therefore rely on analysis and modeling software tools developed by others, tools which overlook important details described herein. To address this oversight, we review the data processing steps required for atomistic modeling of SAS data paying special attention to error propagation, model uniqueness, and data overfitting. Specifically we consider Guinier fitting, information content, data rebinning, ensemble clustering, scaling the model data, and choosing a discrepancy metric. This review aims to provide a guide for the data analysis steps required to identify atomistic models with theoretical scattering that agree with experimental SAS measurements.

A systems approach for modeling the dynamic thermomechanical response of carbon steels

Position 25CS

Shengyen Li, Steve Mates; Mark Stoudt, Carelyn Campbell, Greta Lindwall, and Sindhura Gangireddy

In manufacturing processes, workpiece materials are subjected to rapid heating, high loading rates and large plastic strains. Depending on the temperatures involved, the phase transformations that can occur may significantly affect the mechanical behavior, for example when pearlite transforms to austenite in carbon steel. To capture these processing-structure-properties relations, we have developed a workflow platform to integrate data collection, model simulation, and software applications. Within this platform, microstructure information, thermomechanical data, and mechanical measurements are all easily entered in the Materials Data Curation System (MDCS). This allows the data to be easily transformed and used with other software. For example, simple scripts allow all the SEM micrographs to be accessed and analyzed by ImageJ to determine phase fraction values, which are then stored in the MDCS for later use with other models. CALPHAD-based phase equilibrium calculations are integrated with precipitation and phase transformation models. These results are then integrated with the experimental data and constitutive models to predict time-dependent plastic deformation under rapid heating and loading. This flexible design framework enables the integration of experimental data and composition-dependent models to rapidly develop processing-structure-property relations.

Energy renormalization approach to coarse graining of polymer dynamics

Position 27CS

Wenjie Xia, Jake Song, Cheol Jeong, Frederick R. Phelan, Jack F. Douglas, and Sinan Ketten

A major challenge in soft matter science is the bottom-up prediction of the temperature-dependent behavior of amorphous glass-forming (GF) polymers. Coarse-grained (CG) models derived from atomistic simulation data offer chemical specificity and access to relevant time-scales, but exhibit faster dynamics due to their reduced degrees of freedom. Based on the common notion of a temperature-dependent activation energy in glass formation theories, we find that renormalizing the CG cohesive energy parameters as a sigmoidal function of temperature allows accurate prediction of atomistic polymer dynamics over the Arrhenius, the non-Arrhenius, and the localized elastic regimes. We establish a rigorous approach to enthalpically compensate for the altered configurational entropy and cooperatively rearranging regions (CRRs) in CG modeling. This represents critical progress for building temperature-transferable CG models that predict key properties of a GF polymer. The unique role that cohesive interactions play on GF characteristics as highlighted in this work reveals new opportunities for the tailored design of GF polymer materials.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

The role of local geometry in two-dimensional freezing/melting.

Position 28CS

Tamoghna Das and Jack Douglas

The study of phase transition in particulate systems has been a central research topic for years due to the ubiquity of freezing/melting in nature and its obvious importance in numerous industrial applications. However, our understanding about the microscopic mechanism of this fundamental process is rather incomplete. One of the prominent mechanisms suggests that the melting of crystalline solids happens through the unbinding of topological defects. The theoretical description for the proliferation of such defects and its collective dynamics is often at contest with the experimental findings. Further, a similar description of the same transition point is not possible when approached from the liquid side due to the random structural configuration. On the other hand, the glassy systems, although often out of equilibrium, shows mechanical response similar to that of crystalline media while sharing the structural similarities with the liquids. Importance of the shape fluctuation of the collective excitations in glassy systems are often argued to be the key ingredient to understand its mechanical response. Taking this queue, we study the local geometry of a simple Lennard-Jones systems in both liquid and crystalline states at constant temperature. Generating the configurations using equilibrium molecular dynamics, we identify three distinct populations based on the local packing of particles. Their fluctuation statistics is then studied by using the standard statistical geometric measures. We aim to relate the local stress fluctuation and dynamics with these fluctuations.

Utility of the time-temperature superposition principle for integrating atomistic simulations and experiments to study thermo-mechanical properties

Position 34CS

Ketan S. Khare and Frederick R. Phelan Jr.

One of the major goals of the Material Genome Initiative (MGI) is to integrate experiments, computation, and theory. To this end, we are developing methods for performing accurate simulations of atomistically detailed models of cross-linked epoxy, which is a widely used thermosetting polymer in many industries. Due to the limited time-scales accessible by simulations and the rate-dependent nature of thermo-mechanical properties of polymers, quantitative comparisons between thermo-mechanical data (T_g , creep compliance, etc.) obtained using atomistic simulations and experiments has been difficult. In this work, we show that the time-temperature superposition principle can be successfully employed to make such comparisons between data calculated/measured at time-scales separated by more than ten orders of magnitude. We hope to establish standard procedures for creating models for such materials and calculating thermo-mechanical properties that can then be quantitatively compared with experiments.

How much does the calculation method matter when computing properties using molecular dynamics?

Position 39CS

Lucas Hale, Zachary Trautt, and Chandler Becker

Classical molecular dynamics (MD) is a powerful computational method that allows for complex, dynamic behaviors and mechanisms to be explored at the atomic level. It is well known that different interatomic potentials can give different results, thus making it necessary to evaluate and compare potentials based on how they predict material properties. While many of these properties are thought of as simple calculations, there can be multiple methods for computing the same property. The variation in the measured properties across different methods is largely unexplored.

Here, we compare three methods for computing the lattice and elastic constants across a range of interatomic potentials. This allows for a comparison not only of the potentials themselves, but also the sensitivity to the calculation itself. The results, calculation scripts, and supporting computational infrastructure are openly available to support researchers making informed decisions to help them perform meaningful simulations.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

Diffusion-limited reaction in nanoscale electronics

Position 40CS

Ryan Evans, Anthony Kearsley, and Arvind Balijepalli

Heterogeneous effects of medicine on various sub-populations have motivated an interest in precision medicine; i.e., medicine tailored to one's genetic sequence. Creating precision medicine involves measuring protein-ligand interactions at concentrations well below the sensitivity of current state-of-the-art technology such as Nuclear Magnetic Resonance (NMR), or Mass Spectrometry. Measurements are further obstructed by the need for precise control of the in vitro environment necessary for proteins to function. In response to these challenges, NIST scientists (Arvind Balijepalli) are developing a novel nanoscale electronics instrument capable of measuring protein-ligand interactions at very low concentrations in physiologically realistic environments.

Since interpreting device data relies on a mathematical model, we have developed a coupled Partial Differential Equation model for the nanoscale electronics experiment. Using techniques from asymptotic and complex analysis, we have reduced this model to a single Integrodifferential Equation (IDE)--a reduction which greatly reduces computational effort and time. In the future, we will research using this model to determine instrument sensitivity, and for parameter estimation.

Selection of distributional models to measure similarity between sentences

Position 49CS

Dmitrijs Milajevs

Representation of sentences that capture semantics is an essential part of the natural language processing systems, such as information retrieval or machine translation. The representation of a sentence is commonly built by combining together the representations of words that the sentence consists of. Similarity between words is used as a proxy to evaluate semantic representations. The word similarity models are well studied and correlate with human judgements.

Current evaluation of models of sentential similarity builds on the results obtained in lexical experiments. The main focus is how the lexical representations are used, rather than what they should be. It is often assumed that the optimal representations for word similarity are also optimal for sentence similarity.

This work drops this assumption and systematically looks for lexical representations that are optimal for similarity measurement. We find that the best representations for words similarity are not always the best for sentence similarity and vice versa. However, there are representations that are a good in both tasks. The systematic study of the parameters of similarity models reveals that the more information lexical representations contain, the more attention should be paid to noise.

Understanding convolutional neural networks in the context of feature engineering

Position 54CS

Sarala Padi, Petru Manescu, Peter Bajcsy, and Mary C. Brady

The main objective of this research article is understanding of convolutional neural network models in the context of feature engineering. Convolutional neural network model has two layers; convolutional, and fully connected layer. The first layer does automatic feature engineering and the second layer does nonlinear approximation of extracted features for given analysis. To understand features extracted from the convolutional models, an experimental analysis is designed in selecting the appropriate filters that are known a priori for the given data as opposed to random initialization of convolutional layer filters. This analysis assisted to understanding the features extracted from convolutional model with the human annotated features. In addition to this, the study allows to contemplate the sensitivity analysis of convolutional neural network architecture construction to four factors, namely, a) filter type, b) filters used, c) batch size, and d) neurons used at hidden layer of convolutional model. To support the analysis, convolutional layers are initialized with two kinds of filters, Random and Gabor filters. Experimental results reported in this paper are evident that Gabor initialization of convolutional filters extract meaningful features that are semantically similar to human annotated features prior to feature extraction. It is also shown that appropriate usage of filters at convolutional layers of the CNN model result in faster convergence, minimum number of parameters, and the best accuracy as opposed to randomly initialized filters. The significance of this study provides initial recommendations prior to CNN architecture construction for any given task.

ENERGY, WATER, AND ENVIRONMENT

Quantitative analysis of oxidation state in cerium oxide nanomaterials

Position 3EWE

Christopher Sims, Russell A. Maier, Aaron C. Johnston-Peck, Justin M. Gorham, Alline F. Myers, Vincent A. Hackley, and Bryant C. Nelson

Of the many engineered nanomaterials being incorporated into our society, cerium oxide (ceria, CeO_{2-x}) based nanomaterials (NMs) are receiving increased attention due to their unique chemical properties and vast number of current and potential applications (e.g., automotive catalysts, UV filters, agricultural treatment agents, antioxidant therapeutics.). Previous research designed to understand the potential environmental and toxicological effects of ceria NMs have yielded conflicting results, with ceria NMs found to be both toxic and non-toxic to cells and organisms. As the overall environmental and toxicological outcomes of ceria NMs are not yet fully understood, it is imperative to develop a comprehensive understanding of their physicochemical properties since these properties will influence the interactions of ceria NMs with biological and environmental systems.

Here, we describe the development of an analytical procedure designed to measure the cerium oxidation state in ceria NMs using orthogonal approaches. Preparation of materials for control measurements and methods for optimizing data acquisition and processing were developed to efficiently analyze and objectively interpret the distribution of Ce³⁺ vs. Ce⁴⁺ oxides. Our results demonstrate a high degree of agreement between the utilized techniques (electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), and annular dark field scanning transmission electron microscopy (ADF-STEM)) when stable control materials are employed. The methodology is applied to thoroughly characterize a suite of commercial ceria NMs. In agreement with previous research, our results suggest the primary particle size has a large influence on the oxidation state of the ceria particles, with smaller particles having increased Ce³⁺/Ce⁴⁺ ratios compared to their larger counterparts.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

Atomic-scale interactions of hydrogen with aluminum nanoparticles at room temperature

Position 6EWE

Canhui Wang, Wei-Chang Yang, Devika Sil, Amit Agrawal, and Renu Sharma

Surface plasmons and hot electrons are generated in certain metals such as Au, Ag, Al due to the interaction of photons or electrons with the surface electrons. Recently, optical methods have been used to show that hot electrons generated by surface plasmons can trigger various chemical reactions at room temperature.¹⁻³ Understanding the reactions promoted by localized surface plasmon resonance (LSPR) is important for designing efficient catalytic systems for a wide range of energy and environmental applications. However, a number of important questions related to this type of reaction processes remain unclear due to the complexity of the reaction kinetics, and lack of spatial resolution available with optical methods. Nanoparticles often respond dynamically to the gaseous environment, because gas adsorption on the surfaces affects the free energy of the exposed surfaces and can lead to morphological change or surface oscillations in nanoparticles.^{4,5} Since the LSPR is known to strongly depend on size, shape and dielectric environment of the particles, any change in either of them will also affect the intensity spatial distribution or the center wavelength of the LSPR. Therefore, one of the fundamental questions that needs to be answered is how the change of particle morphology (shape), as well as dielectric environment, during photocatalytic reactions may affect the spatial distribution of LSPR profile on the nanoparticles and if that can be correlated with the locations where each reaction step occurs.

In light of the complexity of the reaction process, we combined an ensemble of techniques to characterize LSPR-promoted chemical reactions at high resolution using an environmental transmission electron microscope (ETEM) with monochromated electron source. In particular, we focus on the LSPR promoted dissociation of hydrogen using Al nanoparticles. An aberration-corrected ETEM is used to generate atomic resolution movies and time-resolved electron energy-loss spectra (EELS) to monitor the crystallographic and chemical change in the particle as well as LSPR locations and shifts during the reaction. Under gaseous environments we observe structure and oscillatory morphological changes in the Al nanoparticle. EELS imaging, with different energy dispersions, is used to acquire both elemental and LSPR maps from the same particle. These combined spectrum images show correlations between the LSPR profile and the morphology of different compounds in the nanoparticle. The comparison between the EELS maps of the particle, before and after H₂ is introduced in the environment, also show the effect of the gaseous environment on the LSPR generated on the nanoparticle surface locally, revealing selective gas adsorption sites. This combined approach to decipher LSPR-promoted reactions provides time-resolved, atomic-scale information on the reaction kinetics and improves the understanding of the dynamics of LSPR promoted relations.

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Room temperature CO dissociation on selective edges of gold nanoparticles

Position 7EWE

Wei-Chang Yang, Canuhui Wang, and Renu Sharma

Au nanoparticles on oxide supports have drawn great interest in catalyst design for low temperature CO oxidation.¹ Both experimental and theoretical results have suggested that adsorption of CO molecules on the Au surface and the following catalytic activity are affected by the coordination number of Au atoms.¹ However, the direct evidence for the location of the active sites on the nanoparticle surface for CO adsorption, which in turn may be the catalytically active sites, is missing.

In the present work, we take advantage of the plasmonic behaviour of Au nanoparticles to measure the energy shifts in localized surface plasmon energy (LSPR) as a function of gas environment using an environmental scanning transmission electron microscope equipped with a monochromated field-emission gun (FEG). We use high energy and spatial resolution electron energy loss spectrum (EELS) imaging to identify the location of CO adsorption on triangular Au nanoparticle, as indicated by the spectral shift of the LSPR energy.² The LSPR peak manifested a blue-shift (≈ 0.05 eV) in CO environment (PCO = 1.1 mbar) with respect to vacuum at the sides of Au triangular nanoparticles, which consisted of the {311} planes of Au, as identified from the diffraction data collected by tilting the particle. The subsequent core-loss EELS revealed that amorphous carbon deposited at the same location. Although the LSPR peak shifted back to its original value after CO was evacuated, the amorphous carbon remained on the ledges, indicating i) the carbon signal is not from the CO, ii) LSPR energy shift is not due to carbon deposition, and iii) therefore, carbon is deposited by the room temperature dissociation of CO. We believe that our results can be compared with the recently reported dissociation of H₂, facilitated by the hot electrons generated from the non-radiative decay of LSPR.³ Similar to H₂, dissociation energies of CO molecules may be lowered as a result of CO adsorption on selective surfaces/ledges as reported for Fe {100} surfaces.⁴ Therefore, the locations that are selective for amorphous carbon deposition may correspond to active sites that display decreased dissociation barriers and enable the hot electron transfer.

Our result suggest that CO is adsorbed preferentially on the ledges of the Au nanoparticles. More interestingly, we discover that LSPR energies can dissociate CO molecules at room temperature as evidenced by the deposition of amorphous carbon on the same ledges.

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Charged grain boundaries reduce the open-circuit voltage of polycrystalline solar cells - analytical description

Position 8EWE

Benoit Gaury and Paul Haney

Despite decades of research, the role of grain boundaries in the photovoltaic behavior of polycrystalline solar cells remains an open question. The high defect density of grain boundaries generally promotes recombination and reduces photovoltaic efficiency. However, thin film polycrystalline photovoltaics such as CdTe and Cu(In, Ga)Se₂ exhibit high efficiencies despite a large density of grain boundaries. Here we present a physical description and analytical expressions for the dark current-voltage $J(V)$ relation of a pn+ junction with positively charged, columnar grain boundaries. We find that grain boundaries contribute substantially to the dark current. Numerical simulations further show that the dark $J(V)$ can be used to determine the open-circuit potential V_{oc} of an illuminated junction for a given short-circuit current density J_{sc} . A precise relation between the grain boundary properties and V_{oc} is provided, advancing the understanding of the influence of grain boundaries on the efficiency of thin film polycrystalline photovoltaics like CdTe and Cu(In, Ga)Se₂.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

Neutron scattering studies of hydrogenous materials for next-generation energy storage

Position 9EWE

Mirjana Dimitrievska, Wan Si Tang, Hui Wu, Wei Zhou, and Terrence J. Udovic

Hydrogen and hydrogenous materials are considered among the most promising choices for providing clean energy for transport and other applications across the world, as well as for future electrochemical energy storage. Understanding the fundamental properties of these materials and their functionality at the atomic and molecular level is crucial to addressing their role in the global challenge confronting renewable energy technologies. Hydrogen has the largest incoherent scattering interaction with neutrons of all the elements in the periodic table and a sizable coherent scattering interaction, making such neutron scattering techniques as neutron powder diffraction (NPD), neutron vibrational spectroscopy (NVS), and quasielastic neutron scattering (QENS) invaluable for elucidating the structures and dynamical natures of these materials over a broad space and time domain. For example, the combination of NPD and NVS coupled with density functional theory (DFT) computations can be highly effective for elucidating the detailed structures and vibrational properties of hydrogenous energy-related materials. Additionally, neutron-scattering fixed window scans (FWS) and QENS can be used to track the mobilities and fundamental dynamical natures of the hydrogen within these materials over a broad temperature range. This work will focus on the recent neutron scattering results from a variety of energy-related materials, ranging from borohydride-based and silanide-based hydrogen-storage materials to novel Li and Na closo-polyborate superionic-conducting solid electrolytes. The relationship among the structural and dynamical properties obtained from these techniques and the thermodynamic and conductivity properties of these various hydrogenous materials will be discussed.

Preliminary results from the NIST supercritical carbon dioxide corrosion test facility

Position 18EWE

Brandi Clark, J. David McColskey, Ross Rentz, and Jeffrey W. Sowards

Carbon dioxide (CO₂) capture and sequestration has been hailed by some as the “critical enabling technology” needed to reconcile climate-change-driven reductions in CO₂ emissions with the use of fossil fuels to meet increasing energy demands. However, transporting large quantities of CO₂ would require a pipeline network the size of the existing natural gas network and a similar level of regulation. Unlike CO₂ currently transported for EOR, anthropogenic CO₂ is expected to contain corrosive contaminants associated with energy production (e.g., H₂O, SO_x, NO_x, H₂S). In order to successfully transport large volumes of anthropogenic CO₂, the level of contaminant removal needed for pipeline safety and integrity will need to be balanced against the cost of CO₂ purification. Gaps in the existing literature demonstrate a need for systematic investigation (through improved metrology) of the effect of expected contaminants on corrosion rate to inform pipeline design decisions. To address this issue, NIST has constructed a supercritical CO₂ corrosion test facility. The facility is equipped with 3 high-temperature, high-pressure vessels and gas-phase FTIR for simultaneous in situ monitoring of key contaminants. This poster will outline the capabilities of the new NIST facility, describe our corrosion test method, and report preliminary test results.

Adsorption properties of shale gas in porous materials

Position 26EWE

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

Shale gas production significantly increases in the past decade in the United States. The total shale gas in place (GIP) and the transport properties of gas molecules in shales are key factors for shale gas production. Due to the presence of abundant nanopores in the shale rocks, the understanding of confinement effects of gas in these pores is essential for the estimation of shale gas storage and transportation. In this study, we investigate the effects of pore size and surface properties on the adsorption behaviors of methane confined in model mesoporous materials, such as MCM-41 and SAB-15, and kerogens by small-angle neutron scattering (SANS). While MCM-41 and SBA-15 have relatively monodisperse pore size distributions, kerogens, which are the organic components of the shale rocks, are heterogeneous porous materials with polydisperse pore size and different surface properties. The adsorption behaviors of methane in these porous materials are investigated using in-situ SANS measurements. Furthermore, we have proposed and developed a new scattering theory to analyze the SANS data that can be used to measure the surface heterogeneity of porous samples.

Neutron reflectometry study of solid electrolyte interface formation on a tungsten film electrode

Position 33EWE

Eric Rus and Joseph Dura

Though the solid electrolyte interface (SEI) is critical to the long term stability of Li-ion batteries, its nature remains elusive, in part due to the relatively low sensitivity of x-ray and electron-based probes to the light element constituents of the SEI. Neutrons, being scattered by the nuclei of atoms rather than by electrons, offer a particularly sensitive probe for light elements such as lithium and hydrogen. Herein, in situ neutron reflectometry (NR) measurements of SEI formation on a tungsten thin film model electrode will be presented. This study builds upon earlier work by optimizing the contrast of the electrode and solution to highlight the growth of a low scattering length density layer at the interface.¹ NR of the bare electrode was first measured in an inert atmosphere, after which the electrode was assembled into a cell with a 1 mol/L LiPF₆ solution in a mixed ethylene carbonate and diethyl-d₁₀ carbonate solvent. NR data were then collected at open circuit (about +2.65 V vs Li/Li⁺), and at a sequence of three fixed potentials: +0.25 V, +2.65 V, and again +0.25 V, with 10 potential cycles between the +2.65 V and final +0.25 V hold. A thin surface layer, presumably oxide, present on the bare electrode was slightly modified by contact with the solution at open circuit, suggesting a reaction with the solution. During the subsequent +0.25 V hold, the NR data were best fit by a model with two surface layers: an inner layer with a high content of Li and/or 1H nuclei, e.g. LiOH or underpotential deposited lithium, and an outer layer richer in 2H, C, O, F, or P - containing species, such as might be derived from LiPF₆ or diethyl-d₁₀ carbonate. Upon increasing the potential to +2.65 V, Li and/or 1H containing species were lost from the inner layer. After potential cycling and returning to +0.25 V, the NR could be fit with a single surface layer with high Li and/or 1H content and of about the same thickness as the two layers present during the first potential hold at +0.25 V. The change from a two to a one surface layer model may be indicative of greater roughness between two surface layers, preventing them from being resolved. These data confirm earlier measurements of SEI thickness and show that the SEI is not immutable once it has been deposited. They also demonstrate the increased sensitivity of W electrodes for elucidating the structure of the SEI. In future work, we plan to apply isotopic substitution to further define the composition of the SEI.

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Neutron radiography as a measurement tool for studying water and solute transport through desalination membranes

Position 35EWE

Devin L. Shaffer, Daniel S. Hussey, Menachem Elimelech, and Edwin P. Chan

Neutron radiography, a non-destructive, two-dimensional imaging technique, is applied for the first time to study water and solute transport through desalination membranes. We demonstrate the use of neutron radiography to measure lithium chloride draw solute concentrations across a thin-film composite membrane during forward osmosis permeation. Neutron radiography provides direct visual confirmation of incomplete membrane support layer wetting and reveals significant dilutive external concentration polarization of the draw solution outside of the support layer. These transport-limiting phenomena have been hypothesized in previous work but are not accounted for in the standard thin-film model of forward osmosis permeation, resulting in inaccurate estimations of membrane transport properties. Our work demonstrates neutron radiography as a powerful measurement tool for studying membrane transport and emphasizes the need for direct experimental measurements to refine the forward osmosis transport model. Neutron radiography is envisioned as a tool for studying a variety of membrane separation processes for liquids and gases.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

The role of the strong metal support interaction on the catalytic activity of Pt deposited on TiO₂ supports

Position 52EWE

Robin Hansen, Richard Phillips, Eric Eisenbraun, and Carl Ventrice

There are a few roadblocks to the widespread commercialization of hydrogen fuel cells, including the stability of the catalysts and their substrates as well as the cost of the Pt catalysts required for the oxygen reduction reaction (ORR). The stability of the fuel cells can be greatly enhanced by replacing the traditional carbon supports with a conductive metal oxide such as TiO₂. In this study Pt was grown by both atomic layer deposition (ALD) and physical vapor deposition (PVD) on reduced TiO₂ samples. The Pt formed islands between 3-8 nm dependent on how much Pt was deposited. One factor which can inhibit the catalytic activity of Pt on a metal oxide is the encapsulation effect known as the strong metal support interaction (SMSI). This where a small overlayer of a reducible metal oxide forms on the surface of Pt during reduction at temperatures as low as 200 °C. This temperature is below that of most ALD processes and as such may inhibit the ability of ALD produced Pt islands from performing the ORR. In order to test this out both methods of preparing Pt was performed on a single crystal rutile TiO₂(110) crystal as well as an ALD produced polycrystalline anatase TiO₂. This allowed a full test for the feasibility of ALD to create both stable and efficient substrates as well as catalysts, which would test the ability to use ALD to coat any nanostructure making it a potential fuel cell. The test of the SMSI and electrochemical activity was performed through cyclic voltammetry (CV). Additional measurements were performed with scanning electron microscopy (SEM), Auger electron microscopy (AES), X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectroscopy (RBS), and four point probe analysis (4pp).

Understanding the shape-based toxicity effects of nanostructures

Position 53EWE

Danielle Gorka, Nick Geitner, Joshua Osterburg, Carly Gwin, Benjamin Colman, Emily Bernhardt, Claudia Gunsch, Richard Di Gulio, Mark Wiesner, and Jie Liu

Nanomaterials are increasingly being used in consumer products due to their unique optical, electronic, and antibacterial properties. However, proliferated use of nanomaterials will lead to increased entrance into the environment where toxicity can occur to plants and other organisms. The focus of my research is to understand the origin of this organismal toxicity and methods for its reduction through engineering. Nano silver was chosen as the subject of study due to its prevalent use in consumer products. Specifically, the effect of three silver nanomaterials (silver nanoparticles, silver nanocubes, and silver nanowires) was examined in environmentally relevant and model organisms including *Lolium multiflorum*, *Danio rerio*, *Caenorhabditis elegans*, and several bacterial strains. Shape was shown to affect the toxicity of silver nanomaterials to *L. multiflorum*; this effect was not found in other species. To further understand the shape-specific toxicity, dissolution was studied. While it is often assumed to be the cause of silver nanomaterial toxicity, we concluded that dissolution alone did not account for all of the toxicity shown. Instead, physical contact between the nanomaterial and plant was found to be necessary for shape-based phytotoxicity. This work will help determine methods of engineer nanostructures to reduce environmental toxicity while retaining functional properties.

PHYSICS

Universal static distortion in pyrochlores

Position 1Ph

Ben Trump, Seyed Koochpayeh, Ken Livi, Jiajia Wen, Kate Arpino, Quentin Ramasse, Rik Brydson, Mikhail Feygenson, Hikaru Takeda, Masashi Takigawa, Kenta Kimura, Satoru Nakatsuji, Collin Broholm, Tyrel McQueen

We report on the structural details of $\text{Pr}_2\text{Zr}_2\text{O}_6\text{O}'$, $\text{La}_2\text{Zr}_2\text{O}_6\text{O}'$, and $\text{Yb}_2\text{Ti}_2\text{O}_6\text{O}'$ in the $\text{A}_2\text{B}_2\text{O}_6\text{O}'$ pyrochlore structure. X-ray and neutron powder diffraction indicate these materials are long-range ordered. On the local scale these materials appear to be disordered despite ideal stoichiometry, ideal cation-ordering, no lone pair-effects, and lack of magnetism (in $\text{La}_2\text{Zr}_2\text{O}_6\text{O}'$); as evidenced by pair-distribution function analysis and selected area electron diffraction at room temperature. High-resolution scanning transmission electron microscopy and 91Zr nuclear quadrupole resonance indicate that this disorder is static and of order 0.01 nm. The magnitude and pattern for displacements is consistent with a β -cristobalite distortion, due to either an electronic (Jahn-Teller) effect or the size mismatch between A and B cations. The evidence for these distortions has significant implications for materials which crystallize in the pyrochlore structure.

Progress towards generating Rydberg state, one-electron ions

Position 4Ph

Joan Dreiling, S.F. Hoogerheide, A.S. Naing, and J.N. Tan

We report on progress towards the goal of producing hydrogen-like ions in Rydberg states for laser spectroscopy measurements of fundamental constants.¹ Such a system can, e.g., provide a value for the Rydberg constant that is free of nuclear size effects, thereby potentially addressing the proton radius puzzle.²

We first create fully stripped neon atoms (NeXI) in the electron beam ion trap (EBIT). These bare nuclei are extracted via a beamline from the EBIT into a second apparatus where they are captured at low energy in a unitary Penning trap.³ The second apparatus has a cross-beam configuration, with a perpendicular beam of laser excited Rb atoms intersecting the ion beam at the Penning trap. While stored in the trap, the ions can interact with the Rb and, through charge exchange interactions, the bare nuclei can capture one or more electrons from the Rb. The charges of the stored ions are then analyzed by dumping the trap to a time-of-flight detector.³

1. U.D. Jentschura et al., Phys. Rev. Lett. 100, 160404 (2008).

2. R. Pohl et al., Annu. Rev. Nucl. Part. Sci. 63, 175 (2013).

3. S.F. Hoogerheide et al., Atoms 3, 367 (2015).

Effective field theory for strongly interacting photons

Position 5Ph

Michael Gullans, J. D. Thompson, Y. Wang, Q.-Y. Liang, V. Vuletic, M. D. Lukin, and A. V. Gorshkov

We develop an effective field theory (EFT) to describe the few- and many-body propagation of one dimensional Rydberg polaritons. We show that the photonic transmission through the Rydberg medium can be found by mapping the propagation problem to a non-equilibrium quench, where the role of time and space are reversed. We include effective range corrections in the EFT and show that they dominate the dynamics near scattering resonances in the presence of deep bound states. Finally, we show how the long-range nature of the Rydberg- Rydberg interactions induces strong effective N-body interactions between Rydberg polaritons.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

Resonant fluorescence of single quantum dot states

Position 12Ph

Olivier Gazzano, T. Huber, V. Loo, S. Polyakov, E. B. Flagg, and G. S. Solomon

The spontaneous emission of an isolated two level system has a Lorentzian spectrum corresponding to the Fourier transformation of its decay rate. However, the line shape will be modified when the emitter dipole is coupled to a reservoir such as a fluctuating electromagnetic environment. The broadening can be Lorentzian (homogeneous) or Gaussian (inhomogeneous) depending on the timescale of the interaction.

In this work, we study the fluorescence emission of single semiconductor InAs quantum dots (QDs) embed in a planar distributed-Bragg reflector cavity. The laser emission is suppressed by an orthogonal, in-plane excitation scheme. We combine resonant photoluminescence and resonant photoluminescence excitation measurements. In particular, we directly observe the QD state inhomogeneous broadening induced by electromagnetic variations in the QD vicinity. The amplitude distribution of the jumps fits a Gaussian line shape.

We show a strong increase of the QD brightness by adding a weak above band laser. We also measure, for the first time, a significant reduction of the inhomogeneous broadening of the QD optical transition by a factor of ~ 2 .

A Monte Carlo simulation models the increased QD brightness and infers that the resonant laser is inducing charge loss. Further, the linewidth narrowing is due to motional narrowing screening or stabilization of nearby states and is predominately independent of the RF increase.

Water dynamics in polymer solution

Position 19Ph

Zhe Zhang, Michael Ohl, Youngkyu Han, Gregory S. Smith, and Changwoo Do

Water and water-containing systems are ubiquitous in nature. Generally, water can be categorized into two populations in water-containing systems: a) bulk water, which exists away from the solute, and therefore, the atomistic and molecular interactions can be ignored; and b) interfacial water, which is usually found close to the solute or interfaces having different properties from bulk water. The interfacial water molecules often demonstrate extraordinary structural and dynamical properties compared to those of the bulk water molecules, and the efforts are still being made to understand the structure and dynamics of interfacial water. Polyethylene oxide (PEO) and Pluronic block copolymer (e.g. L62) aqueous solution are used as model systems in our research. PEO has been widely used as polyelectrolytes in batteries. For PEO solution, we combined quasi-elastic neutron scattering experiments and atomistic molecular dynamics (MD) simulation to study the effect of lithium ions (Li^+) on the dynamics of both bulk water and interfacial water. A detailed analysis of microstructure of PEO- Li^+ -Water complex indicated a cage conformation surrounding the ions. A further investigation with sodium and potassium ions has revealed that the stability of PEO cage is determined by the ionic radius of ions. The composition of L62 is PEO6-PPO34-PEO6, where PPO stands for the polypropylene oxide. The small-angle neutron scattering (SANS) experiments and MD simulation have been applied to understand the distribution of water molecules and water dynamics in different layers of lamellar membrane formed by L62. Water molecules at bulk area are following normal diffusion, while that at lamellar layers are following sub-diffusion.

A fiber pigtailed hemispherical Fabry-Pérot optical cavity for accelerometry

Position 29Ph

Feng Zhou, Yiliang Bao, Jason J. Gorman, and Thomas W. LeBrun

We present a novel fiber-pigtailed hemispherical Fabry-Pérot cavity developed for optomechanical accelerometry and precision sensing. The high finesse ($F > 1000$) and high free spectral range allow the cavity geometry (length, mirror curvature and ellipticity) and the relative phase shift on reflection to be measured in-situ. The relative stability of the resonance frequencies is shown to be better than 7×10^{-6} over one day, limited by drifts in components that will be eliminated with the final phase of fabrication. Using the measured values for cavity geometry/Gouy phase and dispersion of phase shift on reflection allows the frequencies of the measured peaks to be modeled accurately in air with stabilization or correction of environmental variations and with less than $200 \mu\text{W}$ of optical power to avoid self-heating. The cavities also support very high-order modes and allow investigation of still-poorly understood aspects of spherical-mirror Fabry-Perot interferometers including mode mixing and Ince-Gaussian modes. In addition to precision sensing and accelerometry, this can also enable studies of high angular momentum states, photon entanglement and quantum communication.

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Imaging and spectroscopy of individual paramagnetic electronic states on the atomic scale

Position 30Ph

Kapildeb Ambal, C. C. Williams, and C. Boehme

This work presents conduction-atomic force microscopy images of the dangling bond states at silicon surfaces coupled to individual phosphorus donors. Nuclear spins of phosphorus [³¹P] donors in silicon are promising qubit candidates¹, and our methods are a step toward probing individual donors' nuclear spins to make useful quantum devices in silicon.²

Impurities like phosphorus [P] donors in crystalline silicon provide conduction electrons and conductivity at high temperature. But at very low temperature (<20K) the conductivity drops as electrons are localized at the impurity sites. The hypothesis is that tunneling to donor sites occurs through numerous dangling bond states at the silicon surface and therefore, at the nanoscale, the tunneling current density from a scanned tip will be maximum at the donor sites. In this presentation, we focus on identifying individual P-donor and Pb-type dangling bond states by measuring electric current through a crystalline silicon (100) – SiO₂ interface.² The experiments were conducted with simultaneous AFM and local current measurements at low-temperature (T = 4.3 K) and in complete darkness to prevent any optical excitation. I-V responses on these high-current spots further support the hypothesis that individual ³¹P-donor – Pb states are being addressed and that in future work, the spin-states could be probed by monitoring the spin-dependent current change under magnetic resonance condition known as electrically detected magnetic resonance (EDMR).

1. B. E. Kane, Nature 393, 133 (1998)

2. K. Ambal et. al., Sci. Rep. 6, 18531 (2016)

Spectral filtering using symmetry-protected guided modes of photonic crystal slabs

Position 32Ph

Justin Foley, Navin Lingaraju, Yichen Shuai, and John Lawall

Dielectric metasurfaces, including photonic crystal slabs, can be engineered to realize scale invariant planar lenses, broadband reflectors, and narrowband spectral filters, which has led to significant research efforts in recent years. A subclass of these structures, often called high contrast gratings, can be designed to exhibit broadband reflectance near 100% similar to that of distributed Bragg reflectors, albeit in a single-layer dielectric structure. In the context of these structures, we discuss coupling between supported guided modes and incident plane waves. While normally-incident waves are forbidden from coupling to specific modes due to a symmetry mismatch, introducing off-normal light leads to weak coupling to these modes, and as a consequence, narrowband transmission filtering within the established opaque background. We investigate the scale invariant nature of these systems through one- and two-dimensional system studies. Specifically, our work includes one-dimensional silicon structures that operate in the longwave infrared (LWIR, 8-12 μm), as well as a polarization insensitive two-dimensional silicon nitride membranes that operate at telecommunications wavelengths (1550 nm). We discuss our experimental demonstrations of these filters and the computational and symmetry analyses that lay the foundation for their operation.

Measuring flow speed from correlated noise in a long-wavelength acoustic flowmeter

Position 42Ph

John Paul Abbott, K.A. Gillis, M.R. Moldover, and L.J. Gorny

As part of its Greenhouse Gas and Climate Science Measurements Program, the National Institute of Standards and Technology (NIST) has successfully developed long-wavelength acoustic flowmeters (LWAFs) to measure the average flow speed, V , and the speed of sound, c , for a fluid passing through 1:100 scale test model of a coal-burning power plant smokestack with standard measurement uncertainties of less than 1% and 0.1%, respectively. This improves upon the estimated 5-20% standard measurement uncertainty for existing technologies. With this success NIST has constructed a 1:10 scale test model for further investigation. Current LWAF measurement techniques are reliant on a good signal-to-noise ratios (SNR), which may be problematic for the 1:10 scale test model since the amount of turbulence and difficulty generating high-amplitude low-frequency excitation signals at larger scales increases. Anticipating poorer SNRs for larger scale test models, NIST is investigating the use of the LWAF to correlate low-frequency acoustic noise, flow noise, and other excitation signals as an alternative technique to measure V and c with the goal of obtaining the same standard measurement uncertainties of less than 1% and 0.1%, respectively. The latest results of this ongoing investigation are presented.

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Octave-spanning microresonator frequency combs for metrology applications

Position 47Ph

Qing Li, Travis C. Briles, Daron A. Westly, Jordan R. Stone, B. Robert Ilic, Scott A. Diddams, Scott B. Papp, and Kartik Srinivasan

The optical frequency comb is a Nobel-prize-winning (2005) technology that has widespread applications in optical metrology, sensing, high-precision spectroscopy, etc. In particular, a self-referenced comb, which typically requires an octave-spanning spectrum, provides a direct link from radio frequency standards to optical frequencies. To achieve this, conventional technologies typically involve the use of mode-locked lasers and nonlinear spectrum broadening, but the resulting system is usually bulky and consumes a significant amount of power (> 1 W). In this work, we aim to develop nanophotonic technologies for the demonstration of chip-integrated, octave-spanning frequency combs. The core ingredient involved is a high-Q Si_3N_4 microresonator fabricated in the NIST-CNST NanoFab facility. By optimizing the dispersion of the resonator, octave-spanning frequency combs are generated with less than 100 mW pump power. In addition, we are able to generate soliton states that exhibit good coherence properties across the whole comb spectrum, a prerequisite for metrology applications. Finally, we provide a theoretical model that allows us to systematically investigate the accessibility of various soliton states under the given scanning parameters of the pump laser, which agree with the experimental results well.

Optical alignment the easy way: A journey in optimization

Position 48Ph

Eric Zhu and Alan L Migdall

Optical alignment has been the bane of many an optical physicist. Complex optical setups often have many interdependent degrees of freedom that need to be adjusted. Matters are complicated significantly at light levels that require single photon detectors, or when the setup involves an interferometer. In this poster, we present a scheme for the automated alignment of an optical setup with 10 degrees of freedom. The scheme allows us to optimize the coupling efficiency of correlated photon pairs, generated from an interferometer, into optical fiber. At high enough coupling efficiencies, these correlated photons and their detection can then be utilized as a source of randomness.

The precision measurement of the electron-antineutrino correlation in neutron beta decay

Position 50Ph

Md Hassan, Jim Byrne, Brian Collett, Guillaume Darius, Scott Dewey, Gordon Jones, Alex Komives, Jeffrey Nico, George Noid, Melanie Novak, Hyeonseo Park, Ed Stephenson, Fred Wietfeldt, and Boris Yerozolimsky

The angular correlation between the beta electron and antineutrino is characterized by the dimensionless parameter “a” in neutron beta decay. When combined with other neutron decay parameters the value of “a” for free neutron decay can be used to determine the weak vector and axial vector coupling constants g_V and g_A and to test the validity and self-consistency of the Electroweak Standard Model. Previous experiments measuring “a” relied on precise proton spectroscopy and were limited by systematic effects at about the 5% level. We are using a new approach to measure “a” and our goal is to achieve an uncertainty of about 1%. The data analysis of the first phase of the experiment has been completed and the preliminary result will be presented.

Partial breakdown of quantum thermalization in a Hubbard-like model

Position 51Ph

James R. Garrison, Ryan V. Mishmash, and Matthew P. A. Fisher

We study the possible breakdown of quantum thermalization in a model of itinerant electrons on a one-dimensional chain without disorder, with both spin and charge degrees of freedom. The eigenstates of this model exhibit peculiar properties in the entanglement entropy, the apparent scaling of which is modified from a "volume law" to an "area law" after performing a partial, site-wise measurement on the system. These properties and others suggest that this model realizes a new, non-thermal phase of matter, known as a quantum disentangled liquid (QDL). The putative existence of this phase has striking implications for the foundations of quantum statistical mechanics.

POLYMERS

The impact of bromine- and phosphorous-based flame retardants on flame stability and heat feedback from laminar wall flames

Position 10Po

Isaac Leventon, Roland Kraemer, and Stanislav Stoliarov

To improve their resistance and response to fire conditions or simply to meet fire safety regulations and standards, flame retardants are often added to combustible materials such as synthetic polymers. Typically, these flame retardants work by interfering with pyrolysis (e.g. promoting char formation) in the condensed phase of the material, reducing gas phase combustion efficiency, or both. Market demand for flame retardants is estimated at \$2.3 billion with approximately 36% of this market share attributed to brominated flame retardants (BFRs), which are highly effective and relatively low in cost. With the rapid expansion in their use, BFRs have been found across the environment in the atmosphere, soil and sediment, bodies of water, and in the tissue of invertebrates, fish, birds, and mammals. This bioaccumulation has evoked growing concern with regards to the environmental hazards these flame retardants pose and thus industry is moving towards developing safer and equally effective replacements.

To develop new, efficient flame retardants, it is critical to understand the exact mechanisms by which they inhibit flaming combustion. Our research group has developed a systematic methodology to measure flame heat feedback and material burning behavior during upward flame spread over polymeric materials that can be used to quantify these mechanisms of action. Here, a series of experiments was conducted in which flame heat transfer and sample mass loss rate were measured as a flame spread over 7 cm tall, 5 cm wide glass-reinforced PBT samples manufactured with increasing amounts (12, 16, and 24 wt %) of the brominated flame retardant, poly(pentabromobenzyl acrylate) (trade name: FR 1025). In an additional series of tests, similar measurements were obtained for PBT samples manufactured with increasing amounts (8, 12, 16, and 20 wt %) of the phosphorous-based flame retardant, aluminum diethyl-phosphinate (trade name: DEPAL). These tests allow for the study of the impact of flame retardants on three key features of the system: flame height, peak flame heat flux, and flame stability. Current measurements indicate that bromine- and phosphorous-based flame retardants do not affect flame to surface heat transfer in the continuous region of wall flames.

Thiol-ene step growth as a versatile route to functional polymers and gels

Position 14Po

Joel Sarapas, Gregory N. Tew, and Carolyn Watkins

The thiol-ene reaction has been widely used in the field of polymer science for decades, primarily as a network generation and polymer functionalization tool. In this work, we demonstrate the utility of this reaction to form functional, linear polymers capable of undergoing selective redox-tuning via the thioether inherent to this method. We targeted materials containing either a main-chain carbonate, main-chain zwitterion, or side-chain diol, though the possible breadth of this platform is nearly infinite. Selective oxidation of backbone thioethers to either sulfoxides or sulfones was quantitative in all attempts. We also include preliminary data of networks generated and modified through this method. By exposing a thiol-ene network to dilute hydrogen peroxide, the thioether groups are converted to sulfoxides, which in turn causes the network to swell in water. Due to the air, water, and functional group tolerance of this reaction, the thiol-ene step-growth polymerization is a strong addition to the functional polymer synthetic toolbox.

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Spontaneous formation of aqueous droplets in complex coacervate systems

Position 16Po

Samim Ali and Vivek Prabhu

Complex coacervation occurs when a solution of two oppositely charged polymers undergoes liquid-liquid phase separation under suitable conditions. The coacervate forms the highly viscoelastic polymer-rich phase that exhibits very low interfacial tension with the polymer-poor supernatant. This presentation will describe the spontaneous formation of micron-sized aqueous droplets in the polymer-rich coacervate domain as the temperature of the system is increased above a critical value. The spherical droplets, initiated at the liquid-liquid interface, propagates into the bulk coacervate domain as temperature is increased systematically. Moreover, the average size of the droplets increases monotonically with increase in temperature. This results in an optically turbid appearance of the coacervate. We evaluate the role of liquid-liquid interface and polymer structure inside the coacervate phase during such transition using rheological techniques and small-angle neutron scattering. These observations provide a foundation to understand coacervate properties at conditions useful to encapsulation, delivery media, and wet adhesives.

Designing a NIST PR-SoXS station at the National Synchrotron Light Source

Position 21Po

Eliot Gann, Dean DeLongchamp, and Dan Fischer

Polarized Resonant Soft X-ray Scattering (PR-SoXS) is an increasingly important tool used to reveal the nano-level molecular alignment and chemically-sensitive structure within thin polymer films. Performing scattering experiments using specific energies and polarizations of X-rays which excite core electrons into specific, aligned molecular orbitals, we will be able to identify the alignment and domain structure of materials that to classical probes sensitive only to electron density are indistinguishable. Of particular interest in our design is the use of soft X-rays, which require ultra-high vacuum (UHV), to probe liquid, gaseous and other environmental systems which are not typically compatible with UHV. The poster will present the technique and the design of the new scattering station at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory. This station will be a part of the NIST suite of beamlines in sector 7 of the NSLS-II.

Multiscale chain dynamics in polymer nanocomposites: The role of nanoparticle size and architecture

Position 31Po

Erkan Senses, Christopher Kitchens, Siyam Ansar, Madhusudan Tyagi, Suresh Narayanan, Yimin Mao, and Antonio Faraone

Modifying dynamics and entanglements within interphases of polymer nanocomposites can potentially result in responsive and adaptive mechanical behavior. Our work in NCNR aims to understand how local and collective dynamics of polymer chains are altered in the presence of nanoparticles and how these microscopic changes manifest on the macroscopic mechanical behavior of the nanocomposites. In particular, we focused on two fundamental parameters: (i) nanoparticle size relative to entanglement spacing and (ii) nanoparticle architecture.

We studied the effect of particle size in athermal polyethylene oxide-gold nanoparticle system using neutron spin-echo and X-ray photon correlation spectroscopy. The results reveal an $\approx 25\%$ increase in the reptation tube diameter with addition of nanoparticles smaller than the entanglement mesh size (≈ 5 nm), at a volume fraction of 20%. The tube diameter remains unchanged in the composite with larger (20 nm) nanoparticles at the same loading. In both cases, the Rouse dynamics is insensitive to particle size. These results provide the first direct experimental observation of particle size driven disentanglements that can explain non-Einstein-like viscosity trends often reported in polymer nanocomposites.

We investigated the role of filler architecture on chain dynamics using a high- T_g star polymers of various functionality dispersed in a miscible low- T_g linear matrix. Quasielastic neutron scattering results reveal that the segmental dynamics of the matrix chains are significantly slowed-down in the composites; however, the changes are insensitive to filler architecture. Interestingly, highly functionalized compact fillers exhibit accelerated methyl group dynamics in the glassy state compared to neat melt and composites with more open structures. These results have far-reaching implications on tuning mechanical properties and aging of polymeric glasses via chain architecture.

Substrate effect on intrinsic thermal conductivity of ultra-thin amorphous Poly(methyl methacrylate) (PMMA) films

Position 36Po

Ikchhan Kim, Mihai Burzo, Pavel Komarov, Peter Raad, Rick Davis, and Mauro Zammarano

As technology progresses towards smaller and higher density microelectronic devices, we are faced with working with atomic-scale dimensions that present us with challenges but also opportunities. Since mechanical and chemical properties of ultra-thin polymeric films can vary dramatically from their bulk, the thermophysical properties of thin films are also expected to vary. It is known that heat carriers such as electrons and phonons in metallic and dielectric materials, respectively, are influenced by the “size effect” in the micro and nano-scale dimensions. In this work we investigated whether a “size effect” and “substrate effect” on intrinsic thermal conductivity actually exists for amorphous PMMA films with thicknesses ranging from 10 nm to 2 μm and characterization of thin PMMA layers on thermally grown silicon dioxide surface and on gold surface. This approach is based on Time-domain thermoreflectance method, where the change in the surface temperature is measured by detecting the change in the reflectivity of the sample. As we know, intrinsic thermal conductivity of metallic or ceramic thin films is reduced by decreasing dimension of film due to increased carrier scattering by boundary. However, spin coated thin polymer film showed opposite results. The results show that the intrinsic thermal conductivity of layers thinner than 40 nm PMMA film deposited on native silicon oxide is about three times higher as compared to the bulk PMMA value. A similar trend was observed for all ultra-thin (sub 100 nm) PMMA films. The increased thermal conductivity was attributed to the attractive interaction between hydrogen group of PMMA film and the oxide present on the silicon dioxide substrate, which is hydrogen bonds that confined the segmental mobility of the polymer. We suspect that PMMA polymer chains are aligned in the vicinity of substrate surface because of the hydrogen bonds.

Effect of the molecular orientation of polymer nanogratings on the asymmetry of resonant small angle X-ray scattering patterns

Position 37Po

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

Critical dimension small angle X-ray scattering is a variable angle transmission measurement that enables the characterization of the three-dimensional shape of periodic nanostructures. By using this technique at resonant soft X-ray energies with different polarizations to measure soft materials, we not only improve the scattering contrast but also gain information about the preferential molecular orientations of these nanostructures. The information about shape and molecular orientation is convolved in the scattering and must be extracted by comparing it to simulated scattering and fitting using inverse iterative algorithms. We develop a computationally efficient single scattering simulation that takes into account biaxial molecular orientation, and validate it by comparing it to a rigorous coupled wave simulation. We then analyze the ability of various sample models to generate unique best fit solutions by generating simulated parameter sets and fitting the resulting scattering. Distinct asymmetry in the scattering pattern results from the interaction of the measurement geometry and the change in orientation across a periodic repeat unit. Finally, we use this simulation to fit experimental scattering data of linear nanogratings of semiconducting polymers with preferential orientation of the carbon double bond $1s-\pi^*$ transition dipole moments, in order to determine shape and molecular orientation.

Electrophoretic deposition of ultrasonicated and functionalized nanomaterials for multifunctional composites

Position 38Po

Qi An, Andrew Rider, and Erik Thostenson

Recent advances in the synthesis and characterization of nanostructured composite materials have enabled a broad range of opportunities for engineering the properties of polymer-matrix materials. Carbon nanotubes (CNTs) are known to have exceptional mechanical, electrical and thermal properties. Because of their small size, CNTs can occupy regions between traditional micro-scale reinforcements and create a hierarchical micro/nano structure spanning several orders of magnitude. Since CNTs possess critical reinforcement dimensions below 100 nm, new opportunities exist for tailoring the fiber/matrix interphase regions and ultimately the mechanical and electrical performance of advanced fiber-composites with minimal impact on the fiber-dominated properties. This growing interest in nanoscale hybridization with conventional fiber reinforcement has highlighted the need to develop new processing techniques for successful CNT integration.

In this work, a novel and industrially scalable approach for producing multiscale hybrid carbon nanotube/fiber composites using an electrophoretic deposition (EPD) technique has been studied as an alternative to in situ chemical vapor deposition growth (CVD). EPD is a widely used industrial coating process employed in areas ranging from automotive to electronics production. The method has a number of benefits which include low energy use and the ability to homogeneously coat complex shapes with well adhered films of controlled thickness and density. A stable aqueous dispersion of multi-walled carbon nanotubes (MWCNTs) was produced using a novel ozonolysis and ultrasonication (USO) technique that results in dispersion and functionalization in a single step. Networks of CNTs span between adjacent fibers and the resulting composites exhibit significant increases in electrical conductivity and considerable improvements in the interlaminar shear strength and fracture toughness. In order to better understand the underlying mechanisms behind the selective reinforcement of CNTs on the glass-epoxy systems, detailed model interphase study and microdroplet debonding test were conducted to investigate the interfacial properties between an epoxy matrix and glass with the electrophoretically coated CNTs.

Enhanced durability of CNT based hierarchical composites under accelerated aging conditions

Position 41Po

Ajay Krishnamurthy, Donald L. Hunston, Amanda L. Forster, Bharath Natarajan, Andrew H. Liotta, Sunny S. Wicks, Brian L. Wardle, J. Alexander Liddle, and Aaron M. Forster

Multifunctional hierarchical composites are the new generation of structural materials that are capable of replacing traditional fiber reinforced composites in aerospace applications. The main drawbacks of traditional fiber composites include poor out-of-plane strength and inferior electrical properties, which make them vulnerable to shear/compression based failures, along with providing poor functionality towards electrostatic discharges and lightning strikes. By adding highly conductive, multi-walled carbon nanotubes (MWCNTs) as reinforcements, we are able to rectify these issues effectively. The composites were manufactured by depositing MWCNTs on alumina based fiber mat surfaces using a chemical vapor deposition (CVD) process and then infiltrating them with high strength, epoxy resin. The resulting “fuzzy” fiber composites exhibit excellent structural properties in addition to remarkable thermal and electrical properties.

Long term aerospace applications often include a variety of environments where the composites are continually exposed to varying temperature, strain and humidity conditions. The current study involves understanding the changes in the properties of these hybrid materials, when subjected to aggressive hydro (water) and hydrothermal (water and temperature) environments. Upon hydrothermal exposure (60 °C, DI water), the mechanical properties of alumina fiber composites were found to decrease significantly even at short exposure time scales (~ 3 days), while the CNT reinforced composites were found to retain their original mechanical and electrical properties for the entire duration of the study (~ 90 days). The reductions in the strength properties of the alumina fiber composites was attributed to fiber-polymer interfacial debonding caused by the ingress of water at high temperatures, whereas, the presence of interfacial CNT nanofibers provided effective secondary reinforcements in the form of fiber pullout, fiber breakage and crack deflections that extended the life of the nanocomposites even under harsh aging conditions.

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Versatile cholesterol-functionalized block copolymers in aqueous dispersions

Position 43Po

Kenneth Mineart, James Hedrick, Shrinivas Venkataraman, Yi Yan Yang, and Vivek Prabhu

Cholesterol plays an important role in many biological processes, namely regulating the mechanical and transport properties of biomembranes. Biotechnology research attempts to exploit the inherent benefits of cholesterol through its use, for example, in liposomes for drug delivery. The potential applicability of cholesterol can be further extended through its chemical incorporation into random and block copolymers. The controlled segregation of cholesterol moieties into one or more portions (i.e. blocks) of a copolymer produces well-controlled nanostructures (micelles and polymersomes) through self-assembly. Here, we first present structural results for a set of novel cholesterol block copolymers, poly[(ethylene glycol)-b-(cholesterol 2-oxo-1,3,6-dioxazocane-6-carboxylate)] (PEG-b-8C-Chol), self-assembled into micelles. The results provide a direct relation between the number of cholesterol groups per polymer chain (X_n , Chol) and the size and geometry of structures formed. Next, we combine the same PEG-b-8C-Chol copolymers in a minority fraction (~5 mol%) with a common phospholipid in order to form surface-functionalized liposomes varying in insertion moieties per copolymer chain (via X_n , Chol). Again, the major implications relate the molecular structure to the self-assembly behavior. Both studies provide overarching design rules regarding cholesterol-containing block copolymers and could have a major impact in the future synthesis of drug delivery devices and other nanocarriers that utilize cholesterol.

Controlled synthesis of short-chain branched polyethylene via ring-opening metathesis polymerization

Position 44Po

Wesley Farrell, Sara Orski, and Kathryn Beers

Since the discovery of their synthesis over 50 years ago, polyolefins have become one of the most important classes of materials across nearly all aspects of society, and research regarding the synthesis of polyolefins with controlled molecular weights and architectures from inexpensive feedstocks continues today in both academia and industry. As this area of research continues to grow, suitable reference materials to assist in the characterization of new, complex polymers are necessary. In this work, we have explored the use of ring-opening metathesis polymerization (ROMP) of cyclic olefins as a way to prepare model polyolefins with a high degree of control over both the molecular weight distribution and short-chain branching in an effort to build a foundation for the preparation of short-chain branched polyethylene standards.

Dielectric characterization of confined water in nanocellulose

Position 45Po

Caglar Dogu Emiroglu, Bharath Natarajan, Jan Obrzut, and Jeffrey W. Gilman

Nanocellulose has been a continuously emerging area of interest over the recent years due to inexpensive, abundant, and renewable nature of the material source. Cellulose nanocrystals (CNCs) are regarded to be highly useful candidates as a sustainable way of polymer reinforcing. In this regard, investigating the confinement of absorbed water in CNCs is essential to understand the effects on dispersion, wetting, interfacial adhesion, matrix crystallization, and water uptake, all which have critical importance in the utilization and high-scale production of nanocomposites. In this work, we study cellulose nanocrystal films of known mesostructure and functionality, cast from water dispersions under controlled drying rate. Continuous monitoring and control of the drying rate, together with the relative humidity and temperature of the ambient, yields films that are self-organized into well-defined and distinguishably different chiral structures with a characteristic helical modulation length (pitch). Films are studied via reflectance spectroscopy for measurement of their structural periodicity. In addition, scanning electron microscopy (SEM) is used for imaging, and numerical evaluation of the pitch distributions. Reflectance spectroscopy and the SEM analysis results are found to be in strong agreement and directly correlated with the drying rate of the films. For dielectric characterization, a non-contact microwave cavity perturbation method is used. The method enables permittivity measurements with adequate accuracy to investigate water confinement in the CNC films. Through an approach using classical mixing models with randomly oriented ellipsoidal water inclusions, it is found that in the case of hydrophilic Na-CNCs, a decreasing pitch led to greater anisotropy in the shape of moisture inclusions (ellipsoidal or platelet-like). In contrast, the structure of hydrophobic phosphonium-cation modified CNC films are found to have little influence on absorbed water inclusions, which remain predominantly spherical. These results provide a useful perspective on the current state of understanding of CNCs materials and are beneficial for the realization of CNC functional materials and composites.

NIST Chapter of Sigma Xi 24th Annual Postdoctoral Poster Presentation

Structure-property relationships of polymers

Position 46Po

Ying Jin

Microstructure of polymer is crucial to the polymer property and performance. In different polymer systems, we demonstrate microstructures including the composition distribution and chain orientation; monitor the structure evolution under various conditions including heating, stretching and etc. With in-situ experiments, we establish the relationship between the structure and properties such as stability, diffusion and transportation. With these studies, we hope to develop robust and high performance polymeric materials.

Dynamics and structural assembly in weakly-ordered oppositely-charged polyelectrolyte complex solutions

Position 55Po

Anand Rahalkar, Guangmin Wei, Samanvaya Srivastava, Matthew V. Tirrell, and Vivek M. Prabhu

Polyelectrolyte complexes (PEC) are of interest because of their ability to self-assemble and form hierarchical structures. Thus, they have potential applications in drug delivery systems as well as in tissue engineering. Here, we present studies on a system of ABA triblock polyelectrolyte complexes which are formed by combining well-defined polymers which have functionalized polyallyl glycidyl ether end blocks and a polyethylene glycol midblock. PEC of these triblock polyelectrolytes show strong clustering behavior in dilute disordered region. The micelles building blocks hierarchically assemble to form these large-scale clusters in the disordered region. We present insights into the effect of temperature, and polymer concentration on the dynamics, hierarchical structure and phase behavior of these ABA triblock polyelectrolyte complexes.