

CHESS

Users' Meeting 2013

Robert Purcell Conference Center
Cornell University - Ithaca, NY 14853



Tribute to Sol Gruner

- CHESS Director 1996 - 2013



June 4-5, 2013

Tuesday, June 4

Robert Purcell Conference Center

8:00AM **Registration and Poster setup**

Welcome and Introduction

9:00 Status of CHESS – **Sol Gruner, Director & Joel Brock, Associate Director**

9:15 ERL Update – **Bruce Dunham, Project Manager, ERL**

9:30 CHESS Initiatives – **Ernie Fontes, Associate Director**

9:45 Status of MacCHESS– **Marian Szebenyi, Director MacChess**

10:00 BREAK

Invited User Presentations

10:15 **Stephen Meisburger** (Cornell University) – *“Introducing cryo-SAXS: solution scattering from nanoliter volumes”*

10:45 **Nozomi Ando** (Massachusetts of Technology) - *“Radical allostery in a radical protein”*

11:15 **Katsuhiko Murakami** (Pennsylvania State University) *“Structural basis of rifampicin resistance by bacterial RNA polymerase”*

11:45 Group Discussion & Election

12:00PM LUNCH

1:30 **Eaton Lattman** (Hauptman Woodward)

2:00 **Jin Wang** (Advanced Photon Source) *“Ultrafast x-ray imaging of fuel sprays: fluid dynamics on time scale from microseconds to nanoseconds”*

2:30 **Poster Session & coffee break**

4:00 **Tour:** CHESS/ERL

6:15 **Reception:** Statler Hotel

7:00 **Dinner:** Statler Hotel

8:00 **After Dinner Tribute:** Sol Gruner, Chess Director

Wednesday, June 5

Robert Purcell Conference Center

- 8:00AM **Registration**
- 9:00 Welcome
- 9:10 Poster Prize Winner
- Student Paper Prize Talks**
- 9:20 **Ritwaka S. Basu** (Pennsylvania State University) – "*Watching the bacteriophage N4 RNA polymerase transcription by time-dependent soak-trigger-freeze x-ray crystallography*"
- 9:45 **Kaifu Bian** (Cornell University) — "*Comparing the structural stability of PbS nanocrystals assembled in fcc and bcc superlattice allotropes*"
- 10:15 BREAK

Workshop I

MEMBRANE PROTEINS

- 10:30 **Toshi Kawate Hanrath** (Cornell University) – "*Tricks and pitfalls in eukaryotic membrane protein crystallization*"
- 11:10 **Olga Boudker** (Cornell University, Weil Medical College) – "*Crystallographic study of the transport cycle intermediates of a glutamate transporter homologue*"
- 12:00PM LUNCH
- 1:00 **Simon Li** (Yale University) – "*Crystal structure of glycoprotein E2 from bovine viral diarrhea virus*"
- 1:50 **Richard Grisshammer** (National Institutes of Health) – "*Structure of the agonist-bound neurotensin receptor NTS1*"
- 2:30 Concluding Remarks

Wednesday, June 5

Robert Purcell Conference Center

Workshop II

Real Time, In Situ, In Operando Studies

- 10:30 **Josat Vlassak** (Cornell University) – *“Scanning nanocalorimetry combined with time-resolved x-ray diffraction – a new tool for studying transformations with complex materials systems”*
- 11:10 **Jay Schuren** (Air Force Research Laboratory) – *“Changing the paradigm for engineering design by merging high energy x-ray data with materials modeling”*
- 12:00PM LUNCH
- 1:10 **John Smedley** (Brookhaven National Lab) – *“In-situ analysis of alkali antimonide cathode growth”*
- 1:50 **Joel Brock** (Cornell University) - *“Structure of the SrTiO₃ (001) surface during photo-assisted water splitting”*
- 2:30 Concluding Remarks

2013 CHESS Users' Meeting

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Workshop II Abstracts

REAL TIME, IN SITU, IN OPERANDO STUDIES

- Josat Vlassak** Cornell University –
“Scanning nanocalorimetry combined with time-resolved x-ray diffraction – a new tool for studying transformations with complex materials systems”
- Jay Schuren** Air Force Research Laboratory --
“Changing the paradigm for engineering design by merging high energy x-ray data with materials modeling”
- John Smedley** Brookhaven National Lab –
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- Joel Brock**, Cornell University –
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2013 CHESS USERS MEETING

2nd Floor Robert Purcell Conference Center, Cornell University

June 4-5th

2012 EXECUTIVE COMMITTEE

Tobias Hanrath	Cornell University	Term to 2014
Michael Malkowski	SUNY Buffalo	Term to 2014
Nozomi Ando	Mass. Inst. of Tech.	Term to 2013
Jay Schuren	Air Force Research Lab	Term to 2013

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MacCHESS resource is supported by NIH / NIGMS award GM-103485

CHARTER FOR THE CORNELL HIGH ENERGY SYNCHROTRON SOURCE USERS GROUP

The CHESSE Users' Group exists for the purpose of addressing the needs of the user community of the Cornell High Energy Synchrotron Source for establishing general user policy and for fostering communication and free exchange of ideas among users.

A. Organization

1. Membership:
All investigators with active CHESSE projects shall be voting members of the User Group.
2. Election of Officers and Terms of Office:
 - a. The Users Group shall be directed by an Executive Committee (EC) consisting of:
 1. Chairperson
 2. Vice-Chair
 3. two additional members
 4. appointed CHESSE liaison

No less than two members of the EC shall be from outside the Cornell community.

b. Members of the EC will be elected annually for two-year terms. Nominations for the EC shall be made by members of the EC itself as well as by members of the users group at-large during the annual users meeting. Current and past members of the EC are eligible for election.

c. Election of the EC will take place during the annual Users' Meeting and the committee will subsequently meet and elect from its members a Vice-Chairperson who, after one year, will become the Chairperson. In case of incapacity or resignation of the Chairperson, the Vice-Chair will serve for the remainder of the current term and for one additional one-year term.

B. Meetings:

The Users' Group will meet once a year and the EC will meet at that time and at any other time at the discretion of the Chairperson or as called by a majority of the members of the EC.

C. Procedures:

- a. A quorum of the EC will require the presence of at least three of the members and decisions will be determined by simple majority. No official action on behalf of the Users' Group will be taken by the EC without the majority consent of a quorum of the EC or a simple majority of the respondents of a poll of the membership.
- b. Minutes of all the meetings of the EC shall be recorded and distributed to all members of the EC. The same will apply to the annual users meeting.
- c. This Charter and any proposed future amendment will require approval by 2/3 of the responding membership for its passage.

Invited Talks Abstracts

Introducing cryo-SAXS: solution scattering from nanoliter volumes

Steve P. Meisburger, Matthew Warkentin, Andrea Katz, Jesse B. Hopkins, Huimin Chen, Richard E. Gillilan, Robert E. Thorne and Lois Pollack
Cornell University

Abstract: Small angle X-ray scattering (SAXS) is an increasingly popular technique for obtaining low resolution solution structures of dynamic macromolecules and complexes. Because SAXS does not require special sample preparation beyond that needed to ensure monodispersity, it is commonly used to probe the dependence of macromolecular conformation or association on different solution conditions (such as temperature, pH, and ionic strength). Such combinatorial experiments are often limited by consumption of both sample and synchrotron time. Therefore, for high throughput applications of SAXS, it is desirable to find ways to economize sample and to accelerate data collection. Although modern X-ray sources can deliver sufficient flux for millisecond data acquisition in micron-scale samples, the high sensitivity to radiation damage of macromolecules in solution demands that the total dose be distributed over a large volume (typically >10 microliters), either by defocusing the beam or flowing the sample through it. Furthermore, frequent, aggressive cleaning of X-ray windows of the sample cell is often required due, for example to protein adsorption. Experience from electron microscopy (EM) and X-ray crystallography (MX) suggests that the maximum allowable radiation dose may be significantly larger at low temperatures than at ambient conditions. In addition to reducing radiation damage, cryocooling prevents evaporation of the sample droplet, and therefore “window-free” sample holders may be used.

While cryocooling is now standard practice for EM and MX, it has not yet been embraced by the SAXS community. Because of the difficulty in producing homogeneous and reproducibly vitrified solutions, the requirement of accurately measuring and subtracting the solvent background scattering for SAXS was seen as incompatible with cryocooling. From a series of experiments performed at CHESS beamlines F2, C1, and G1, we identified cryoprotectants that produce homogeneously vitrified droplets by rapid cooling in a 100 K gas stream. Scattering profiles from similarly vitrified, macromolecule-containing solutions resemble those acquired at room temperature. The ability to expose for longer periods of time before damaging the sample more than compensates for the reduction in signal to background resulting from the cryoprotectants. As a result of increased dose tolerance, the sample volume can be reduced by orders of magnitude relative to room temperature. We collect cryo-SAXS data of sufficient quality to determine molecular shape reconstructions from illuminated volumes as small as 100 nanoliters. Studies to date show minimal artifacts introduced by

cryoprotectant and cooling. Possible applications of cryo-SAXS will be discussed, as well as remaining technical challenges for high throughput data collection.

Structural basis of rifampicin resistance by bacterial RNA polymerase

Katsuhiko Murakami

Pennsylvania State University

Abstract: Tuberculosis (TB) is one of the most significant global challenges to human health. For over four decades, Rifampicin (Rif, aka Rifampin), a semi-synthetic derivative of Rifamycin, has been used as a first line antibiotic treatment of TB and is the cornerstone of current short-term TB treatment. The mode of action involves tight Rif binding to a beta subunit of bacterial RNA polymerase (RNAP) (K_d is sub nanomolar) to inhibit RNA transcription. Although many Rif resistant (Rif^R) strains with mutations in the Rif-binding pocket can be isolated in bacterial culture, only three specific Rif^R mutations account for over 80 % of *Mycobacterium tuberculosis* (MTB) Rif^R strains in clinical isolates due to Rif^R associated fitness costs. Recently, we have shown that the *Escherichia coli* RNAP can be prepared from a convenient overexpression system and its X-ray crystal structure can be determined (1). We have also shown that the *E. coli* RNAP crystal can be used for finding the binding site of ligand such as bacterial alarmone (p)ppGpp (2) and for investigating the interaction between RNAP and benzoxazinorifamycins, rifampicin-derivatives having superior affinity toward Rif^R RNAP mutants (3). In this study, we have determined the crystal structures of the *E. coli* RNAP Rif^R mutants each having one of three major Rif^R mutations found in clinical isolates. Each Rif^R RNAP structure shows a unique conformation of the Rif binding pocket and their structural deviations from the wild-type Rif binding pocket are consistent with their Rif resistances suggesting that the Rif^R results from alternating the shape complementary between the Rif binding pocket and Rif in addition to disrupting hydrophilic and hydrophobic interactions. This study provides an important step toward developing superior Rif analogues for the Rif^R MTB.

1. K.S. Murakami. The X-ray crystal structure of *Escherichia coli* RNA polymerase sigma70 holoenzyme. *J. Biol. Chem.* 2013, 288, 9126-9134.
2. U. Mechold, K. Potrykus, H. Murphy, K.S. Murakami and M. Cashel. Differential regulation by ppGpp versus pppGpp in *Escherichia coli*. *Nucleic Acids Research* 2013, in press.
3. V. Molodtsov, I.N. Nawarathne, N.T. Scharf, P.D. Kirchhoff, H.D.H. Showalter, G.A. Garcia and K.S. Murakami. X-ray crystal structures of the *Escherichia coli* RNA polymerase in complex with Benzoxazinorifamycins. *J. Medicinal Chem.* in press.

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Radical allostery in a radical protein

Nozomi Ando

Massachusetts Institute of Technology

Structural basis of rifampicin resistance by bacterial RNA polymerase

Katsuhiko Murakami

Pennsylvania State University

Sol Gruner and the Other Phase Problem

Eaton Lattman

Hauptman Woodward

Ultrafast x-ray imaging of fuel sprays: fluid dynamics on time scale from microseconds to nanoseconds

Jin Wang

Advanced Photon Source

Research Paper Prize Winner(s) Abstract

Watching the Bacteriophage N4 RNA Polymerase Transcription by Time-dependent Soak-trigger-freeze X-ray Crystallography

Ritwaka S. Basu

Pennsylvania State University

The challenge for structural biology is to understand atomic-level macromolecular motions during enzymatic reaction. X-ray crystallography can reveal high

resolution structures; however, one perceived limitation is that it reveals only static views. Here we use time-dependent soak-trigger-freeze X-ray crystallography, namely, soaking nucleotide and divalent metal into the bacteriophage RNA polymerase (RNAP)-promoter DNA complex crystals to trigger the nucleotidyl transfer reaction and freezing crystals at different time points, to capture real-time intermediates in the pathway of transcription. In each crystal structure, different intensities and shapes of electron density maps corresponding to the nucleotide and metal were revealed at the RNAP active site which allow watching the nucleotide and metal bindings and the phosphodiester bond formation in a time perspective. Our study provides the temporal order of substrate assembly and metal co-factor binding at the active site of enzyme which completes our understanding of the two-metal-ion mechanism and fidelity mechanism in single-subunit RNAPs. The nucleotide-binding metal (Me^{B}) is coordinated at the active site prior to the catalytic metal (Me^{A}). Me^{A} coordination is only temporal, established just before and dissociated immediately after phosphodiester bond formation. We captured these elusive intermediates exploiting the slow enzymatic reaction *in crystallo*. These results demonstrate that the simple time-dependent soak-trigger-freeze X-ray crystallography offers a direct means for monitoring enzymatic reactions.

Comparing the Structural Stability of PbS Nanocrystals Assembled in fcc and bcc Superlattice Allotropes

Kaifu Bian
CHESS

We investigated the structural stability of colloidal PbS nanocrystals (NCs) self-assembled into superlattice (SL) allotropes of either face-centered cubic (fcc) or body-centered cubic (bcc) symmetry. Small-angle X-ray scattering analysis showed that the NC packing density is higher in the bcc than in the fcc SL; this is a manifestation of the cuboctahedral shape of the NC building block. Using the high-pressure rock-salt/orthorhombic phase transition as a stability indicator, we discovered that the transition pressure for NCs in a bcc SL occurs at 8.5 GPa, which is 1.5 GPa higher than the transition pressure (7.0 GPa) observed for a fcc SL. The higher structural stability in the bcc SL is attributed primarily to the effective absorption of loading force in specific SL symmetry and to a lesser extent to the surface energy of the NCs. The experimental results provide new insights into the fundamental relationship between the symmetry of the self-assembled SL and the structural stability of the constituent NCs.

Workshop I Abstracts

Tricks and pitfalls in eukaryotic membrane protein crystallization

Toshi Kawate
Cornell University

Crystallization of eukaryotic membrane proteins is extremely challenging due to a number of technical difficulties, and, in fact, there are only less than 70 reported structures compared to more than 86,000 structures for proteins of other kinds. While the rate of successful crystallization has been drastically increasing, there is no golden standard for eukaryotic membrane protein crystallization. Therefore, crystallographers still rely on methods based on their own experience or published techniques, which typically contain only successful attempts. In this talk, I will present unpublished stories behind the successful P2X receptor crystallization, comprising mostly unsuccessful trials. The seven years' worth of my struggle will hopefully help the audience succeed in their challenges.

Crystallographic study of the transport cycle intermediates of a glutamate transporter homologue

Olga Boudker
Cornell University & Weill Medical College

Ion-coupled membrane transporters undergo cycles of conformational changes associated with binding of ions and substrates from the extracellular space, their translocation across the membrane and release into the cytoplasm, and finally the return of the unbound transporter into the initial state. To visualize the key structural states along this cycle crystallographically, it is necessary to isolate them out of the dynamic conformational ensemble sampled by the transporter solubilized in detergent. To achieve this, we have developed several methodologies, including cross-linking of strategically placed cysteines, site directed mutagenesis aided by spectroscopic methods, manipulation of crystallization conditions and crystal soaking. Using these methods, we have determined the structures of several key states of a glutamate transporter homologue, GltPh, providing structural snapshots along the transport cycle and revealing a striking dynamic nature of these transporters.

Crystal structure of glycoprotein E2 from bovine viral diarrhea virus

Simon Li

Yale University

Pestiviruses, including bovine viral diarrhea virus (BVDV), are important animal pathogens and are closely related to hepatitis C virus (HCV), which remains a major global health threat. They have an outer lipid envelope bearing two glycoproteins, E1 and E2, required for cell entry. They deliver their genome into the host-cell cytoplasm by fusion of their envelope with a cellular membrane. The crystal structure of BVDV E2 reveals a novel protein architecture consisting of two Ig-like domains followed by an elongated beta-stranded domain with a new fold. E2 forms end-to-end homodimers with a conserved C-terminal motif rich in aromatic residues at the contact. A disulfide bond, across the interface explains the acid resistance of pestiviruses and their requirement for a redox activation step to initiate fusion. From the structure of E2, we propose alternative possible membrane fusion mechanisms. We expect the pestivirus fusion apparatus to be conserved in HCV.

Structure of the agonist-bound neurotensin receptor NTS1

Reinhard Grisshammer

National Institutes of Health

Neurotensin (NT) is a 13 amino acid peptide that functions as both a neurotransmitter and a hormone through activation of the neurotensin receptor NTS1, a G protein-coupled receptor (GPCR) signaling preferentially through Gq. In the brain, NT modulates activity of dopaminergic systems, opioid-independent analgesia, and the inhibition of food intake, and in the gut NT regulates a range of digestive processes. We have solved the structure at 2.8 Å resolution of NTS1 in an active-like state, bound to NT8-13, the C terminal portion of NT responsible for agonist-induced activation of the receptor. Because wild-type NTS1 is unstable and thus not amenable to crystallization, we used alanine-scanning mutagenesis to stabilize NTS1 and to select for an active-like conformation in the presence of agonist, which combined with the bacteriophage T4 lysozyme fusion protein strategy and the lipidic mesophase crystallization method, resulted in diffracting crystals. The agonist binding pocket is located at the extracellular receptor surface. The peptide agonist binds to NTS1 in an extended conformation nearly perpendicular to the membrane plane with the C-terminus oriented towards the receptor core. The NTS1 structure bears many hallmark features of an active-like receptor conformation such as an outward-tilted

transmembrane helix 6 at the cytoplasmic surface and key conserved residues in positions characteristic for active but not for inactive GPCRs. Our findings provided for the first time insight into the binding mode of a peptide agonist to a GPCR.

Workshop II Abstracts

Scanning nanocalorimetry combined with time-resolved x-ray diffraction - a new tool for studying transformations in complex materials systems

Joost Vlassak
Harvard University

Changing the paradigm for engineering design by merging high energy x-ray data with materials modeling

Jay Schuren
Air Force Research Laboratory

In-situ analysis of alkali antimonide cathode growth

John Smedley
Brookhaven National Lab

Structure of the SrTiO₃ (001) surface during photo-assisted water splitting

Joel Brock
Cornell University

Poster Abstracts

Double Laue Monochromator for High Energy X-rays: Designing and Commissioning of a Prototype, and Planned Upgrade

J. Y. Peter Ko¹, Benjamin B. Oswald¹, James J. Savino¹, Alan K. Pauling¹, Darren S. Dale¹, Margaret K. A. Koker¹, Matthew P. Miller^{1,2}, Joel D. Brock^{1,3}

¹ Cornell High Energy Synchrotron Source, Cornell University, Ithaca, NY

² Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY

³ School of Applied and Engineering Physics, Cornell University, Ithaca, NY

High-energy X-rays are efficiently focused in the out of scattering plane direction by a set of sagittally-bent, asymmetric Laue crystals [1]. The main advantage of the Laue geometry over the Bragg geometry is the smaller beam footprint on the crystals, and the ability to utilize the anticlastic bending in the meridional plane to eliminate the chromatic aberration of the diffracted beam by working on the Rowland circle [2]. We have designed, built, and commissioned a prototype double-crystal Laue monochromator optimized for high energy X-rays. We characterized several performance parameters such as flux, focal size, energy bandwidth, and angular divergences. Here, we report our design of novel prototype sagittal bender and highlight results from recent characterization experiments. The design of the bender combines the tunable bending control afforded by previous leaf spring designs with the stability and small size of a four bar bender. The prototype monochromator focuses a 25 mm-wide 30 keV X-rays at the upstream monochromator crystal to a 0.6 mm beam waist in the hutch. Compared to flux in the same focal spot, the prototype Laue monochromator delivered 60 times more flux at 30 keV. In addition, the horizontal divergence of the beam can be controlled precisely by varying opening width of the horizontal slits in front of the upstream monochromator without affecting the size of the focal spot in the hutch. Based on the lessons learned from the commissioning experiments, we have designed an improved version of Laue monochromator, which will be installed at the F2 beamline as part of the high-energy X-ray beamline upgrade. The design considerations include bending mechanisms, twist controls, desired ranges and precisions of various movements of the monochromator crystals, and cooling of the upstream monochromator crystal. The beamline is expected to provide the X-rays ranging from 40 to 90 keV, with the beam size of ~1 mm horizontal (focused), and ~3 mm vertical (unfocused). The flux in the focused spot at 40 keV is expected to be 7.5×10^{12} ph/s, with

$\Delta E/E$ of 2×10^{-3} . The installation of the monochromator will take place this summer and commissioning experiments will be performed this fall.

- [1] Z. Zhong, C. C. Kao, D. P. Siddons, J. B. Hastings, J. Appl. Cryst. **34**, 504-509 (2001)
- [2] Z. Zhong, C. C. Kao, D. P. Siddons, J. B. Hastings, J. Appl. Cryst. **34**, 646-653 (2001)

The Status of CHESS Capillary Optics Development

Rong Huang and Thomas Szebenyi

CHESS, Cornell University

Ellipsoid shaped single-bounce glass capillaries, fabricated at CHESS, have been used as achromatic X-ray focusing optics for various applications at beamlines. Capillary's compact dimension provides a high demagnification configuration with short focal distance in both transverse directions, and the capillary's 360 degree of azimuth angle interception can provide a large X-ray acceptance or a large numerical aperture. Capillary fabrication at CHESS can be customized according to requirements of particular applications, such as microbeam X-ray fluorescence, confocal X-ray microscopy, microcrystallography, small-angle X-ray scattering, high resolution X-ray diffraction and microbeam standing wave technique, high pressure experimentation with diamond anvil cells, full-field transmission X-ray microscopy (TXM), X-ray emission spectroscopy etc.

The features of capillary optics will be briefly summarized in this poster, followed by examples of recently progress on capillary optics development. As we gradually improve the capillary quality, we have successfully achieved $4\mu\text{m}$ focal size with capillary fully illuminated and $2.7\mu\text{m}$ focal size with capillary partially illuminated. One latest application was using CHESS capillaries as the condenser for the APS transmission X-ray Microscopy using the high resolution and high numerical aperture zone-doubled Fresnel Zone Plates (FZPs), which demonstrated that CHESS capillaries are suitable for such large numerical aperture focusing applications. The compact dimension of capillary makes it not only suitable as primary focusing optics but also as secondary focusing optics for maximal flux acceptance, with an example shown in this poster. As capillary fabrication improves, we are also developing a new capillary metrology setup based on a customized airbearing stage to improve measurement accuracy and resolution. Finally, to give users and beamline scientists a good grasp of the

broad range of applications of CHESS capillaries, exemplar experiments on several synchrotron facilities in recent years are also given in this poster.

Tunable 2D nanoparticle crystallization in high salt and divalent salt environments with non-base-pairing DNA

Shawn J. Tan †*, Jason S. Kahn §, Thomas L. Derrien §, Michael J. Campolongo †, Mervin Zhao §, Detlef-M. Smilgies #, Dan Luo §†*

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Cornell High Energy Synchrotron Source, Cornell University, Ithaca, New York 14853, USA

The multiparametric nature of nanoparticle self-assembly make it challenging to circumvent the instabilities that lead to aggregation and achieve crystallization under extreme conditions. With non-base-pairing DNA as a model ligand, we demonstrate that long-range 2D DNA-nanoparticle crystals can be attained in extreme high salt conditions and in divalent salt environment. We further report an empirical model for engineering the interparticle spacing in high monovalent and divalent salt conditions based on ligand length and ionic strength.

Designer Solids: Ambient Structural Control

Detlef-M. Smilgies

CHESS D1 Station

Designer solids consist of complex objects that form regular lattices - the standard example is nanocrystal superlattices, where nanocrystals comprise an inorganic core surrounded by an organic ligand shell [1]. We have found that such materials can be highly tailored to obtain specific lattice parameters and symmetries [2-3]. Another intriguing feature is the ability to orient faceted nanocrystals on their lattice sites within a superlattice [4]. The structural control is achieved by judicious choice of deposition and annealing parameters [5]. We

have used in-situ deposition via drop casting [6] or shear coating [7] as well as controlled vapor treatment [8] and drying [6] to prepare well-ordered phases of a specific symmetry. A fascinating aspect is the observation of phase transitions [4,9] as a result of the offered partial pressure of solvent vapor. The controlled vapor environment can also be employed to prepare and study perfectly equilibrated systems [10]. The next step in this project will be to correlate structural properties of the materials with their collective behavior, such as magnetic and optical properties – some first D1 experiments show great promise [11, 12]. As structural properties may depend delicately on environmental conditions such as solvent vapor pressure, such measurements should be done in-situ under structural control via x-ray scattering.

- [1] C. P. Collier, T. Vossmeier, and J. R. Heath, *Annu. Rev. Phys. Chem.* 49 (1998) 371–404.
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X-RAY DIFFRACTION OF ORGANIC CATHODE MATERIALS IN LITHIUM-ION BATTERIES

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The Abruña research group has developed and characterized numerous promising materials for battery and fuel cell applications. In the present context, we focus on organic-based battery materials and intend to investigate how molecular structure relates to bulk characteristics of the materials of interest, with emphasis on charge storage. Conventional lithium-ion batteries employ inorganic oxides (e.g. LiCoO₂) and graphite (LiC₆) as cathode and anode electrodes, respectively. The charge/discharge process involves (de)intercalation events which are known to be kinetically slow, resulting in low rates of charge and discharge. An alternative, yet relatively unexplored, approach is the use of electroactive organic molecules (in place of the metal oxide) as the cathode in a

lithium-ion battery (LIB). Through computational design and screening, combined with synthesis, organic molecules can be tuned over a broad parameter space to yield materials that can exchange multiple electrons per formula unit, leading to high gravimetric capacities. In addition, the formal potentials can be tuned so that theoretical energy densities in excess of 1,500 Wh/kg are possible.

To date, the interactions of lithium ions with these organic materials within a working cell are not well understood. How is the lithium incorporated? Does it intercalate between layers within microcrystals? Does it ionically coordinate to electronegative moieties? By monitoring structural changes of the organic compounds via X-ray diffraction as a function of the state of charge, we can begin to elucidate the molecular mechanism of lithium incorporation that leads to charge storage. Our test system includes anthraquinone and two derivatives with different electron-withdrawing groups. A deeper physical understanding of these materials will allow for a more rational design and, ultimately, more efficient devices.

Global studies of single-stranded nucleic acid conformation

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Unstructured regions of RNA molecules require flexibility to accomplish many biological tasks such as conformational switching and protein recognition. Due to its highly charged backbone, the flexibility of single-stranded RNA is influenced by counterions. In this presentation, we continue to explore RNA flexibility using single-stranded nucleic acid homopolymers as a model system [1]. We investigate the role of counterion valence in nucleic acid flexibility using a combination of small-angle X-ray scattering (SAXS) and single-molecule Förster resonance energy transfer (smFRET). We also study how charge-screening of these model systems are affected by mono- and divalent ions in competition. The results imply that various factors can alter the polymeric properties of unstructured nucleic acids, and may be important for tuning RNA conformational dynamics *in vivo*.

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Using Smart Polymers to Regulate DNA-mediated Nano Assembly

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In this paper we describe the use of a temperature responsive polymer to regulate DNA interactions in both a DNA-mediated assembly system, as well as a DNA encoded drug delivery system. A thermo-responsive pNIPAAm-co-pAAm polymer, with a transition temperature (TC) of 51C was synthesized with thiol modification, and grafted to gold nanoparticles (Au NPs) also containing single stranded oligonucleotides (ssDNA). The thermo-responsive behavior of the polymer allowed for regulating the accessibility of the sequence-specific hybridization between complementary DNA functionalized Au NPs. At $T < TC$ the polymer was hydrophilic and extended, blocking interaction between the complementary sequences at the periphery of the hydrodynamic diameter. In contrast, at $T > TC$, the polymer shell undergoes a hydrophilic to phobic phase transition and collapses, shrinking below the outer ssDNA, allowing for the sequence-specific hybridization to occur.

Confined but Connected Quantum Dot Solids

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Confined but connected quantum dot solids (QDS) combine the advantages of tunable, quantum-confined energy levels with efficient charge transport through enhanced electronic interdot coupling. We report the fabrication of QDSs by treating self-assembled films of colloidal PbSe quantum dots with polar nonsolvents. Treatment with dimethylformamide balances the rates of self-assembly and ligand displacement to yield confined but connected QDS structures with cubic ordering and quasi-epitaxial interdot connections through facets of neighboring dots. The QDS structure was analyzed by a combination of transmission electron microscopy and wide-angle and small-angle X-ray scattering. Excitonic absorption signatures in optical spectroscopy confirm that quantum confinement is preserved. Transport measurements show significantly enhanced conductivity in treated films.

In-situ GIXS Study of P3HT:PCBM Thin Films During Solvent Vapor Annealing and Film Drying

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The obvious difference between thin films and bulk materials is that a thin film can be considered as under two dimensionally confined, which in turn may affect polymer crystallization behavior and crystal structures, molecular ordering, morphology, etc. In recent years poly(3-hexylthiophene) (P3HT):1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C61 (PCBM) thin film has drawn tremendous research attention. P3HT is a semicrystalline material, while PCBM is a crystallizable small molecule. Even though this film is extensively studied after post processing by solvent annealing, in-situ solvent annealing study of such films is rather rare. In-situ study enabled us to capture frame by frame GIWAXS images during solvent annealing process. In this way P3HT and PCBM crystal dissolution and growth kinetics during such solvent annealing is directly probed. All studies were conducted approximately for 20 minutes of solvent annealing and subsequent 20 minutes for drying. In this study we varied substrate surface energy and solvents. It is observed that substrate surface energy has immense effect on P3HT crystal growth kinetics. From exposure normalized images it is found that on self-assembled monolayer (SAM) coated silicon (surface energy $\sim 40\text{mJ/m}^2$) P3HT crystal dissolution is much faster than that of UVO treated silicon (surface energy $\sim 70\text{ mJ/m}^2$). All surface energies were obtained by contact angle measurement method. Effect of solvents on crystal dissolution and growth kinetics is rather complex. Crystal dissolution rate largely depends on solubility of P3HT and PCBM, volatility and partial pressure of the solvent under study. However, in all cases much of the crystal dissolution occurs in first minute. During drying cycle crystal formation largely depends on volatility of solvent under study. In the cases where o-xylene, chloroform, toluene and chlorobenzene, were used as solvent for annealing, crystal growth rate is fast during drying cycle. However, we did not observe much crystal growth during drying cycle in the case where o-dichlorobenzene was used during annealing cycle. Since our study only captured 20 minutes of drying in ambient condition it is most likely that absorbed non-volatile o-dichlorobenzene was not evaporated during that time frame. X-ray reflectivity shows that film thickness and roughness increase during solvent annealing and reduce in drying cycle when o-xylene, chloroform, toluene and chlorobenzene, were used during annealing cycle. Smoothness of the films remained intact throughout the study when annealing solvent was o-dichlorobenzene.

Introducing Cryo-SAXS for Measuring Low Resolution Macromolecular Structure without Radiation Damage

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Small angle X-ray scattering (SAXS) is an increasingly popular technique for obtaining low resolution structures of macromolecules and complexes in solution. However, the susceptibility of biomolecule solutions to damage by ionizing radiation can complicate SAXS experiments. Many potentially interesting proteins, such as light sensors and metalloenzymes, require flow cells to distribute the X-ray dose over a large volume. The high sample consumption in these cases can be prohibitive. To circumvent radiation damage, we explore whether cryo-cooling of samples to temperatures of 100 K can prevent aggregation and fragmentation during data collection. We identify SAXS-friendly cryoprotectant conditions that suppress ice formation upon rapid cooling, and compare cryo-SAXS profiles with room temperature measurements for a variety of standard molecules. From scattering volumes as small as 100 nL, we obtain data of sufficient quality for envelope reconstruction, and find good agreement between cryo-SAXS data and known atomic structures. Strikingly, cryo-cooled samples can withstand doses that are 2-3 orders of magnitude higher than typically used for SAXS at room temperature, comparable to those used in cryo-crystallography. While practical challenges remain, this breakthrough opens the possibility of using SAXS with new, high brightness X-ray sources for high throughput applications.

Mechanistic Study of High Performance Triblock Terpolymer Ultrafiltration Membrane Formation via In Situ GISAXS

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The application of block copolymer self-assembly towards membrane separations has received significant attention over the past several years due to the potential for significantly improved performance. In particular, the combination of self-assembly and non-solvent induced phase separation (SNIPS)¹ produces integral isoporous membranes. Using this facile and industrially scalable method, membranes have been fabricated from a variety of block copolymers, including poly(styrene-*b*-4-vinyl pyridine),² poly(styrene-*b*-2-vinyl pyridine),³ poly(styrene-*b*-ethylene oxide),⁴ poly(styrene-*b*-2-vinyl pyridine-*b*-ethylene oxide),⁵ and poly(isoprene-*b*-styrene-*b*-4-vinyl pyridine).⁶ These SNIPS membranes exhibit exceptional fluxes and high-resolution separations, as well as the capacity for post-functionalization, leading to temperature-dependent performance⁷ and charge-based separations⁸. While functional membranes can be fabricated, a detailed understanding of their formation mechanism has yet to be fully elucidated. To further understand the formation mechanism in these

SNIPS membranes, in situ block copolymer membrane formation that relies on self-assembly of doctor bladed solutions was observed using grazing incidence small-angle X-ray scattering (GISAXS). The evaporation dependent evolution of a disordered to an ordered structure in a film of the triblock terpolymer poly(isoprene-b-styrene-b-4-vinyl pyridine) dissolved in 1,4-dioxane and tetrahydrofuran was observed. The GISAXS pattern of the film exhibited Bragg spots consistent with a bcc structure between evaporation times of 37 s and 58 s, with the most intense Bragg spots occurring after 46 s of evaporation. Projections of the GISAXS patterns were consistent with solution small angle X-ray scattering. Such in situ methods offer the potential to optimize the key parameter of evaporation time in the production of isoporous integral block copolymer membranes.

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High-energy x-ray beamline at Cornell High Energy Synchrotron Source for in situ materials studies

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The F2 beamline at CHESS (Cornell High Energy Synchrotron Source) is currently undergoing an extensive upgrade to facilitate high energy direction microscopy (HEDM) experiments. This project is a collaborative effort of CHESS, the Air Force Research Laboratory, and the Energy Materials Center at Cornell (emc2). HEDM experiments are ideal for the non-destructive study of mechanical properties and their connection to the microstructure. Part of the project focuses on capabilities needed to perform in situ mechanical loading and heating, namely for investigations of material at extremes. By studying crystal-scale mechanics, a deeper understanding of fundamental grain mechanics, and therefore dramatically improved modeling capabilities, can be achieved. Ideally, such experiments provide insight into the deformation processes occurring in materials in real engineering applicable environments. The beamline will also host a wide variety of other applications such as in operando studies of energy-related materials and high-resolution pair-distribution function studies. Features of the new beamline include a horizontally focused beamsize of 1:2 mm (vertically unfocused, 3 mm), a range of achievable hard x-ray energies (nominally 40{90 keV), an overall increase in ux, the precision mechanical positioning of specimens, the implementation of high resolution area detectors capable of capturing an evolving microstructure, and in situ loading and heating equipment for real-time experiments.

Instantiation of Virtual Polycrystals for Simulation of Deformation Induced Twinning

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Most high strength structural alloys are polycrystalline materials - meaning they contain regions (grains) that have different crystallographic orientations. The grains can vary widely in size and shape, depending on its processing history. Important design properties, such as stiffness and strength, are sensitive to these features of the microstructure. For example, Ti-6Al-4V, a widely used aerospace alloy, exhibits a wide array of microstructures with attributes that depend strongly on its processing history. Additionally, Ti-6-4 is a two-phase material - meaning it has two co-existing crystalline structures (one hexagonal and the other cubic)

present at temperatures below 1000 C. To design machines that are both safer and more economical, better understanding of the structure-properties links in critical, load-bearing materials is paramount. A more fundamental understanding of these links begins with more refined modeling of the microstructure. Higher fidelity microstructural representations can be combined with simulations of the mechanical behavior (finite element analysis) to create tools to emulate experiments in which we can observe responses at the microstructural level through x-ray diffraction. Diffraction provides a non-destructive way of measuring important behavior of specimens throughout different stages of mechanical loading, which in turn lends actual physical insight to the micromechanical behavior of the material, while conventional methods measure.

Spatially Resolved Standing Wave Experiment With Coherent, Monochromatic Gaussian X ray Beams

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X ray standing wave is an experimental technique used for, among other purposes, vertically resolving atoms adsorbed on crystal surfaces. Since it uses plane waves, due to their infinite transverse extent, it cannot provide horizontal resolution. We propose to extend the standing wave technique to provide horizontal resolution by using coherent, monochromatic gaussian beams. Our proposed technique relies on interaction of curved wavefronts of incident and reflected beams to modulate the fluorescence. We demonstrate our technique using numerical simulations of copper adsorbed on Si 111 crystal surface.

Duplex DNA, RNA and DNA/RNA Hybrid Condensation by Spermine

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Due to the biological significance of DNA condensation and the potential use of packaged RNA for therapeutics, the behavior of nucleic acids in the presence of condensing agents is a topic of great interest. Following the discovery that double-stranded RNA resists condensation in solutions containing cobalt

hexamine [1], we studied short double-stranded DNA, RNA and a DNA/RNA hybrid in the presence of polyamines using UV spectroscopy and small and wide angle x-ray scattering. Polyamine-induced condensation of the nucleic acid constructs will be discussed.

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Structural and Biochemical Studies of the CRISPR-associated Protein Cas5a from *A.fulgidus*

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Bacteria and archaea acquire resistance to viruses and plasmids by integrating short foreign DNA fragments into their CRISPRs (clustered regularly interspaced short palindromic repeats). These repetitive loci contain genetic records of all prior encounters with foreign transgressors. CRISPR is transcribed and the long primary transcript is processed into a library of short CRISPR-derived RNAs (crRNAs) that contain a unique sequence complementary to a foreign nucleic acid challenger. The *E.coli* CRISPR-associated complex for antiviral defense (CASCADE) is central in targeting invading DNA, composed of five proteins (CasA, CasB, CasC, CasD and CasE) and CasE-processed crRNA. While the CASCADE of the bacteria *B. halodurans* is composed of three proteins (Cas5d, Csd1 and Csd2) and Cas5d-processed crRNA. In the archaea *A. fulgidus*, its CASCADE is composed of four proteins (Csa2, Cas5a, Cas6 and Csa5) and Cas6-processed crRNA. Here we report the structural and functional characterization of Cas5a (aCas5a) from *A. fulgidus*. Unlike Cas5d from *B. halodurans* (bCas5d) which has RNase activity, aCas5a does not have nuclease activity. The crystal structure of aCas5a has been solved using SAD method. Though the overall structures of aCas5a and bCas5d are similar, the two structures have significant difference: aCas5a lacks the RNA-binding site found in bCas5d, so it does not have nuclease activity as bCas5d does.

In-Situ Diffraction Measurements of Plastically Deforming Silicon Using High Energy Synchrotron X-Rays

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Silicon has proven to be an ideal material for studying plasticity mechanisms in crystalline materials due to the availability of large single crystals with low defect concentrations. However, there is still a great deal to learn about the interactions of defects and subsequent misorientation that develops within the bulk of

crystalline materials due to the plasticity mechanism of crystallographic slip. Synchrotron radiation can be used as an effective tool to observe misorientations as they develop in silicon single crystals in-situ. The evolving diffracted intensity distributions are directly related to internal structure within the silicon single crystal and the “smearing” that is observed during plastic deformation at high temperatures is consistent with its evolving misorientation distribution. A unique load frame / diffractometer has been built for use in the A2 station at the Cornell High Energy Synchrotron Source (CHESS) which can simulate processing conditions causing plastic deformation while allowing for in-situ interrogation of crystalline samples using high-energy synchrotron x-rays. The experimental set-up and results from an experiment probing silicon as it is compressed at high temperature are presented.

Crystal Structure of the C2A Domain of DOC2a

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Neurotransmitter release in brain synapses occurs in three kinetically distinct phases: one phase is tightly coupled to action potentials, in which Ca^{2+} influx triggers rapid synchronous release with a time course of several milliseconds (synchronous); the second phase is immediately following action potentials and can last for tens or hundreds of milliseconds (asynchronous); the third one occurs as stochastic events in the absence of action potentials (spontaneous). It has been found that synchronous release involves the Ca^{2+} sensors synaptotagmin-1, -2, or -9, which are anchored in the vesicle membrane and contain two cytoplasmic C2 domains that bind phospholipids in a Ca^{2+} -dependent manner and interact with the SNARE complex. Recently, it has been found that DOC2 is required for asynchronous neurotransmitter release (Yao et al., 2011, Cell) and spontaneous neurotransmitter release (Groffen et al., 2010, Science). Similar to synaptotagmin, DOC2 is a Ca^{2+} sensor containing two tandem C2 domains (designated C2A and C2B) connected by a short linker. Unlike synaptotagmin, DOC2 is a cytoplasmic protein. Here we reported the Ca^{2+} free crystal structure of the C2A domain of DOCa. The structure consists of a compact β -sandwich formed by two four-stranded β -sheets. It contains all the acidic residues responsible for Ca^{2+} binding, in agreement with its Ca^{2+} -dependent membrane-binding properties. Similar to other C2 domains, its electrostatic surface is highly basic, for its membrane-binding.

A SAXS Study of the CRISPR associated gene (cas) Csn2 in the presence and absence of Ca^{2+}

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Small angle X-ray scattering (SAXS) was used to study the solution structures of the *E. Faecalis* Csn2 protein, a cas gene required for DNA spacer acquisition as part of the CRISPR defense system. Crystallographic study of this protein illustrates a tetrameric ring that facilitates the binding of ds-DNA. Interestingly, monomeric Csn2 is not observed in our solution scattering study. In 2 mM or higher Ca²⁺ concentrations when Csn2 has strong DNA-binding affinity, our SAXS data agree with the calculated scattering from the crystalline tetramer and consequently elucidate the importance of Ca²⁺ ions in its ring structure formation and biological function. When the [Ca²⁺] is lowered or completely chelated by EGTA, a conformational change followed by higher order oligomerization was observed through direct comparison of the normalized scattering profiles. Analysis of the SAXS data by R_g and P(r) analyses and shape reconstruction shows that the conformational change is consistent with a pore elongation in 1.5 mM Ca²⁺. These biochemical and biophysical results lead us to propose a physiological model for the functioning of the Csn2 protein upon phage invasion.

CESR & CHESS UNDULATOR UPGRADE

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"Upgrades to CHESS Beamlines for undulator Operation"

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Over the next two years, the wigglers that provide beam to CHESS A, G, and F lines will be replaced with undulators currently under development and testing. This, in combination with upgrades to CESR, will provide greatly enhanced flux (a factor of 40) and brightness (a factor of 100) to these beamlines. In order to accommodate these more intense beams, the optical elements of these beamlines will be replaced with state of the art commercial optics. In 2014 two canted short (1.7m) undulators will be installed in CHESS west allowing independent operation of each station on A-line and G-line (fed by the same undulators). Cryocooled silicon monochromators will be used on A-line, while

multilayer optics will be maintained on G-line with internal cooling if required. Following in 2015, a second set of undulators will be installed on F-line for F1 and F2. The flexibility of the undulator design allows us to tailor its design to compliment the high energy needs of the F2 station and its Laue based high energy monochromator.

Rocking Curve Mapping of defects in large Lab-grown Single Crystal Diamonds plates

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Mapping the crystalline quality of the entire surface of 5mm x 5mm-sized diamond crystal plate with arc second angular resolution is of great interest in the growing field of diamond technology and in particular for the diamond radiation detectors and reflectors plates in Synchrotron machines. Using the Cornell High Energy Synchrotron Source equipped with CCD detectors, we obtained rocking curves from a total of 25, (001)-oriented single crystal diamonds (SCD) plates grown under high pressure high temperature (HPHT) and plasma enhanced chemical vapour deposition (CVD). The average full width at half maximum (FWHM) for the HPHT grown crystals is 13.1 mRad and were narrower than CVD grown (type Ila) SCD crystal plates. For type Ila diamonds, we found that the average FWHM of 10 plates of light-shades is 29.2 mRad, which are generally narrower than the average FWHM of 49.9 mRad of 10 plates of dark-shades SCD plates. Using birefringence microscopy, it was shown that highly stressed areas show huge broadening in the full-width half-maximum (FWHM) of the rocking curve. This broadening was attributed to bending, tilts, and twinning during crystal growth as well as residual strain at the surface induced by polishing.

We note that the average FWHM of the rocking curves correlate with the C-H impurities measured using FTIR and the density of nitrogen vacancies (NV) obtained from Raman/PL spectroscopy. Broadening of FWHM from lattice imperfections due to impurities are more subtle compared to lattice parameter variations caused by tilts, bending and stress points. This spatially resolved crystal quality of diamond has vital role on the performance of diamonds in wide range of applications

G-Line High Precision Optical Table & Gantry System

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In this poster we present two independent high precision motion systems that were designed for the G-Line at CHESS. The G-Line station make use of radiation from the same 49-pole wiggler that feeds the A1 and A2 hutches at CHESS West; the 5.3 GeV electron beam circulates counterclockwise and produces X-rays for A1 and A2, while the positron beam circulates clockwise and feeds G1, G2 and G3. The high intensity available at the G3 station is used by a wide variety of research groups from Cornell University and others around the world, to study the structure and dynamics of matter at the atomic scale. The G3 station generally operates from 8 to 12 keV, and combines horizontal and vertical focusing with synthetic multilayer monochromator pairs to deliver upwards of 5×10^{13} photons/sec/mm², at the sample.

The first system is the optical table, a 3 axis motion. The linear motion is supported by THK HSR35 guide rails and bearings. A preloaded 20x5 mm ball screw coupled to a NEMA 23 motor and a 10:1 gear reduction allows the unit to have a 2.5 μm resolution. The vertical motion consists of 4 ADC 5kN Utility Jacks that are geared to be driven off of one motor. The one motor approach is preferred to avoid the potential binding of the jacks that is common with driving each jack individually. The rotary motion for this optical table provides a full 360° rotation, and is equipped with fully adjustable limit switches to set travel limits as necessary. The second system consists of a Gantry System with 5 motions, including 3 linear slides providing X, Y and Z translations, and 2 rotary stages providing the pitch and yaw rotations. The members of the frame are steel tubes which are welded to steel plates that contain slotted holes for alignment of the unit. The frame is designed to be modular in construction so that it can be assembled efficiently. Maximum rigidity is assured through the use of preloaded linear guide rails. Each slide also features two fully adjustable, normally closed, limit switches to define the extents of travel. These stages not only give an exceptionally high running accuracy, but allow for large radial and thrust loads as well. Each stage is driven by a precision ground worm gear set and a high resolution, high torque stepper motor. Backlash is reduced by employing a flexure style shimming technique to preload the worm and worm wheel.

Area detector development at Cornell

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We present an overview of the work done at Cornell to develop area detectors that will meet and anticipate the needs of the x-ray science community. Our focus is on area detectors based on direct detection of x-rays in a silicon sensor. Direct conversion of absorbed x-rays to charge carriers in silicon provides high-fidelity measurements of total absorbed x-ray energy, and high-resolution spatial data.

Pixel array detectors (PADs) allow for a highly flexible detector that is made by coupling commercially fabricated CMOS with high-quality, pixelated silicon diode sensors. Using commercial CMOS processes allows for efficient and custom processing of x-ray generated signal. PADs developed in our lab have been used in experiments at CHESS and the APS, with applications ranging from coherent diffractive imaging to time-resolved studies of materials science samples.

Direct-detection CCDs combine the high spatial resolution offered by direct conversion in silicon with the smaller pixel sizes available in CCD technology. A prototype direct-detection CCD has been used to successfully collect protein crystallography data at CHESS beamline F1.

Thermal Processing of Binary Nanoparticle Superlattices

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Binary nanoparticle superlattices (BNSLs) make use of progress in the synthesis of colloidal nanoparticles with size dependent properties to create new designer materials. Like conventional table salt, made from Na and Cl atoms but with its own properties, BNSL's exhibit novel properties above and beyond the properties of the nanoparticle building blocks¹. We use GISAXS to determine the structure of the BNSLs and then investigate the structural evolution during equilibrium and non-equilibrium thermal processing. In situ GISAXS at the CHESS D1 station allows real time observation of the structural evolution with increasing annealing temperature. We also examine structural changes due to Laser Spike Annealing (LSA) and find that non-equilibrium processing methods allow for processing at higher temperatures while maintaining superlattice structure. LSA shows promise as a processing technique for structural control and thermal annealing of both single and multicomponent nanoparticle superlattices.

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Energy and Power in Li-Ion Battery through Synchronized Process and Crystal Engineering

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Throughout the history of materials science, existing self-assembled natural and synthetic materials have often provided inspiration for future materials. A central challenge in applied materials science is the development of high-quality materials with useful properties that can be efficiently and consistently manufactured on a large scale. Although sound progress is being made, the link between crystallographic engineering and process engineering still needs to be strengthened in order to produce solids with desired properties more effectively. It has also been observed that the same material can behave very differently in different structural forms, such as bulk solids and nano-scale powders. Therefore, structure and process engineering play an important role in tuning a material's desired properties, especially in the battery industry. More effective design and prediction of new crystal structures for cathode and anode materials may be achieved by using a posteriori analysis of similar existing structures. This can help with the identification of relevant crystallographic factors, which will in turn aid in the development of future materials. This process may serve as a blueprint for both crystal engineering and particle engineering.

The primary objective of the current presentation is to demonstrate a fundamental understanding of crystal engineering, and how it can be applied to particle engineering in order to continually develop better performing battery materials. An especially important tool in this process is systematic, real-time materials analysis using synchrotron x-ray beams.

X-ray Crystal Structure and Biophysical Analysis of a Class 2 PreQ₁ Riboswitch[†]

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Riboswitches are *cis*-acting RNAs that regulate gene expression via ligand binding. Typically located in the 5'-leader sequences of bacterial genes, riboswitches have potential as novel antimicrobial targets. Of special interest are riboswitches that bind ligands that are unique to the bacterial metabolome. One such molecule is preQ₁, a pyrrolopyrimidine that interacts with a cognate riboswitch in >29 bacterial species including several human pathogens. To date two classes of preQ₁ riboswitches (termed preQ₁-I and preQ₁-II) have been described but structural information has been described only for class 1. Here we present the structure of a 77-mer, class 2 preQ₁ riboswitch in the ligand-bound state at 2.3 Å resolution. The structure was solved by SAD phasing from co-crystallized, site-bound Cs⁺ ions. The preQ₁-II riboswitch differs completely from preQ₁-I riboswitches in terms of its fold and mode of ligand recognition. The preQ₁-II architecture adopts a "J"-like conformation in which helices P1, P2 and P3 adopt a 75 Å co-axial stack. The topology is that of an H-type pseudoknot in which the entire ribosome-binding site (RBS) is sequestered in helix P3, which abuts the preQ₁-binding pocket located at the confluence of the P2-P3-P4 helical junction. Non-Watson-Crick readout of preQ₁ occurs within one tier of a three-layer U•A-U major-groove base triple; we validated this mode of ligand recognition using isothermal titration calorimetry. Notably, the preQ₁-II U•A-U major-groove base triples are structurally homologous to those of human telomerase RNA (rmsd 1.46 Å) in which disruption of any base in the layer equivalent to that which binds preQ₁ was shown to cause global hTR destabilization. By analogy our solution analysis by in-line probing showed that base-triple formation and adjacent RBS sequestration depends on ligand binding, thus providing a plausible mechanism for preQ₁-dependent translational regulation. The results are broadly applicable to other riboswitches that control gene regulation at the level of translation, and expand the known repertoire of ligand-binding modes used by functional RNAs.

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Collecting sub-second images @ MacCHESS

David J. Schuller
MacCHESS

Single crystal macromolecular diffraction at MacCHESS usually involves rotating

a sample crystal through an angle while diffracting monochromatic X-rays from it (Bragg scattering). A set of such exposures cover the necessary region of reciprocal space to enable Fourier analysis. A typical single exposure may cover 0.3 - 1.0 degrees and last 1-120 seconds. Recent experiments with diffuse scattering led to the revelation that the equipment at MacCHESS performs poorly for exposures much less than one second. The routines controlling the X-ray shutter and rotation motor have been examined and reworked for better chronological control and more uniform angular coverage. As proof of principle, a set of data consisting of 30 millisecond exposures was collected and processed, and the results compared to data sets of longer exposures.

The CAPER α UHM Provides a Potential Means for Alternative Splice Site Regulation

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CAPER α is of major medical interest as it plays a crucial role in tumor growth and angiogenesis in Ewing sarcoma¹ and other cancers. In its physiological function, CAPER α is responsible for the alternative splicing of genes under the control of certain steroid receptor promoters. However, the molecular mechanisms and pathways of splice site regulation by CAPER α remain unknown. CAPER α contains a putative U2AF homology motif (UHM), a domain frequently found in early 3' splice site recognition factors. UHMs recognize a key tryptophan in short sequences termed "U2AF ligand motifs" (ULM)². We determined structures of the CAPER α UHM bound to a prototypical ULM at 1.74 Å resolution, and for comparison, in the absence of ligand at 2.20 Å resolution. The binding pocket for the ULM key tryptophan appears pre-formed in the apo-structure (rmsd 0.667 Å). The UHM/ULM-interactions authenticate CAPER α as a bona fide member of the UHM-family of proteins and suggest possible regulation of UHM-interactions by phosphorylation within the ULM. Furthermore, we identified the spliceosome subunit SF3b155 as a relevant binding partner for CAPER α . Because SF3b155 also interacts with UHMs of constitutive splicing factors, this work demonstrates a new interface for the regulation of alternative and constitutive pre-mRNA splicing.

¹ G. Huang, Z. Zhou, H. Wang, E.S. Kleinerman (2011) *Cancer* 118(8):2106-2116.

² C.L. Kielkopf, S. Lucke, M.R. Green, U2AF homology motifs: protein recognition in the RRM world. *Genes Dev* **2004**, 18 (13), 1513-1526.

Effect of Changes of the Surface Structure of SrTiO₃ on the Catalysis of Photo-Assisted Water Splitting

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Although many experiments and models have been conducted and proposed about adjusting the bulk and electronic structure of electrode materials to optimize the catalytic properties [1,2], much less has been known about the surface transformations during the photo catalytic reaction. Moreover, the contribution of the surface structure to the catalytic properties remains unknown.

In this poster, we report the evolution of the surface of the SrTiO₃ (001) during photo-assisted electrocatalysis, and the surface-dependent activity towards the water splitting at open circuit potential. By means of *in situ* high-energy X-ray reflectivity, we calculate the electron density of the SrTiO₃ electrode surface during electrochemical reaction. The photo catalytic properties have been studied with *in situ* scanning electrochemical microscopy. “Training” the surface by biasing to potentials where photo electrochemical oxygen evolution occurs in basic medium, both irreversibly alters the surface structure to more stable surface structure and increases three times the water splitting activity at open circuit.

Reference:

[1]Suntivich, J.; May, K.J.; Gasteiger, H.A.; Goodenough, J.B.; Shao-Horn, Y. *Science* **2011**, *334*, 1383-1385.

[2] Kudo, A.; Miseki, Y. *Chem. Soc. Rev.* **2009**, *38*, 253–278

X-RAY DIFFRACTION OF ORGANIC CATHODE MATERIALS IN LITHIUM-ION BATTERIES

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The Abruña research group has developed and characterized numerous promising materials for battery and fuel cell applications. In the present context, we focus on organic-based battery materials and intend to investigate how molecular structure relates to bulk characteristics of the materials of interest, with emphasis on charge storage. Conventional lithium-ion batteries employ inorganic oxides (e.g. LiCoO₂) and graphite (LiC₆) as cathode and anode electrodes, respectively. The charge/discharge process involves (de)intercalation events which are known to be kinetically slow, resulting in low rates of charge and discharge. An alternative, yet relatively unexplored, approach is the use of electroactive organic molecules (in place of the metal oxide) as the cathode in a lithium-ion battery (LIB). Through computational design and screening, combined with synthesis, organic molecules can be tuned over a broad parameter space to yield materials that can exchange multiple electrons per formula unit, leading to high gravimetric capacities. In addition, the formal potentials can be tuned so that theoretical energy densities in excess of 1,500 Wh/kg are possible.

To date, the interactions of lithium ions with these organic materials within a working cell are not well understood. How is the lithium incorporated? Does it intercalate between layers within microcrystals? Does it ionically coordinate to electronegative moieties? By monitoring structural changes of the organic compounds via X-ray diffraction as a function of the state of charge, we can begin to elucidate the molecular mechanism of lithium incorporation that leads to charge storage. Our test system includes anthraquinone and two derivatives with different electron-withdrawing groups. A deeper physical understanding of these materials will allow for a more rational design and, ultimately, more efficient devices.

What's in the Eye of the Lamprey? A Look at Five Sea Lamprey Lenses, from A(u) to Z(n)

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Sea lamprey (*Petromyzon marinus*) are among the most primitive of extant fishes. As such, they lack true otoliths, and instead have primitive hearing/balance structures called statoliths. Research into whether statoliths can be used to determine the provenance of adult lampreys has shown that these organs transform chemically when the fish metamorphoses from its larval, stream-bottom-dwelling form to its adult, parasitic form. However, in fishes, eye lenses are permanent structures that retain elemental concentrations in a manner similar to otoliths, and might prove to be superior to statoliths in terms of linking adult lampreys back to their natal streams.

We examined lamprey eye lenses from 5 newly transformed sea lampreys (larva to adult form) from Mount Hope Brook that drains into southern Lake Champlain. Lenses were analyzed with scanning x-ray fluorescence microscopy (SXFM) at the F3 beamline at CHESS. All 5 lenses showed uptake of the same dozen elements, albeit with some spatial variation and differences in concentration. However, the “signature” was very clear and dominated by Cu, Hg, Rb, Se, and Zn. We conclude that the method shows great promise as a forensic tool to determine the natal origins of sea lamprey.

Thermal stable Si nanocrystal superlattice drop-cast from colloidal dispersion

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Si is one of the most commercially important semiconductors. Si nanocrystals can exhibit bright, size-tunable, visible photoluminescence and

electroluminescence, which make them especially interesting for optoelectronic applications requiring light emission. Si quantum dots are also being explored as a laser source. Photovoltaic devices utilizing Si quantum dots have also been proposed because of their size-tunable optical absorption edge, much higher absorption coefficient and the potential for multi-exciton generation (MEG). Most collections of Si nanocrystals studied to date have been disordered with a significant size distribution. We obtained FCC superlattices with size-selected organic capped Si nanocrystal by drop casting. The superlattice structure was determined to FCC through grazing incidence small angle X-ray scattering (GISAXS). The superlattice was found to be stable up to 280 °C, which is much more thermally stable than other colloidal nanocrystals, like Au, Ag, or PbSe.

CHES Rocking Curve Measurements of Thin Diamonds for the GlueX Experiment

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University of Connecticut

The GlueX experiment at the Thomas Jefferson National Lab in Newport News, Virginia is a photonuclear experiment designed to explore the excited gluonic bonds between quarks. The excitation of the bonds is induced by the absorption of a polarized high energy photon by a proton in a liquid hydrogen target. To create a well collimated polarized photon beam, coherent bremsstrahlung radiation was chosen. A 12GeV electron beam will pass through a 20 μ m thick diamond wafer and undergo the bremsstrahlung process. The spread of photon production is not only a function of the thickness of diamond, but also of its planarity. The lattice structure of an ideal diamond makes it a good choice, however modern machining techniques tend to leave the diamonds curved and stressed resulting in a wide bremsstrahlung peak. The collaboration group at UConn has developed a laser ablation process to create 20 μ m CVD diamond radiators free from strain and warping. Rocking curve measurements taken at CHES and surface profiles are presented which demonstrate that this process results in diamond radiators which meet the GlueX criteria for thickness, flatness, and crystal mosaic spread.

Artifacts in grating interferometry data

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Since grating interferometry data have sinusoidal character, it is natural to want to use the Discrete Fourier Transform to extract the sinusoid parameters. However, in the presence of thermal distortion of the interferometer or drift in beamline optics, the DFT tends to recover the parameters incorrectly, in such a way that "shadows" of the original moiré fringes remain in the processed image. Markov chain Monte Carlo methods can be used to correctly recover dataset parameters in situations where the DFT fails catastrophically.

Identification of good conditions for solvent vapor annealing of block copolymer thin films

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Nanostructured block copolymer thin films are used as templates for inorganic nanostructures, where a perfect alignment of the structures is mandatory for their technological application. Solvent vapor annealing has emerged as a promising and highly versatile method to improve ordering in nanostructured thin film. We show how alignment of nanostructures in a thin block copolymer film can be controlled and improved by carefully selecting solvent annealing conditions during swelling and during drying. The model system studied are thin films of lamellae-forming poly(styrene-*b*-butadiene) (P(S-*b*-B)) in cyclohexane vapor, a solvent slightly selective for PB. The dry film features lamellae parallel to the substrate surface with a number of orientational defects. We have developed a protocol for solvent annealing, where the control parameters are the rates of swelling and drying as well as the maximum degree of swelling of the film. The structural changes during swelling and drying are monitored in-situ using time-resolved grazing-incidence small-angle X-ray scattering (GISAXS) and ex-situ using X-ray reflectometry. For a sufficiently high maximum degree of swelling, good alignment of the lamellar nanostructure is achieved. This alignment is improved during drying, provided the rate of drying is sufficiently low. Thus, to obtain well-ordered lamellar nanostructures in block copolymer thin films, it is important to cross the glass transition of both blocks, but not the order-disorder transition, that the film is dried sufficiently slowly. Our study opens the route to

obtain and control well-ordered block copolymer thin films, which appears to be widely applicable to post-processing of soft materials after deposition.

Photo-Induced Disorder in Block Copolymer/Additive Composite Films for Hierarchical Pattern Formation

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Ordered structures can be generated through selective hydrogen bonding between organic or nanoparticle additives and one block of weakly segregated block copolymers to increase the segregation strength in hybrid materials. Here, we report the use of enantiopure tartaric acid as the additive to dramatically improve ordering in poly(ethylene oxide-block-tert-butyl acrylate) (PEO-b-PtBA) copolymers. TEM, atomic force microscopy (AFM) and X-ray scattering were used to study the phase behavior and morphologies within both bulk and thin films. With the addition of a photo acid generator, photo-induced disorder in PEO-b-PtBA/tartaric acid composite system can be achieved upon UV exposure to deprotect PtBA block to yield poly(acrylic acid) (PAA), which is phase-miscible with PEO. Due to the strong interaction of tartaric acid with both blocks, the system undergoes a disordering transition within seconds during a post-exposure baking, which can be tracked by GISAXS to optimize the conditions. With the assistance of trace-amounts of base quencher, high resolution, hierarchical patterns of sub-micron regions of ordered and disordered domains were achieved in thin films through area-selective UV exposure using a photo-mask.

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Advances in colloidal chemistry have enabled the synthesis of anisotropic nanostructures like rods with exquisite control over their aspect ratios. The quality of these materials facilitates their organization into ordered superlattices that exhibit unique properties and functionalities depending on the material composition and assembly structure. Previously, we demonstrated that solvent vapor annealing can be employed towards preparing ordered superlattices of isotropic nanocrystals. In this study, we investigate how the same technique can be used to assemble films of core/shell cadmium selenide/cadmium sulfide nanorods into vertically oriented superlattices by controlling the cell's solvent

composition and inlet gas temperature. The structural evolution of these materials are monitored by in-situ GISAXS and GIWAXS, whereas their optical properties are recorded using in-situ UV-Vis spectrometer. Ex-situ optical experiments were conducted to confirm the orientation-dependence of the optical properties and to define our material's structure-property relationships. Our study indicates that solvent vapor annealing can be used as a robust technique for assembling large-scale arrays of nanorods into superlattices with orientation-dependent functionalities.

Fabrication of Spoked Channel Arrays for 3D micro-Xray Fluorescence

David Agyeman-budu
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The Hard X-ray Polarimeter X-Calibur Astrophysical Motivation and Performance

Kenneth Finkelstein
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X-ray Emission Collected Using a Novel Energy Dispersion Method

Kenneth Finkelstein
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Advances in BioSAXS at MacCHESS

Richard Gillilan
MacCHESS, Cornell University, Ithaca, NY

In-plane anisotropy of organic semiconductors revealed by in situ structural monitoring in doctor blade casting

Ruipeng Li

Cornell University, Ithaca, NY

What's New at MacCHESS

Marian Szebenyi

MacCHESS, Cornell University, Ithaca, NY

High pressure SAXS/WAXS/Spectroscopy at CHESS (B1): opening new dimension of nanocrystal supercrystals

Zhongwu Wang

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Graphene as a protein crystal mounting method for reducing background scatter

Jennifer Wierman

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