



SXNS 14

14th International Conference on
Surface X-ray and Neutron Scattering



July 10-14, 2016
Charles B. Wang Center
Stony Brook University

Conference Program



Conference Agenda

14th International Conference on Surface X-ray and Neutron Scattering (SXNS14)		
Sunday, July 10	Monday, July 11	Tuesday, July 12
	8:00 Check In and Registration	8:00 Check In and Registration
	8:50 Opening Remarks Ben Ocko, Doon Gibbs, <i>BNL</i> ; Richard Reeder, <i>SBU</i>	8:50 Session III - Introductory Remarks Milan Sanyal, <i>SINP</i> (Session Chair)
	Session I Andrei Fluerasu, <i>BNL</i> (Session Chair)	9:00 Tim Salditt <i>Georg-August-Universität Göttingen</i>
	9:10 Sunil Sinha <i>University of California at San Diego</i>	9:30 Jakub Drnec <i>European Synchrotron Radiation Facility</i>
	9:40 Hyunjung Kim <i>Sogang University</i>	9:50 Ralf Roehlsberger <i>Deutsches Elektronen-Synchrotron</i>
	10:00 Karl Ludwig <i>Boston University</i>	10:20 Coffee Break (provided)
	10:30 Coffee Break (provided)	Claudio Mazzoli, <i>BNL</i> (Session Chair)
	Tad Koga, <i>SBU</i> (Session Chair)	10:50 Changyong Song <i>Pohang University of Science and Technology</i>
	11:00 Marie-Ingrid Richard <i>Marseille University</i>	11:20 Gennady Pospelov <i>Forschungszentrum Juelich GmbH</i>
	11:30 Randall Headrick <i>University of Vermont</i>	11:40 June Hyuk Lee <i>Korea Atomic Energy Research Institute</i>
	11:50 Andrej Singer <i>University of California at San Diego</i>	12:00 Valeria Lauter <i>Oak Ridge National Laboratory</i>
	12:10 Anders Madsen <i>European XFEL</i>	12:20 Lunch (provided) and International Meeting to decide the location of SXNS15
	12:40 Lunch (provided)	1:30 Session IV - Introductory Remarks Mark Schlossman, <i>U. Illinois</i> (Session Chair)
	1:40 Session II - Introductory Remarks Donald Walko, <i>ANL</i> (Session Chair)	1:40 Jean Daillant <i>Synchrotron SOLEIL</i>
	1:50 Beatriz Noheda <i>University of Groningen</i>	2:10 Irena Kiesel <i>Institut Laue-Langevin</i>
	2:20 Michael Bedzyk <i>Northwestern University</i>	2:30 Luigi Cristofolini <i>University of Parma</i>
	2:40 Ullrich Pietsch <i>University of Siegen</i>	2:50 Keiji Tanaka <i>Kyushu University</i>
	3:00 Steve May <i>Drexel University</i>	3:20 Poster Session #2, Group Photo and Coffee Break (provided)
	3:30 Poster Session #1 and Coffee Break (provided)	John Ankner, <i>ORNL</i> (Session Chair)
	Matt Dawber, <i>SBU</i> (Session Chair)	5:20 Michael Kent <i>Sandia National Laboratories</i>
4:00 - 6:30 Check In and Registration at Hilton Garden Inn Stony Brook	5:30 Yaohua Liu <i>Oak Ridge National Laboratory</i>	5:50 Hanna Wacklin <i>European Spallation Source ERIC</i>
	6:00 G. Brian Stephenson <i>Argonne National Laboratory</i>	6:20 Wenjie Wang <i>Ames Laboratory</i>
6:30 - 8:30 Welcome Reception at Hilton Garden Inn Stony Brook	6:20 John Smedley <i>Brookhaven National Laboratory</i>	7:15 Dinner at the Hilton Garden Inn (provided)
	7:15 Dinner at the Hilton Garden Inn (provided)	8:00 Wang Center closes for the evening
	8:00 Wang Center closes for the evening	

Wednesday, July 13	Thursday, July 14	Legend
8:00 Check In and Registration	8:00 Check In and Registration	Special Talks and Remarks
8:50 Session V - Introductory Remarks Sushil Satija, <i>NIST</i> (Session Chair)	8:50 Session VI - Introductory Remarks Cheng Wang, <i>LBNL</i> (Session Chair)	Invited Talk
9:00 Peter Pershan <i>Harvard University</i>	9:00 Gila Stein <i>University of Houston</i>	Contributed Talk
9:30 Philippe Fontaine <i>Synchrotron SOLEIL</i>	9:30 Adrian Rennie <i>Uppsala University</i>	Poster Session
9:50 Moshe Deutsch <i>Bar-Ilan University</i>	9:50 Bulent Akgun <i>Bogazici University</i>	Session Chairs
10:20 <i>Coffee Break (provided)</i>	10:20 Jaydeep Basu <i>Indian Institute of Science</i>	
Paul Fenter, <i>ANL</i> (Session Chair)		
10:50 Ian K. Robinson <i>BNL/London Center for Nanotechnology</i>	10:50 <i>Coffee Break (provided)</i>	
11:20 Bridget Murphy <i>University of Kiel</i>	Ron Pindak, <i>BNL</i> (Session Chair)	
11:40 Ahmet Uysal <i>Argonne National Laboratory</i>	11:20 Kevin Yager <i>Brookhaven National Laboratory</i>	
12:10 Jochim Stettner <i>Kiel University</i>	11:50 Kim Nygard <i>University of Gothenburg</i>	
12:30 <i>Lunch (provided)</i>	12:10 Zhang Jiang <i>Argonne National Laboratory</i>	
Tom Arnold, <i>Diamond Light Source</i> (Session Chair)	12:40 Closing Remarks	
1:30 Hans-Georg Steinrück <i>SLAC National Accelerator Laboratory</i>	12:50 <i>Box Lunch (provided)</i>	
1:50 Mark Dean <i>Brookhaven National Laboratory</i>	1:19 SBU train to NYC (on campus)	
2:10 Jaseung Koo <i>Korea Atomic Energy Research Institute</i>	2:46 Next SBU train to NYC (on campus)	
2:30 Poster Winner Talks		
3:10 Bus A departs for BNL (tours #1-3)		
3:30 Bus B departs for BNL (tours #4-6)		
4:00 BNL (NSLS-II/740) tours #1-3		
4:30 BNL (NSLS-II/740) tours #4-6		
4:45 Bus A departs from SBU Wang Center for the Riverhead Aquarium, stopping at BNL.		
5:20 SBU bus departs from BNL Berkner to SBU		
5:30 Bus A and B depart from NSLS-II for Riverhead		
6:00 Buses arrive in Riverhead		
6:00 Banquet Dinner (separate cost; tickets required)		
10:00 Buses depart for hotels and SBU		
10:45 Buses arrive at hotels and SBU		

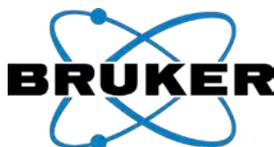
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National Synchrotron
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Center for Functional
Nanomaterials



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SBU Campus Map	Inside back cover

Welcome

On behalf of the National Synchrotron Light Source II (NSLS-II) and Stony Brook University (SBU), we warmly welcome you to the 14th International Conference of Surface X-ray and Neutron Scattering (SXNS14), which is taking place this year in the Wang Center on the SBU campus. This biannual conference is the prime forum in our community to highlight scientific and technical advances in surface scattering.

The conference has an exciting program designed to foster discussion with focused sessions on hard, soft and biologically relevant interfaces, ionic liquid and electrified interfaces, coherence, and methods. The program includes 21 invited talks, 22 contributed talks, approximately one hundred posters, and three short poster award presentations. The conference will commemorate 30 years of surface x-ray scattering at the NSLS with special talks by Professors Peter Pershan and Ian K. Robinson. Participants will have the opportunity to tour the newly commissioned NSLS-II, the brightest light source in operation.

We are grateful to the generous support provided by NSLS-II, NSLS-II UEC, and the Center for Functional Nanomaterials at Brookhaven National Laboratory, the National Institute of Standards and Technology (NIST), and Stony Brook University. We also recognize the invaluable role of our vendors and sponsors in making this event a success. A list of the conference supporters can be found in this booklet.

It is a true privilege to serve this community by organizing SXNS14. We owe many thanks to those who made this conference possible including members of the Local Organizing and the Scientific Program Committees, our co-chairs, Matt Dawber and Tad Koga, along with Mercy Baez, Nancye Wright, Gretchen Cisco, and Ron Pindak for their dedicated support of this endeavor throughout the past year.

We wish everyone a productive conference and an enjoyable stay on Long Island.

Benjamin Ocko

Chair, 14th International Surface X-ray and Neutron Scattering Conference
NSLS-II, BNL

Sushil Satija

Scientific Chair, 14th International Surface X-ray and Neutron Scattering Conference
NIST

Local Organizing Committee

Matt Dawber (Stony Brook University, Co-Chair)
Masa Fukuto (Brookhaven National Laboratory)
Maya Endoh (Stony Brook University)
Tad Koga (Stony Brook University, Co-Chair)
Claudio Mazzoli (Brookhaven National Laboratory)
Ben Ocko (Brookhaven National Laboratory, Chair)
Ron Pindak (Brookhaven National Laboratory)
Miriam Rafailovich (Stony Brook University)
Peter Stephens (Stony Brook University)
Kevin Yager (Brookhaven National Laboratory)
Mercy Baez (Brookhaven National Laboratory, Conference Coordinator)

Program Committee

Sushil Satija (National Institute of Standards and Technology, Chair)
Elaine DiMasi (Brookhaven National Laboratory)
Giovanna Fragneto (Institut Laue-Langevin, France)
Mike Fitzimmons (Oak Ridge National Laboratory)
Oliver Seeck (DESY)
Oleg Shpyrko (University of California, San Diego)
Dillion Fong (Argonne National Laboratory)
Yusuke Wakabayashi (Osaka University)
Kwanwoo Shin (Sogang University)
Zhang Jiang (Argonne National Laboratory)
Tad Koga (Stony Brook University)

Conference Events

Registered attendees are invited to attend the welcome reception, banquet dinner and NSLS-II Facility Tour. Please visit the Registration Desk for further details.

Sunday Night Welcome Reception – 6:30 PM-8:30 PM

Hilton Garden Inn Stony Brook

1 Circle Road, Stony Brook, NY 11794

No charge for registered attendees; additional cost for guests.

SXNS14 Poster Session

All posters must be dropped off at the registration desk by 10:30 a.m. on Monday and picked up no later than 1:00 p.m. on Wednesday.

NSLS-II Facility Tour

Participants can tour the NSLS-II on Wednesday, July 13. Please visit the registration desk to sign up. Tour sign-up is available during Conference Registration while space is available. Buses start departing at 3:10 p.m.

Important Note: NSLS-II is posted a Controlled Radiation Area. Minors under the age of 10 years old are not allowed to tour the facility. Guests must wear **long pants and flat, closed-toe shoes**. Access may be restricted if proper attire is not worn.

No charge for registered attendees. Transportation will be provided.

Wednesday Night Banquet – 6:00 PM-10:00 PM

Long Island Aquarium & Exhibition Center

431 East Main Street, Riverhead, NY 11901

Please visit the registration desk to purchase your banquet ticket. Transportation provided to banquet location.

International Advisory Committee

Milan K. Sanyal (Saha Institute of Nuclear Physics)

Jens Als-Nielsen (Niels Bohr Institute)

John Ankner (Oak Ridge National Laboratory)

Michael Bedzyk (Northwestern University)

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Andreas Stierle (DESY)

Metin Tolan (Universitat Dortmund)

Jin Wang (Argonne National Laboratory)

John White (Australian National University)

Sunday, July 10, 2016

- 4:00 pm to 6:30 pm Check In and Registration at Hilton Garden Inn
6:30 pm to 8:30 pm Welcome Reception at Hilton Garden Inn

Monday, July 11, 2016

- 8:00 am Check In and Registration at Wang Center
- 8:50 am Opening Remarks
Ben Ocko, *Brookhaven National Laboratory*, Doon Gibbs, *Brookhaven National Laboratory*, Richard Reeder, *Stony Brook University*
- Session I**
Andrei Fluerasu, *Brookhaven National Laboratory* (Session Chair)
- 9:10 am “Some Recent Developments in the Analysis of Grazing Incidence and Coherent Scattering from Surfaces” – Invited (I-1)
Sunil Sinha, *University of California at San Diego*
- 9:40 am “Strain Development of Pt Nanocrystal during Catalytic Process by Coherent X-ray Diffraction Imaging” – Contributed (C-1)
Hyunjung Kim, *Sogang University*
- 10:00 am “Co-GISAXS as a New Tool to Investigate Surface Growth Dynamics” – Invited (I-2)
Karl Ludwig, *Boston University*
- 10:30 am Coffee Break (provided)
Tad Koga, *Stony Brook University* (Session Chair)
- 11:00 am “Structural X-ray Studies of Nanostructures using X-ray Nanobeams” – Invited (I-3)
Marie-Ingrid Richard, *Marseille University*
- 11:30 am “Observation of Heterodyne and Homodyne Mixing in X-ray Photon Correlation Spectroscopy during Thin Film Deposition” – Contributed (C-2)
Randall Headrick, *University of Vermont*
- 11:50 am “Enhancement of Charge Ordering by Dynamic Electron-Phonon Interaction. A Pump-Probe Study at LCLS” – Contributed (C-3)
Andrej Singer, *University of California at San Diego*
- 12:10 pm “Materials Imaging and Dynamics Station at the European X-Ray Free-Electron Laser Facility” – Invited (I-4)
Anders Madsen, *European XFEL*

- 12:40 pm Lunch (provided*)
- 1:40 pm **Session II – Introductory Remarks**
Donald Walko, *Argonne National Laboratory* (Session Chair)
- 1:50 pm “Self-Assembly and Control of Periodic Nano-Domains in Ferroelastic Thin Films” – Invited (I-5)
Beatriz Noheda, *University of Groningen*
- 2:20 pm “Templated Functionalization of Epitaxial Graphene” – Contributed (C-4)
Michael Bedzyk, *Northwestern University*
- 2:40 pm “In-situ X-ray Diffraction Studies during GaAs MBE Nanowire Growth” - Contributed (C-5)
Ullrich Pietsch, *University of Siegen*
- 3:00 pm “Scattering Approaches for Characterizing Octahedral Rotations and their Physical Effects in Oxide Heterostructures” – Invited (I-6)
Steve May, *Drexel University*
- 3:30 pm Poster Session #1 and Coffee Break (provided)
Matt Dawber, *Stony Brook University* (Session Chair)
- 5:30 pm “Insight into Spintronics from Neutrons and X-rays” – Invited (I-7)
Yaohua Liu, *Oak Ridge National Laboratory*
- 6:00 pm “In Situ Studies of GaN Vapor Phase Epitaxy on Various Surface Orientations” – Contributed (C-6)
G. Brian Stephenson, *Argonne National Laboratory*
- 6:20 pm “Alkali Antimonides: from Photocathodes to Solar Cells” – Contributed (C-7)
John Smedley, *Brookhaven National Laboratory*
- 7:15 pm Dinner at the Hilton Garden Inn (provided*)
- 8:00 pm Wang Center closes for the evening

Tuesday, July 12, 2016

- 8:00 am Check In and Registration at Wang Center
- 8:50 am **Session III – Introductory Remarks**
Milan Sanyal, *Saha Institute of Nuclear Physics* (Session Chair)
- 9:00 am “X-ray Waveguide Optics and Imaging at the Nanoscale” – Invited (I-8)
Tim Salditt, *Georg-August-Universität Göttingen*
- 9:30 am “Unlocking the Power of 2D Detectors in Surface X-ray Diffraction: Data Reduction and Visualization” – Contributed (C-8)
Jakub Drnec, *European Synchrotron Radiation Facility*

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- 9:50 am "Quantum Optics with X-rays using Thin-Film Cavities" – Invited (I-9)
Ralf Roehlsberger, *Deutsches Elektronen-Synchrotron*
- 10:20 am Coffee Break (provided)
Claudio Mazzoli, *Brookhaven National Laboratory* (Session Chair)
- 10:50 am "Dynamic Imaging of Nanostructures using Femtosecond X-ray Laser Pulses" – Invited (I-10)
Changyong Song, *Pohang University of Science and Technology*
- 11:20 am "BornAgain: Simulation and Fitting Framework for Scattering Experiments at Grazing Incidence and Reflectometry" – Contributed (C-9)
Gennady Pospelov, *Forschungszentrum Juelich GmbH*
- 11:40 am "Probing Dynamic Layer Rearrangement during the Growth of Ruddlesden-Popper Series Thin Films through Surface X-ray Scattering" – Contributed (C-10)
June Hyuk Lee, *Korea Atomic Energy Research Institute*
- 12:00 pm "Reaching High-Temperature Magnetism in Intrinsic Topological Insulator - Ferromagnetic Insulator Heterostructures" – Contributed (C-11)
Valeria Lauter, *Oak Ridge National Laboratory*
- 12:20 pm Lunch (provided*) and International Meeting to decide the location of SXNS15
- 1:30 pm **Session IV – Introductory Remarks**
Mark Schlossman, *University of Illinois at Chicago* (Session Chair)
- 1:40 pm "Reduction in Tension and Stiffening of Lipid Membranes in an Electric Field Revealed by X-Ray Scattering" – Invited (I-11)
Jean Daillant, *Synchrotron SOLEIL*
- 2:10 pm "Biomimetic Model Membranes for Investigation of Membrane Transport Processes with Reflectometry" – Contributed (C-12)
Irena Kiesel, *Institut Laue-Langevin*
- 2:30 pm "Different Effects of Hydrophilic and Hydrophobic Silica Nanoparticles on the Dynamics of Phospholipid Films" – Contributed (C-13)
Luigi Cristofolini, *University of Parma*
- 2:50 pm "Aggregation States of a Highly Bio-inert Polymer Blend at Water Interface by Neutron Reflectivity" – Invited (I-12)
Keiji Tanaka, *Kyushu University*
- 3:20 pm Poster Session #2, Group Photo and Coffee Break (provided)
John Ankner, *Oak Ridge National Laboratory* (Session Chair)
- 5:20 pm "Combining Neutron or X-ray Reflectivity with Hydrogen-Deuterium Exchange Mass Spectrometry to Resolve Conformations of Membrane Associated Proteins" – Invited (I-13)
Michael Kent, *Sandia National Laboratories*

- 5:50 pm “Probing the Structure and Antibiotic Susceptibility of Yeast Membranes using Neutrons - Effect of Lipid Composition on the Mechanism of Amphotericin B” – Invited (I-14)
Hanna Wacklin, *European Spallation Source ERIC*
- 6:20 pm “Two-Dimensional Assembly of Gold Nanoparticles at Vapor/Liquid Interfaces” – Contributed (C-14) Wenjie Wang, *Ames Laboratory*
- 7:15 pm Dinner at the Hilton Garden Inn (provided*)
- 8:00 pm Wang Center closes for the evening

Wednesday, July 13, 2016

- 8:00 am Check In and Registration at Wang Center
- 8:50 am **Session V – Introductory Remarks**
Sushil Satija, *National Institute of Standards and Technology* (Session Chair)
- 9:00 am “From Liquid Crystals to Liquid Metals: The Birth and Maturation of Liquid Surface Scattering” – Special (S-1)
Peter Pershan, *Harvard University*
- 9:30 am “Ionic Liquids at Interfaces” – Contributed (C-15)
Philippe Fontaine, *Synchrotron SOLEIL*
- 9:50 am “Alkyl Chain Length Dependence of the Interfacial Structure of Ionic Liquids” – Invited (I-15)
Moshe Deutsch, *Bar-Ilan University*
- 10:20 am Coffee Break (provided)
Paul Fenter, *Argonne National Laboratory* (Session Chair)
- 10:50 am “The Original NSLS CTR Beamline: X16A” – Special (S-2)
Ian K. Robinson, *Brookhaven National Laboratory/London Center for Nanotechnology*
- 11:20 am “Temperature- and Potential-Dependent Structure of the Mercury-Electrolyte Interface” – Contributed (C-16)
Bridget Murphy, *University of Kiel*
- 11:40 am “Molecular Scale Structure and Dynamics of Concentrated Electrolytes at Charged Interfaces” – Invited (I-16)
Ahmet Uysal, *Argonne National Laboratory*
- 12:10 pm “Transmission Surface Diffraction: A Novel Method for Operando Studies of Electrochemical Interfaces” – Contributed (C-17)
Jochim Stettner, *Kiel University*
- 12:30 pm Lunch (provided*)

Conference Program

Tom Arnold, *Diamond Light Source* (Session Chair)

- 1:30 pm “Nanoscale Structure of Si/SiO₂/Organics Interfaces” – Contributed (C-18)
Hans-Georg Steinrück, *SLAC National Accelerator Laboratory*
- 1:50 pm “Orbital Polarization Driven by Anisotropic Hybridization in a Nickelate Heterostructure determined by Resonant Inelastic X-Ray Scattering” – Contributed (C-19)
Mark Dean, *Brookhaven National Laboratory*
- 2:10 pm “Reduced Diffusion Dynamics of Polymer Thin Films near Graphene Oxide Surfaces: Neutron Reflectivity Studies” – Contributed (C-20)
Jaseung Koo, *Korea Atomic Energy Research Institute*
- 2:30 pm Poster Winner Talks
- 3:10 pm Bus A departs for BNL (tours #1-3)
- 3:30 pm Bus B departs for BNL (tours #4-6)
- 4:00 pm BNL (NSLS-II/740) tours #1-3
- 4:30 pm BNL (NSLS-II/740) tours #4-6
- 4:45 pm Bus A departs from SBU Wang Center for the Riverhead Aquarium, stopping at BNL.
- 5:20 pm SBU bus departs from BNL Berkner to SBU
- 5:30 pm Bus A and B depart from NSLS-II for Riverhead
- 6:00 pm Buses arrive in Riverhead
- 6:00 pm Banquet Dinner (separate cost; tickets required)
- 10:00 pm Buses depart for hotels and SBU
- 10:45 pm Buses arrive at hotels and SBU

Thursday, July 14, 2016

- 8:00 am Check In and Registration at Wang Center
- 8:50 am **Session VI – Introductory Remarks**
Cheng Wang, *Lawrence Berkeley National Laboratory* (Session Chair)
- 9:00 am “Grazing-Incidence X-Ray Scattering From Thin Polymer Films” – Invited (I-17)
Gila Stein, *University of Houston*
- 9:30 am “Wetting, Alignment and Roughness - lamellar Phases at Solid Interfaces” – Contributed (C-21)
Adrian Rennie, *Uppsala University*

- 9:50 am “Effect of Chain Architecture on the Interdiffusion in Thin Polymer Films” – Invited (I-18)
Bulent Akgun, *Bogazici University*
- 10:20 am “Surface X-ray Scattering Probes Dynamical Anomalies of Polymer Grafted Nanocolloids in Polymer Films” – Invited (I-19)
Jaydeep Basu, *Indian Institute of Science*
- 10:50 am Coffee Break (provided)

Ron Pindak, *Brookhaven National Laboratory* (Session Chair)
- 11:20 am “Photothermal Assembly of Block Copolymers” – Invited (I-20)
Kevin Yager, *Brookhaven National Laboratory*
- 11:50 am “Anisotropic de Gennes Narrowing in Confined Fluids” – Contributed (C-22)
Kim Nygard, *University of Gothenburg*
- 12:10 pm “High-resolution Grazing-incidence X-ray Scattering for Three-dimensional Structures in Thin Films and Buried Nanostructures” – Invited (I-21)
Zhang Jiang, *Argonne National Laboratory*
- 12:40 pm Closing Remarks
- 12:50 pm Box Lunch (provided*)
- 1:19 pm SBU train to NYC (on campus)
- 2:46 pm Next SBU train to NYC (on campus)

*Meals provided for non-BNL registered attendees only.

Oral Presentation Abstracts





Some Recent Developments in the analysis of Grazing Incidence and Coherent Scattering from Surfaces

Sunil K. Sinha

University of California San Diego

email : ssinha@physics.ucsd.edu

We shall discuss recent advances in the application of the Distorted Wave Born Approximation (DWBA) often used to analyze Grazing Incidence Small Angle or Diffuse Scattering, including the incorporation of Parratt-like slicing methods, the development of user-friendly software, and tests of the accuracy of the DWBA. We shall also discuss the extension of the DWBA to the scattering of coherent radiation and its application to coherent diffraction imaging at grazing incidence. Finally, we will reexamine the old question of resolution vs. partial coherence and discuss the interpretation of X-ray Photon Correlation Spectroscopy (XPCS) on spin systems.

Strain development of Pt nanocrystal during catalytic process by coherent X-ray diffraction imaging

Dongjin Kim^a, Jerome Carnis^a, Myungwoo Chung^a, Jinback Kang^a, Sungwon Kim^a, Kyuseok Yun^a, Jaeseung Kim^a, Wonsuk Cha^b, Mathew J. Cherukara^c, Ross Harder^c, Alexey Zozula^d, Michael Sprung^d, Hyunjung Kim^a

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Metal nanoparticles are of primary interest for heterogeneous catalytic processes due to their large surface area, the number of under-coordinated atoms, and the coexistence of different low-index facets which lift kinetic barriers. They have been used for major environmental applications such as automotive catalytic converters. In this case, the effect of surface oxidation along the catalytic process is of particular importance to the development of new processes resulting in higher efficiency and thus a reduction of the cost. However, it is not yet fully understood how the oxidation or surface adsorption of reactants on the nanoparticle and further resultant lattice distortion affect the internal strain of the nanoparticles during catalytic process.

Coherent X-ray diffraction imaging (CXDI) allows determining the shape of the nanoparticles and the deformation field by mapping the phase through the crystal structure. Even though the spatial resolution of CXDI at current stage is yet ~10nm, a resolution in the displacement retrieved from the phase is less than 0.1 nm. In this study, we observed the deformation field distribution of Pt nanoparticles during the oxidation process of methane. Retrieved phases indicate changes above the activation temperature of methane oxidation. Because of the binding (or surface adsorption) energy of the gases, we observed the different magnitude of the deformation field distribution along the catalytic oxidation process. In addition, our simulation results show that the structural deformation is related to the interaction between the catalysts and the reactants and the adsorption of reactants can be varied with the crystal facets and edges.

This research was supported by the National Research Foundation of Korea (Nos. NRF-2014R1A2A1A10052454, 2015R1A5A1009962, 2016R1A6B2A02005468) and Samsung Electronics and Samsung Display.

References

- [1] J. Carnis, Coherent X-ray scattering study of Dynamics and Nanostructures, Ph.D. Thesis, Sogang University (2015).
- [2] W. Cha, et al., Core-shell strain structure of zeolite microcrystals. *Nature Materials* **12**, 729 (2013).
- [3] M. Watari, et al., Differential stress induced by thiol adsorption on faceted nanocrystals. *Nature Materials* **10**, 862 (2011).

Co-GISAXS as a New Tool to Investigate Surface Growth Dynamics

M.G. Rainville^a, C. Wagenbach^a, J.G. Ulbrandt^b, S. Narayanan^c, A. Sandy^c, H. Zhou^c, M. Mokhtarzadeh^d,
R.L. Headrick^b and K.F. Ludwig^{a,d}

^aDiv. of Materials Sci. & Eng.; Boston University, ^bDept. of Physics; Univ. of Vermont, ^cAdvanced Photon Source, Argonne National Laboratory, ^dDept. Of Physics; Boston University

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A detailed quantitative measurement of surface dynamics during thin film growth is a major experimental challenge. Recently we have used X-ray Photon Correlation Spectroscopy with coherent hard X-rays in a Grazing-Incidence Small-Angle X-ray Scattering (i.e. Co-GISAXS) geometry as a new tool to investigate nanoscale surface dynamics during sputter deposition of a-Si and a-WSi₂ thin films. For both films, kinetic roughening during surface growth reaches a dynamic steady state at late times in which the intensity autocorrelation function $g_2(q,t)$ becomes stationary. For the most surface-sensitive experimental conditions, the $g_2(q,t)$ functions exhibit compressed exponential behavior at all wavenumbers studied. The overall dynamics are complex, but the structure factor and correlation time exhibit power law behaviors consistent with dynamical scaling [1]. Simulations were performed to better compare the observed kinetics with predictions of linear and nonlinear growth models.

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Structural X-ray studies of nanostructures using x-ray nanobeams

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Characterizing the structural properties (strain gradients, chemical composition, crystal orientation, defects, ...) inside thin film and nanostructures is a grand challenge in materials science. This contribution will illustrate how advanced synchrotron x-ray techniques can be utilized to address this challenge for crystalline nanostructures.

The availability of x-ray nanobeams is a fundamental change for the study of nanostructures. An optimized fast-scanning x-ray microscopy (SXDM) technique called quick continuous Mapping (K-Map) and developed at ID01-ESRF, will be shown [1]. This method, which consists of a two-dimensional mapping of a sample with a nano-focused x-ray beam, is used to directly image structural inhomogeneities (strain, composition, thickness and lattice tilt) down to the sub-micrometer scale. Here, the spatial resolution is defined by the beam size (100 nm). We will demonstrate the capabilities of this fast technique on functional Ge layers grown on graded SiGe buffers for sub-10 nm CMOS applications [2,3]. With the availability of detectors that can operate in the kilohertz regime, the scanning speed is ultimately limited by the brilliance of the source. The technique will benefit from the ESRF Extremely Brilliant Source (EBS) Upgrade (scheduled in 2018/2019) and is likely to become a routine analysis technique with *in situ* and operando capabilities to study processed semiconductor devices.

In the case of Bragg coherence diffraction imaging (Bragg-CDI), where coherent diffraction patterns are reconstructed, the spatial resolution depends on the data quality, which is determined by the coherent flux and ultimately limited by the wavelength. A resolution of the structural properties of less than 10 nm is achieved up-to-date for Bragg CDI [4]. The capabilities of the Bragg CDI technique will be demonstrated on nanowires [4,5] and highly faceted Pt nanoparticles for enhanced catalysis. The Bragg CDI technique allows understanding the interplay between shape, size, strain, faceting, composition and defects at the nanoscale. This technique opens pathways to investigate *in situ* and operando the internal structural evolution of nanoparticles in various gaseous and liquid environments during reaction.

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Oral Abstracts

Observation of heterodyne and homodyne mixing in X-ray photon correlation spectroscopy during thin film deposition

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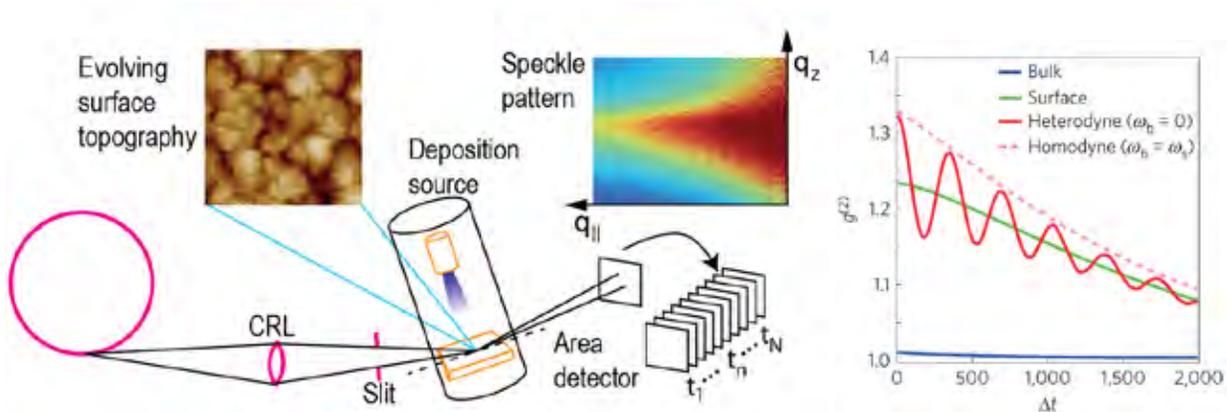
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The properties of artificially grown thin films are often strongly affected by the dynamic relationship between surface growth processes and subsurface structure. Coherent mixing of X-ray signals promises to provide an approach to better understand such processes. Continuously variable mixing of surface and bulk scattering signals during real-time studies of sputter deposition of a-Si and a-WiSi₂ films has been observed by controlling the X-ray penetration and escape depths in coherent grazing incidence small angle X-ray scattering (Co-GISAXS). Under conditions where the X-ray signal comes from both the growth surface and the thin film bulk, oscillations in temporal correlations arise from coherent interference between scattering from stationary bulk features and from the advancing surface. [1] The absence of oscillations at larger in-plane wavevector transfer is interpreted as evidence that elongated bulk features propagate upward at the same velocity as the surface. Additionally, a highly surface sensitive mode is demonstrated that can access the surface dynamics independently of the subsurface structure. [2] A schematic diagram of the experiment and an example of the autocorrelation signal is shown below.

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Enhancement of charge ordering by dynamic electron-phonon interaction. A pump-probe study at LCLS.

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Symmetry breaking and the emergence of order is one of the most fascinating phenomena in condensed matter physics. It leads to a plethora of intriguing ground states found in antiferromagnets, Mott insulators, superconductors, and density-wave systems. Exploiting states of matter far from equilibrium can provide even more striking routes to symmetry-lowered, ordered states.

The advent of x-ray free-electron lasers opened up new routes to study structural dynamics on femto-second time scales, particularly in technologically relevant nanoscale materials such as thin films. Here, by utilizing the unique capabilities of the LCLS we demonstrate that moderate photo-excitation in elemental chromium can transiently enhance the charge-density-wave (CDW) order by up to 30% above its equilibrium value, while strong excitation leads to an oscillating, large-amplitude CDW state that persists above the equilibrium transition temperature [1] (see Figure 1). By experimentally discerning multiple time scales thus revealing the underlying physics we conclude that both effects result from dynamic electron-phonon interaction. The interaction between these degrees freedom also provides an efficient mechanism to selectively transform a broad excitation of the electronic order into a well-defined, long-lived coherent lattice vibration. This mechanism may be exploited to transiently enhance the order parameter in other systems with coupled electronic and lattice orders.

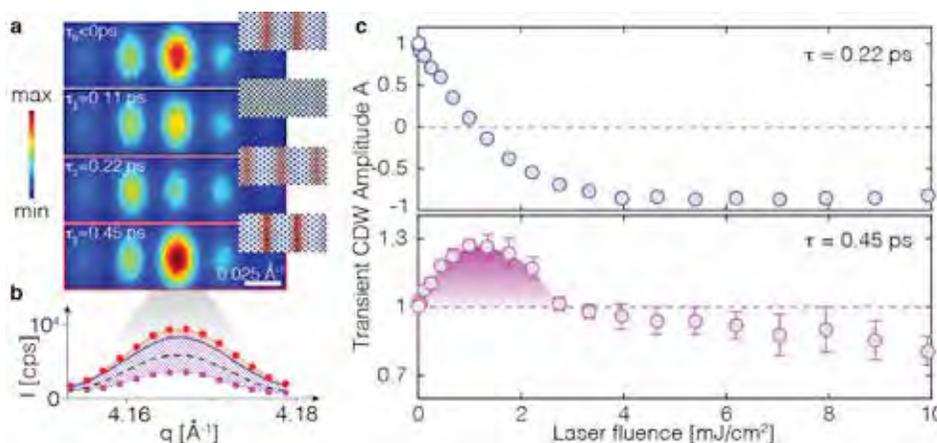


Figure 1. (a) Time resolved x-ray diffraction around the CDW satellite peak and the integral along the vertical direction (b) following photo excitation. Insets show schematic representations of the charge density consistent with the x-ray data for different time delays. (c) The transient amplitude of the CDW at 0.22 ps (top) and 0.45 ps (bottom) normalized to the value in equilibrium. The shaded region indicates the CDW enhancement.

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Oral Abstracts

Materials Imaging and Dynamics Station at the European X-Ray Free-Electron Laser Facility

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A new international X-Ray Free-Electron Laser facility, European XFEL, is under construction in the Hamburg area in Germany. Several stations will provide new capabilities for experiments using FEL radiation both in the soft- and hard X-ray regime. Experiments at the Materials Imaging and Dynamics (MID) station will seek to exploit the exceptional coherence properties, the high flux, and the short duration (fs) of XFEL pulses. The MID instrumentation allows experiments to be carried out in a surface sensitive grazing angle geometry, also on liquid surfaces, potentially combined with a synchronized optical pump laser for sample excitation. Experiments on solid samples in a He cryostat will be possible at MID that covers both the SAXS and WAXS regimes with a variable photon energy from 5 to 25 keV. Focusing of the beam is possible in the range from about 10 micron to 100 nm. First experiments at MID are planned for summer 2017.

Self-Assembly and Control of Periodic Nano-Domains in Ferroelastic Thin Films

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Control of domains in ferroelectric and ferromagnetic materials is of crucial importance because domains determine, to a large extent, the electrical and magnetic responses of these materials. In thin films and nanostructures, domains form in richer configurations and larger densities, making the significance of nano-domains and their control even greater. Moreover, the fact that the density of domain walls scales inversely with the size of the crystal, makes the distinct contribution of these objects non-negligible in nanoscaled ferroics. The spread and availability of local probe techniques has recently led to great progress in the study of domain walls and it has been shown that domain walls display their own functionalities¹, quite different from those of the parent material. This is due to the symmetry breaking that takes place at the boundaries between domains and/or, in the case of ferroelastic domain walls, to the local strain gradients², which can directly alter the ferroelectric properties³, promote local accumulation of defects⁴, or even change the chemistry of the materials selectively at the wall⁵. It has, then, become important to have control of the formation, configuration and densities of nanodomains, as a way to tune the domain walls properties in order to investigate their use as nanodevices. In this talk I will describe our main contributions to this field, discussing our work on epitaxial thin films of strain-modified $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$, BiFeO_3 , BaTiO_3 and TbMnO_3 , for which x-ray diffraction has played an essential role.

This work is done in collaboration with a large number of people among which I would like to mention: my current and past group members Arnoud Everhardt, Saeedeh Farokhipoor, Oleksiy Nesterov, Sylvia Matzen, Diego Rubi, Christophe Daumont and Gustau Catalan; collaborators at the Zernike Institute (Groningen) S. Venkatesan, Bart Kooi, Maxim Mostovoy and Coen de Graaf; in Toulouse and Zaragoza (CEMES-CNRS-INA) Etienne Snoeck and Cesar Magen; in Düsseldorf (MPIE) Sriram Venkatesan and C. Scheu, and in Luxembourg (LIST), Jorge Iñiguez.

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Templated Functionalization of Epitaxial Graphene

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Nanoscale control and integration of disparate materials on graphene is a critical step towards the development of graphene-based electronics and sensors. Among different graphene substrates, epitaxial graphene (EG) on SiC provides several advantages for functionalization, including high electronic quality, tunable substrate coupling, wafer-scale processability, and crystalline ordering that can template commensurate growth. Exploiting the wafer-scale registry of EG on SiC to template self-assembly and heterostructure materials; we have demonstrated multiple avenues toward functionalization which each offering distinct modifications to the electronic and chemical properties of the underlying graphene.

The local functionalized structure and electronic nature is revealed through scanning tunneling microscopy (STM) and atomic force microscopy (AFM). The precise multi-length scale structure at and below the top surface layer is determined via simultaneous grazing incidence small- and wide- angle X-ray scattering (GISAXS/GIWAXS). GISAXS/GIWAXS gives the relative orientation of the EG, SiC, and functionalized material atomic planes. GISAXS/GIWAXS reveals the orientational registry of the functionalized system with respect to the underlying graphene. We used this scan-probe/X-ray scattering method to examine systems of epitaxial MoS₂ and organically templated ZnO nanowires on EG.^{1,2}

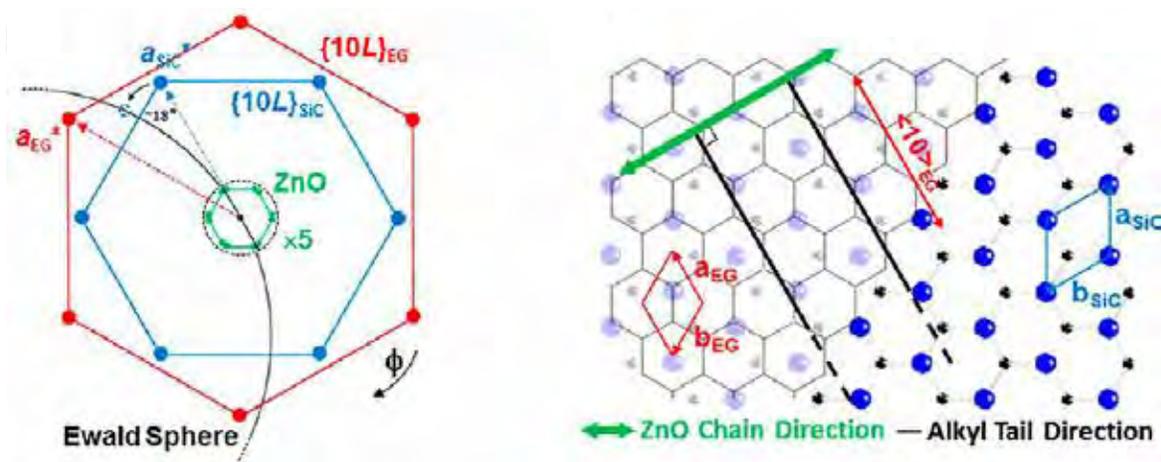


Figure 1: Reciprocal space lattice corresponding to real space 2D crystal structures of epitaxial ZnO nanowires templated by self-assembled organic molecules on EG on SiC(001).

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In-situ x-ray diffraction studies during GaAs MBE nanowire growth

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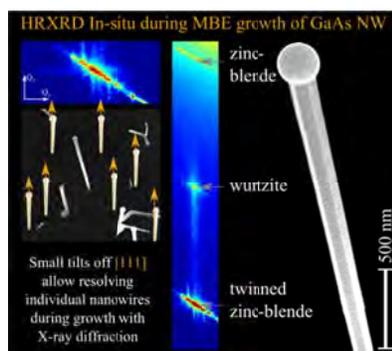
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Catalyst-free MBE nanowire growth along the [111] crystallographic orientation suffers from wurtzite-zincblende polytypism. Typically XRD studies of polytypism are performed ex-situ after removal of sample from MBE chamber. Therefore after growth modifications of the structure are not accessible. We report on in-situ x-ray diffraction experiments during GaAs MBE growth to explore the dynamic relation between the growth conditions and the structural composition of the nanowires.

Using our own portable MBE growth chamber we investigated the evolution of polytypism in self-catalyzed GaAs nanowires on Si (111) with time-resolved in situ x-ray diffraction at ANKA synchrotron. We observed the temporal evolution of faultless wurtzite and zinc blende and interpret our data in the framework of a height dependent Markov model [1]. This allows for extract quantitative information on the differences of the nucleation barriers of both phases.

Using the same portable MBE chamber we realized first in-situ growth experiment at P09 beamline of PETRA III using a 40x40 μ m beam illuminating a small NW ensemble. Because of the very parallel beam and because most of the NWs are slightly tilted with respect to [111] we could separate a very few NWs for structure analysis. In particular, we studied the evolution of mean nanowire diameter, tapering and polytypism during the growth. In combination with *ex-situ SEM* we could disentangle processes of radial growth responsible for tapering due to catalytic growth and step-flow mediated facet growth [2]. Further we did first re-growth studies probing nanowire length and diameter for of rising temperature and as function of time revealing different behavior for NWS and parasitic islands.



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Scattering approaches for characterizing octahedral rotations and their physical effects in oxide heterostructures

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Rotations and distortions of the corner-connected BO_6 octahedra are known to play a central role in the physical properties of ABO_3 perovskites. While these rotations are tuned using cation substitution in bulk materials, epitaxial strain and interfacial coupling provide means to achieve non-bulk-like structural distortions, thereby enabling new strategies to spatially modulate and realize new physical properties in complex oxides. In this talk, I will discuss how synchrotron diffraction can be used to quantify octahedral rotations, revealing how the octahedral network responds differently to strain and superlattice formation.[1,2] Building on this structural understanding, examples of how interfacial modifications to octahedral rotations and distortions alter local magnetic and electronic properties in $La_{0.7}Sr_{0.3}MnO_3$ -based heterostructures, as revealed by polarized neutron reflectivity and x-ray spectroscopy, will be presented.[3,4] Finally, the response of in-phase octahedral rotations to strain and substrate imprinting will be presented and the implications for designing hybrid improper ferroelectrics will be discussed.

This work is supported by the National Science Foundation (DMR-1151649) and the US Army Research Office (W911NF-15-1-0133).

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Insight into Spintronics from Neutrons and X-rays

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Spintronics, where the functional components are built from magnetic heterostructures, has become an increasingly important field in magnetism. Fundamentally new physics and valuable functionalities that are not found in individual components have been discovered in magnetic heterostructures in the last few decades. Examples include giant magneto-resistance, tunneling magneto-resistance, novel low-dimensional magnetization, interlayer exchange coupling, exchange bias, proximity effects and spin injection. By combining the complementary polarized neutron reflectometry (PNR) and polarized x-ray absorption spectroscopy (XAS) techniques, one can determine element-specific and spatially resolved magnetization structures, which have provided significant insights into the underlying physics in this rapidly developing field (1). Here I will present two examples. In the first case, we found an anomalous decrease of the tunnel magnetoresistance at low temperatures in magnetic tunnel junctions (MTJs) consisting of ferromagnetic $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and insulating $\text{PrBa}_2\text{Cu}_3\text{O}_7$. With a combined approach of PNR and x-ray magnetic circular dichroism (XMCD), we found this anomalous behavior can be attributed to the competition between the positive spin polarization of the manganite contacts and the negative spin-filter effect from the interface-induced Cu magnetization (2). In the second one, we demonstrated a nonvolatile electric control on magnetism in heterostructures consisting of ferromagnetic Co (or CoFeB) and dielectric $\text{Gd}_2\text{O}_{3-x}$. XAS and XMCD experiments show that the voltage-induced oxygen migration gives rise to the redox of the interfacial Co layer, which changes its magnetic properties (3). With XMCD experiments in situ applying an electric field and magnetotransport measurements, we have demonstrated that both the magnetic anisotropy and the interlayer coupling are tunable by applying a voltage of 5 V. Recent work supported by Scientific User Facilities Division of the Office of Basic Energy Sciences, US Department of Energy.

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In Situ Studies of GaN Vapor Phase Epitaxy on Various Surface Orientations

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While the use of non-polar and semi-polar surface orientations is a potentially powerful approach to enhance the performance of GaN-based devices [1], complex growth behaviors observed on these orientations has introduced new challenges [2]. The surface symmetries of the non-polar and semi-polar facets of wurtzite GaN suggest that they will exhibit highly anisotropic surface energies and kinetics [3]. Opportunities for optimal process and device design depend upon understanding of fundamentals such as adatom surface diffusion anisotropy, step edge energies, impurity incorporation, interactions of the surface species with step edges, and elucidating how these fundamentals affect crystal growth.

Using *in situ* synchrotron x-ray scattering, we have been investigating the effects of crystal surface orientation on the atomic mechanisms of metal-organic vapor phase epitaxy (MOVPE) of GaN. These experiments employ a vertical-flow growth chamber with a fused quartz wall designed for real-time surface x-ray scattering. We use high energy x-rays from the Advanced Photon Source to penetrate the chamber walls and the reactive vapor phase. Here we compare growth behavior on polar +c-plane (0001), non-polar m-plane (10-10) [4], and semi-polar (20-21) surfaces, mapping the transitions between step-flow, layer-by-layer, and 3-dimensional homoepitaxial growth modes on these surfaces as a function of temperature and growth rate.

Further insights can be gained by comparing the experimental results with kinetic Monte Carlo simulations designed to model MOVPE growth. During growth on the m-plane surface, both simulations and x-ray scattering experiments show the presence of anisotropic islands elongated along <11-20>-type directions, whose spacing in [0001] as a function of flux follows a very weak (-1/4) power law dependence. The simulations allow us to understand how this anisotropic growth is related to underlying anisotropies in both the step edge energies and the diffusion kinetics.

With the expected continued increase in coherent flux at high x-ray energies delivered by advanced synchrotron radiation facilities, x-ray photon correlation spectroscopy and related techniques promise to become powerful tools for in-situ studies of synthesis, revealing the atomic-scale fluctuation dynamics [5] that underlies epitaxial growth. We present simulations of speckle dynamics in coherent scattering from surfaces, both at equilibrium in the growth environment at high temperature, and during non-equilibrium crystal growth. Initial exploration of surface coherent diffraction imaging will also be discussed.

Work supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Division of Materials Sciences and Engineering.

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Alkali Antimonides: from Photocathodes to Solar Cells

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Alkali antimonide photocathodes have been the go-to option for low visible light photodetectors and image intensifiers for decades. These materials are relatively easy to grow and more robust to contamination than other options (Cs:GaAs). Recently they have been investigated for use as a high-current, low emittance electron source [1] for accelerator applications such as LCLS-II. These applications require high quantum efficiency and long operational lifetime, just as photodetectors do, but also require good correlation of the emitted electrons (low beam emittance). Unfortunately, while the traditional growth methods produce cathodes with a peak quantum efficiency in excess of 30%, these films are very rough [2], and this roughness impacts the beam emittance [3].

Using *in situ* x-ray analysis tools during growth [4], we have developed methods of growing alkali antimonide films with far less roughness than traditional methods – from an RMS roughness of 25 nm to a less than 1 nm. This process required understanding the formation chemistry of these materials through x-ray diffraction, while measuring the stoichiometry with x-ray fluorescence and the roughness with x-ray reflectivity. We discovered that the roughening of the surface occurred as the crystalline antimony was converted first into amorphous potassium antimonide, and then into crystalline potassium antimonide. We investigated several methods to avoid this step, including sputter deposition of this material (which, while well known for other ionic compounds, had not been demonstrated for the alkali antimonides).

Solving the roughness problem of the alkali antimonides does more than just enable higher brightness photoinjectors, however. It opens the possibility of these materials being used for more traditional semi-conductor applications. One natural application is photovoltaics, where the high optical density of these materials, coupled with the wide array of band gaps (0.7-1.6 eV) available within this material family, lead to very thin, very efficient materials. This presentation will cover both what has been accomplished through surface x-ray analysis in this material system, and the promise of things yet to come.

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X-ray waveguide optics and imaging at the nanoscale

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X-rays deeply penetrate matter and thus provide information about the functional (interior) architecture of complex samples, from biological tissues and cells to nanoscale composite materials. Until recently, however, this potential of hard x-rays in view of penetration, spatial resolution, contrast, and compatibility with environmental conditions was significantly limited by the lack in suitable x-ray optics. With the advent of highly brilliant radiation, and the development of lens-less diffractive imaging and coherent focusing, the situation has changed. Here we discuss how coherent optics and imaging can be implemented based on *compound reflective optics* including focusing mirrors and waveguides [1-5]. Besides full field imaging and tomography, we discuss coherent imaging of interfaces, including dynamic phenomena [6].

We explain how the central challenge of inverting the coherent diffraction pattern can be mastered by different reconstruction algorithms in the optical far and near-field. In particular, we present full field projection imaging at high magnification, recorded by illumination with advanced x-ray waveguide optics [2,5], and show how imaging and diffraction can be combined to investigate biomolecular structures within biological cells [5].

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Unlocking the power of 2D detectors in Surface X-ray diffraction: data reduction and visualization

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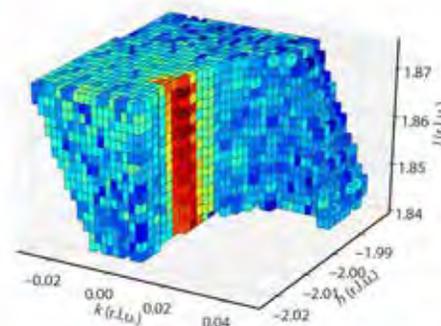
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Over the past decade there have been several developments that have radically changed data acquisition in X-ray diffraction experiments. The primary development is that nearly all point detectors have been replaced by two-dimensional detectors, that collect spatially resolved information from a region in reciprocal space in a single shot. Secondly, by synchronizing the data acquisition with the actuation of the diffractometer motors, it is now possible to perform continuous scans during diffractometer movements. However, the lack of knowledge of suitable data acquisition techniques or the absence of appropriate post data analysis methods not only means that the full advantages of using two-dimensional detectors may not be realized, but might also lead to misinterpretation of the experimental data.

In this contribution we discuss two integration methods to determine the structure factors along a surface diffraction rod measured with a two-dimensional detector [1]. The first method applies the classic way of calculating integrated intensities in angular space. This is adapted to work efficiently with two-dimensional data. The second method is based on integration in reciprocal space. An intensity map is created in the reciprocal space and the integration is then performed directly on this map. A theoretical framework, as well as a comparison between the two integration methods, is provided. Although integration in reciprocal space is a more universal approach, the integration in direct space is sufficient in many cases and does not require extensive programming and computational power.

To compute the reciprocal space maps in surface X-ray diffraction experiments we developed the BINoculars: a software tool for data reduction and analysis of large datasets that have been acquired with a 2D detector [2]. The intensity of each pixel of a two-dimensional detector is projected onto a three-dimensional grid in reciprocal-lattice coordinates using a binning algorithm. This allows for fast acquisition and processing of high-resolution data sets and results in a significant reduction of the size of the data. It has evolved from the specific needs of the ID03 beamline at the ESRF, but it has a modular design and can be easily adjusted and extended to work with data from other beamlines or from other measurement techniques. BINoculars is used to greatly improve the workflow of surface X-ray diffraction measurements and analysis as it unlocks the full power of two-dimensional detectors and helps visualize surface diffraction patterns to an extent that was previously only achievable with low-energy electron diffraction or by taking an impractical amount of time.



Example of BINoculars reciprocal space reconstruction.

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Oral Abstracts

Quantum Optics with X-rays using Thin-Film Cavities

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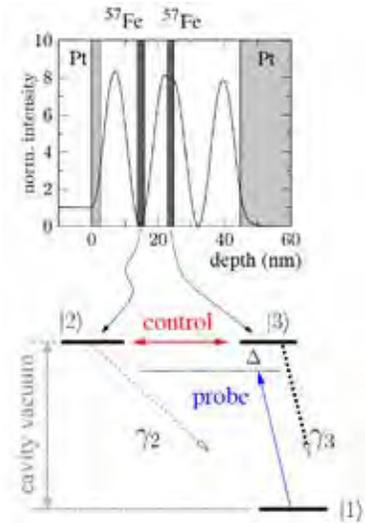
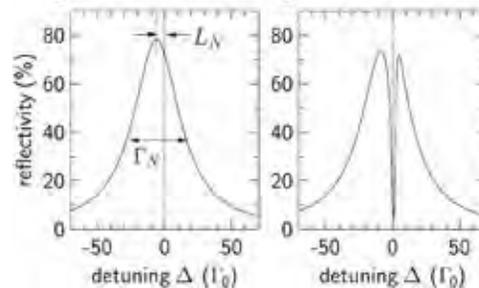
G-1

Planar thin-film waveguides have a long-standing history in x-ray physics [1]. Resonantly enhanced standing waves forming in the guided modes of such layer structures [2] have been used to amplify various signals originating from the x-rays in these modes, including fluorescence yield from metal atoms embedded in them [3], grazing incidence diffraction from thin films [4], and GISAXS from nanoparticles [5], to name a few. The coherent beam that leaves the waveguide at its exit has been used for x-ray imaging applications with sub-micron resolution [6].

A new research field, nuclear quantum optics, has been opened recently when ensembles of Mössbauer nuclei were coupled to the guided modes of x-ray waveguides. The cavity environment stimulates an enhanced exchange of real and virtual photons amongst the nuclei, leading to superradiance and a shift of the ensemble's nuclear resonance energy, the collective Lamb shift [7] (Fig.1, left). This experiment formed the starting point to transfer concepts of quantum optics into the regime of hard x-rays. One of the most intriguing phenomena of quantum optics is electromagnetically induced transparency (EIT): Exposing a medium to intense laser light of a certain wavelength makes it transparent for light of a different wavelength for which it would be completely opaque otherwise.

In our new approach to EIT, the interaction of two nuclear ensembles in a node and an antinode of the resonant wavefield in a cavity (Fig.2, top) leads to an almost complete cancellation of nuclear absorption, manifesting as a transparency window in the spectrum of the cavity reflectivity (Fig.1, right) with the same appearance as in optical EIT, indicating that the cavity has effectively converted the Mössbauer nuclei into 3-level systems [8].

Fig. 1: The left panel shows the collective Lamb shift L_N of resonant Mössbauer nuclei in a cavity. The right panel displays the EIT transparency window at zero detuning that shows up when two nuclear ensembles interact with the cavity field (see Fig. 2).



In this contribution I will explain the basics of nuclear quantum optics enabled by x-ray cavities, and discuss applications and perspectives.

Fig. 2: Layer configuration (top) and effective level scheme (bottom) of a cavity with two ^{57}Fe layers, resulting in nuclear EIT as displayed in Fig. 1, right panel.

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Oral Abstracts

Dynamic imaging of nanostructures using femtosecond X-ray laser pulses

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I-10

Interest in high-resolution, both in space and time, structure investigation has been zealous especially with the advent of X-ray free electron lasers (XFELs). The intense and femtosecond-short X-ray laser pulses have introduced new routes to explore structures and dynamics of single macromolecules, functional nano-materials and complex electronic materials. Femtosecond X-ray pulses capture atomic structures at nearly radiation-damage free conditions, which facilitates ambient temperature crystallography and environmental imaging. In the last several years, we have developed XFEL single-shot diffraction imaging to unveil internal structures of nano-bio composite particles and to visualize 3D structures of high-index Au nano-particles. Further, dynamic diffraction imaging was realized using femtosecond (<10 fs in FWHM) hard X-ray laser (probe) synchronized to the femtosecond (50 fs) optical laser (pump) at 1 ps resolution. Sequential procedures involved in structure deformations were directly visualized via coherent diffraction imaging (CDI) at several nm resolution. This XFEL pump-probe imaging provides new insight into the dynamic deformation process of nanoparticles. We expect this femtosecond dynamic imaging to open new science opportunity with XFELs.

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BornAgain: simulation and fitting framework for scattering experiments at grazing incidence and reflectometry

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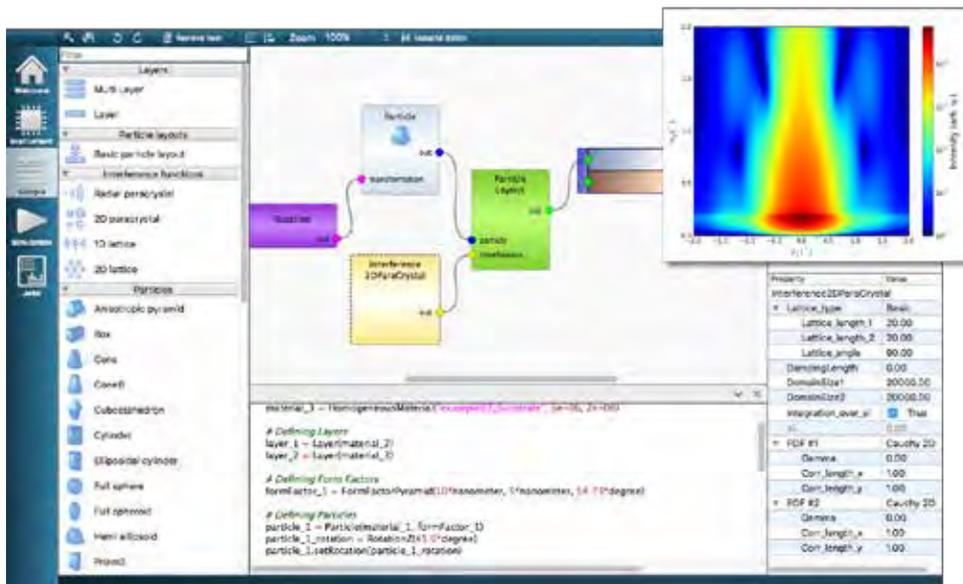
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C-9

A common software for simulation and data analysis in the field of surface X-ray and neutron scattering is of key importance for scientists running their experiments at various synchrotron and neutron facilities. BornAgain [1] is a free and open-source project that provides scientists with the means to simulate and fit their specular, off-specular and GISAXS data within a single framework. The name of the software, BornAgain, indicates the central role of the distorted-wave Born approximation in the physical description of the scattering process. The software is capable of modeling multilayer samples with smooth or rough interfaces, various types of embedded nanoparticles and various models to treat finite size effects and the coupling between the type and position of a particle. In this way, it reproduces and enhances the functionality of the well known IsGISAXS software [2]. BornAgain goes beyond IsGISAXS by supporting an unrestricted number of layers and particles, the diffuse reflection from rough layer interfaces, particles with inner structures, neutron polarization and magnetic scattering. Carefully designed for a broad community of users, BornAgain offers a modern graphical user interface with the possibility to perform real-time simulations and to fit experimental data. An advanced Python API lets experienced users create complex models. BornAgain is a multi-platform software released under the GPL3 license. It is adherent to object-oriented design, fosters a professional approach to software development and lays a solid foundation for future extensions in response to specific user needs.



BornAgain graphical user interface

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Oral Abstracts

Probing Dynamic Layer Rearrangement during the Growth of Ruddlesden-Popper Series Thin Films through Surface X-ray Scattering

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The (AO)(ABO₃)_n Ruddlesden-Popper homologous series, consisting of AO and BO layers, exhibits a wide variety of functionalities including dielectric, ferroelectric, magnetic, and catalytic properties. Unfortunately, the synthesis of such layered oxides has been a major challenge owing to the occurrence of growth defects that result in poor materials behavior in the higher-order members [1]. To understand the fundamental physics of layered oxide growth, we have developed a reactive molecular beam epitaxy system with in situ synchrotron X-ray surface scattering capability at Advanced Photon Source [2]. We present results demonstrating that layered oxide films can dynamically rearrange during growth, leading to structures that are highly unexpected on the basis of the intended layer sequencing [3]. Density functional theory calculations indicate that layer rearrangement can occur in many layered oxides and suggest a general growth strategy that may be essential for the synthesis of metastable Ruddlesden-Popper phases. Utilizing rearrangement, we perform the first atomically controlled synthesis of single-crystalline La₃Ni₂O₇ and higher-order members [4].

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Oral Abstracts

Reaching High-temperature Magnetism in Intrinsic Topological Insulator - Ferromagnetic Insulator Heterostructures

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New functionality often arises at the mesoscale at the interfaces. Generating exchange-induced ferromagnetism on the surface of a topological insulator (TI) with a ferromagnetic insulator (FMI) provides a clean approach for realizing many potential device applications exhibiting novel quantum functionality. We demonstrate a fundamental step towards realization of high temperature magnetization in TI and FMI heterostructures through observation of magnetic proximity-induced via the exchange interaction. We have successfully introduced the ferromagnetic order onto the surface of epitaxial Bi₂Se₃ films employing the ferromagnetic insulator EuS. Polarized Neutron Reflectometry allows to efficiently discriminate the magnetism at the surface of TI from the magnetization distribution in FMI layer and provides direct evidence that Bi₂Se₃-EuS heterostructures exhibit proximity-induced interfacial magnetization in the top 2 QL (~2 nm) layer of Bi₂Se₃. We show that this effect originates through exchange interaction, without structural perturbation at the interface.

The Bi₂Se₃ is spin polarized in the surface plane, accompanied by magnetic order in the immediate region of the interface and decaying into the TI layer. This interfacial ferromagnetism persists up to room temperature, even though the T_c of FMI (EuS) < 17 K. The induced magnetism at the interface resulting from the large spin-orbit interaction and spin-momentum locking property of the TI surface is found to greatly enhance the magnetic ordering (Curie) temperature of the TI/FMI bilayer system. Due to the short range nature of the ferromagnetic exchange interaction, the time-reversal symmetry is broken only near the surface of a TI, while leaving its bulk states unaffected [1].

The TI ferromagnetism is observed reproducibly in a variety of bi-layer samples with different combinations of thicknesses, providing a mechanism to control this effect. These findings of locally-induced ferromagnetic order on the TI surface extending over macroscopic areas without impurity doping open the door for an energy efficient topological control mechanism for future spin-based technologies. Work supported by U.S. DOE, Office of Science, BES.

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Oral Abstracts

Reduction in Tension and Stiffening of Lipid Membranes in an Electric Field Revealed by X-Ray Scattering

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The effect of ac electric fields on the elasticity of supported lipid bilayers is investigated at the microscopic level using grazing incidence synchrotron x-ray scattering. A strong decrease in the membrane tension up to 1 mN/m and a dramatic increase of its effective rigidity up to 300 k_BT are observed for local electric potentials seen by the membrane <1 V.

The experimental results are analyzed using detailed electrokinetic modeling and nonlinear Poisson-Boltzmann theory. Based on a modeling of the electromagnetic stress, which provides an accurate description of the bilayer separation versus pressure curves, we show that the decrease in tension results from the amplification of charge fluctuations on the membrane surface whereas the increase in bending rigidity results from the direct interaction between charges in the electric double layer.

These effects eventually lead to a destabilization of the bilayer and vesicle formation. Similar effects are expected at the tens of nanometers length scale in cell membranes with lower tension, and could explain a number of electrically driven processes.

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Biomimetic model membranes for investigation of membrane transport processes with reflectometry

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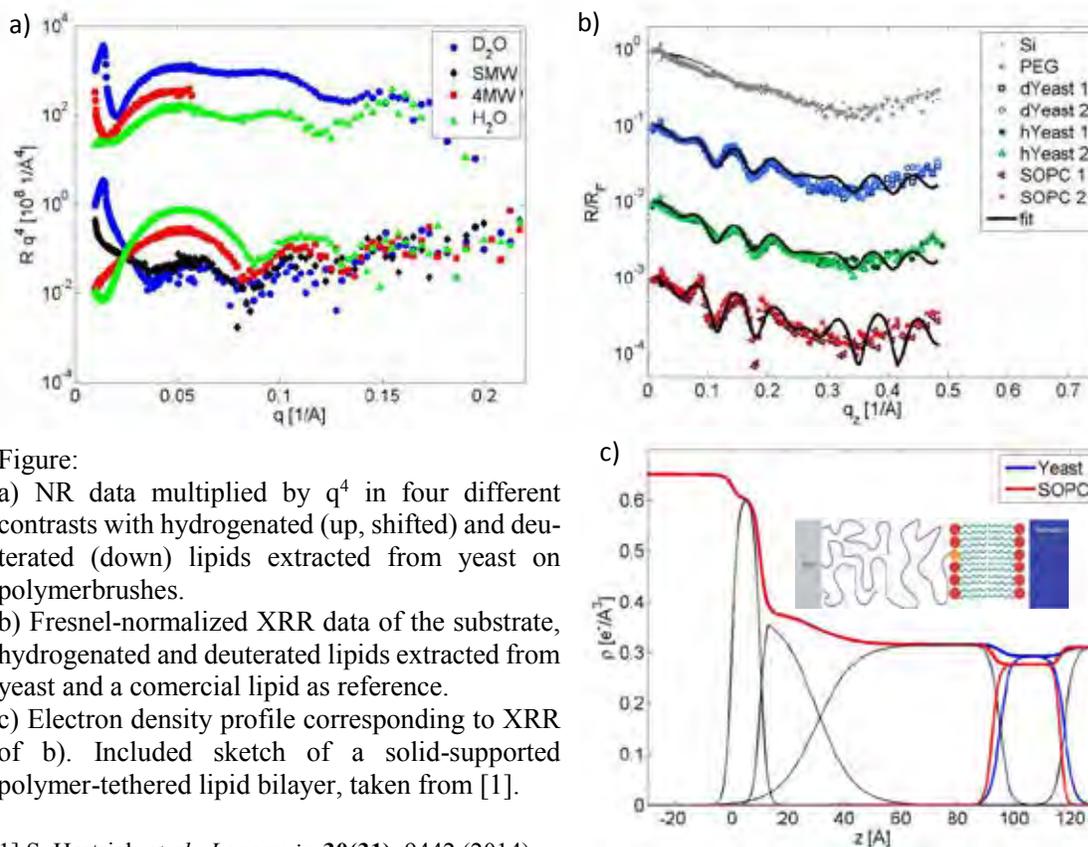
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C-12

Transport processes through membranes are fundamental for the biological function. To investigate these processes, e.g. transport of drugs into cells, it is necessary to build a reproducible and stable membrane model system, accessible for analytical methods. Surface-sensitive techniques as X-ray- or neutron reflectivity (XRR, NR) allow a high resolution investigation of solid-supported lipid bilayers that act as model membrane. In order to allow the penetration of guest molecules through lipid bilayers, it is necessary to use a highly hydrated spacer e.g. polymer brushes [1] or protein layer [2]. Furthermore, natural membranes are composed by several different saturated and unsaturated lipid species, which is in contrast to common model systems that use one or few commercially available lipid species. Extracted lipids from *Pichia pastoris yeast* [3] are used here in order to model a more natural mimicking membrane. The availability of natural extracts in both hydrogenated and deuterated forms allow the use of the so-called contrast variation method with neutrons.

We will present results from structural investigations on these model membranes with XRR, NR and complementary methods (AFM, fluorescence microscopy, QCM-D) in order to create reproducible, stable and tethered model membranes to allow the investigation of transport processes through membranes. A current challenge in the developing is to built membranes with a low roughness and waviness to enable high resolution studies with reflectometry.



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Oral Abstracts

Different effects of hydrophilic and hydrophobic silica nanoparticles on the dynamics of phospholipid films

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Silica nanoparticles (SiNP) of different hydrophilicity are used in drug delivery platforms to improve the stability and control the release rate of drugs. The fine-tuning of these systems requires detailed understanding of their dynamics. Recent X-ray reflectivity experiments [1] demonstrated opposite structural effects of hydrophobic / hydrophilic SiNP on phospholipids: hydrophilic SiNP stabilize the liquid-condensed phospholipid domains, while hydrophobic SiNP induce the formation of a highly ramified structure. While these structural effects are understood, much less is known about the effects on the dynamics of these layers, which in turn determine molecular diffusivity and the possibility of drug release.

We combined Grazing Incidence X-ray Photon Correlation Spectroscopy (XPCS) with microscopy tracking, and Epifluorescence Discrete Fourier Microscopy to cover a broad temporal and Q-range. In this way we characterized the dynamics of mixed Langmuir layers made of phospholipid (DPPC) and hydrophobic/hydrophilic SiNP (Fig. 1). In phospholipid/ hydrophilic SiNP layers we find –upon compression- a transition from Brownian diffusion to an arrested glassy phase of repulsive disks [2]. On the contrary, in phospholipid/ hydrophobic SiNP layers we obtain evidence for the onset of an arrested state characterized by intermittent stress-relaxation rearrangement events, corresponding to a 2D gel network dominated by attractive interactions [3]. We believe that this information shall help the development of new, highly refined drug-delivery platforms.

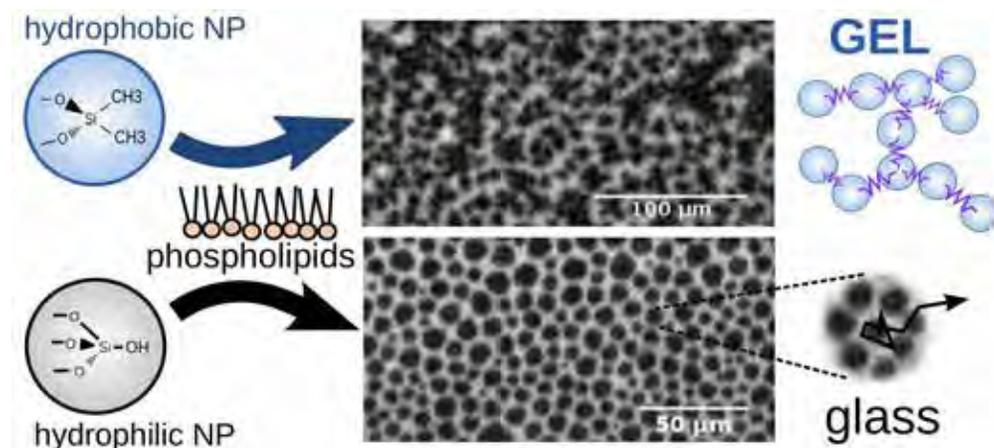


Fig. 1: artist's impression of the effects of Silica NP of different hydrophilicity interacting with phospholipid monolayers

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Oral Abstracts

Aggregation States of a Highly Bio-inert Polymer Blend at Water Interface by Neutron Reflectivity

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Some synthetic polymers exhibit excellent bio-inert properties, like poly(2-methoxyethyl acrylate) (PMEA). However, a universal explanation about the biocompatibility of polymers is far from clear due to a lack of structural information of the PMEAs/water interface. To apply interfacial-selective characterization techniques, the geometry of a thin film on a solid substrate is highly desired. However, a stable thin film of PMEAs is difficult to prepare due to its lower glass transition temperature. Thus, we have designed a mixture of PMEAs with a typical glassy polymer, poly(methyl methacrylate) (PMMA) [1]. Neutron reflectivity (NR) measurement was performed for the blend films in water on Soft Interface Analyzer (SOFIA at beam line No.16 in Materials and Life Science Facility, Japan Proton Accelerator Research Complex, Japan) [2,3]. Here, perdeuterated species of PMMA (dPMMA) and water were used. Figure 1(a) shows the scattering vector (q) dependence of NR for a PMEAs/dPMMA blend film contacted with D₂O. A solid curve denotes the calculated reflectivity on the basis of a model (b/V) profile shown in Figure 2(b). To simplify the fitting model, the film was divided into three layers, as shown in Figure 1(c). The PMEAs component was enriched at both D₂O and substrate interfaces. Panel (d) shows the depth dependence of the volume fraction for PMEAs and D₂O in the blend film in close proximity to the water interface. Since the blend film contains three components, PMEAs, dPMMA and D₂O, the profile is drawn by combining the NR data for the PMEAs/dPMMA blend film in D₂O with the one for the PMEAs/PMMA blend film in D₂O. In the region extending to 5 nm, the outermost region of the PMEAs/dPMMA blend film is composed only of PMEAs with D₂O. Sum-frequency generation spectroscopy revealed that the orientation of PMEAs segments at the water interface became random, resulting in an increase in the fractional amount of lower-coordination water molecules, including monomeric isolated waters, at the interface. We will show that the interfacial water structure and the polymer dynamics are related to the bio-inertness of PMEAs [2,3].

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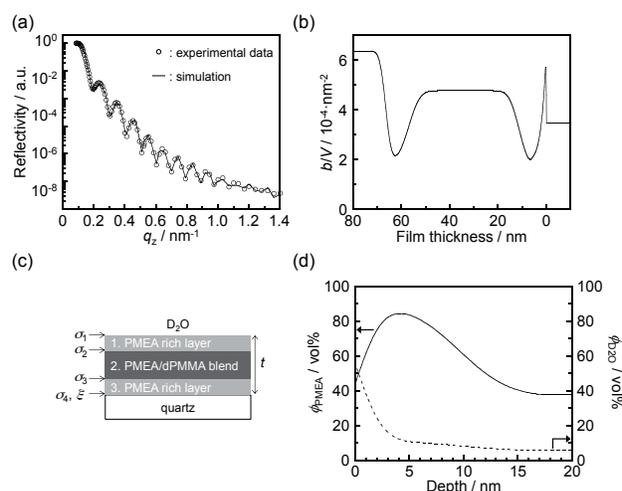


Figure 1. (a) NR curve for the PMEAs/dPMMA film in D₂O. A solid line is drawn on the basis of (b) the (b/V) profile of the blend film in D₂O. (c) A schematic illustration of the model used for fitting. Here, t , σ_1 and ξ represent the total thickness, roughness, and the decay length of D₂O molecules at the substrate interface, respectively. (d) Depth dependence of the volume fraction of PMEAs and D₂O in the blend film.

Combining Neutron or X-ray Reflectivity with Hydrogen-Deuterium Exchange Mass Spectrometry to Resolve Conformations of Membrane Associated Proteins

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Membrane association plays an essential role in the structure and regulation of many proteins. A common example is the conversion from a nonfunctional cytoplasmic form to a membrane-associated active form. In addition to promoting conformational changes, association of proteins with membranes can position motifs at specific distances from the membrane or in specific orientations to facilitate interactions with other proteins. Examples of important cellular processes that involve membrane-induced changes in protein structure include specific molecular recognition events that alter signaling and regulatory functions, the fusion of enveloped viruses with host cell membranes, budding of viruses from host cells, production of infectious virions, cytosolic delivery of bacterial toxins, and apoptosis. While X-ray crystallography and NMR are available to determine the structure of folded proteins in solution, few methods can resolve structural details for membrane-associated proteins. Recently neutron and X-ray reflection (NR and XR) have emerged as useful methods to derive structural information for membrane-associated proteins. However, while NR and XR provides the overall residue distribution normal to the membrane, information pertaining to specific residues is not available from these methods. Toward addressing this deficiency we combined NR and XR with hydrogen-deuterium exchange mass spectrometry (HDX-MS).¹⁻³ HDX-MS has proven useful in studying protein complexes and binding of drug molecules to proteins in solution. We combined these methods to study the structure of membrane-associated HIV Nef. Nef is an HIV-1 accessory protein and an essential factor in AIDS progression. Nef exists in both membrane-associated and cytosolic fractions. Membrane-association is achieved by an N-terminal myristoylation essential for the virus in vivo as well as a cluster of basic residues within the N-terminal arm. NR and XR revealed that upon insertion of the myristate and residues from the N-terminal arm, Nef transitions from a closed to open conformation that positions the core domain 70 Å from the lipid headgroups. Deuterium exchange of HIV-1 Nef was analyzed in solution and also when membrane-associated. Significant differences in deuterium uptake between the solution form and lipid-associated state reveal the disposition of an important regulatory loop and the oligomeric state upon binding. Hundreds of proteins are known to be lipidated and many are potential targets for therapeutic intervention. The present approach will be useful to resolve the membrane-bound conformations of these proteins, and to inform on the effects of protein-protein interaction at the membrane and disruption of said interactions with pharmacological agents.

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Oral Abstracts

Probing the structure and antibiotic susceptibility of yeast membranes using neutrons - effect of lipid composition on the mechanism of Amphotericin B

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TUE

I-14

Millions of people suffer invasive life-threatening fungal infections every year, but there are still only a limited number of antifungal agents, whose application is often restricted by toxicity, antifungal resistance and low bioavailability. The existing drugs, discovered several decades ago, target the fungal sterol ergosterol, either by preferentially binding to it in fungal membranes, or by preventing its biosynthesis. Ergosterol is key to their function but the precise mechanism of action, and how it is related to the toxic side effects is still a matter of debate. A fuller understanding of the mode of functioning of the current drugs is critical for designing better, safer antifungal therapeutics.

Amphotericin B (AmB) has the broadest spectrum of antifungal activity and has been used as an antibiotic against systemic fungal and parasitic infections for more than 50 years without the development of significant microbial resistance. AmB interacts preferentially with ergosterol, but also to a lower extent with cholesterol, giving rise to toxic side effects that are often dose-limiting and still represent a major problem.

The vast majority of biophysical AmB studies have been carried out on model membranes consisting mainly of synthetic phospholipids. The complex lipid composition of natural cell membranes is however essential for biological functions and influences the membrane structural organisation. We have recently carried out a detailed characterization of the lipid composition and structure of reconstituted fungal membranes from *Pichia pastoris* yeast[1], as well as the structural consequences of AmB[2] using neutron reflection. The structure of yeast membranes differs considerably from typical model lipid bilayers composed of synthetic lipids and depends on the degree of lipid polyunsaturation. AmB inserts in yeast membranes both in the absence and presence of ergosterol, and our results confirm directly that AmB forms an extramembraneous aggregate, proposed recently to act as an ergosterol-extracting sponge[3]. In contrast, AmB has only a limited interaction with typical model lipid membranes composed of POPC, but is activated by addition of PLPC in which the sn2-oleyl (C18:1) chain has been replaced by the doubly unsaturated linoleyl (C18:2) chain.

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Two-dimensional assembly of gold nanoparticles at vapor/liquid interfaces

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Various experimental conditions, such as subphase contents, pH, surface charge density, have been employed to assemble nanoparticles (NPs) into orderly 3D and 2D structures [1-6]. Here, we use liquid surface scattering and spectroscopy techniques to unravel the multi-parameter space of 2D assembly of AuNPs in both Langmuir monolayer and Gibbs monolayer scenarios. It is found that the ionic content is crucial in regulating the interfacial assembly. For instance, divalent ions Mg^{2+} and Ca^{2+} efficiently promote the adsorption of DNA-capped nanoparticle to an air/water interface, and at a threshold concentration even lead to 2D crystallization. The grazing incidence x-ray reflectivity (XR) and small-angle scattering (GISAXS) provide the in-depth and in-plane structure of the AuNPs. Moreover, the grazing incidence fluorescence spectroscopy provides direct evidence of the surface AuNPs aggregation mediated with divalent ions (i.e. Ca^{2+}). Quantitative analysis reveals that divalent cations screen the charge of ssDNA, and that the hydrophobic hexyl-thiol group commonly used to functionalize the ssDNA (for capping the AuNPs) is likely the driving force for the accumulation of the NPs at the interface. Our finding as that of others [6] shows that the DNA plays a role of a simple polyelectrolyte. We have thus extended our study beyond DNA-capped AuNPs systems and have successfully assembled 2D ordered structure of polymer-capped AuNPs.

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Ionic Liquids at Interfaces

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WED

C-15

Room temperature ionic liquids [ILs] are an important class of new solvents often considered as environmentally friendly media for chemical processes [1]. Accordingly, a large number of applications in several fields of science and technology [2] have been proposed [5]. ILs consist solely of ions which bulky and irregular shape, often comprising hydrocarbon chains and rings, inhibits solidification near room temperature [1]. The peculiar physicochemical properties of ILs are often associated with their mesoscopic organization or local order [6] and with the formation of nanostructured domains resulting from the self-aggregation of the apolar and polar components of the ILs into domains [7]. Detailed knowledge of the structure of the interface of ILs is also of major importance to the rational design of ionic-liquid-based chemical processes. In fact many of these processes depend of the ions organization at the interface. We propose to obtain a better understanding of the behavior of ILs at interfaces by studying two kinds of systems: the free surface of bulk ionic liquid, and thin films at the air-water interface through the Langmuir procedure. We will present results obtained on Langmuir monolayers of ILs by π -A isotherm, Brewster Angle Microscopy, Grazing Incidence X-ray Diffraction and Fluorescence and on the free surface of ILs by surface pressure measurements, X-ray surface scattering and fluorescence. The structure obtained will be compared with the structure of bulk ILs and computer simulations.

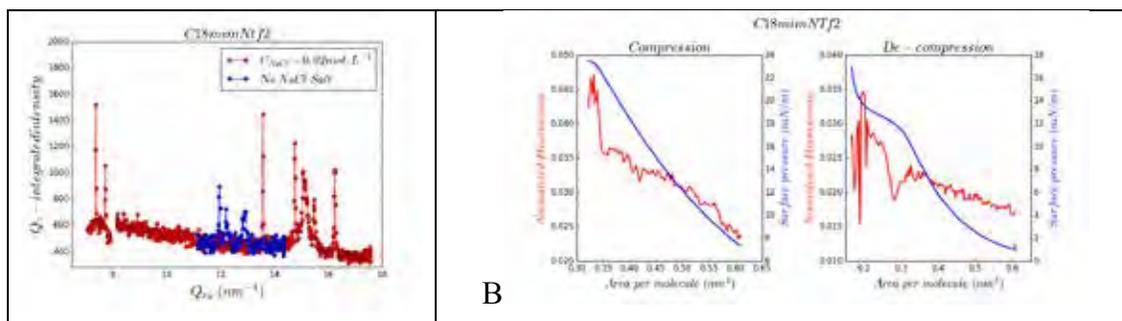


Fig. 1 – A: Q_z -integrated GIXD spectrum at $\pi=24\text{mN/m}$ of a Langmuir monolayers of ionic liquid C18mimNTf2 on aqueous subphase with and without NaCl. B: $K\alpha$ Sulfur fluorescence evolution and surface pressure with area per molecule of a Langmuir monolayer of ionic liquid C18mimNTf2 during compression and de-compression of the monolayer. The sulfur atom belong to the NTf2 counterion.

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Oral Abstracts

Alkyl chain length dependence of the interfacial structure of ionic liquids: From Coulomb to van der Waals domination

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Room-temperature ionic liquids (RTILs), an important new class of solvent-free electrolytes and reaction media, have many applications involving interfaces. Comprising a large variety of interactions, they are of great interest for basic science as well, particularly under the topological constraints imposed on their structure by various interfaces. While RTIL interfaces have been intensely studied over the last decade, including by Angstrom-resolution x-ray methods [1], a systematic molecular-resolution study of the evolution of the interface structure with the cation's alkyl chain length over a broad homologous RTIL series is still missing. Following a brief introductory overview of the field, we will present a high-resolution x-ray study [2] of the evolution with chain length of the RTIL/air interface structure for a homologous series of RTILs with alkyl chain lengths ranging from 2 to 22 carbon atoms. This study highlights the evolution from a surface structure dominated by the Coulomb interaction of the headgroups to that dominated by the van der Waals interaction of the alkyl tails. For the same homologous series, x-ray measurements of the RTIL/sapphire interface structure will also be briefly presented.

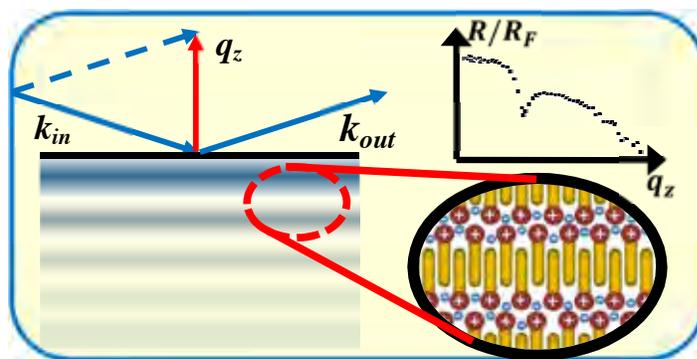


Fig. 1: (Left) Cartoon showing the interfacial layering and x-ray reflectivity geometry. (Right) Top: Typical Fresnel-normalized reflectivity curve. Bottom: Molecular cartoon of the derived interfacial layering for the longer chains. The rod and circles are, respectively, the interdigitated chains (not necessarily surface-normal or fully extended) and charged moieties.

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Oral Abstracts

Temperature- and potential-dependent structure of the mercury-electrolyte interface

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The atomic-scale structure of the mercury-electrolyte (0.01 M NaF) interface was studied as a function of temperature and potential by x-ray reflectivity and x-ray diffuse scattering measurements. The capillary wave contribution is determined and removed giving access to the intrinsic electron density profile at the interface, especially to the surface layering in the Hg phase. A temperature dependent roughness anomaly known from the Hg-air interface is found to persist also at the Hg-electrolyte interface. Additionally, a temperature dependence of the layering period was discovered. The increase in the layer spacing with increasing temperature is approximately four times larger than the increase expected from thermal expansion. Finally, the interface is found to broaden

towards the electrolyte side as the potential becomes more negative, in agreement with the Schmickler-Henderson theory. Our results favour a model for the interface structure, which is different from the model formerly used in comparable studies.

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WED

G-16

Molecular Scale Structure and Dynamics of Concentrated Electrolytes at Charged Interfaces

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WED

I-16

How ions interact with charged surfaces and interfaces is crucial to many scientific and technological phenomena, such as electrochemical energy storage, biomineralization and liquid-liquid extraction. Although the century-old Gouy-Chapman theory works sufficiently in numerous circumstances, it usually breaks down at high ionic concentrations or when mixture of ions with different valencies and sizes coexist. Therefore, direct structural observations of such systems at nanoscale, supported with molecular dynamics (MD) simulations, is necessary to advance our limited knowledge and support new technologies in a wide range of applications.

Firstly, we will discuss the potential dependent structure and dynamics of room temperature ionic liquids (RTILs), which are essentially molten salts with very high ionic concentration [1, 2]. In situ, real-time X-ray reflectivity (XR) integrated with fully atomistic (MD) simulations elucidate the interfacial ionic liquid structure and dynamics at epitaxial graphene electrode during cyclic voltammetry and potential steps. Our results suggest that the graphene-RTIL interfacial structure is bistable in which the EDL structure at any intermediate potential can be described by the combination of two extreme-potential structures whose proportions vary depending on the polarity and magnitude of the applied potential. This picture is supported by the EDL structures obtained by MD simulations at various static potentials. The potential-driven transition between the two structures is characterized by an energy barrier (~ 0.15 eV) that is independent of temperature. The model nicely explains the coexistence of distinct anion and cation adsorbed structures and provides further insights to ultra-slow response of the interfacial structure to potential steps.

Secondly, we will examine the competition between monovalent Cl^- and divalent chlorometallate anions (PtCl_6^{2-} and PdCl_4^{2-}) at amine functionalized surfaces, which is highly relevant to liquid-liquid extraction technologies used in majority of global rare earth and precious metal production, as well as processing of other heavy elements, such as actinides. Unlike the adsorption of metal cations that is driven by dative (i.e. coordinating) interactions with ligating groups on the surface, anions are extracted via a competitive 'anion exchange' mechanism. Based on electrostatics, the divalent ions should adsorb more strongly; however, higher charge density (charge/molecular volume) of Cl^- should play a role in the opposite direction. In situ XR experiments reveal that the electrostatics is the dominant factor even at significantly high Cl^- concentrations.

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Oral Abstracts

Transmission surface diffraction: a novel method for operando studies of electrochemical interfaces

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WED

C-17

A new surface diffraction method for in situ studies of electrochemical interfaces is presented, which employs synchrotron X-ray radiation of high photon energy and, instead of using grazing incidence angles [1], a transmission geometry where the X-ray beam passes through the sample. Transmission surface diffraction (TSD) is a powerful and user-friendly method that enables simultaneous imaging of the full in-plane structure of solid surfaces. It furthermore allows surface X-ray diffraction studies with micrometer spatial resolution, opening up the way to map the atomic interface structure of spatially inhomogeneous systems or to study the surface properties of small samples. The feasibility of this approach is demonstrated by TSD measurements of Co electrodeposition on Au(111) electrodes [2], performed at beamline ID 31 of the ESRF. The formation of the Co crystal truncation rods (CTRs), shifts in the Au CTRs due to epitaxial strain, and the disappearance of the rods corresponding to the $(22 \times \sqrt{3})$ phase of the Au surface reconstruction can be directly observed without lengthy searches in reciprocal space. In addition, in situ microscale mapping of the deposit and substrate properties and studies during Co dissolution are discussed.

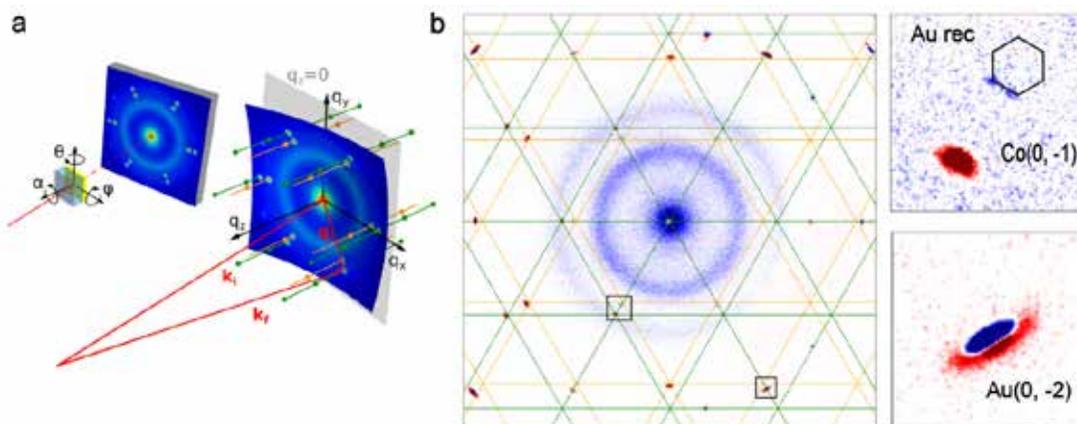


Fig. 1 (a) Real space and reciprocal space geometry of TSD. (b) In situ TSD of Au(111) in 0.1 M NaClO₄ + 1.3 mM HCl + 1mM CoCl₂, recorded at 40 keV. Shown is the intensity difference between detector images of the Au sample at -0.2 V_{Ag/AgCl} and after electrodeposition of a 20 ML thick epitaxial Co(001) film at -1.05 V_{Ag/AgCl}.

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Oral Abstracts

Nanoscale Structure of Si/SiO₂/Organics interfaces

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Single-crystalline silicon is by far the most widely used substrate for the deposition of organic thin films. Its surface is invariably terminated by a few nanometer-thick amorphous native SiO₂ layer. The structure of the transition layer between the silicon and its oxide is neither well characterized nor well understood at present.

Using high-resolution x-ray reflectivity measurements of increasingly more complex interfaces involving silicon (001) substrates, we reveal the existence of a low-density, few-Ångstrom-thick, transition layer at the Si/SiO₂ interface [1]. The importance of accounting for this layer in modeling silicon/liquid interfaces and silicon-supported monolayers is demonstrated by comparing fits of reflectivity curves by models including this layer and the widely used Tidswell model [2], which does not include this layer (see Fig. 1). The 6-8 electrons per silicon unit cell area missing in the transition layer support previous theoretical models and simulations of the Si/SiO₂ interface [3].

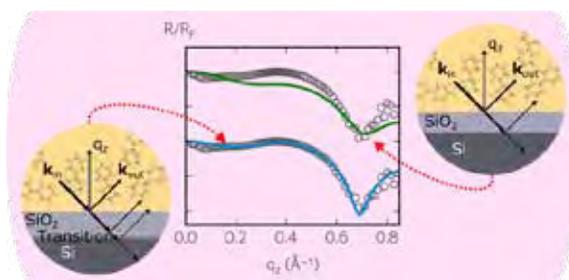


Fig. 1: Measured, Fresnel-normalized, X-ray reflectivity (symbols) from a silicon/bicyclohexyl solid/liquid interface. Lines show fits to a distinct oxide layer, excluding (green) and including (blue) a depletion layer at the SiO₂/silicon interface. The corresponding real space schematics are shown on the left, and right, respectively.

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Oral Abstracts

Orbital Polarization Driven by Anisotropic Hybridization in a Nickelate Heterostructure determined by Resonant Inelastic X-Ray Scattering

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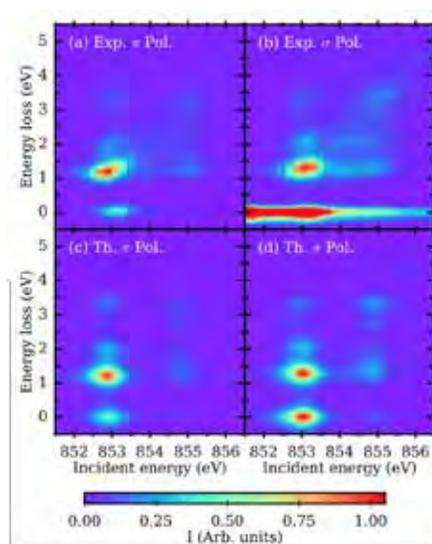
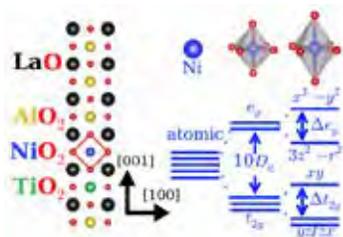
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Heterostructures built from one-unit-cell thick layers of transition metal oxides (TMOs) represent an exciting opportunity to design new electronic states with improved properties. LaNiO₃-based systems are a prototype for such efforts ever since it was predicted that it might be possible to reconstruct its electronic structure into a state that is analogous to the cuprate high temperature superconductors [1]. This involves breaking the symmetry of the initially degenerate e_g states to generate a half-filled 3d x²-y² ground state and an unoccupied 3z²-r² orbital – generating what is called “orbital polarization”. To date, these effects have been interpreted in terms of changing the energies of the orbitals, which naturally causes preferential occupation of the lower energy orbital. We use Ni L-edge resonant inelastic x-ray scattering to determine the Ni electronic configuration in LaTiO₃/LaNiO₃/(LaAlO₃)₃ heterostructures, a model system with exceptionally large orbital polarization [2] shown in Fig. 1. We find that charge transfer from Ti to Ni drives LaNiO₃ out of its initial itinerant state into a localized Ni d⁸-ligand hole state that we model in detail using multiplet calculations plotted in Fig. 1. Surprisingly, octahedral elongation generates only minor changes in the Ni 3d crystal fields that were previously thought to be the driving force behind the observed large orbital polarization. Instead, orbital polarization is caused by an anisotropic reconstruction of the Ni 3d – O 2p states, in which the 3d x²-y² orbital is significantly more hybridized with O 2p than the 3d 3z²-r² [3]. We therefore suggest that efforts to target new electronic properties that require large orbital polarization focus on anisotropic hybridization, rather than orbital energy levels, in order to generate the largest effects.

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Figure 1: Left: the basic structural unit studied here composed of LaTiO₃, LaNiO₃ and LaAlO₃ layers in a 1:1:3 ratio with a related Ni orbital energy level diagram. Right: RIXS measurements of the heterostructure (a)&(b) plot the measured intensity with π and σ polarized incident x-rays. (c)&(d) plot our corresponding multiplet calculations for the two different polarizations.



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Oral Abstracts

Reduced diffusion dynamics of polymer thin films near graphene oxide surfaces: neutron reflectivity studies

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Neutron reflectivity (NR) technique was used to study the diffusion dynamics of polymer chains confined between graphene oxide (GO) layers. The densely packed 2-D monolayers of graphene oxide were prepared on 3-inch substrates for neutron reflectivity samples by applying Langmuir–Schaefer or Langmuir–Blodgett technique. The bilayers of polymethylmetacrylate (PMMA)/ deuterated PMMA (d-PMMA) films and polystyrene (PS)/d-PS films with various film thicknesses were then sandwiched between graphene oxide monolayers. The PMMA/dPMMA bilayers between the solid PS layers also prepared for the comparison. From the NR results, we found that the diffusion dynamics of the PMMA thin films was reduced near the GO surface while that for the PS was not significantly changed. The PMMA diffusion dynamics sandwiched between the PS layers became even faster as the thickness of the PMMA/dPMMA bilayers decreased. This difference is due to the various interactions between polymers and solid surfaces (the GO or the PS layer). In this talk, these diffusion results will be compared with dewetting dynamics of polymer thin films on the GO monolayers. Since dynamics of the confined polymer thin films between graphene sheets is closely correlated to thermal stability issues for graphene-based nanoelectronic device applications, this study could provide a route for improved lifetimes of heterojunction devices for polymer photovoltaic (OPV) applications.

Grazing-Incidence X-Ray Scattering From Thin Polymer Films

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Grazing-incidence X-ray scattering is widely used to analyze crystallinity and nanoscale structure in thin polymer films. However, ionizing radiation will generate free radicals that initiate cross-linking and/or chain scission, and such damage can impact ordering kinetics, thermodynamics, and crystallinity in many polymers. We describe a simple methodology to screen for damage that is based on lithographic principles: thin films are exposed to patterns of x-ray radiation, and changes in polymer structure are revealed by immersing the film in a solvent that dissolves the shortest chains¹. Experiments are implemented at high throughput using standard beam line instrumentation and a typical grazing-incidence configuration². The extent of damage (at fixed radiation dose and photon energy) depends on a range of intrinsic material properties and experimental variables, including the polymer chemistry and molecular weight, exposure environment, film thickness, and angle of incidence. Simulations of the energy profile through the film thickness (using the distorted-wave Born approximation) explain many of the observed trends. The “solubility switch” for common polymers is detected within 10–60 sec at ambient temperature, and we verified that this first indication of damage corresponds with the onset of network formation in glassy polystyrene and a loss of crystallinity and functionality in polyalkylthiophenes³. Therefore, grazing-incidence X-ray “patterning” offers a simple approach to optimize data acquisition times for small-angle and wide-angle experiments.

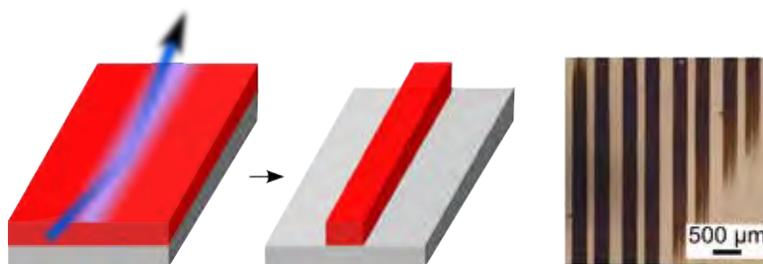


Figure 1: When irradiated at a shallow angle of incidence (7.35 keV photons), a thin film of polystyrene is rapidly cross-linked into a network. The damage is revealed by immersing in toluene, which washes away the un-exposed areas of the film.

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Wetting, alignment and roughness - lamellar phases at solid interfaces

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Amphiphiles form liquid crystalline mesophases at high concentrations in aqueous solution. One example is the formation of lamellar structures of surfactant bilayers. Solid boundaries perturb these structures in interesting ways. This talk will describe two different types of surfactants that form structures which align strongly at a boundary. Theoretical descriptions indicate that fluctuations of the lamellar layers are important as regards stability¹. The anionic surfactant aerosol-OT forms layers that are separated by water and a composition that represents a volume fraction of about 0.1 wets a range of different interfaces and aligns even when the bulk concentration is much lower². The intensity of the Bragg peaks can be used to estimate the flexural modulus. Static perturbations such as interface roughness change the structure. New data for a non-ionic surfactant, C₁₂EO₄ in D₂O with three different roughness are shown in Figure 1. Scattering has allowed the degree of alignment to be investigated. Comparison with spherical filler particles that are known to strongly perturb the phase behaviour will be presented.

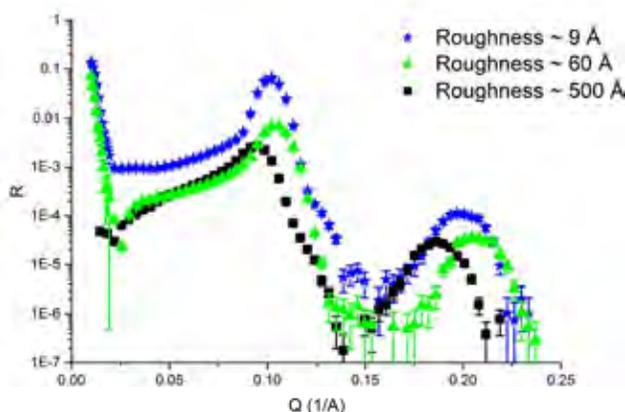


Figure 1. Reflectivity for C₁₂EO₄ in D₂O (mass fraction 0.55) at silica surfaces with different roughness³.

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Effect of Chain Architecture on the Interdiffusion in Thin Polymer Films

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Branched polymer chains have been widely used in industrial applications as additives. In recent years, they are also used in biomedical applications [1], controlled drug release [2,3], electrochromic displays [4], pressure sensitive adhesives [5], and in photoresists [6,7]. In these applications where they are confined in thin layers, it is important to understand the mobility of branched polymers under confinement to be able to determine the processing conditions. Interdiffusion measurements for bilayer thin films can provide the vertical mobility of polymer chains across the interfaces. Earlier studies investigated the diffusion between the layers of linear chains [8] and layers of cyclic chains [9] using neutron reflectivity (NR). Eliminating the chain ends clearly altered the diffusion characteristics of cyclic chains compared to their linear counterparts [9] and demonstrated the key role of the chain architecture on mobility.

Here we have investigated the effect of the number of arms and arm molecular weight on the diffusion in thin polymer films using star and linear polymers of same total molecular weight by NR. Diffusion of either 4-arm or 8-arm star polystyrene (PS) and deuterated PS chains is studied in a bilayer geometry with various film thicknesses to understand the effect of the confinement on each star PS as well.

Our measurements indicate that for the same total molecular weight, 8-arm chains have higher mobility than 4-arm and linear chains for the whole thickness range studied. This is expected since the viscosity of 8-arm chains is smaller than the viscosity of both 4-arm and linear chains. For 8-arm and 4-arm chains as the films get thinner the diffusion coefficient seems to get slightly smaller first but the difference is not significant compared to their linear counterparts. As the film thickness decreases further to roughly 1.5 Rg for bottom and top layers then the diffusion of branched chains get faster again.

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THU

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Surface X-ray Scattering Probes Dynamical Anomalies of Polymer grafted Nanocolloids in Polymer Films

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One of the central dogmas of fluid physics is the no-slip boundary condition, whose validity has come under scrutiny, especially in the fields of micro and nano-fluidics. Although various studies show the violation of the no-slip condition its effect on flow of colloidal particles in viscous media has been rarely explored. Using a combination of techniques including X-ray photon correlation spectroscopy (XPCS) we report unusually large reduction of effective viscosity experienced by polymeric nano-colloids moving through a highly viscous and confined polymer, well above its glass transition temperature. The extent of reduction in effective interface viscosity increases with decreasing temperature and polymer film thickness. Concomitant with the reduction in effective viscosity we also observe apparent divergence of the wave vector dependent hydrodynamic interaction function of these colloids with an anomalous power law exponent of ~ 2 at the lowest temperatures and film thickness studied. Such strong hydrodynamic interactions are not expected for polymeric colloidal motion in polymer melts. We suggest hydrodynamics, especially slip present at the colloid-polymer interface which determines the observed reduction in interface viscosity and presence of strong hydrodynamic interactions. Our observations point to rich Physics at play in such complex confined fluids and the role played by combination of surface X-ray scattering techniques - using both coherent and incoherent X-rays- in providing critical insight into these phenomena.

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Photothermal Assembly of Block Copolymers

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This talk will discuss recent work on the use of photothermal methods to control the ordering of block copolymer thin films. Photothermal methods can be used to generate temperature gradients and shear fields, which have a strong influence on block copolymer assembly. Self-assembly can be accelerated, and morphology can be aligned. These methods also highlight the non-equilibrium, pathway-dependence of self-assembly. We present examples of exploiting these effects to control alignment, and to iteratively construct arbitrary lattice symmetries. Grazing-incidence small-angle x-ray scattering (GISAXS), including a grazing-transmission variant (GTSAXS), are used to characterize order in these nano-materials.

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I-20

Anisotropic de Gennes narrowing in confined fluids

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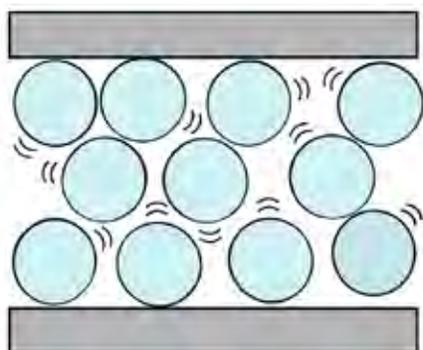
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Spatial confinement induces anisotropy in the fluid's pair distributions [1], which is expected to show up as strongly direction-dependent collective diffusion. However, verification of this hypothesis is missing. We have recently developed methodology for probing anisotropic structure factors [2] and density fluctuations [3] in spatially confined fluids, based on small-angle x-ray scattering (SAXS) from colloid-filled nanofluidic containers. Here we extend the methodology for simultaneous high-energy SAXS and x-ray photon correlation spectroscopy studies on the static structure and the collective diffusion in confined fluids [4]. We find the collective diffusion to be wave vector dependent, scaling as the inverse of the static structure factor, similar to de Gennes narrowing typically observed in bulk fluids. In stark contrast to isotropic bulk fluids, however, the static structure factor is anisotropic for confined fluids. Consequently we also observe anisotropic de Gennes narrowing in confinement. These experimental observations are essential in order to develop a microscopic theoretical description of collective diffusion of dense fluids in confined geometries.

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High-resolution Grazing-incidence X-ray Scattering for Three-dimensional Structures in Thin Films and Buried Nanostructures

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Grazing-incidence X-ray Scattering (GIXS) can provide invaluable data to reveal structure of surfaces, interfaces and thin films. Here, a deeper understanding of GIXS will be discussed beyond how GIXS is typically analyzed nowadays. The general perception has been that GIXS data yields mostly the in-plane structure and its correlation in planar and thin film samples, for example, defects and disordering in 2D nanoparticle superlattices. To obtain the structure information of nanometer or even sub-nanometer resolution along the 3rd dimension, one may take advantage of the interference of the scattering from parallel surfaces of a thin film to enhance or reduce the scatterings from certain depths of the film (so called X-ray standing wave or waveguide effect). That requires both a high-resolution grazing-incidence instrument and an appropriate surface scattering theory for the data analysis. The multi-layer DWBA theory we have developed takes into account the depth-dependent electric field intensity profile [1], and thus it affords a nanometer or even sub-nanometer spatial resolution on the depth information of the buried nanostructures, along with the in-plane correlation of the structures. Examples will be provided on self-assembled block-copolymer thin films [2] and nanoparticle membranes [3].

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Poster Presentation Abstracts





Poster Presentation List

Poster	Presenting Author	Institution	Title
P-1	Adlmann, Franz	Uppsala Universitet	'Överlåtaren' a fast way to transfer and orthogonalize 2D offspecular reflectivity data in q-space
P-2	Anada, Masato	Osaka University	Reverse Monte-Carlo analysis of CTR data from perovskite-type oxide thin films
P-3	Ankner, John	Oak Ridge National Laboratory	Deuteration, Mass Balance, and Constrained Models: Comprehending Polyelectrolyte Chemistry using Neutron Reflectometry
P-4	Arnold, Thomas	Diamond Light Source Ltd.	Surfactant and Phospholipid behaviour on the surface of Deep Eutectic Solvents
P-5	Barbour, Andi	Brookhaven National Laboratory	Study of Electrochemical Oxidation and Reduction of Pt(111) Using X-ray Crystal Truncation Rods Acquired with an Area Detector
P-6	Barkley, Deborah	Stony Brook University	Chain conformation near the substrate interface in nanoparticle stabilized polymer thin films
P-7	Basutkar, Monali	The University of Akron	Tuning Ordering Dynamics for Orientation Control in Cold Zone Annealed Block Copolymer Thin Films
P-8	Begam, Nafisa	Indian Institute of Science	Kinetics of dispersion of nanoparticles in thin polymer films at high temperature
P-9	Browning, Jim	Oak Ridge National Laboratory	Using Neutron Reflectometry to Investigate Solid-Electrolyte Interphase Formation, in situ, in Energy Storage Materials Formation, in situ, in Energy Storage Materials
P-10	Bu, Wei	University of Chicago	High Energy X-ray Scattering in the Reflection Model from a Rare Earth Ion Aqueous Solution
P-11	Cao, Chuntian	SLAC National Accelerator Laboratory	In-situ study of silicon electrode lithiation via X-ray reflectivity
P-12	Choi, Yongseong	Argonne National Laboratory	Correlating interfacial octahedral coupling with electronic properties in nickelate heterostructures
P-13	Chu, Miaoqi	Northwestern University	Direct observation of anion crowding at an electrode-ionic liquid interface using X-ray reflectivity
P-14	Coati, Alessandro	Synchrotron SOLEIL	In-situ study of AuCu NanoParticles epitaxied on TiO ₂ (110): Synthesis, structure and behaviour at low pressure of reactant
P-15	Coati, Alessandro	Synchrotron SOLEIL	Surfaces and Interfaces X-ray Scattering (SixS) beamline at SOLEIL
P-16	Coppola, Roberto	ENEA-Casaccia	Small-angle scattering studies of irradiated steels for nuclear applications
P-17	De Jeu, Wim	DWI–Leibniz Institute for Interactive Materials	Thin films of substituted thiophenes: Order and frustration
P-18	Dogan, Susanne	DELTA, TU Dortmund	pH- and surface pressure-depend adsorption of human apolipoprotein A1 at solid/liquid- and gas/liquid-interfaces.
P-19	Dugger, Jason	Oak Ridge National Laboratory	Determining the Electromechanical Response Mechanism of Nanostructured Ionic Block Copolymers
P-20	Festersen, Sven	Kiel University	Utilization of curved edges for XRR measurements on liquid samples
P-21	Fister, Tim	Argonne National Laboratory	Solvation, sorption, and electrodeposition in multivalent batteries
P-22	Fontaine, Philippe	Synchrotron SOLEIL	Semifluorinated Alkanes Monolayer at the Air Water Interface
P-23	Fontaine, Philippe	Synchrotron SOLEIL	SIRIUS: GIWAXS, GISAXS and surface spectroscopy beamline in the tender x-ray range at SOLEIL Synchrotron

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P-24	Forov, Yury	DELTA, TU Dortmund	Ions at hydrophobic interfaces
P-25	Fukuto, Masafumi	Brookhaven National Laboratory	Transmission X-ray Scattering as a Probe for Complex Liquid-Surface Structures
P-26	Garreau, Yves	Synchrotron SOLEIL and CNRS-Université d'Orléans	In-situ Anomalous X-ray Scattering: Chemical Order in AgCo Nanoparticles during Growth and Annealing
P-27	Gura, Anna	Stony Brook University	Investigation of Domain Behaviour in PbTiO ₃ /SrTiO ₃ Superlattices using X-Ray Diffraction Methods
P-28	Haddad, Julia	Bar-Ilan University	Order and Melting in Self-Assembled Alkanol Monolayers on Amorphous SiO ₂
P-29	Han, Young-Soo	Korea Institute of Geoscience and Mineral Resources	Synchrotron X-ray Beam-Induced Oxidation/Reduction of Arsenic during As K-edge X-ray Absorption Spectroscopy Measurements
P-30	Headrick, Randall	University of Vermont	NLSL-II beamline for Integrated In-Situ and Resonant X-ray Studies (ISR)
P-31	Hejral, Uta	Deutsches Elektronen-Synchrotron (DESY)	Tracking the shape-dependent sintering of Pt-Rh model catalysts under operando conditions
P-32	Hori, Koichiro	High Energy Accelerator Research Organization	Aggregation Structure and Molecular Motion of Polybutadiene Bound Rubber on Carbon Surface
P-33	Huber, Patrick	Technische Universität Hamburg	Formation of Periodically Arranged Nanobubbles in Mesopores: Capillary Bridge Formation and Cavitation during Sorption and Solidification in an Hierarchical Porous SBA-15 Matrix
P-34	Jeon, Tae-Yeol	Pohang Accelerator Laboratory	Relationship between Potentials of Zero Charge and Geometric Properties of Transition Metal Nanocatalysts
P-35	Jiang, Naisheng	Stony Brook University	In-situ X-ray Reflectivity and Microscopy Studies on Irreversibly Adsorbed Polymer Layers on Solids
P-36	Kaganer, Vladimir	Paul-Drude-Institut für Festkörperelektronik	Strain relaxation in coalesced GaN nanowires: an x-ray diffraction study
P-37	Kusano, Shogo	Kwansei Gakuin University	Development of CV-XAFS method for studying electrode/electrolyte reactions on catalysts
P-38	Lee, Hyun Hwi	Pohang Accelerator Lab	Noncontact Selective Modification and Chain Alignment of Conducting Polymer Blend Films by an Ultrafast laser writing
P-39	Lee, Jeong-Soo	Korea Atomic Energy Research Institute	Cold Neutron Reflectometer (CN REF-V) at the HANARO
P-40	Lhermitte, Julien	Brookhaven National Laboratory	In Situ Spatial Structural Characterization of Meso Scale Structures Using X-rays
P-41	Li, Hongfei	Stony Brook University	A study of the influence of graphene and graphene oxide nanoparticles on the self-diffusion coefficient of PMMA
P-42	Li, Hongfei	Stony Brook University	Enhancing the performance of BHJ solar cell via self-assembly tem-plates in active layer
P-43	Lin, Binhua	University of Chicago	The Role of Ligand in the Mechanical Properties of Self-Assembled Nanoparticle Films
P-44	Lippmann, Milena	Deutsches Elektronen-Synchrotron (DESY)	A new setup of high resolution in-situ X-ray reflectivity experiments
P-45	Liu, Rui	Stony Brook University	Rapid in-situ x-ray diffraction during the growth of ferroelectric superlattices
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P-49	Lützenkirchen-Hecht, Dirk	Bergische Universität Wuppertal	In-situ investigation of NiAl alloy formation in Ni-Al multilayers by combined specular and non-specular reflectivity EXAFS investigations
P-50	Majewski, Pawel	Brookhaven National Laboratory	GISAXS Studies of Laser-Induced Block Copolymer Self-Assembly
P-51	Mattepanavar, Shidaling	Bangalore University	Evidence for magnetoelectric and spin - lattice coupling in PbFe _{0.5} Nb _{0.5} O ₃ multiferroic
P-52	Mezger, Markus	Max Planck Institute for Polymer Research	Barrier Formation at Ionic liquid Surfaces
P-53	Miller, Mitchell	Northwestern University	Observation of Ordered Structures in Counterion Layers Near Wet Charged Surfaces
P-54	Mukhopadhyay, Mrinmay K.	Saha Institute of Nuclear Physics	Lateral Organization of Cholesterol in Phospholipid Membrane
P-55	Murphy, Bridget	Kiel University	X-ray pump - optical probe capability at LISA Liquid Surface Diffractometer
P-56	Nakamura, Masashi	Chiba University	Structural dynamics of the initial stage of Cu deposition/dissolution on Au(111) electrode
P-57	Nase, Julia	DELTA, TU Dortmund	Hydrophobic interfaces at increased hydrostatic pressures
P-58	Nesamony, Victor Jaya	Anna University	Preparation and characterization of mono dispersed silica spheres embedded with a Fe ₂ O ₃ Nanocrystals for biomedical applications
P-59	Nesamony, Victor Jaya	Anna University	In-Situ High Pressure Studies on Nanocrystalline Mercury Sulphide
P-60	Nikolaev, Konstantin	University of Twente	Study of crystal surface with asymmetric X-Ray diffraction
P-61	Park, Jin Hee	Korea Institute of Geoscience and Mineral Resources	Arsenic incorporation by iron minerals applicable to natural attenuation of arsenic
P-62	Passariello, Nicole	Stony Brook University	Anti-biofouling property of adsorbed polymer nanolayers
P-63	Phan, Minh Dinh	Sogang University	Intrinsic Dynamic Difference Between Hydrogenated and Deuterated Lipids and Packing Effect on Their Transbilayer Movement
P-64	Ruett, Uta	DESY Photon Science	"GIXD measurements on monolayers at the water/air interface with hard and high
P-65	Ruett, Uta	DESY Photon Science	MBE: Time Resolved Studies with High Energy Photon GIXD
P-66	Salmen, Paul	DELTA, TU Dortmund	Lysozyme at the solid - liquid interface - A high pressure X-ray reflectivity study
P-67	Salunke, Namrata	The University of Akron	Wetting/non-wetting transition in FOSM-DMA-FOSM hydrogel triblock copolymer thin films
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P-69	Shi, Xiaowen	Diamond Light Source Ltd.	Hard x-ray diffraction imaging in Bragg geometry
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P-74	Su, Yunlan	Institute of Chemistry, Chinese Academy of Sciences	Nanoparticle Enlarged Interfacial Effect on Phase Transition of 1-Octadecanol/Silica Composites
P-75	Surmeier, Göran	DELTA, TU Dortmund	Solid-supported DMPC multilayers containing cholesterol at high hydrostatic pressure
P-76	Wakabayashi, Yusuke	Osaka University	External field control of self-assembled monolayer on Au(111)
P-77	Walko, Donald A.	Argonne National Laboratory	Photoinduced dynamic phase competition probed by surface x-ray diffraction
P-78	Wang, Cheng	Lawrence Berkeley National Laboratory	Resonant Soft X-ray Scattering for Soft Materials
P-79	Wiegart, Lutz	Brookhaven National Laboratory	Coherent Hard X-ray Scattering Beamline for Structure and Dynamics Investigations at Liquid and Solid Interfaces
P-80	Yang, Zhenhua	Stony Brook University	Ternary blend polymer solar cells with self-assembled structure for enhancing power conversion efficiency
P-81	Yano, Yohko F.	Kindai University	A simultaneous multiple angle-wavelength dispersive X-ray reflectometer applied to the dynamical study of soft matter interfaces
P-82	Yuan, Guangcui	National Institute of Standards and Technology	Liquid-solid transition in colloidal system with added adsorptive polymer
P-83	Zhernenkov, Mikhail	Brookhaven National Laboratory	Design of Soft Matter Interfaces beamline at NSLS-II
P-84	Zhernenkov, Mikhail	Brookhaven National Laboratory	Thermoresponsive PNIPAM coatings for tissue engineering studied by neutron reflectometry

'Överlåtaren' a fast way to transfer and orthogonalize 2D offspecular reflectivity data in q-space

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Neutron reflectivity techniques offer several unique opportunities in materials research. However the possibility to fully take advantage of the data being taken depends entirely on the software available for analysis and visualization.

This limitation becomes obvious in terms of accessing off-specular data in momentum transfer space [1]. This is a specific capability, which has been proven to be needed for the analysis of hierarchical structures [2] as often found in soft matter [3] and 3D magnetic structures [4].

We present a new program package (see figure1), that conducts generic 2D transformations to an orthogonal grid. It is specifically set for transferring instrument data into momentum transfer space. The method is designed and optimized for repeatable operations as they occur as standardized instrument settings being common on large scale facilities.

In this contribution, we prove the operational capabilities of our package by showing artificial and real data from instruments at ORNL and ILL.

Further the limitations and an outlook for future capabilities and applications, such as coherent reflectivity [5] and true background reduction, will be presented.

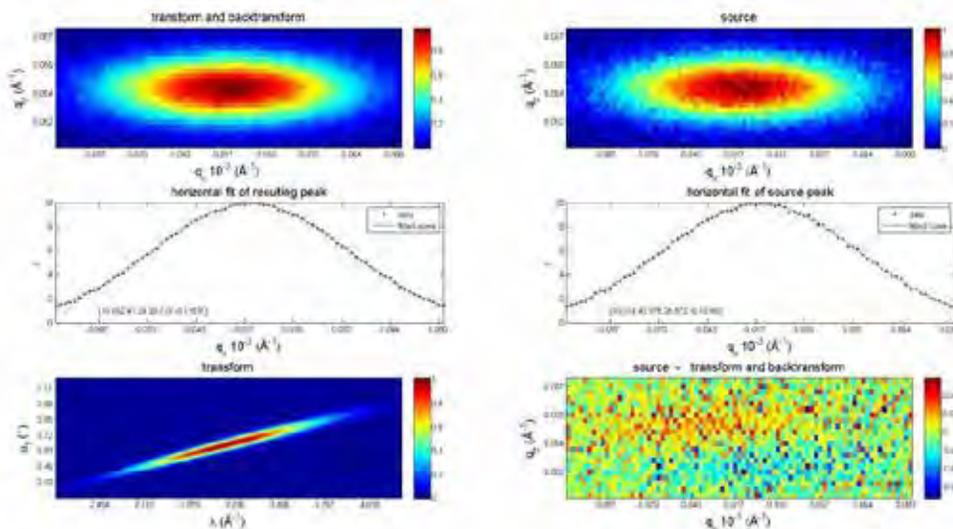


Figure 1: Showing artificial data with SNR 20 proving that the resulting error of two transformations is lower than the noise level. The quality of the fit proves shape preservation.

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Reverse Monte-Carlo analysis of CTR data from perovskite-type oxide thin films

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Interfaces between perovskite oxides are one of the central issues in solid state physics because of their emergent properties that may open a new way to achieve new electronic devices [1,2]. For better control of interfacial structures as well as better understanding of the interfacial physics, quick and user-friendly analyzing techniques for heterostructures are demanded. Therefore, we started to develop a reverse Monte-Carlo software for such a purpose.

The results of CTR measurements of the 5-unit cell-thick LaAlO₃ ultra-thin film made on SrTiO₃ substrate [3] were used as the reference data. Grid search followed by the Metropolis method gave a satisfactory fit as shown in Figure 1. Obtained real space structure was basically the same as the reported ones. [3] We could obtain a result equivalent to the analysis in 2 days.

Knowledge of local polarization around the interface is useful to understand the physical property of perovskite heterostructures. The estimation of local polarization requires the depth dependence of atomic positions of metal and oxygen sites with 0.1Å resolution. Therefore, we examined the precision of the structure parameters from the information scientific point of view. The Monte-Carlo method provides the magnitude of the error of parameters even if the parameters have correlations. The error estimation was conducted by making histograms of all parameters during the Monte-Carlo calculation. The peak gives the plausible value, and the width gives the precision. Two dimensional histograms provide the information on the parameter correlation as shown in Figure 2. The impact of the statistical and systematic noise on the resulting structure will be also reported.

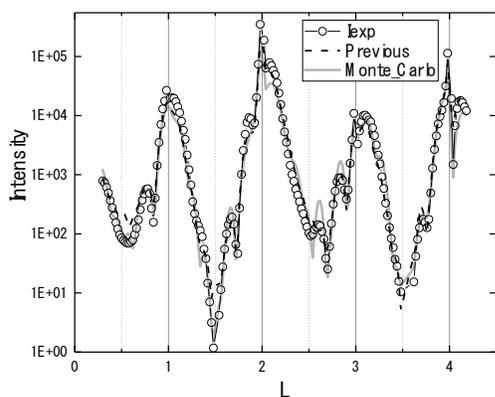


Fig 1 Experimental result for 00L rod and the results of fitting

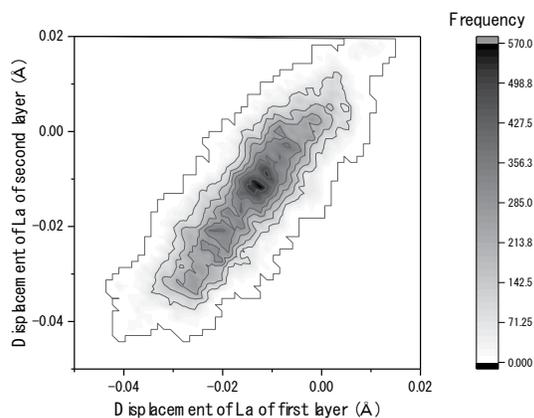


Fig 2 The typical two dimensional histogram of atomic positions

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Deuteration, Mass Balance, and Constrained Models: Comprehending Polyelectrolyte Chemistry using Neutron Reflectometry

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Proton-deuteron substitution is a time-honored tool for elucidating the structure of soft matter using neutron scattering. In reflectometry, where model uniqueness is a particular concern, deuteration, careful experiment design, and the application of mass balance across different sample states greatly enhance the quality of information extracted from specular reflectivity data. The variation of poly(methacrylic acid) brush extension and hydration with pH [1] is a good example of the use of mass balance under multiple pH conditions. Deuterated marker layers reveal both the extent of interlayer penetration and its variation with distance from the substrate in layer-by-layer (LbL) growth [2,3]. An important application of LbL-grown films is the creation of templated hydrogels, where in post-deposition processing either the polycation or polyanion is driven off in a crosslinking step [4]. These hydrogels are remarkable for their “memory” of the original LbL stack and how this can be used to specify the swelling properties and pH-responsiveness of the hydrogel [5]. Recently, we have applied these sample principles to track the reactive modification of polymer azlactone-based polymer films [6]. In each case, application of conservation rules, simple math, and careful synthesis reveals the nanoscopic structure of polymer films.

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Surfactant and Phospholipid behaviour on the surface of Deep Eutectic Solvents

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Deep Eutectic Solvents (DES) resemble ionic liquids but are formed from an ionic mixture instead of being a single ionic compound. DES are potentially very useful as “green solvents”, particularly since they can be made from common non-toxic species. Recently we have begun an investigation into the behaviour of common surfactants in DES, using Small-Angle-Scattering and Reflectometry to gain a detailed picture of how the solvent affects the self-assembly and adsorption processes of these materials [1]. Further it has recently been suggested that small molecules found in the interior of cells, e.g. fructose or malic acid, are also capable of forming DES [2]. There is also some evidence that DES may form within the crowded cellular environment and could assist in solubilizing biological species in an intermediate environment between that of the hydrophobic phospholipids and highly polar water rich regions, particularly assisting survival under extreme conditions e.g. low temperature or drought where the water content of cells is restricted. In order to understand how such conditions may affect the properties of phospholipid membranes, we have begun a systematic investigation of phospholipid monolayers on DES sub-phases.

We will present an outline of our studies of surfactants in DES together with more recent results for phospholipids on the surface a sub-phase made from a prototypical DES: Choline Chloride / Glycerol. The results demonstrate behaviour analogous to that seen on water. A combination of Langmuir Isotherms, X-ray & Neutron Reflectometry and Grazing Incidence Diffraction allows us to obtain information about both tail and head groups for a range of phospholipids even at temperatures close to 0°C. The results will be compared with the well-studied behaviour on water.

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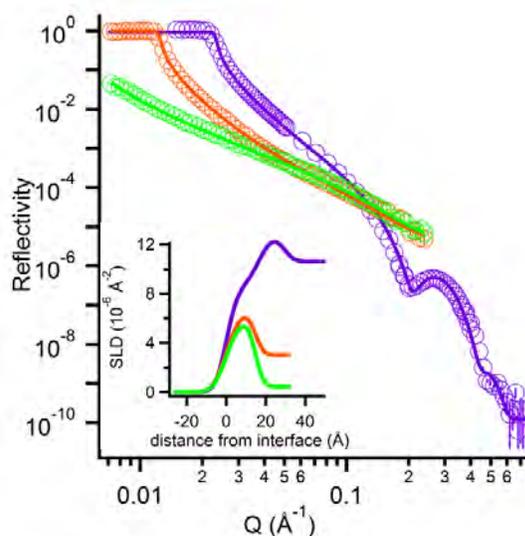


Figure: Reflectivity data from DPPC on the surface of a Deep Eutectic Solvent. Data from X-ray (purple) and two neutron contrasts corresponding to d-DPPC on a fully protonated (green) and a 50% deuterated mixture solvent (red). (Inset) SLD profiles for the fits shown.

Study of Electrochemical Oxidation and Reduction of Pt(111) Using X-ray Crystal Truncation Rods Acquired with an Area Detector

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X-ray crystal truncation rods were measured with an area detector (Pilatus 100K) to obtain data with greater detail than previously reported for the electrochemical surface oxidation and reduction of Pt(111) (Fig. 1). Initial data evaluation during the X-ray scattering experiment was simplified by mathematical operations on carefully selected regions of interest. Building on reported findings [1], the final data reduction and analysis suggests that the surface oxidation results in the buckling of the top-most platinum layer prior to the electrochemical place-exchange (Fig. 2). [2] Given the industrial importance of platinum, the observed surface buckling is an important pre-oxidation step that is dependent on the oxygen coverage. [3]

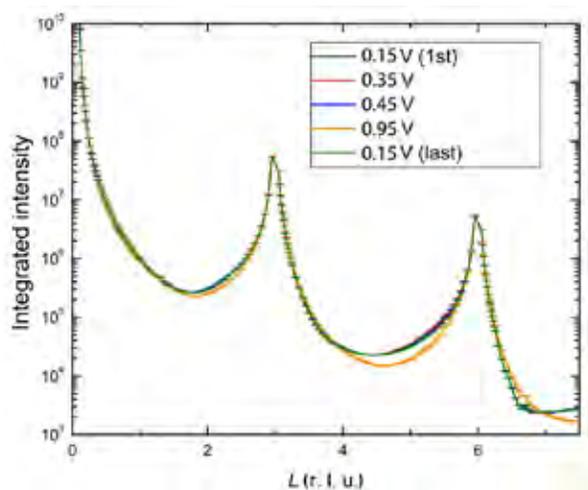


Figure 1. 00L crystal truncation rod of Pt(111) at various electrochemical potentials in 0.1M HClO₄ electrolyte. The horizontal lines for each point denote the error bars.

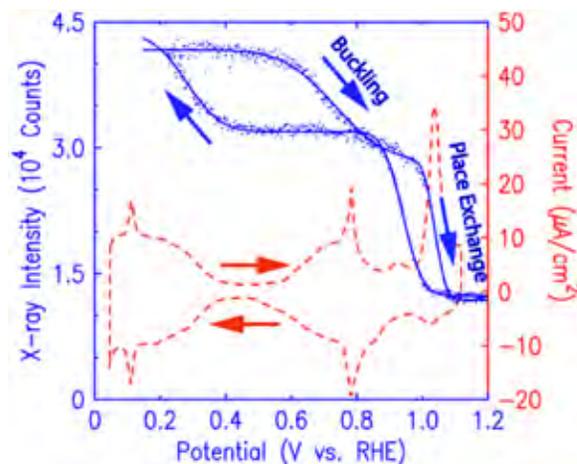


Figure 2. Pt(111) specular anti-Bragg intensity measured during a simulated or X-ray cyclic voltammogram (XCV) compared to a typical CV (on right).

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Chain conformation near the substrate interface in nanoparticle stabilized polymer thin films

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P-6

Nanocomposite thin films have significant applications as optical and electronic layers. When nanoparticles are added to polymer thin films, they often enhance the mechanical properties of the film. The migration of the particles to the film-substrate interface serves to screen the polymer-substrate interaction and suppress dewetting. An unsolved question is how the conformations of the polymer chains in the layer are affected by the nanoparticles and the relationship with the improvement of film stability. To address the question, dodecane thiol-functionalized gold nanoparticles (2.8 nm in diameter) and polystyrene (PS, Mw = 30 kDa and 50 kDa) were used as a rational model. We found that the Au nanoparticles induce complete dewetting suppression of 20 nm-thick PS/Au thin films on cleaned Si substrates at 0.25% (volume of the particle/volume of the polymer). To investigate the interfacial structures at the polymer-solid interface, we rinsed the annealed PS/Au thin films with toluene and characterized the residual interfacial layers by using various x-ray and neutron scattering techniques. The results indicate that when nanoparticles are added, the conformation of the polymer chains becomes elongated and the adsorbed chains can act as connector molecules to stabilize the thin film.

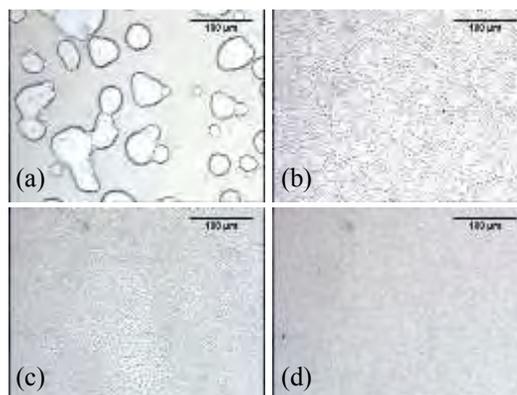


Fig. 1 Optical micrographs of the PS30k/Au 20 nm thick films after annealing 18 h at 150 °C: (a) pure PS, (b) 0.05 % Au; (c) 0.1 % Au; (d) 0.25 % Au.

Tuning Ordering Dynamics for Orientation Control in Cold Zone Annealed Block Copolymer Thin Films

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Block copolymers (BCPs) comprise of two or more chemically distinct polymeric chains that are covalently connected to each other. Repulsion between the blocks due to their incompatibility, countered by their connectivity results in microphase separation of the blocks into nano-scaled periodic morphologies¹. The high degree of control over the size, shape and orientation of the microphase separated BCP nanodomains as well as their in-plane order makes BCP thin films attractive candidates for applications like nanolithography², nanoporous membranes for filtration³, and high density information storage media⁴. External fields such as electric⁵, shear⁶, magnetic⁷ and surface fields⁸ have been induced to obtain BCP nanopatterns based on long range ordering of the nanodomains. Among the above fields used for annealing, most being batch processes, only some methods are applicable to large scale continuous production of desired BCP morphology required for several commercial applications. At the same time, the slow ordering kinetics of some annealing processes limits their applications to lab scale. Here, we demonstrate the fabrication of highly ordered lamellar nanodomains of BCP thin films via rapid dynamic continuous processing Cold Zone Annealing (CZA). This technique utilizes a thermal gradient for localized melting followed by recrystallization as the block copolymer film is moved at a constant velocity over this temperature gradient^{9, 10}. We illustrate that BCP morphologies can be finely tuned by controlling the CZA parameters like temperature gradient, maximum temperature of the hot wire, and sweep rate. Polymer relaxation and preferential surface wetting dynamics are two of the most important factors affecting the final BCP morphology. By optimizing the mentioned annealing conditions, we obtain dominance over these factors to achieve vertical lamellar morphologies over the competing energetically favored substrate-wetting parallel lamellar morphology. Small angle scattering and reflectivity experiments are a great tool to study the molecular arrangements of the BCP nanostructures being zone annealed. Scattering experiments help to characterize the internal ordering and average interfacial structure, both out-of-plane and in-plane and help us tune BCP properties via process parameter control. This control over desired properties enables us to apply directed self-assembly of BCPs for desired applications.

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Kinetics of dispersion of nanoparticles in thin polymer films at high temperature

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Dispersion of particles in polymer nanocomposite (PNC) thin films has been found to be the key in tapping the different novel properties like optical, thermal and magnetic [1]. It has been reported earlier both by our group [2] and others that thermal annealing plays a major role in tuning the dispersion state. However, how the dispersion state evolves from a non-equilibrium state to equilibrium state during annealing remains open. Herein we report the *in-situ* X-ray scattering measurements vindicating the evolution of the dispersion of polymer grafted gold nanoparticle dispersed in homopolymer matrix in a thin film [3,4]. X-ray reflectivity measurements were done on these films before annealing, during annealing and after annealing. Electron density profiles (EDP) have been extracted from X-ray reflectivity profile using Parrat formalism with three layer model- *surface*, *bulk*, *interface*. The resultant volume fraction of particle for these three layers with time is shown in Fig. 1. It is clear from figure that the segregated un-annealed film is becoming homogeneous during annealing. The diffusion coefficient has been calculated using an error function fit to the EDP. The average diffusion coefficient turns out to be $0.014 \text{ \AA}^2/\text{s}$ which is two orders of magnitude slower than bulk diffusion of particles in polymer melts.

The in-plane observation we have also probed the in-plane diffusion characteristics of the particles with x-ray diffuse scattering (XDS) measurements (Fig-2). As is visual from the data, there is an evolution of the length scale with time and it varies with time as a power law with an exponent > 1 indicating a super-diffusive motion along the lateral direction. This slow out-of-plane and superdiffusive in-plane motion simultaneously helps it to make a homogeneously dispersed film.

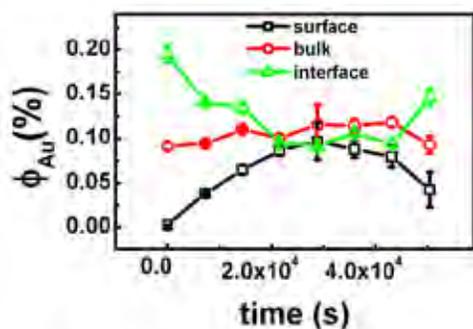


Fig-1: Time evolution of dispersion (gold volume fraction, ϕ_{Au} vs time) for different layers as specified in the figure (time zero points and end points correspond to room temperature data)

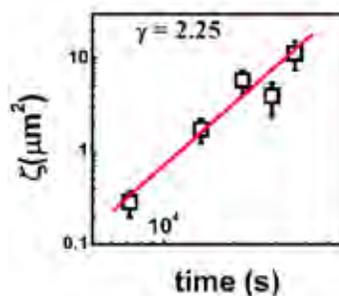


Fig-2: Evolution of length scale with time along the plane of film.

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Poster Abstracts

Using Neutron Reflectometry to Investigate Solid-Electrolyte Interphase Formation, *in situ*, in Energy Storage Materials

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The reaction between the aprotic liquid electrolyte and a lithium ion battery electrode material is arguably the most important process for rechargeable batteries. This reaction occurs when an aprotic electrolyte is reduced, or oxidized, on the surface of an electrode at a given potential forming the so-called solid-electrolyte interphase (SEI). This reduction/oxidation reaction forms a passivating layer, which has been shown to be a mixture of inorganic (e.g. LiF, POF) and organic/polymeric (e.g. C-O-C, Li-ROCO₂) species that build up on the surface. A properly formed SEI prevents additional reduction/oxidation reactions from occurring and enables long term cycling. A poor SEI layer leads to safety issues, such as fires and gassing, as well as lifetime and power limitations due to consumption of electrolyte and the resistance of the SEI to both ionic and electronic transport. Understanding these reactions *in situ* is difficult since they occur at the liquid-solid or solid-solid interface of optically absorbing materials that hinder the use of traditional spectroscopic techniques. Furthermore, since some interfaces involve liquids it is necessary to use an analytical technique that can “see” through structural materials required to contain the liquid. Neutron reflectometry (NR) is a neutron scattering technique highly sensitive to morphological and compositional changes occurring across surfaces and interfaces, including buried interfaces and those occurring at the boundary between a liquid and a solid. Neutrons, by virtue of their nature, are deeply penetrating and therefore ideally suited as a probe to study materials in complicated environments, such as electrochemical cells. NR can be used to study thin film morphology and composition over lengths scales extending 1 nm to hundreds-of-nanometers. We will present results of the application of NR to the study of SEI formation on anode and cathode materials recently carried out on the Liquids Reflectometer at the Spallation Neutron Source at ORNL.

High Energy X-ray Scattering in the Reflection Model from a Rare Earth Ion Aqueous Solution

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The interface between the air and 1 M ErCl₃ (pH=2) solution is studied by high energy X-ray scattering technique in the reflection model. The local coordination of Er at the surface and in the bulk can be carried out with the incident beam below and above the critical angle, respectively, by taking advantage of the X-ray penetration depth dramatically varying from nanometers to micrometers across the critical angle. Measurements with various geometric setups were performed systematically to validate the self-consistency of the data. The geometric setups significantly influence the scattering intensity by changing the scattering volume, whose calculation is presented in detail. Normalization of the scattering volume collapses experimental data above the critical angle with various geometric setups to one master data without any adjustable parameters, which is in a good agreement with the data taken in the transmission model. The success on the bulk measurements makes it feasible to extract the local coordination of metal ions at the interface by lowering the incident angle below the critical angle.

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In-situ study of silicon electrode lithiation via X-ray reflectivity

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A better understanding of the lithiation of Si is essential to provide insights into the observed capacity fading in Si anode based batteries and to develop approaches to eliminate this issue. To address this, we have designed an electrochemical X-ray cell for *real time, in-situ* X-ray reflectivity (XRR) experiments to study the (de)lithiation process of Si wafer electrode.

We focus on a well-defined model system consisting of a single crystal Si electrode in a half cell configuration, with Li metal as counter/reference electrode in non-aqueous electrolyte solution (1 M LiPF₆ in 1:1 ethylene carbonate (EC) and dimethyl carbonate (DMC)). We have performed *operando* XRR under galvanostatic cycling to provide insight into the reaction front at the lithiated Si (Li_xSi) and crystalline Si interface, as well as into the solid-electrolyte interphase (SEI), which is the reaction product at the electrolyte-anode interface. XRR yields sub-Angstrom resolution insight into the surface normal electron density profile, and is operated under real electrochemistry reaction condition with adequate time resolution of minutes, allowing us to develop a more detailed, mechanistic model of lithiation process in crystalline Si.

From our results, we propose a three stage lithiation process of crystalline silicon (see Fig. 1): (1) In the early lithiation stages, the SEI is formed. (2) Subsequently, the native oxide is lithiated and becomes part of the SEI. This is accompanied by the “initial” lithiation of Si, where we observe diffusion of Li-ions into Si. Finally (3), the “deep lithiation” of Si occurs. During this stage, a few nanometer thick and high density layer is observed at the Li_xSi/Si interface, and is interpreted as Li-ion incorporation into the silicon matrix at the interface. This, together with that fact that Li_xSi/Si interface remains smooth throughout the entire first discharge cycle, suggests a layer-by-layer interface reaction limited process.

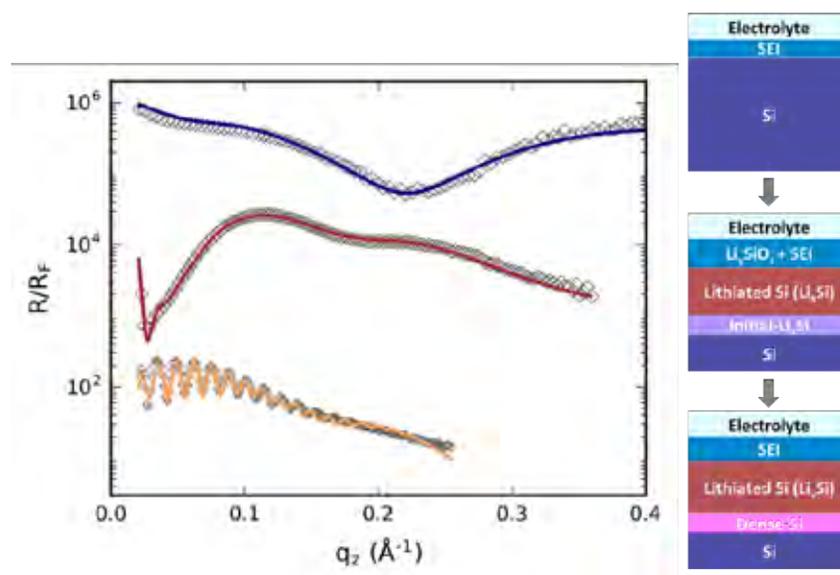


Fig 1.: Part of the in-situ XRR data (black markers) and fitted curve (solid lines) on Si electrode. (1) Initial SEI growth (blue line). (2) Native oxide lithiation and Li⁺ diffusion (red line). (3) Bulk Si lithiation (yellow line). On the right are schematic figures drawings to show the surface layers on Si electrode.

P-11

Correlating interfacial octahedral coupling with electronic properties in nickelate heterostructures

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In a heterogeneous layered film, materials with similar structures but with dissimilar properties are forced to coexist at the boundary, giving rise to emergent interfacial properties. Perovskite oxide heterostructures provide an opportunity to study novel interfacial coupling phenomena. In RNiO_3 (R=rare earth), strongly correlated electronic behavior gives rise to unconventional transport and magnetic properties. Tuning octahedral symmetry through artificial perovskite nickelate superstructures can bring about functional changes in electronic behavior. We investigate the role of interfacial coupling in the metal-to-insulator transition in epitaxial nickelate films. Taking advantage of element-selectivity of x-ray resonant scattering and spectroscopy techniques, we study the magnetic and electronic order of nickel atom across the heterogeneous interfaces. Varying the incident x-ray linear polarization provides further insight into the anisotropic structural response and electronic transition of each individual layers.

P-12

Direct observation of anion crowding at an electrode-ionic liquid interface using X-ray reflectivity

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Room temperature ionic liquids (RTILs) are molten salts with molecular anion/cations at/near room-temperature. They have high ion concentrations and wide electrochemical windows (EW). RTILs are novel electrolytes and solvents that may have important applications in batteries, supercapacitors, electro-tribology, etc. Understanding the behavior of RTIL ions at electrified surfaces is key for these applications.

It has been theoretically predicted that RTILs form alternating anion/cation layers (overscreening) when the electrode surface is slightly charged, and “crowded” thick layers of counterions when the surface is highly charged [1]. Overscreening has been observed in several previous experiments with X-ray reflectivity [2] and AFM [3].

Using in-situ synchrotron X-ray reflectivity (XRR), we have studied the interfacial structure of [TDTHP][NTF2] on the surface of silicon as a function of applied voltage in a transmission cell. [TDTHP][NTF2] has a wide EW, which enabled us to apply higher voltage without electrolysis. Silicon has electron density only slightly higher than the electrolyte, which improves the density contrast compared to metal electrodes such as gold, which are so dense that they dominate the reflectivity. These choices combined with synchrotron radiation at APS enabled us to detect and characterize crowding in an RTIL.

Analysis of our XRR data reveals that an anion-rich layer develops at the interface above a threshold voltage of +1.75v, and the layer thickness increases rapidly with voltage, reaching $\sim 65\text{\AA}$ at +2.64v. This thickness is much larger than the anion size. Instead of a pure counterion layer as predicted, the interfacial layer is a mixture of anions and cations [4]. It is theoretically predicted [1] that the thickness of the crowded layer will increase as \sqrt{V} ; we find that it increases as $\sqrt{(V-V_{th})}$ where V_{th} is the threshold voltage at which crowding appears. The static differential capacitance calculated from X-ray measurements shows an increase at higher voltage, consistent with a recently published zero-frequency measurement on a different ionic liquid, but inconsistent with AC capacitance measurements.

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In-situ study of AuCu NanoParticles epitaxied on TiO₂(110): Synthesis, structure and behaviour at low pressure of reactant

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Specific properties for applications in electronics, optics, magnetism or catalysis can be achieved using materials based on nanoparticles (NPs). The development and characterization of the bimetallic NPs and the understanding of their physical and chemical properties are thus crucial steps for their technological applications. Among them, a promising field is the heterogeneous catalysis: Au NPs have become a paradigm of size effects on the catalytic properties. To improve the catalytic activity of Au-based NPs, a promising method is to use bimetallic NPs that can exploit the synergy between two metals for catalytic reactions. For example, Au-Cu/silica NPs display a better activity for CO oxidation than pure Au or Cu NPs and a better selectivity for preferential oxidation (PROX) [1]. However, the synergies between the two metals and the substrate are not clearly understood.

Scanning tunneling microscopy (STM) and grazing-incidence X-ray diffraction (GIXD) have been used to follow *in situ* the growth and the structure of Au-Cu nanoparticles (NPs) formed on TiO₂(110) by successive metal evaporations [2]. STM observations of the same area of the substrate highlight the strong dependence between the sequence of deposition and the final result. Deposition of Cu first leads to a system where both Au-Cu and pure Au NPs coexist. Deposition of Au first ensures growing mostly bimetallic NPs. GIXD results show that Cu alloys instantaneously with Au NPs at room temperature. Reciprocal space map measurements reveal different epitaxial relationships for crystallized particles and a diffuse ring due to the presence of icosahedral NPs that have not specific orientations.

In the presence of oxygen (10^{-7} mbar), STM experiments show that Cu NPs of size smaller than 1 nm are unstable [3] but that a small amount of Au (<20%) is enough to ensure their stability [4]. However, GIXD measurements show that the nanoalloys structures are strongly modified during O₂ exposure: the lattice constant of the NPs increases, meaning that Cu segregates at the NPs surface and Au enriches in the core of the NPs. The core-shell configuration obtained is stable at room temperature, even under CO exposure, but annealing above 200°C allows the system to release oxygen and let the Cu diffuse back in the core of the NPs. We also have evidence a reorganization of small non-oriented NPs toward one specific epitaxial relationship in the presence of a CO+O₂ gas phase (10^{-5} mbar).

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Surfaces and Interfaces X-ray Scattering (SixS) beamline at SOLEIL

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SixS (Surface Interface X-ray Scattering) is a wide-energy range (5 -20 keV) beamline dedicated to structural characterization of interfaces (gas-solid, solid-solid or solid-liquid), as well as nano-objects. The techniques available are: Grazing Incidence X-ray Diffraction (GIXD), Crystal Truncation Rods (CTR), Grazing Incidence Small Angle X-ray Scattering (GISAXS), Anomalous Surface X-ray Scattering, X-ray Reflectivity (XRR), Magnetic Surface X-ray Scattering (in the near future). There are two experimental stations each hosting one 4+3 circles diffractometer, i.e. MED and UHV. The MED station has a multi-environment diffractometer, which can accommodate various sample environments such as high-pressure reactivity chambers, electrochemical cells, Langmuir troughs. The second station – UHV – is hosting diffractometer coupled to a stationary assembly of UHV chambers equipped with the standard UHV tools (evaporators, ion-guns, etc.) and surface science methods (STM, LEED, AES).

The SixS beamline is now equipped with a 2D hybrid detector coupled with an automatic attenuators system that allows data recording accounting for the (strong) intensity variations, preserving the 2D detector in its safe and linear range. The acquisition system is based on a “flyscan” mode, opening to unprecedented acquisition speeds across the reciprocal space. The flyscan mode in the reciprocal (and in the angular) space exploits the accuracy of the diffractometer encoders and guarantee a very high resolution of the measurements. Moreover, the fast data acquisition allows to perform quantitative measurements of systems that can evolve in short time. The aim of this contribution is to present the first results obtained using the flyscan@SixS

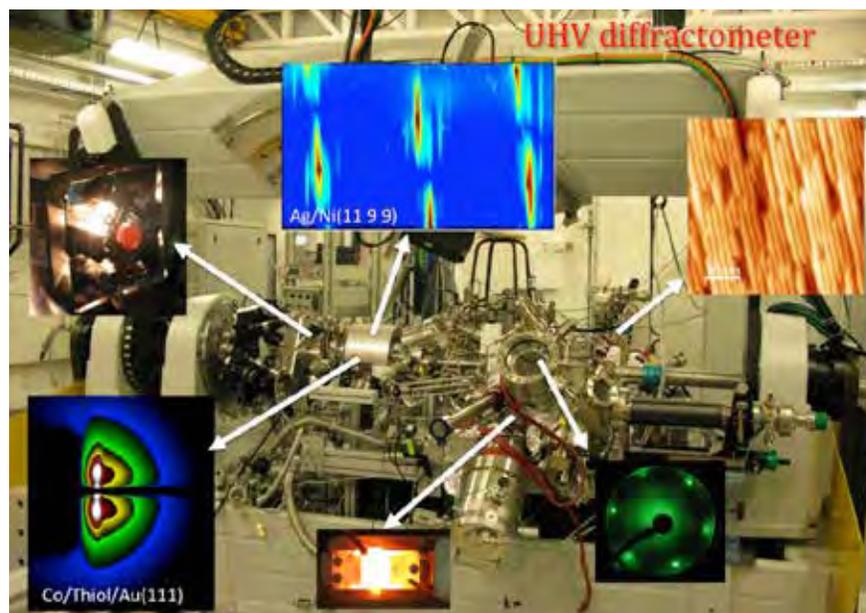


Figure 1: The UHV end-station of the SixS beamline. The diffractometer hosts an assembly of UHV chambers equipped with standard surface science tools and allows using various surface sciences techniques (STM, LEED, AES) coupled with x-ray scattering.

Small-angle scattering studies of irradiated steels for nuclear applications

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The microstructural characterization of radiation damage is an essential step in the development of innovative steels for nuclear applications and, more specifically, for future fusion reactors, where very high damage rates and helium concentrations will be produced by exposure to 14 MeV neutrons. Bulk irradiated specimens for post-irradiation mechanical and microstructural characterization are usually obtained by neutron irradiation, while ion implantation, generally limited to very low thicknesses, is more relevant to fundamental modeling studies. In both cases, small-angle scattering, of neutrons or X-ray, constitutes a powerful experimental tool to complete the information obtainable by electron microscopy.

This poster contribution will show SANS results obtained on irradiated steels developed as structural materials for fusion reactor technology. Both neutron irradiated steels [1] and α -implanted ones [2] have been successfully characterized, determining the size distributions of the microstructural defects produced under the different irradiation conditions (micro-voids, helium bubbles). The interest of SAXS/GISAXS and reflectometry applications (for samples as thin as a few μm) will be discussed in the light of ongoing European research programs relating to the development of innovative nuclear steel and fundamental understanding of radiation damage produced by different irradiation technologies.

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Thin films of substituted thiophenes: Order and frustration

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Thin organic films are an inspiring field of study for surface x-ray techniques [1]. Furthermore, understanding order, packing and frustration of conjugated molecules in thin films allows the development of new components for molecular electronics. We report on substituted septithiophenes with alkylated end groups, either asymmetric [2] or symmetric with rather different bulkiness [3]. The thiophene cores prefer to pack parallel to optimize their π - π interactions, leading to relatively high electric mobilities. However, this becomes sterically difficult for increasing bulkiness of the end groups (see Figure a). The way out of this packing dilemma is toward liquid-crystal phases of higher dimensionality in the order smectic \rightarrow columnar \leftrightarrow bicontinuous cubic. For films each of these structures leads to its own stringent packing considerations and different types of boundary interactions may compete [4].

Using scanning force microscopy (SFM), x-ray reflectivity and grazing-incidence diffraction we found a difference between monolayer and three-layer films, in which the monolayers appear to escape from packing frustration by generating superstructures. For the bulkier end groups the x-ray measurements allow proposing a basic structure of columns parallel to the substrate with short-range helical order along the column axes. This provides a compromise between preserving some π - π interactions and optimum packing.

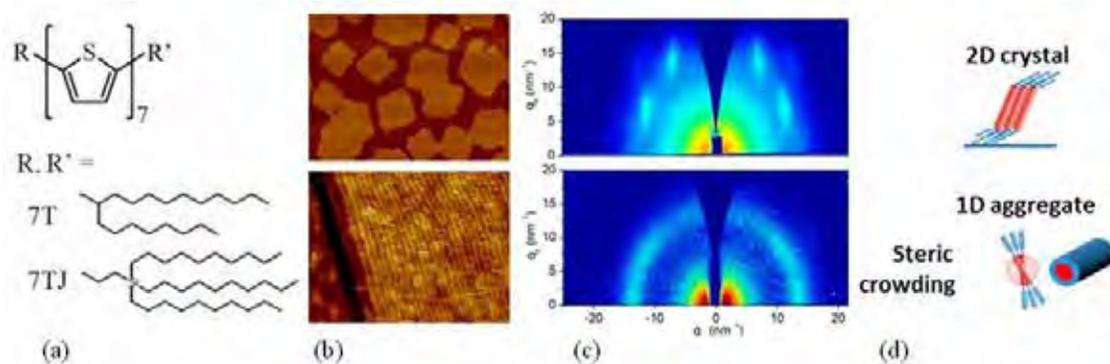


Figure 1. (a) Structure of substituted septithiophenes, (b) SFM and (c) GIWAXS of monolayers of 7T (top) and 7TJ (bottom), (d) proposed modelling.

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pH- and surface pressure-depend adsorption of human apolipoprotein A1 at solid/liquid- and gas/liquid-interfaces

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In natural cells, proteins face a very complex environment, in which crowding and confinement can affect the conformational stability and the adsorption behavior of proteins or even lead to aggregation. Thus, interactions of proteins with solid surfaces are major issues in a number of fields of research such as biology, medicine, or biotechnology [1, 2]. Apolipoprotein A1 (apoA1) is an important protein of high density lipoproteins (HDLs) and plays a vital role in reverse cholesterol transport. Reduced plasma levels of HDL and apoA1 are the key risk factors for atherosclerosis and cardiovascular disease [3]. Lipidfree apoA1 is the main constituent of amyloid deposits found in atherosclerotic and senile plaques, an acquired type of amyloidosis [4, 5]. Due to its anisotropic surface, apoA1 is able to interact with surfaces or interfaces via different interaction mechanisms including the hydrophobic and electrostatic interaction.

Studies of the molecular mechanisms of the lipid association and the conformational flexibility of apoA1 are essential for understanding the structure/function relationships and pathophysical reactions at surfaces like biological membranes or implants.

We investigated the adsorption behaviour of apoA1 at hydrophilic silicon dioxide surfaces as a function of the pH-value and the surface pressure-depend adsorption behaviour at DOTMA/DOPC-monolayer by means of x-ray reflectivity (XRR). To measure protein adsorption, different surface-sensitive XRR setups were chosen. The pH-depend adsorption behavior of apoA1 was examined at BL9 at the synchrotron light source DELTA (Dortmund, Germany) at the solid/liquid-interface. Hydrophilic silica wafers were prepared by etching with piranha solution. Surface pressure-depend adsorption measurements were conducted at the gas/liquid-interface using a Langmuir trough with a Bruker-AXS D8 diffractometer. The pH-value of the buffer solution was varied between 3 and 7 and the surface pressure between 10 mN/m and 20 mN/m.

The pH-depend measurements show that apoA1 adsorbs in different conformations depending on the microenvironment. Between pH 4 and pH 6, an adsorption window with different electron densities and layer thicknesses is determined. The adsorption within this window is mainly driven by electrostatic interactions, since the protein and surface are oppositely charged in the region of these pH-values. The protein is described as a molten globule with a loosely fold state [6] which are able to adsorb at the interface. With lowering the pH-value in the acidic region the protein undergoes molecular transitions where the α -helical segments are reduced and the protein gets into a random coil state [7].

At the cationic DOTMA/DOPC-monolayer apoA1 causes a complete reduction of the electron density without changing the layer thickness. It seems that apoA1 adsorbs, penetrates and finally solubilizes the lipids into solution. These processes are surface-pressure dependent and occur predominantly at low pressures.

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Poster Abstracts

Determining the Electromechanical Response Mechanism of Nanostructured Ionic Block Copolymers

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The electromechanical response of ionic polymers to an applied electric field places ionomeric systems in a position to be of immense use to a variety of fields including flexible electronics, biomimetic devices, and nanofluidics.¹ While the use of common ionic polymers such as Nafion as actuators has been thoroughly studied,² the literature lacks a complete knowledge of the complex interplay of an electromechanical response and the chemical structure, morphology, and ion mobility of these ionomeric systems. The actuating behavior of ionic polymer systems results from deformation due to electric/Maxwell stress (electrostatics of ion distribution) as well as viscous/hydrodynamic stress (properties of the polymer structure and chemical identity). A fundamental understanding of how each of these parameters affects the electromechanical response would allow for the rational design of ionic polymer systems that give rise to specific functionality. To this end, we are in the early design phase of constructing a sample cell for the Liquids Reflectometer (BL-4B) at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL) that is capable of applying an electric field to a sample during neutron reflectometry measurements. While this sample cell would be of general use to a wide variety of research areas, we intend to investigate how the system morphology and chemical composition of ionic block copolymer systems affects the electrostatic interactions that occur under an applied electric field by monitoring ion and polymer migration through a thin film. The sensitivity of neutron reflectometry to scattering length density as well as subnanometer changes in thickness make it an ideal tool for investigating polymer and counterion mobility under applied fields. We have utilized raft polymerization to synthesize AB and ABA block copolymers where the ionic B block contains charged imidazolium groups to impart electromechanical responsiveness and a polystyrene A block providing structural integrity to the film. It is our hypothesis that copolymer morphologies containing conducting channels (cylindrical and gyroid) will best facilitate ion transport, leading to a more pronounced electromechanical response.

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Utilization of curved edges for XRR measurements on liquid samples

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X-ray reflectivity (XRR) studies of liquid interfaces can be currently performed only at few synchrotron beamlines due to the necessity to bend the beam onto the horizontal sample. Here, we present a relatively simple method that allows XRR measurements of liquid surfaces and interfaces at virtually any synchrotron or FEL beamline without changes to the existing diffractometer setup. In the presented geometry, the natural curvature of a liquid drop in gas or in another liquid is used to reflect the incoming horizontal beam (Fig. 1a).

Two variations of this method are discussed: In the first approach, a beam of small height (in the order of 100 nm) is reflected. This results in a very narrow distribution of incidence and reflection angles. By changing the sample height, full reflectivity curves can be obtained serially, similar to conventional XRR techniques. In the second variant, a beam of a vertical size in the range of a few micrometers is employed. Here, the reflection angles are spread out over a large range, thus allowing to probe a large part of the XRR curve in one single shot.

Tests of both reflection modes on the mercury/vapor (Fig. 1b), water/vapor and mercury/electrolyte interfaces yielded results in very good agreement with those obtained by conventional XRR techniques.

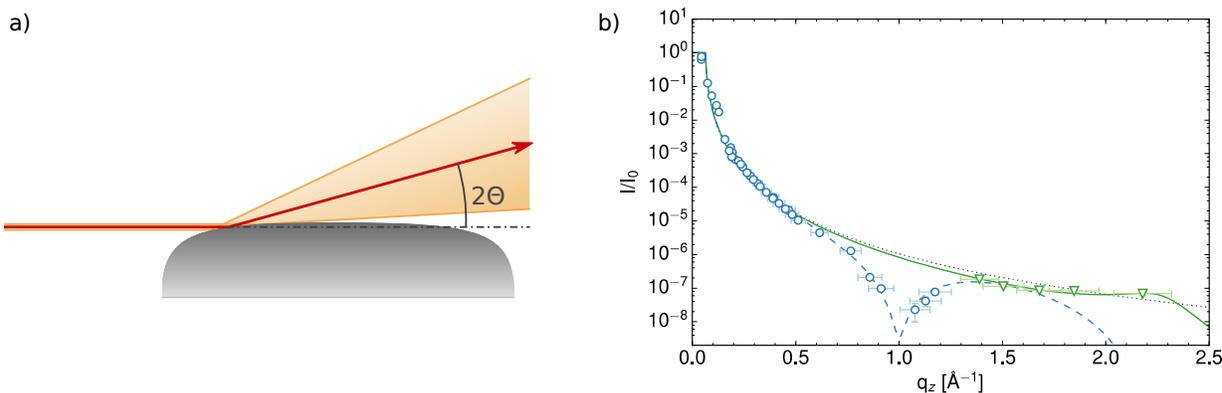


Figure 1: a) Schematic of the reflection geometry. b) Reflectivity of the mercury/vapor interface recorded using a nanometer beam.

Solvation, sorption, and electrodeposition in multivalent batteries

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Multivalent ion chemistries (Mg^{2+} , Zn^{2+} , Al^{3+} , etc) have the potential to leapfrog analogous lithium ion batteries by incorporating ions with multiple charge transfers and energy-dense metal anodes. However these batteries are limited by transport in the cathode and electrolyte, overpotentials and hysteresis of plating/stripping at the anode, and passivation of the metal surface. Here we study the solvation structure of electrolytes of nonaqueous electrolytes in the bulk and at a charged electrode surface using EXAFS and resonant scattering, finding evidence of ion pairing at high concentrations in each case. Using powder diffraction and x-ray reflectivity we also follow zinc and magnesium electrodeposition on platinum thin film current collectors. We find that the morphology and reversibility of the deposition process can be modified electrochemically due to passivation and alloying processes revealed by diffraction.

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Semifluorinated Alkanes Monolayer at the Air Water Interface.

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Despite the lack of polar head group semifluorinated alkanes ($C_nF_{2n+1}C_mH_{2m+1}$, FnHm for short) form Langmuir monolayers ie. mono-molecular thick layer at the air-water interface. Grazing Incidence Small Angle X-ray Scattering (GISAXS) demonstrated that these molecules on liquid surface self assemble in a hexagonal array of nano-domains with a very large parameter (typ. 30 nm) [1] (Fig 1-A). This network is observed on water for different hydrocarbon chain length [2]. This structure is in agreement with the domain size observed by Atomic Force Microscopy (AFM) on silicon substrate [3]. However, the stability even after collapse [4] of such domains remains puzzling. On high-resolution AFM images after transfer on solid substrate, the domains shape appears as separated by a hump (Fig. 1-B). Macroscopic measurement combined with GISAXS and wide-angle x-ray scattering (GIXD) suggest that some molecules do not belong to the domains made of upright molecules. Indeed, Q_{xy} - Q_z GISAXS spectrum can be simulated by considering a corona representing lying molecules around the domains (Fig. 1-C). The presence of such lying molecules could explain the stability of the structure against coalescence of the domains upon compression of the monolayer in relationship with the polar nature of the substrate and the dipole of the SFA molecules.

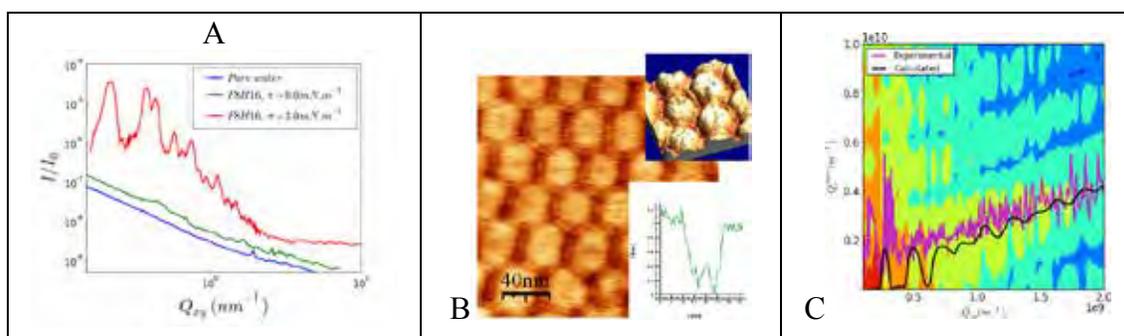


Fig. 1 – A: Q_z -integrated GISAXS spectrum of a F8H16 monolayer. All diffraction peaks can be indexed on a hexagonal lattice of parameter 33.6nm. B: AFM image of a spin-coated F8H18 layer on silicon substrate. C: Simulated GISAXS spectra of FnHm domains surrounded by a corona of lying molecules, lines are the position of the maximum of intensity along Q_z for simulation and experiment.

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Poster Abstracts

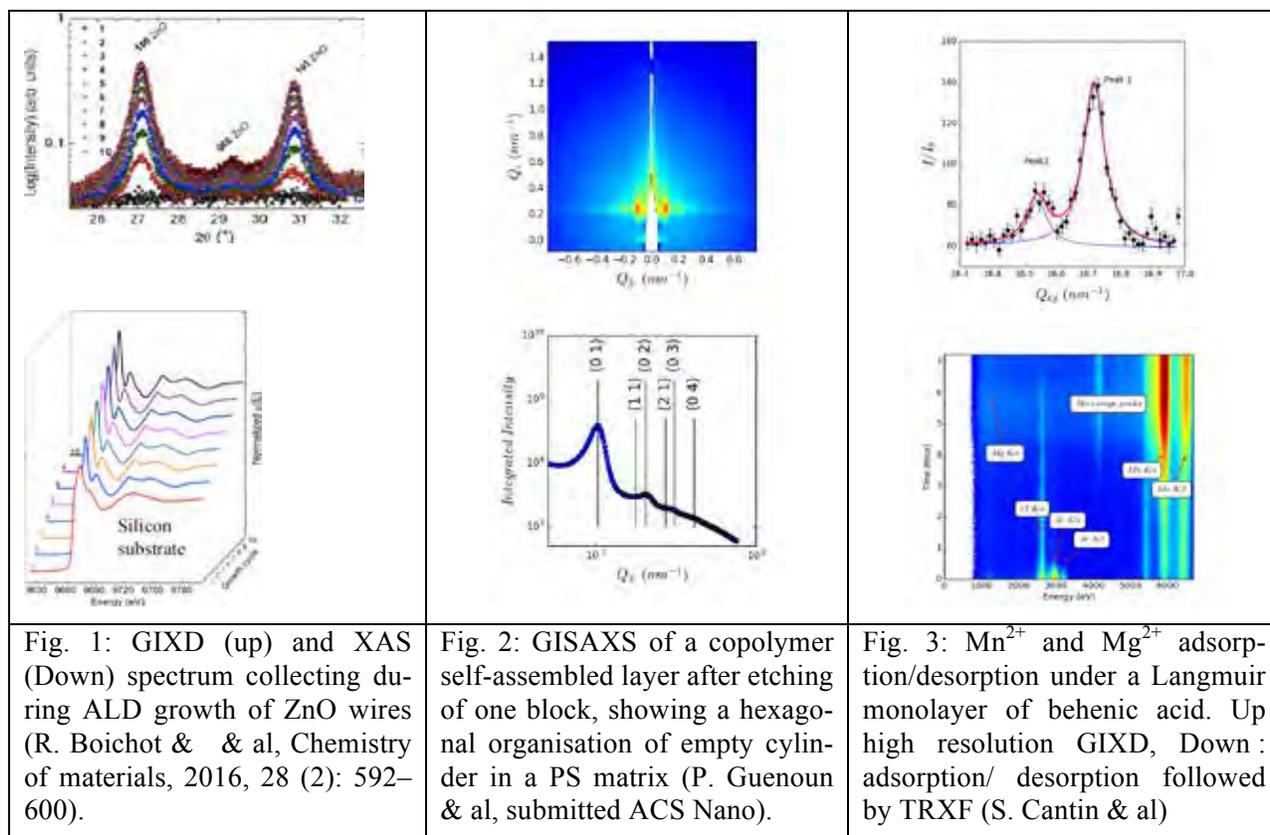
SIRIUS: GIWAXS, GISAXS and surface spectroscopy beamline in the tender x-ray range at SOLEIL Synchrotron

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On the French synchrotron facility (SOLEIL), the SIRIUS beamline is devoted to surface scattering and spectroscopy in the tender/hard x-ray range (1.4 – 12 keV) [1]. The beamline intends to serve two communities: the one studying soft interfaces (liquid/air interface, biomimetic systems, Langmuir monolayers, polymer layers...) and the one studying semiconductor or magnetic nanostructures (III-V materials, quantum wells and dots, metal and oxide magnetic multilayers). The beamline implements most of the x-ray grazing incidence techniques (wide angle diffraction - GIXD, small angle scattering - GISAXS, fluorescence – TRXF, surface x-ray absorption spectroscopy).



We will present the main features [1] that are implemented on SIRIUS for the optimization in the tender x-ray range of a scattering beamline with energy scanning ability and the first, obtained results demonstrating the possibility of the instrument (*eg.* figures) with coupled measurements: wide and small angle scattering, x-ray fluorescence and scattering, surface x-ray absorption spectroscopy and grazing incidence x-ray spectroscopy on biomimetic systems, polymer layers, metal-oxide ALD growth.

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Ions at hydrophobic interfaces

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The investigation of the microscopic structure of water is one of the important areas of modern research [1]. In particular, the understanding of the behavior of water at interfaces is essential for the explanation of interfacial phenomena in several natural and technological environments [2]. Therefore, many experimental and theoretical studies (mainly molecular dynamic (MD) simulations) on solid-liquid and liquid-gas interfaces have been published. Hereby, one important research field is the behavior of ions at hydrophobic interfaces [3, 4]. Much pioneer work has been done to describe the interactions between ions and hydrophobic surfaces, but a complete description of the physical mechanism for the hydrophobic interaction is still pending [5]. From MD simulations, different parameters like polarizability, size and charge have been identified, effecting the accumulation of ions at interfaces. In general, these parameters code-terminate the ion's hydration enthalpy and the ions's ability to break or to stabilize the water network. Thus, a variation of hydration enthalpy has an impact on the hydrophobic interaction between ions and interfaces. In the past, the ion distribution at liquid - gas interfaces was in the focus of interest, using several experimental technics, yielding different conclusions. However, liquid - gas interfaces are modulated by capillary waves, which are not considered in MD simulations and cause a convolution of the simulated density profiles. The proposed ion density excess at the liquid – gas interface might be significantly reduced by capillary waves. The use of hydrophobic solid – liquid interfaces avoids this problem. Especially the use of octadecyltrichlorosilane (OTS) coated surfaces seems to be very promising because of the existence of the so-called hydrophobic gap [6], which shows a strong signature in the reflectivity signal. This signature is very sensitive on the adsorption of material at the interface and can be used to analyze the formation extreme thin layers.

We measured the adsorption behavior of ions at hydrophobic interfaces as a function of different ion radii and ion concentrations by means of x-ray reflectivity (XRR) at ambient conditions. The use of high energy x-rays allows the analysis of buried interfaces and thin films in-situ and thus can be used for studying different properties of a (multi-) layer system at interfaces, such as layer thickness, roughness, and electron density. First high resolution electron density profiles from the solid-liquid interface between salts of different combinations of alkali metals and halogens (e. g. NaCl, NaBr or KCl) and OTS-coated silicon wafers will be shown as a function of salt concentration at ambient conditions. We observed changes both in the shape of the hydrophobic gap and the OTS monolayer with rising salt concentrations. Furthermore, changes in the electron density profiles for different salt types at the same concentrations will be discussed. Therefore, the variation of the ion radii of either the anion (at NaF, NaCl, NaBr and NaI) or the cation (at LiCl, NaCl, KCl, RbCl and CsCl) has been investigated.

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Transmission X-ray Scattering as a Probe for Complex Liquid-Surface Structures

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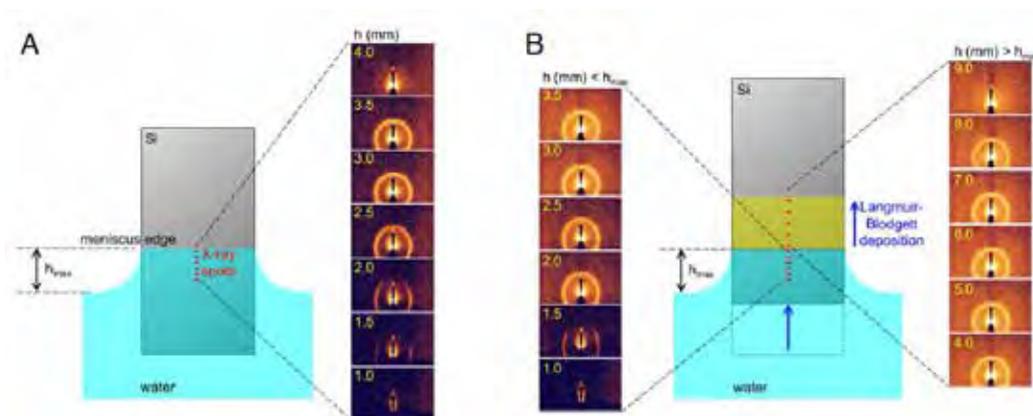
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The need for functional materials calls for increasing complexity in self-assembly systems. As a result, the ability to probe both local structure and heterogeneities, such as phase-coexistence and domain morphologies, has become increasingly important to controlling self-assembly processes, including those at liquid surfaces. The traditional x-ray scattering methods for liquid surfaces, such as reflectivity and scattering at grazing incidence, are not well suited to spatially resolving lateral heterogeneities due to large illuminated footprint. A possible alternative approach is to use scanning transmission x-ray scattering to simultaneously probe local intermolecular structures and heterogeneous domain morphologies on liquid surfaces. To test the feasibility of this approach, we recently carried out transmission small- and wide-angle x-ray scattering (SAXS/WAXS) studies of Langmuir films formed on water meniscus against a vertically immersed, hydrophilic Si substrate. First-order diffraction rings were observed in SAXS patterns from a monolayer of hexagonally packed gold nanoparticles (figure) and in WAXS patterns from a monolayer of fluorinated fatty acids, both as a Langmuir monolayer on water meniscus and as a LB monolayer on substrate. The patterns taken at multiple spots have been analyzed to extract the shape of the meniscus surface (i.e., surface tilt vs. meniscus height) and the crystalline monolayer coverage vs. meniscus height. Our results, together with continual improvement in the brightness and spot size of x-ray beams available at synchrotron facilities, raise the possibility of using scanning transmission x-ray scattering to characterize heterogeneous structures at liquid surfaces.



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In-situ Anomalous X-ray Scattering: Chemical Order in AgCo Nanoparticles during Growth and Annealing

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Nanoalloys are investigated for their promising physico-chemical properties, which are governed by the nanoparticles (NPs) size, morphology, structure, and also by the chemical order. In the case of bi-metallic systems, several chemical orders as alloyed, core-shell, or Janus (etc) particles can be achieved, allowing to tune the NPs properties [1]. Therefore, it is essential to develop experimental methods that provide morphological and structural information with a chemical selectivity, in order to access to the degrees of mixing or segregation of the metals in the NPs.

Anomalous X-ray scattering is a non-destructive technique that can be used to study in-situ and in real-time the morphological and structural evolutions of nanoalloys. This method exploits the variations of the contribution of one element to the scattering as a function of the energy close to an absorption edge. Thus, combining Anomalous Small and Wide Angles X-ray Scattering in Grazing Incidence (A-GISAXS [2] and A-GIWAXS [3]), the chemical order in supported nanoalloys can be investigated.

This experimental work focuses on the AgCo system whose phase diagram presents immiscibility gap. Supported bi-metallic NPs, smaller than 3nm, are prepared by UHV deposits on an amorphous substrate. Thanks to this method, the NPs composition can be controlled, and the metals can be deposited simultaneously or sequentially. The aim of this work is to investigate the stability of the NPs and their equilibrium configurations during their growth and annealing, in order to determine the impact of the competition between the thermodynamic principles and experimental kinetic parameters.

In situ A-GISAXS and A-GIWAXS measurements were performed on the SixS beamline at synchrotron SOLEIL. The experimental setup allows achieving a significant anomalous effect despite the weak amount of matter involved.

The AgCo NPs exhibit a core-shell configuration after deposition at RT, with a Co core and an Ag shell, that tends to metals segregation towards Janus NPs during annealing.

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Investigation of Domain Behaviour in PbTiO₃/SrTiO₃ Superlattices using X-Ray Diffraction Methods

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The discovery of two-dimensional electron gas (2DEG) formation at the oxide interface of the band insulators lanthanum aluminate (LaAlO₃) and strontium titanate (SrTiO₃) has sparked interest in these kinds of systems due to its variety of interesting effects. This 2DEG formation is thought to be a consequence of a polar catastrophe, in which an electronic reconstruction results from the energetically costly polar discontinuity at the interface between the polar insulator LaAlO₃ and non-polar insulator SrTiO₃. In this work we explore the possibility of the formation of 2DEG in a system in which the polar material is ferroelectric, where the spontaneous polarization would be the driving force for the polar discontinuity. Using an off-axis rf-magnetron sputter deposition technique, we grew a series of ferroelectric superlattices composed of lead-titanate (PbTiO₃) and SrTiO₃, with varying volume fractions of the ferroelectric layers of PbTiO₃. Experimental results, mainly reciprocal space maps obtained by X-Ray diffraction, show us that at a certain threshold of PbTiO₃ volume fraction there is a peculiar behavior of electric polarization domain periodicity within the superlattice structure. Rather than following the Kittel scaling law for ferroelectrics, we observe a spike in domain periodicity indicating the possibility of an alternate screening mechanism within the system. Utilizing nanofabrication techniques, this work focuses on measuring the electrical resistance at the interfaces of PbTiO₃/SrTiO₃ superlattices.

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Order and Melting in Self-Assembled Alkanol Monolayers on Amorphous SiO₂

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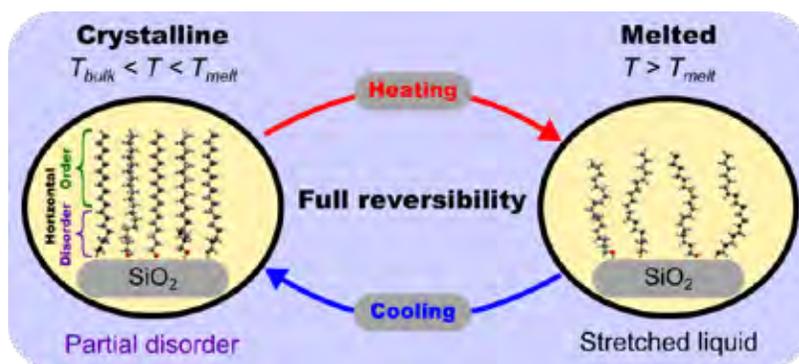
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Self-assembled organic monolayers (SAMs) play an important role in wide-ranging nano and microscale applications in many fields including nanoscience, organic chemistry and material science. Understanding their molecular level structure is therefore of prime importance. Employing surface-specific synchrotron x-ray scattering methods, we have resolved the Å-scale structure of the earliest and simplest SAM, octadecanol on an amorphous-SiO₂- terminated Si (001) substrate, and determined the structure's temperature evolution [1]. At low temperatures, lateral hexagonal order exists, with close-packed, surface-normal molecules. At ~12 °C above the alkanol's bulk melting temperature, T_{bulk}=60°C, a fully reversible disordering transition occurs to a novel "stretched liquid" phase, where the SAM is laterally disordered, but only ~15% thinner than in the crystalline phase. The octadecanol SAM persists on the substrate to ≥100 °C. A thermodynamic model yields a headgroup-substrate bond energy ~40% lower than that of an octadecanol SAM on crystalline sapphire [2], highlighting the importance of the substrate's order and near-epitaxy (on sapphire) for the SAM's structural properties and stability.



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Poster Abstracts

Synchrotron X-ray Beam-Induced Oxidation/Reduction of Arsenic during As K-edge X-ray Absorption Spectroscopy Measurements

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X-ray absorption spectroscopy (XAS) is a widely used application in the study of Arsenic (As) that is interacted with its hosting minerals. Particularly, since As exists as a trace element in environmental samples, a small amount of As in a tested sample often undergoes transformation of its oxidation state during the beam-radiation. Previous studies have been reported many cases of beam-induced As oxidation and suggested several precautions to avoid this change using special conditions such as cryogenic temperature or oxygen-free atmosphere. In this study, various oxidation state of FeS reacted with As(III) or As(V) were tested to observe the occurrence of beam-catalyzed change of As during XAS measurement. Our results showed that both beam-catalyzed oxidation and reduction were observed in tested samples. The main controlling factors caused beam-catalyzed change seem to be redox state of As-hosting FeS and the chemical species of As reacted with its hosting FeS. If the As-hosting FeS was under reducing conditions, the As-interacted with surface of FeS was reduced during the XAS measurement; the opposite reaction occurred when FeS was under oxidizing conditions. Based on this results, the observed As transformation was confirmed as a beam-catalyzed reaction. This study also discusses the precautions in As XAS measurement and its data analysis to avoid the error from the beam-catalyzed sample change.

Key words: Beam-induced transformation, oxidation/reduction, arsenic, X-ray absorption spectroscopy

NLS-II beamline for Integrated In-Situ and Resonant X-ray Studies (ISR)

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Three endstations are served by a 2.8 m long, 23 mm period, in-vacuum undulator (IVU) source: (1) a base diffractometer accommodating large magnets in Hutch C; (2) a psi 6-circle diffractometer in Hutch C; a base diffractometer accommodating custom large environment chambers (Hutch D). The X-ray energy range is 2.4-23 keV for resonant studies of a very wide range of important elements. Key capabilities include full polarization control, circular and variable linear, and polarization analysis, and 1 μm vertical focusing. Coherence-preserving optics allow for studies of nanoscale dynamics and complementary imaging studies in complex environments. The beamline is capable of combining a wide range of techniques for integrated materials investigations including: polarized XRD, RXS, CTR, XRR, GISAXS, GID, XPCS, and XMCD. Scientific directions include correlated electron systems, functional surfaces and interfaces, and thin film growth processes during growth by techniques such as thermal deposition, pulsed laser deposition, sputter deposition, and atomic layer deposition.

Tracking the shape-dependent sintering of Pt-Rh model catalysts under operando conditions

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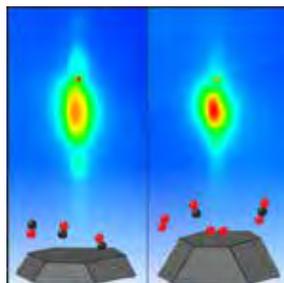
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Alloy Pt-Rh nanoparticles are widely employed in chemical industry and in automotive exhaust control where they are employed to catalyze the oxidation of CO among other reactions [1]. Sintering – i.e. the unwanted agglomeration and coalescence of particles into larger ones – is regarded as one of the major causes of catalyst deactivation and lifetime reduction. Therefore it is of paramount scientific and economic interest to find ways to prevent it.



Average shape as determined for the pure Pt nanoparticles before (left side) and after (right side) the CO oxidation induced sintering. The use of high photon energies combined with a 2D detector (background: respective particle (3-11) Bragg peaks) allowed for the operando monitoring of the particle sintering.

Here we present our recently published results [2] on the composition- and hence shape-dependent three-dimensional restructuring of epitaxial Pt-Rh alloy nanoparticles supported on α -Al₂O₃(0001) as observed operando during CO oxidation performed at 550 K and at near-atmospheric pressures. The experiments were carried out in a dedicated flow-reactor [3] installed on the high energy micro-diffraction setup at beamline ID15A (ESRF, E=78.8 keV) by combining high energy grazing incidence x-ray diffraction, complementary x-ray reflectivity measurements, in-situ mass-spectrometry and a combinatorial sample design. Our results disclose a tremendous sintering in height for the pure Pt and Pt-rich particles at the expense of the total particle coverage on the sample surface. Furthermore, we find this restructuring to be progressively reduced for particles with increasing Rh content. We explain our findings by a reaction-induced non-classical Ostwald ripening process in which the sintering particles use the energy released in the reaction to obtain a more three-dimensional and accordingly more stable shape.

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Aggregation Structure and Molecular Motion of Polybutadiene Bound Rubber on Carbon Surface

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Introduction

In general, the performance of a nanocomposite, which is materials composed of polymers mixed with inorganic fillers, strongly relies on the interfacial structure and physical properties of the composite. This means that understanding interfaces is a first step to achieve to construct functionalized materials. Applying to the case of tire material, elastomer and carbon black, main components of the tire, are corresponding to the polymer and the filler. In the tire material, a nanometer-thick layer, so-called bound rubber layer (BRL) is typically formed on the carbon surfaces. In theory, the interactions between polymer and carbon material surface restrict a molecular motion which correlates with increased resistance to mechanical deformation. However, it have not yet been fully clarified a role of the BRL because of lack of knowledge about the aggregation structure and thermal molecular motion of the elastomer molecules in BRL. In this study, to understand the role of BRL in tire material, aggregation structure and thermal molecular motion of the layer was investigated.

Experimental

As a material, 1,4-cis polybutadiene (PB) with number-average molecular weight and polydispersity index of 190k and 2.3 was used. Diamond like carbon (DLC) film, as a model material of carbon black, was prepared on the Si wafers by plasma-enhanced chemical vapor deposition method. PB film was spin coated on the DLC film from toluene solution and dried under vacuum more than 12 hours at room temperature. After that, the PB films were rinsed by large amount of toluene. Then, the film was again dried under vacuum more than 8 hours at room temperature. This procedure can extract BRL and leads to evaluate thermal molecular motion of the layer directly. The mechanical properties of the rinsed film on the DLC were measured on the basis of force-distance curves derived from atomic force microscopic observation. A cantilever with spring constant and Young's modulus of $1.6 \text{ N}\cdot\text{m}^{-1}$ and 80 GPa were used. The approach-retract speed for a tip was set at $20 \text{ nm}\cdot\text{s}^{-1}$.

Results and discussion

Prior to the force-distance curves measurement, density profile of BRL along the direction normal to the surface was examined by X-ray reflectivity measurement. As a result, it has been found that density of BRL was much higher than bulk one. This implies that not only the aggregation structure but also thermal molecular motion of BRL is different from those of bulk. Figure 1 shows temperature dependence of force-distance curves for BRL. When the cantilever tip contacts with a specimen in the approach direction, the normal force drops because of Van der Waals force between them. If BRL is glassy state, the normal force immediately increases with decreasing the Z-sample position. On the other hand, when BRL is rubbery state, the normal force doesn't increase because BRL is distorted by a pressure from the cantilever. Although glass transition temperature (T_g) of bulk PB was 170 K, the normal force immediately increased at 298 K. On the other hand, in case of the measurement temperature is higher than 378 K, the normal force didn't increased just at Z-sample position is around 0 nm, suggesting that the BRL is in glassy state. We will show detail in the presentation.

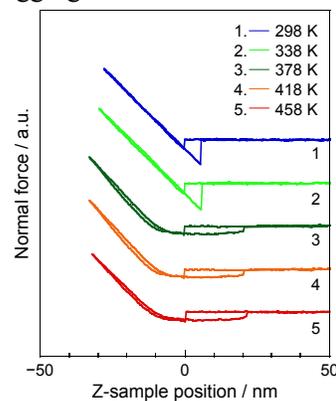


Figure 1 Temperature dependence of force-distance curve for BRL.

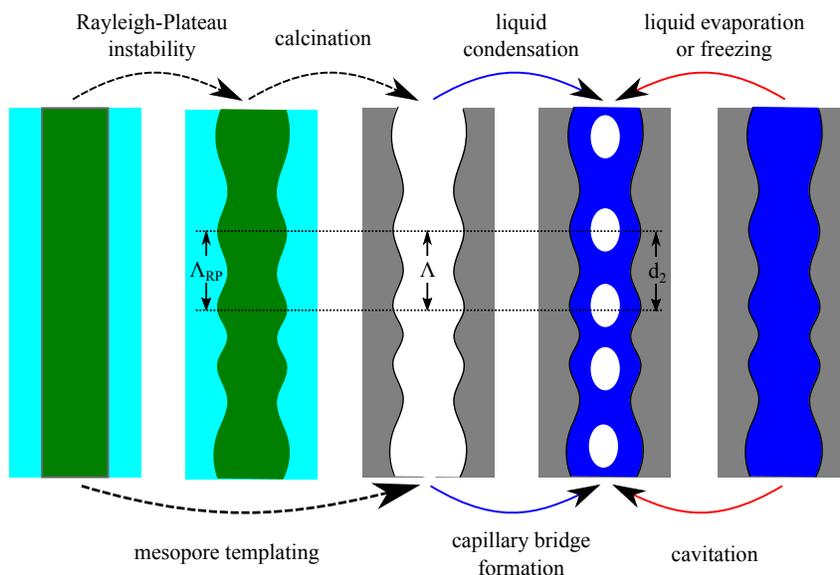
Formation of Periodically Arranged Nanobubbles in Mesopores: Capillary Bridge Formation and Cavitation during Sorption and Solidification in an Hierarchical Porous SBA-15 Matrix

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We report synchrotron-based small-angle X-ray scattering experiments on a template-grown porous silica matrix (Santa Barbara Amorphous-15) upon in-situ sorption of fluorinated pentane C_5F_{12} along with volumetric gas sorption isotherm measurements [1]. Within the mean-field model of Saam and Cole for vapor condensation in cylindrical pores, a nitrogen and C_5F_{12} sorption isotherm is well described by a bimodal pore radius distribution dominated by meso- and micropores with 3.4 and 1.6 nm mean radius, respectively. In the scattering experiments, two different periodicities become evident. One of them ($d_1 = 11.5$ nm) reflects the next nearest neighbor distance in a 2D-hexagonal lattice of tubular mesopores. A second periodicity ($d_2 = 11.4$ nm) found during in-situ sorption and freezing experiments is traced back to a superstructure along the cylindrical mesopores. It is compatible with periodic pore corrugations found in electron tomograms of empty SBA-15 by Gommers et al. (*Chem. Mater.* 2009, 21, 1311–1317). A Rayleigh–Plateau instability occurring at the cylindrical blockcopolymer micelles characteristic of the SBA-15 templating process quantitatively accounts for the superstructure and thus the spatial periodicity of the pore wall corrugation. The consequences of this peculiar morphological feature on the spatial arrangement of C_5F_{12} , in particular the formation of periodically arranged nanobubbles (or voids) upon adsorption, desorption, and freezing of liquids, are discussed in terms of capillary bridge formation and cavitation in tubular but periodically corrugated pores.



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Relationship between Potentials of Zero Charge and Geometric Properties of Transition Metal Nanocatalysts

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Potential of zero charge (pzc), which is also called the potential of zero free charge (pzfc) or the potential of zero total charge (pztc), has been regarded as a key factor to evaluate electronic and geometric effects on the electrochemical properties at the metal-electrolyte interface. According to the introduction by Frumkin and Petrii [1], adsorption behavior at the metal-electrolyte interface is closely connected to the pztc. The underlying background for that can be conceptually understood in terms of specific adsorption and work function.

In UHV, the pzfc indicates the potential at which charge density on the metal surface equals zero. It is directly related to the metal work function or Fermi level. In electrochemical cell, however, there are various species that can be adsorbed onto the electrode surface and participate to the charge transfer process. At a given applied potential, the work function of the metal electrode is also changed regardless of the work function of the metal. The compensation of the difference between the metal work function and the electrode potential generates different excess charge and consequent specific adsorption. Therefore, the pztc is the potential at which the excess charge density becomes equal to the charge density transferred during adsorption process.

On the basis of the conceptual understanding, we have studied various mono- and bi-metallic nanoparticles with different surface structures in the combination of both electrochemical measurements and synchrotron X-ray techniques. The electrocatalytic performance as fuel cell catalyst, i.e., activity and stability, will be also discussed.

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In-situ X-ray Reflectivity and Microscopy Studies on Irreversibly Adsorbed Polymer Layers on Solids

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Abstract

The solid-polymer melt interface is of great scientific interest due to its vital impact on various physical and mechanical properties of thin polymer films prepared on solid substrates. Recent studies have evidenced the formation of irreversibly adsorbed polymer layers at the solid-polymer melt interface with thickness of much less than the radius of gyration of unperturbed macromolecules (R_g), even when interactions between polymers and solids are weak. In this work, the detailed structure and thermal properties of adsorbed polystyrene and poly (2-vinylpyridine) layers prepared on silicon substrates were investigated by a combination of in-situ X-ray reflectivity (XR) and atomic force microscopy (AFM) techniques. The effects of the polymer/substrate interaction and molecular weight on the surface morphology and thermal property were revealed. It was evidenced that the temperature-dependent morphological evolution of the adsorbed layer is in good agreement with previous theoretical and experimental findings. These results would provide a better understanding of the underlying thermodynamics at the solid-polymer melt interface.

Strain relaxation in coalesced GaN nanowires: an x-ray diffraction study

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GaN nanowires form spontaneously on various substrates without requiring a metal droplet to induce growth. A decisive advantage of this spontaneous formation is the possibility to synthesize abrupt axial heterojunctions. However, the spontaneous formation inevitably results in dense arrays, and thus in subsequent nanowire coalescence during growth [see Fig. 1(a)]. We have found that the process of coalescence is governed by nanowire bundling, which reduces the surface energy of the side facets at the expense of elastic bending energy [1]. In the present work, we study the strain state of GaN nanowire ensembles by laboratory x-ray diffractometry in conjunction with an analysis of the energetics of nanowire bundling. Our results demonstrate that the elastic bending of nanowires caused by their bundling gives rise to a large elastic strain, which is reduced plastically via the creation of dislocation walls at the joints.

The shape of the bundled nanowires in Fig. 1(b) and the elastic energy of bending are deduced in the framework of the elasticity of thin rods. Alternatively, dislocations at the joints form small angle boundaries, as shown in Fig. 1(c). This introduction of dislocations is found to significantly reduce the total energy of the bundle. The relative misorientation of the nanowires at the joint due to the small-angle boundary reduces the nanowire curvature by an order of magnitude and hence gives rise to narrower diffraction lines.

Figure 1(d) compares the experimental x-ray diffraction profiles from a spontaneously formed GaN nanowire ensemble on Si(111) in successive reflection orders [2] with the calculated profiles. The calculation is performed with a Monte Carlo average over random lengths, diameters, and distances between nanowires, as well as random orientations of the bundled pairs. We also take into account the vertical divergence of the x-ray beam in a laboratory diffraction experiment, which gives rise to the asymmetry of the profiles [2] observed in Fig. 1(d). The calculated x-ray diffraction profiles for elastically bent rods lead to the line widths much larger than experimentally observed. The calculated profiles presented in Fig. 1(d) are for dislocated bundles and are narrow due to the reduction of the nanowire curvature compared to the case of purely elastic bundling. Thus, our x-ray diffraction experiments show that a major part of the elastic bending energy of the nanowires is released by creation of dislocations at the coalescence joints.

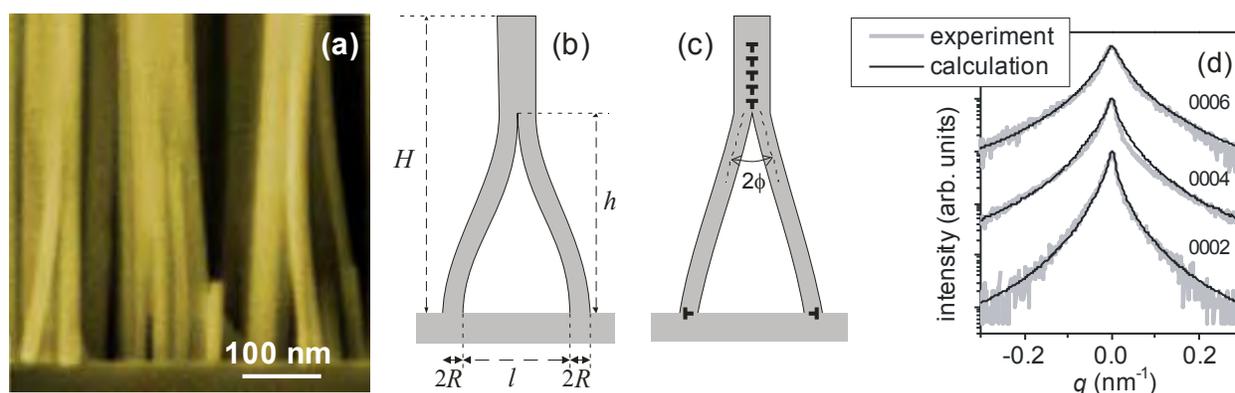


Fig.1: (a) Bottom part of coalesced nanowires, (b) coalescence by bending, (c) coalescence with creation of dislocations at the joint, (d) experimental and calculated x-ray diffraction profiles from bundled nanowires.

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Poster Abstracts

Development of CV-XAFS method for studying electrode/electrolyte reactions on catalysts

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To fully understand the mechanisms of electrochemical reactions and to apply these reactions to fuel cells, sensors, and molecular devices, it is important to know the evolution of atomic arrangements and their related electronic structures at the electrode/electrolyte interfaces under working condition in real time. Oxygen reduction reaction (ORR) in liquid fuel cell is one of the electrochemical reactions at the electrode/electrolyte interfaces and is a key role to design catalysts with high-performance, reaction selectivity, and long-life. Cyclic Voltammetry (CV) is a well-known method to study the electrochemical reactions [1]. However, no direct information on atomic and electronic structures related to the reactions at the electrode/electrolyte interfaces are derived by the CV method. In order to overcome this problem, we have developed the method of CV combined with X-ray Absorption Fine Structure (XAFS) spectroscopy, named "CV-XAFS" which is *in situ* and real time XAFS, and applied it to studying the reaction behavior of Pt/C cathode catalyst for ORR.

XAFS measurements were carried out in wavelength dispersive mode at BL14B1 of SPring-8 in Japan. Fig. 1 shows electrochemical cell developed for the present study, and x-rays can pass through window and catalyst. The three electrodes were immersed into oxygen or nitrogen saturated 1 M KOH. Carbon paper coating Pt/C catalyst is on the carbon electrode used as working electrode. Pt coil and Hg/HgO were used as counter and reference electrode, respectively. Scan rates of CV were chosen at 2 mV/s (Fig. 2a), 10 mV/s, and 50 mV/s.

Fig. 2 shows the results of CV-XAFS with Pt L_{III} edge. The comparison between oxygen and nitrogen atmosphere indicates different behaviors of the reaction on the surface with and without ORR condition. It is found that the current due to the ORR begins to be observed at around 0.08 V although the Pt valence remains almost no changing. Also from the observation of the hysteresis in Fig. 2c the electronic structure of the catalytic surface for ORR is different between negative and positive potential scan direction. These observations allow us to discuss the surface dynamics related to electrochemical reactions.

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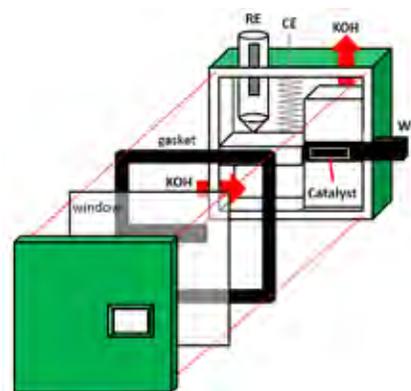


Fig. 1. Schematic of internal structure for electrochemical cell

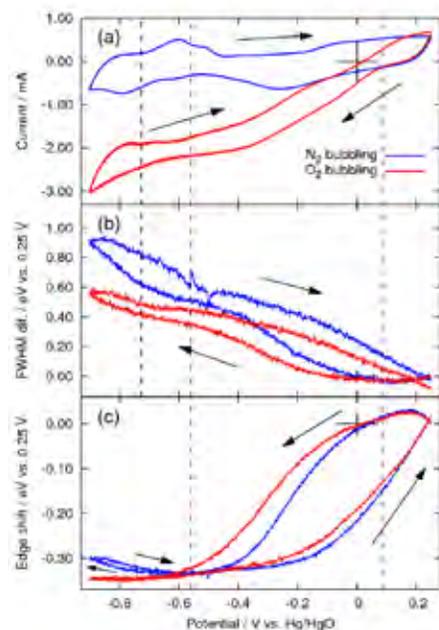


Fig. 2. The results of CV-XAFS for (a) cyclic voltammogram and shifts of (b) width of the white line and (c) edge position from 0.25 V at 2 mV/s

Noncontact Selective Modification and Chain Alignment of Conducting Polymer Blend Films by an Ultrafast laser writing

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We propose a novel direct writing technique with a femtosecond laser enabling selective modification of not only the morphology of conducting polymer thin films but also the orientation and alignment of the polymer crystals. Surface relief gratings resulting from photoexpansion on poly(3-hexylthiophene)(P3HT):[6,6]-phenyl-C61-butylric methyl ester (PCBM) thin films were fabricated by a femtosecond laser direct writing. The photoexpansion was induced at laser fluence below the ablation threshold of the thin film. The morphology (size and shape) of photoexpansion could be quantitatively controlled by laser writing parameters such as focused beam size, writing speed, and laser fluence. Grazing incidence x-ray scattering results showed that the amount of face-on P3HT crystals were largely increased in the photoexpansion in comparison with pristine region of the thin film. In addition, the P3HT polymer chains in the photoexpansion were highly aligned along the polarization of the laser. The micro-RAMAN spectra confirmed that neither chemical composition change nor the polymer chain breaking was observable after femtosecond laser irradiation. We believe that this laser direct writing technique opens a new door to the fabrication of more efficient organic semiconductor devices via non-contact, toxic-free approach.

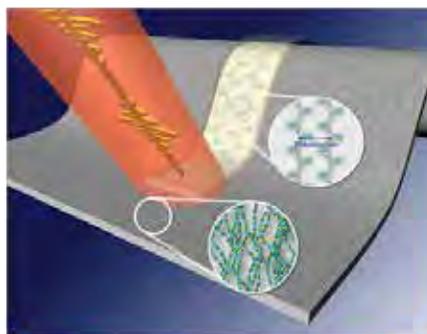


Figure. Schematic illustration showing an ultrafast laser induced photoexpansion process and polymer chain alignment during direct laser writing.

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Cold Neutron Reflectometer (CN REF-V) at the HANARO

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Neutron reflectometer, CN REF-V has been installed at CG1A guide in the cold neutron laboratory building (CNLB) at the high-flux advanced neutron application reactor (HANARO) at the Korea [1]. The instrument operates in a monochromatic, angular dispersive mode and collects the reflectivity data as a function angle in the horizontal scattering geometry. In general, we use two modes such as fixed-slit and variable-slit scan for the measurement of the neutron reflectivity profile for a thin film sample [2]. We determined the instrument resolution for the two measurement modes by theoretically and experimentally [3]. In consideration of instrument user's convenience, we made a new data reduction program which can automatically correct the footprint effect appearing during the measurement of reflectivity profiles in fixed-slit scan mode [4].

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In Situ Spatial Structural Characterization of Meso Scale Structures Using Xrays

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The high degree of coherence and flux of xrays from next generation synchrotron sources permits the measurement of structural information from less ordered systems over larger ranges of length scales. One such interesting length scale is the mesoscale (100nm – 1 micron) range. This talk will discuss the application of coherence-based correlation techniques, especially Xray Cross Correlation Analysis (XCCA), applied to various nano- and meso-structures. Correlation techniques hold the promise of extracting subtle structural features from xray scattering data. The experimental setup, data analysis, and initial results will be presented, along with some discussion of the limitations and capabilities.

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A study of the influence of graphene and graphene oxide nanoparticles on the self- diffusion coefficient of PMMA

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Graphene and graphene Oxide nanoparticles have recently attracted a great deal of attention as modifier of polymer thermal and electric properties. Recently it has been illustrated that they can compatibilize polymer blends[1] as well as assist in exciton migration in two phase bulk heterodyne junction photovoltaic cells[2]. In both cases, graphene and graphene oxide serve to modify the interfacial energies between two polymers phase segregating in a blend and produce morphologies which enhance the properties of the material[3]. Rather than rely on trial and error, its optimal to be able to model the influence of graphene or graphene oxide on polymer blend interfaces. In order to be able to set up the models though it is essential that the interaction energies between the graphene and graphene oxide nanoparticles and the host matrices be known. One method, which we have previously shown to be very useful, is the determination of the self-diffusion coefficient in a homopolymer in the presence of the nanoparticles. If the interaction is attractive, adsorption of the chains onto the nanoparticle surfaces increases the diffusion coefficient while a neutral or unfavorable interaction results in no change of the polymer dynamics in the presence of the particles. The experiments involve measuring the diffusion coefficient in a bilayer sample composed of monodisperse polymers of DPMMA/HPMMA with added graphene or graphene oxide nanoparticles in either one of both of the layers. Sample preparation was done at Stony Brook University and the neutron reflectometry was measured on NG-7 at NIST-NCNR.

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Enhancing the performance of BHJ solar cell via self-assembly templates in active layer

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The bulk heterojunction (BHJ) solar cell is an important example of a polymer solar cell technology that has been proposed in recent years. However, due to the disordered inner structures in the active layer, control of the inner structure within the active layer is required to enhance the efficiency [1]. In our approach, a self-assembly of tertiary polymer blend film is confined between the air and solid interfaces [2]. The principal has been proved using a blend of PMMA: P3HT: PCBM where we showed that the PMMA phase formed a column structure in the P3HT, which template the PCBM phase between the electrodes. Neutron reflectometry was used to demonstrate the confinement of PCBM at the interface between P3HT and PMMA in the active layer. The columnar structured template is investigated under atomic force microscopy (AFM) and transmission electron microscopy (TEM). SCLC mobility measurement indicated an obvious improvement on both hole and electron mobility. The different morphological structures formed via phase segregation are correlated with the performance of the PEV cells fabricated at the BNL-CFN and significant enhancement for the efficiency is observed.

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The Role of Ligand in the Mechanical Properties of Self-Assembled Nanoparticle Films

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Films of ligand-capped metal nanoparticles self-assembled at the air/water interface exhibit rich mechanical responses to compression including hashing, wrinkling, and folding, which are a result of ligand-based interactions. Previous studies have shown that a high concentration of ligands inhibits wrinkling and folding, but the mechanism remains elusive. By using inductively coupled plasma optical emission spectrometry (ICP-OES) to measure the ligand concentration of our NP solutions and then back-adding excess ligands at controlled amounts, we precisely control ligand-based interactions, enabling an investigation of how they guide self-assembly and correspondingly the mechanical properties. Liquid surface grazing incidence x-ray diffraction (GIXD) performed at ChemMatCARS, Sector 15-ID (APS/ANL) and transmission electron microscopy (TEM) experiments reveal that increasing the ligand concentration of the films causes the formation of free-ligand islands in addition to an increase in the interparticle separation. These effects are correlated with the previously observed inhibition of wrinkling and folding, as well as a decrease in the dilatational and shear moduli. This work was supported by the University of Chicago Materials Research Science and Engineering Center, NSF/DMR-1420709. ChemMatCARS is principally supported by CHE and DMR at NSF (NSF/CHE-1346572).

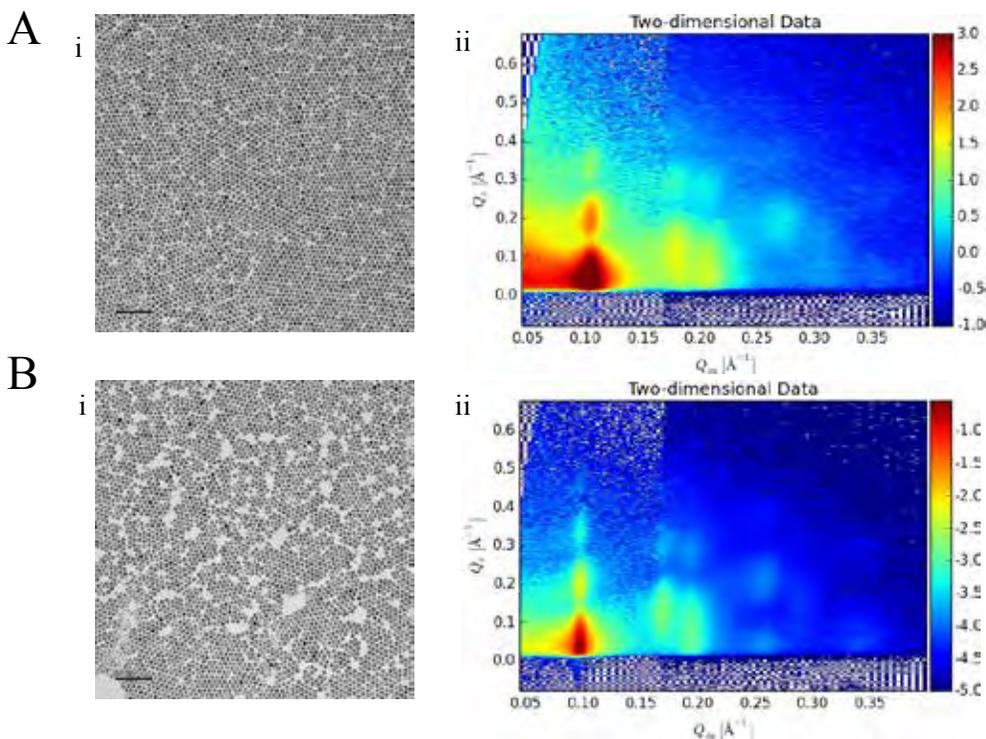


Figure 1: (i) TEM image and (ii) 2-D GIXD (Intensity vs. Q_z vs. Q_{xy}) of 5nm Au nanoparticle monolayers having (A) 11% ligand mass concentration and (B) 60% ligand mass concentration. At high concentrations, islands of free ligands are seen in the TEM images, and an increase in interparticle spacing as well as more pronounced Bragg peaks are seen in the GIXD data. The scale bars on the TEM

A new setup for high resolution in-situ X-ray reflectivity experiments

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A new method for fast x-ray reflectivity data acquisition is presented. The method is based on a fast rotating, slightly tilted sample reflecting to a stationary mounted position sensitive detector (see Fig.1). Since $\theta/2\theta$ scans are not performed the method allows for measurements of reflectivity curves in a quarter of a second. The actual time resolution of the data acquisition depends on the speed of the rotation table, the photon flux and the sample detector distance. Maximum q_z -values of 1 \AA^{-1} can be achieved. The resolution mainly depends on the beam properties and the pixel number and size of the detector (here a Mythen detector with 1280 pixels at $50 \mu\text{m}$ height was used). The main challenges were to cope with the high flux in forward direction and with the high background scattering which swamps the reflectivity at large q_z . The high flux in forward direction, which would saturate the detector, was reduced by a specially designed fixed absorber. The contribution of the background signal is suppressed by a knife-edge blade placed just above the sample and short consecutive exposures with short acquisition times (typically 0.05 to 0.1 s). This acquisition time turns out to be an important parameter for high quality data and the complete reflectivity has to be recorded over several tens of frames. The reconstruction of the reflectivity curve is done by means of program script.

The time-temperature depending structure changes of poly(N-isopropylacrylamide) (PNIPAM) samples has been measured by the new method. It will be presented as application example. For this we used a photon energy of 18 keV, achieved a time resolution of two seconds and an accessible q_z -range of 0.5 \AA^{-1} (see Fig. 2).

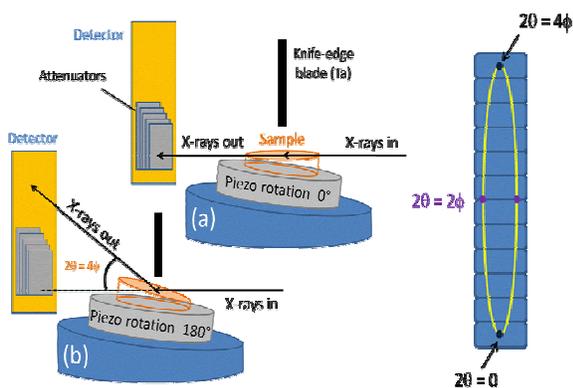


Figure 1. Schematic view of the setup. (a) Piezo rotation = 0° , $\theta = 0^\circ$ (b) Piezo rotation = 180° , $\theta = 2\phi$.

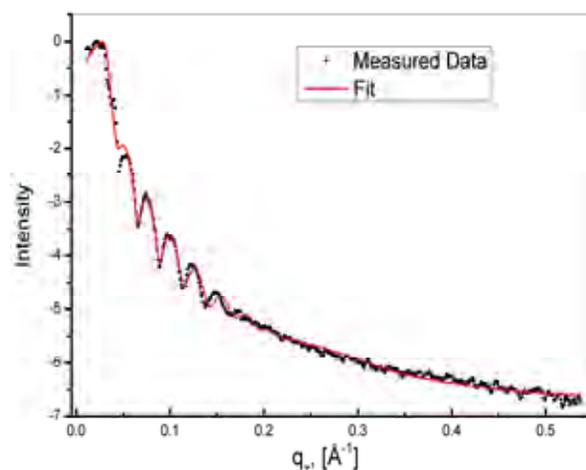


Figure 2. Reflectivity curve of PNIPAM thin film recorded in two seconds. The measurements are done at PETRA III, P08 beamline, DESY, Hamburg

Rapid in-situ x-ray diffraction during the growth of ferroelectric superlattices

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In epitaxially strained ferroelectric thin films and superlattices, the ferroelectric transition temperature can lie above the growth temperature. Ferroelectric polarization and domains should then evolve during the growth of a sample, and electrostatic boundary conditions may play an important role. In this work, Ferroelectric domains, surface termination, average lattice parameter and bilayer thickness were monitored using in-situ synchrotron x-ray diffraction during the growth of BaTiO₃/SrTiO₃ (BTO/STO) superlattices by off-axis RF magnetron sputtering. A new x-ray diffraction technique was employed which makes effective use of the custom growth chamber, pilatus detector and synchrotron radiation available at beamline X21, NSLS, BNL. The technique allows for scan times substantially faster than the growth of a single layer of material, enabling continuous monitoring of multiple structural parameters as the film grows. Due to the large compressive strain experienced by the BTO layers in these substrates these superlattices are ferroelectric when grown and display continuous evolution of the polarization during growth. The effect of electric boundary conditions was investigated by growing the same superlattice alternatively on STO substrates and 20nm SrRuO₃ (SRO) thin films grown on STO substrates. The experiments provide insight into the formation and evolution of ferroelectric domains in the situation when the sample is ferroelectric during the growth process. Besides the fundamental knowledge gained from these studies, being able to monitor the structural parameters of a growing ferroelectric superlattice at this level of detail provides numerous insights which can guide the growth of higher quality ferroelectric superlattices in general. Looking to the future, an updated system for real-time X-ray scattering analysis of complex oxide thin film growth will be installed at the NSLS-II in-situ and resonant scattering beamline in 2016, providing enhanced capabilities and enabling the next generation of these experiments to be performed.

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Recent Progress of CORELLI: The Elastic Diffuse Scattering Spectrometer at SNS

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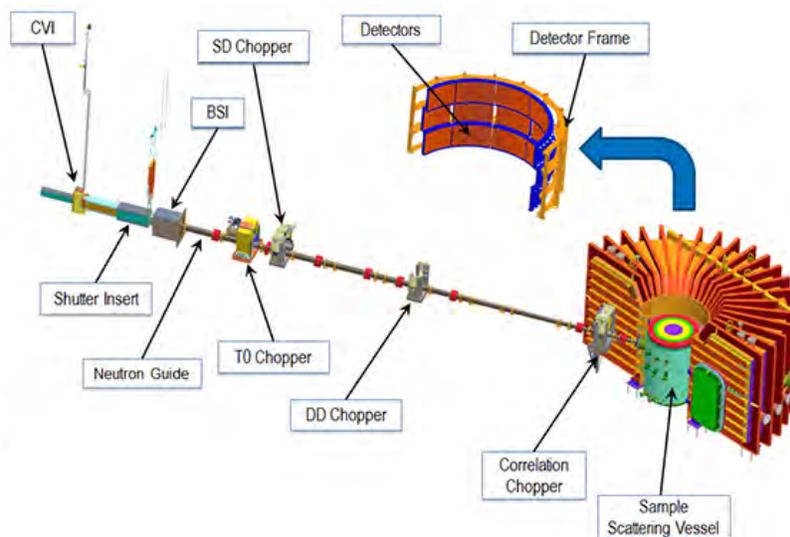
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The CORELLI spectrometer combines the high efficiency of white-beam Laue neutron diffraction with unique (quasi-)elastic discrimination by modulating the incident neutron beam with a statistical chopper. It is located on the BL-9 thermal moderator at the Spallation Neutron Source at the Oak Ridge National Laboratory and has entered into the full user program recently (2016). This instrument can be used for single crystal and epitaxial film neutron diffraction experiments, and is particularly optimized for studying elastic diffuse scattering. The momentum transfer ranges from 0.5 to 18 Å⁻¹, the energy of incident neutrons ranges from 10 to 200 meV, and the detector coverage is -21.9° to +148.2° horizontally and +/- 28.5° vertically. Data can be reduced and visualized both onsite and offsite via the Mantid package, which also allows the users to implement their own tailored analysis algorithms. We have commissioned a rich set of sample environments that are of interest to condensed matter physicists and materials scientists, including ultra-low temperature (300 mK), high temperature (1500 K), high magnetic field (5 T static field and 25 T pulsed field), electric field (5 kV) and high pressure (1.8 GPa), and are making steady progress in further upgrading sample environments and reducing the background scattering. It has been demonstrated that within a reasonable period weak elastic scattering signal can be measured, including elastic diffuse scattering from correlated local disorder in crystalline materials and magnetic diffraction from epitaxial thin films. Selected examples will be presented. CORELLI can have an impact on a range of research areas, such as spintronics, unconventional superconductors, frustrated magnetism, fast ion conductors, quasi-crystals, ferroelectrics, thermoelectrics, multiferroics, molecular solids and microporous framework systems. Work supported by Division of Scientific User Facilities of the Office of Basic Energy Sciences, US Department of Energy.



Grazing incidence X-ray Studies on the Morphology of Organic Bulk Hetero-junction Solar Cells

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Nowadays, solar industry becomes the fastest growing industry due to the rising demands to solve energy crisis and environmental problems. Organic photovoltaic (OPV) devices, as one of the most promising technologies offering low-cost, light weight and flexible solar cells, have attracted more and more attentions [1]. The main challenge of OPV devices is the relatively low power conversion efficiency due to limitations in exciton diffusion, charge separation and transportation inside the organic active layers. It is widely believed that the morphology of the active layer is closely related to these electronic properties, and thus crucial to the device performance. Here, I am going to present our recent work on the active layer morphology and its correlations with device performances for several different OPV systems. Grazing incidence X-ray scattering techniques have been employed to investigate the active layer morphology: grazing incidence wide-angle X-ray scattering (GIWAXS) for Angstrom-scale ordering, such as molecular packing and orientation; grazing incidence small-angle X-ray scattering (GISAXS) for nano-scale ordering, such as donor-acceptor phase separation and miscibility.

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Combining specular and non-specular reflectivity EXAFS investigations by using 2D-area detectors for the study of annealing processes in metal bilayers

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In a grazing incidence X-ray scattering experiment, distinct scattering peaks besides the specular reflected beam may occur (Yoneda-peaks, [1]). While the specular reflection contains information about the structures perpendicular to the surface such as surface and interface roughness and the density of surface layers, the diffuse scattering is related to the in-plane and out-of-plane structure of the involved interfaces [1]. By measuring the X-ray absorption fine structure in the Yoneda peak, i.e. by scanning the photon energy in the vicinity of an X-ray absorbing element inside the sample, we have recently shown that a site-selectivity to a selected interface may be obtained [2], similar to the grazing incidence diffraction anomalous fine structure (DAFS, [3]) or the X-ray reflection anomalous fine structure [4]. In those experiments, the exit angle for the diffuse intensity measurement was selected by a slit system, and the scattered intensities were measured by means of ionization chambers [1]. Therefore, these experiments are extremely time-consuming for multilayered samples, because different exit angles have to be selected and measured consecutively, eventually for several different edge energies. Therefore, those measurements were only feasible for static samples. In particular, interface reactions at buried interfaces that are closely related to the presence of diffusion processes cannot be monitored.

We therefore have used a 2-dimensional X-ray detector (Pilatus 100K) in order to collect the entire scattering pattern for each energy in an EXAFS scan. The desired scattering intensities for the different Yoneda peaks and the specular reflectivity were extracted from the measured scattering patterns after the completion of the energy scan, that can now be performed within typically less than 50 minutes on a state of the art 3rd generation synchrotron beamline. Thus in-situ studies of annealing processes of multilayered samples are feasible.

Here we will discuss results from bismuth-gold and gold-bismuth bilayers on glass substrates, that were subjected to an annealing process in a high-vacuum environment. The combined scattering and spectroscopic X-ray experiments sensitively show that gold diffusion starts at about 120°C, however without formation of Au-Bi-intermetallic compounds such as AuBi or AuBi₂.

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In-situ investigation of NiAl alloy formation in Ni-Al multilayers by combined specular and non-specular reflectivity EXAFS investigations

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Combustion synthesis is a widely used technique for the preparation of intermetallic compounds such as nickel or titanium aluminides, and molybdenum silicides. In most cases the synthesis uses μm -sized powders as reactants (e.g. [1]), but alternating stacks of elemental metal films can also be employed [2, 3]. In any case, an ignition is required to initiate the combustion reaction. In the case of NiAl, the reaction is highly exothermic, thus the reaction may freely propagate after initiation. For multilayered Ni-Al-samples, the ignition temperature strongly depends on the individual foil thickness, and for very thin individual layers in the range of several nm only, the prepared layers are metastable and may ignite instantaneously even at room temperature [4]. Although the NiAl compound is thermodynamically the most stable $\text{Ni}_x\text{-Al}_y$ -material, some previous investigations have shown the presence of additional phases such as Ni_2Al_3 or NiAl_3 after cooling the combustion product to room temperature [3]. However, in-situ experiments performed in the course of the reaction do not reveal any indications for reaction intermediates [1, 5, 6].

In the present study, Ni-Al-multilayered films were prepared by subsequent thermal evaporation of Ni and Al on float glass substrates under high-vacuum conditions. The as-deposited films were mounted in a small vacuum chamber and slowly heated to temperatures in the range of 200°C to 300°C. In-situ investigations of the NiAl-intermetallic compound formation were performed using specular and non-specular grazing incidence X-ray absorption spectroscopy.

The reflection mode grazing incidence EXAFS results show that for a thickness of the individual layers of about 50-80 nm, the reaction begins in a narrow temperature window at about 200-210°C, and is finished at about 230°C. While all the elemental Ni inside an Al/Ni/Al – trilayer may be fully transformed to the NiAl-phase, Al-Ni- bilayers only partially reacted, with remaining elemental Al and Ni above and below a buried, inner NiAl-layer, respectively. The present measurements gave no indications for Ni_xAl_y – stoichiometries other than NiAl.

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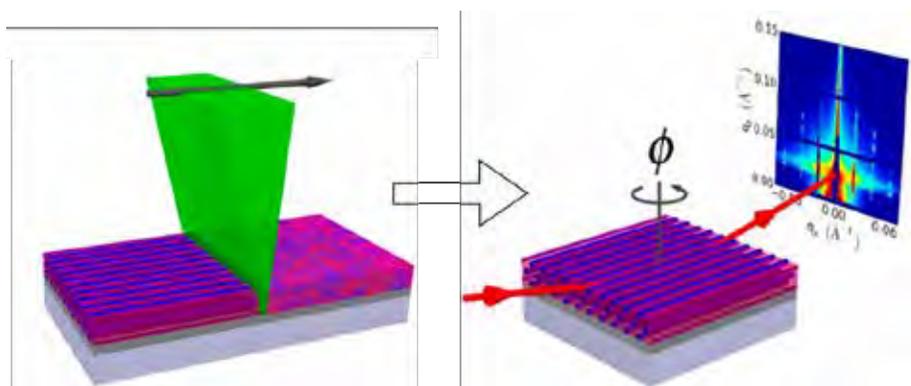
GISAXS Studies of Laser-Induced Block Copolymer Self-Assembly

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We present a novel method of accelerated self-assembly of block copolymer thin films utilizing laser light, called Laser Zone Annealing (LZA). In our approach, steep temperature transients are induced in block copolymer films by rastering narrowly focused laser line over the light-absorbing substrate. Extremely steep temperature gradients accelerate the process of self-assembly by several orders-of-magnitude compared to conventional oven annealing, and, when coupled to photo-thermal shearing (Soft-Shear LZA), lead to global alignment of block copolymer domains assessed by GISAXS diffraction studies and real-space SEM imaging. [1]



We demonstrate monolithic alignment of various block-copolymer thin films including PS-*b*-PMMA, PS-*b*-PEO, PS-*b*-P2VP, PS-*b*-PI and observe different responsiveness to the shearing rate, depending on the characteristic relaxation timescale of the particular material.[2] We also investigate a pathway-dependence of ordering in block copolymer films under ultra-fast soft-shear LZA conditions, which we term “latent ordering”.[3] Our investigation of this phenomenon helps to understand fundamental mechanisms of the self-assembly and to engineer an optimal approach for processing these materials.

Subsequently, we utilize our findings to obtain LZA-aligned polymeric films which are used as templates for synthesis of single- and multi-layered arrays of inorganic, metallic or semiconducting nanowires and nanomeshes.[4]

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Evidence for magnetoelectric and spin – lattice coupling in $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ multiferroic

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Neutron diffraction (ND) studies were carried out on polycrystalline single phase multiferroic $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PFN) in the temperature range of 290 – 2 K to understand the structural and magnetic properties as a function of temperature. ND data was refined using the Rietveld refinement method for both crystallographic and magnetic structures. The structure at room temperature was found to be monoclinic, in Cm space group. No structural transition was observed till 2 K. At low temperatures (i.e., from $T < T_N$; $T_N = 155$ K), an additional peak appears at scattering vector, $Q = 1.35\text{\AA}^{-1}$, indicating the onset of antiferromagnetic ordering. The magnetic structure was found to be commensurate with the crystallographic structure and could be refined using the propagation vector, $k = [0.125, 0.5, 0.5]$. Magnetization, ferroelectric P - E loops and dielectric measurements on PFN reveal a strong anomaly at the antiferromagnetic transition temperature (T_N) indicating the magneto-electric coupling. The refined temperature dependent structural parameters such as unit cell volume and monoclinic distortion angle (β) reveal pronounced anomalies at the magnetic ordering temperature (T_N), which indicates strong spin-lattice coupling. An anomaly in lattice volume was observed with a small negative thermal expansion below and a large thermal expansion above the T_N , respectively. It shows the occurrence of isostructural phase transition accompanying the magnetic ordering below $T_N \sim 155$ K, leading to significant change in ionic polarization, octahedral tilt angle and lattice strain around T_N . These detailed studies confirm the magneto-electric and spin-lattice coupling in PFN across T_N .

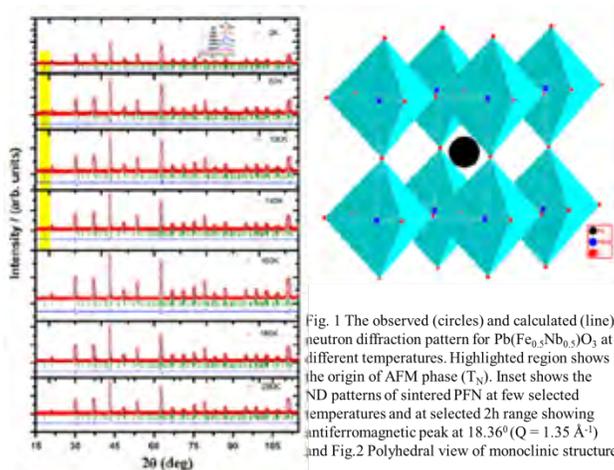


Fig. 1 The observed (circles) and calculated (line) neutron diffraction pattern for $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ at different temperatures. Highlighted region shows the origin of AFM phase (T_N). Inset shows the ND patterns of sintered PFN at few selected temperatures and at selected 2θ range showing antiferromagnetic peak at 18.36° ($Q = 1.35\text{\AA}^{-1}$) and Fig.2 Polyhedral view of monoclinic structure

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Barrier Formation at Ionic liquid Surfaces

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Ionic Liquids (ILs) are promising candidates in a variety of applications such as heterogeneous catalysis. In the SILP (Supported Ionic Liquid Phase) catalysis the chemical reaction takes place in a thin IL film, wetting a solid support material with high surface area. Recently, it has been proposed that the observed performance degradation is related to aggregation of side products at the IL/gas interface, forming diffusion barriers for educts and products. However, for an in-depth understanding of the processes influencing the transport properties of reactants and products across the liquid/gas interface, knowledge of the interfacial structure of ILs on a molecular length scale is essential. As a model system, we studied the near surface structure of an alkane containing IL by x-ray reflectivity. Analysis of the experimental data revealed the pinning of bulk correlations at the surface, surface induced smectic ordering, and surface segregation of the alkanes, affecting the interfacial ion profiles.

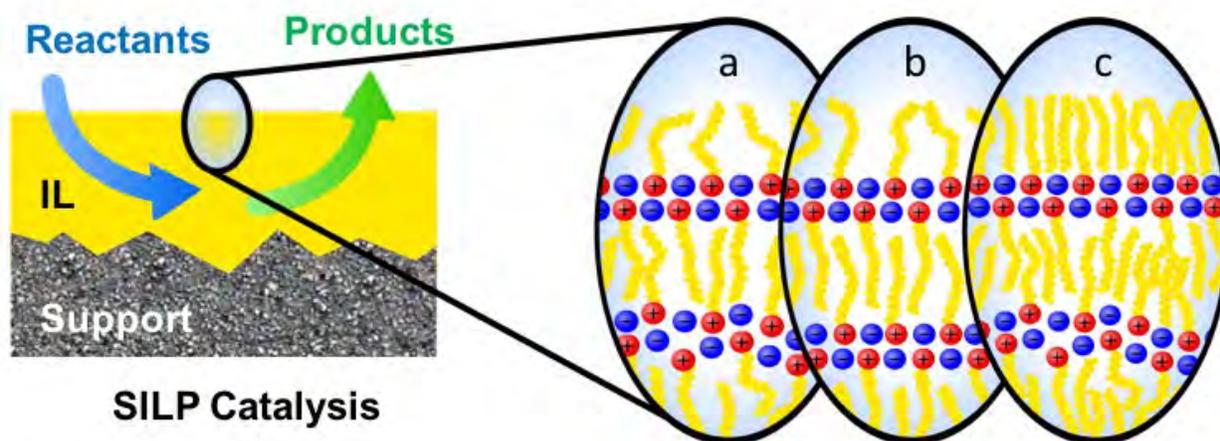


Figure: Sketch of the SILP process. The transport properties of reactants and products across the liquid/gas interface can be affected by the near surface structure that is governed by (a) the pinning of bulk correlations, (b) surface induced smectic ordering, and (c) surface segregation of impurities and side products.

Observation of Ordered Structures in Counterion Layers Near Wet Charged Surfaces

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Charged particles in aqueous solutions sometimes behave as though their effective charge has been completely reversed, rather than simply reduced or neutralized, by counterions.^[1] One proposed mechanism to explain this counterintuitive phenomenon is the formation of lateral ordering in the counterion layer, which may reduce the overall free energy^[1]. Grazing incidence x-ray diffraction (GIXD) allows us to probe these charged surfaces *in situ* and directly observe any ordering that occurs.

We detect sharp diffraction peaks from an incommensurate Er³⁺ counterion layer near the charged surface formed by a floating molecular monolayer^[2]. Since this counterion lattice is incommensurate with the lattice of the floating molecular layer, there is no specific adsorption of the ions to molecules, and the ionic lattice structure is not imposed by the molecular layer. Thus, the ionic lattice must be formed due to interactions between charges in the counterion layer. This indicates that counterion ordering is a realistic mechanism for charge inversion. (Previous studies of divalent ions under Langmuir monolayers found commensurate structures only.)

In addition, we have observed several different ordered counterion structures using other trivalent lanthanides and molecular monolayers. There are transitions between these structures as a function of atomic number that appear to be inconsistent with the physical properties of the lanthanide series. This elemental series undergoes what is known as “lanthanide contraction,” the continuous reduction in atomic radius as *Z* increases. Our discrete transitions suggest that some property other than atomic radius governs the interaction between the counterions and the molecular monolayer.

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Lateral Organization of Cholesterol in Phospholipid Membrane

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Raft structures in lipid membranes are believed to control many important cellular processes like protein functioning, protein sorting, signal transduction, drug delivery etc. and cholesterol is a major constituent of these raft phases in lipid bilayer membranes [1]. Here lateral organization of cholesterol and its effect on regulating the phospholipid membrane properties is investigated for a variety of cholesterol molar percentages using Langmuir monolayer pressure-area ($\Pi - A$) isotherm studies and x-ray reflectivity (XRR) measurements. $\Pi - A$ isotherm of DMPC-cholesterol system at 15 °C is shown in figure (a) and the compressibility modulus (C_s) extracted from the isotherms are in the inset. X-ray reflectivity measurements were done from bilayers deposited on polymer cushion [2] in a specially designed water cell as the bilayers are stable only under water. The fitted reflectivity profiles and the corresponding EDPs are shown in figure (b). The analyzed reflectivity profiles show the electron density region corresponding to the polymer, bilayer and water on top of silicon substrates and to clearly identify the region corresponding to the bilayer on top of polymer films we have marked it with a shaded box.

Isotherm measurement suggests cooperativeness between cholesterol and phospholipid depending on the cholesterol molar concentration. Isothermal compressibility modulus shows the coexistence of liquid expanded (LE) and liquid condensed (LC) phases for the lipid monolayer at 15 °C. The XRR measurements predict the organization of cholesterol in the bilayer membrane as the cholesterol tries to mix with the lipids at low molar concentration but higher cholesterol concentration induces tilting in the head group of the lipids causing a change in size along the depth and reducing the electron density. In addition, a change in the length of hydrophobic region has also been observed at higher cholesterol concentration. These observations clearly indicate the coexistence of all the physical models [3] namely the Umbrella Model, the Condensed Complex Model and the Super Lattice Model. At low concentration, the Umbrella Model along with the cholesterol condensing effect gives satisfactory result. At some specific percentages (near 25% and 75%) the Super Lattice Model works very well. At high concentration regime (above 25%) cholesterol produces condensed complex with the lipid molecule. Results suggest the existence of a critical molar concentration of cholesterol beyond which inhomogeneity in mixture settles in, that can lead to the formation of lipid rafts.

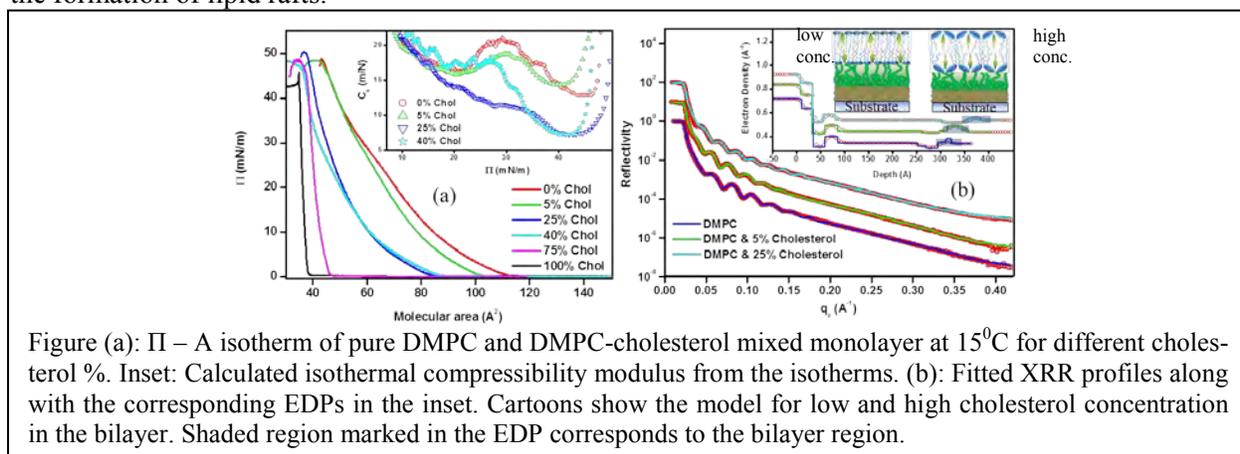


Figure (a): $\Pi - A$ isotherm of pure DMPC and DMPC-cholesterol mixed monolayer at 15°C for different cholesterol %. Inset: Calculated isothermal compressibility modulus from the isotherms. (b): Fitted XRR profiles along with the corresponding EDPs in the inset. Cartoons show the model for low and high cholesterol concentration in the bilayer. Shaded region marked in the EDP corresponds to the bilayer region.

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Poster Abstracts

X-ray pump - optical probe capability at LISA Liquid Surface Diffractometer

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The LISA diffractometer [1], installed at the P08 beamline at the PETRA III synchrotron radiation source in Hamburg, is a specialized instrument for hard X-ray scattering studies of liquid surfaces and interfaces. The setup takes advantage of the specific design of LISA, where all scattering studies can be performed without moving the sample.

Here, we describe the extension of this instrument's capabilities by an optical pump - X-ray probe option, which will allow investigations of ultrafast processes at liquid interfaces. This includes installation of a synchronized fs-laser system and optics for directing the laser pulse onto the sample surface. First results from pump probe X-ray reflectivity experiments at the liquid - air interface, confirming a time resolution better than 100ps will be shown. These new capabilities will provide access to structural changes induced via optical excitation allowing us to understand the non-equilibrium processes on liquid interfaces.

We thank the BMBF (05K13FK2) for funding this project.

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Structural dynamics of the initial stage of Cu deposition/dissolution on Au(111) electrode

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A well-defined epitaxy layer on single crystal surface is formed by the underpotential deposition (upd) of metal ions. Therefore, the understanding of upd processes is useful for fundamental research as an initial model of metal deposition. Detailed structures of well-defined upd layer at the constant potential have been studied using scanning tunneling microscopy and X-ray diffraction. The understanding of transient structure is also necessary to elucidate deposition/dissolution processes. In this study, deposition/dissolution processes of Cu cation and counter anion on Au(111) were investigated by using time resolved X-ray diffraction. Transient structures of metal cation and counter anion in the electrical double layer were captured at the time resolution of micro – millisecond.

X-ray diffraction measurements were performed with a multi-axis diffractometer at BL13XU (SPring-8). Diffracted X-ray was counted with the time resolution of 500 μ s. The multichannel scaler was synchronized with the function generator. The electrolyte concentration was 0.5 M H₂SO₄ + 1 mM CuSO₄. In sulfuric acid, Cu and sulfate anion are coadsorbed on Au(111) with the $\sqrt{3} \times \sqrt{3}$ honeycomb structure at the first upd step. A rectangular potential wave was applied between the $\sqrt{3} \times \sqrt{3}$ upd and non-upd potentials.

Fig. 1 shows the (0 0) CTR at the $\sqrt{3} \times \sqrt{3}$ upd and non-upd potentials. Fig. 2 presents transient diffraction intensity at the peak position of the (0 0 1.4) reflection. After the potential is stepped from non-upd potential (350 mV) to $\sqrt{3} \times \sqrt{3}$ upd potential (-250 mV), the CTR intensity between Bragg peaks is reduced because of the interference between the Au substrate and the Cu adlayer. However, the intensity at (0 0 1.4) increases within 5 ms and then decreases over the next 400 ms. Structural analysis was performed from time-resolved measurements at the peak positions along the CTR. Intensity increase at the initial step suggests the presence of the outer layer species at 0.35 nm from the Au surface, and we assigned this species to the hydrated Cu ion. During Cu deposition, hydrated Cu ions approach to the outer layer and then Cu ions are adsorbed on Au(111) with the destruction of hydration shell.

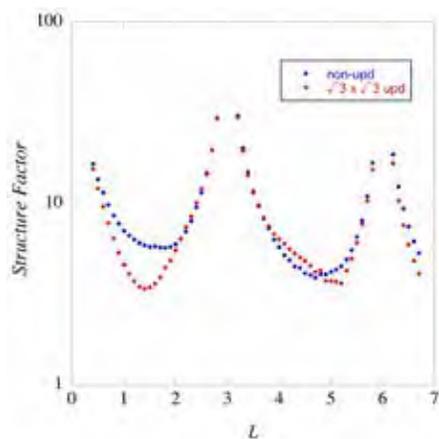


Fig. 1 Specular CTR at upd and non-upd potentials.

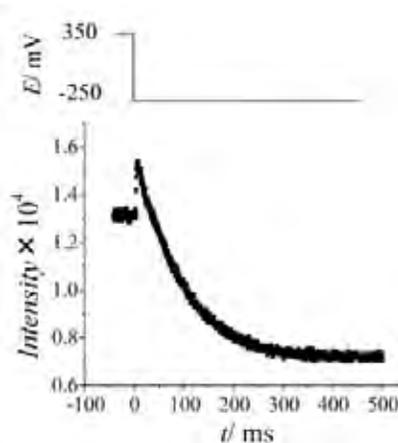


Fig. 2 Transient diffraction intensity at (0 0 1.4).

Hydrophobic interfaces at increased hydrostatic pressures

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Hydrophobic interfaces play an important role in nature. The folding process of proteins is in vast parts governed by hydrophobic interactions, and the structure of cell membranes, consisting of amphiphilic lipid molecules, is controlled by hydrophobic/hydrophilic forces. Naturally, biological structures are dissolved in water, and the contact area of the hydrophobic parts with water is minimized. When water meets hydrophobic surfaces, the electron density at the interface decreases below the level of bulk water. This electron-depleted region next to the interface is commonly named as *hydrophobic gap* and was in the focus of scientific discussion among physicists and chemists. It was observed both in experiments and simulations [1-5]. While the exact size of the gap region was under discussion in the literature, its existence, with a size on the order of a few Ångstrom, is now generally accepted [3-5]. Mezger *et al.* determined an integrated density deficit of $1.1 \text{ \AA g cm}^{-3}$ at an OTS (octadecyltrichlorosilane)-water interface, smeared out over a region of up to 6 Å thickness [4].

On the experimental side, hydrophobic substrates consisting of self-assembled monolayers (SAMs) with a dense layer of saturated hydrocarbon chains at the surface were studied. On such a methyl group-terminated hydrophobic interface, the CH₃ group contributes to some extent to a decrease in the electron density at the interface [6]. However, it was shown that at least the first monolayer of the surface water is disturbed by the presence of a hydrophobic surface [7].

In this work, we used pressure variation to study the response of the interfacial gap region towards density changes in the bulk water phase and structural modifications that go in hand with increased hydrostatic pressure. The structure of bulk water is known to be changed upon pressurization, since the second hydration shell collapses with increasing pressure at approximately 2 kbar and molecules are pushed into the first hydration shell [8]. Simulations results predicted that the gap size has a compressibility that is approximately five times larger than the bulk compressibility of water for pressures up to 2 kbar [2]. In the current study, we applied X-ray reflectivity measurements to determine the exact vertical density profile of OTS samples in contact with water at pressures up to 5 kbar. We show that the compressibility in the gap region is increased as compared to the bulk compressibility up to a pressure of 2 kbar, while it equilibrates to the bulk value at pressures above. These results are in agreement with molecular dynamics simulations.

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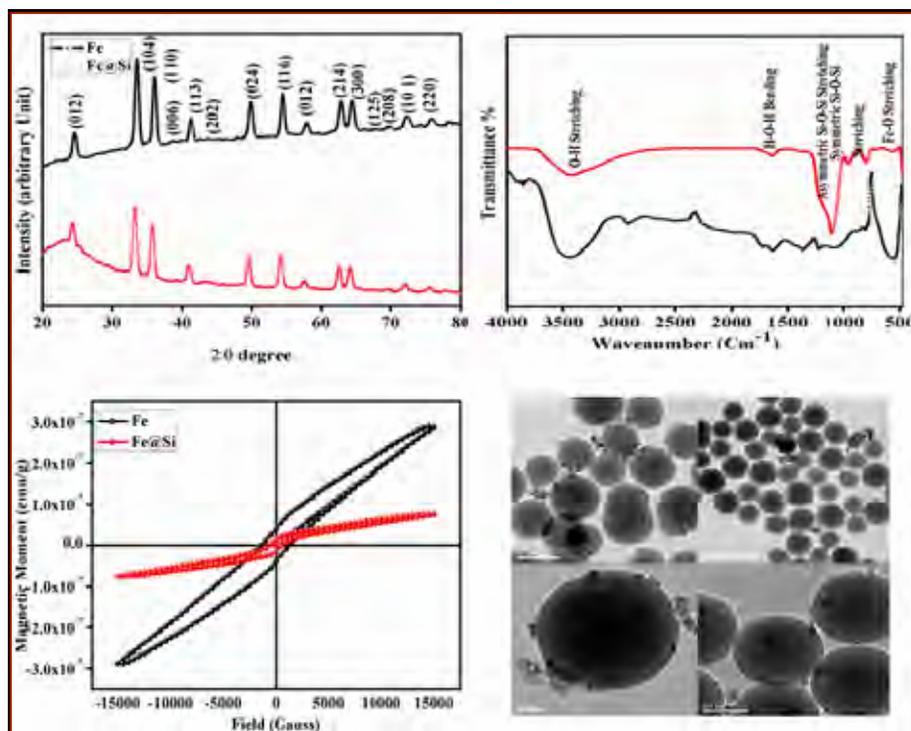
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Preparation and characterization of mono dispersed silica spheres embedded with a Fe_2O_3 Nanocrystals for biomedical applications

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Monodispersed colloidal spheres with desirable optical and magnetic properties have attracted a great deal of attention owing to their unique physicochemical properties and potential applications in plentiful areas such as magnetic sensors, magnetic fluids, magneto-optical devices, data storage devices and especially in biomedicine/biotechnology [1-7]. Herein, we report a simple and cost effective two step preparation of highly monodispersed magnetic $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ nanocomposite spheres. The resultant nanocomposite exhibited a smooth spherical morphology made up of SiO_2 nanospheres and $\alpha\text{-Fe}_2\text{O}_3$ Nanocrystals embedded over it. The phase purity and micro structural parameters of the samples were analysed using powder X-Ray diffraction. Si-O stretching and M-O stretching vibrations observed in FTIR spectrum confirm the formation of successful formation of nanocomposites. Optical absorption studies carried out with UV-Vis spectrophotometer shows a broad absorption in the visible region in addition to Fe^{3+} ligand field transitions. The observed shift in the band edge is attributed to electronic structural modification arising as a result of interaction between Silica spheres and Fe_2O_3 . Magnetic behaviour of the samples was analysed using vibrating sample magnetometer. Both bare Fe_2O_3 and $\text{SiO}_2\text{-Fe}_2\text{O}_3$ compounds exhibits room temperature ferromagnetism with well defined hysteresis loops. These biocompatible and large ferromagnetic nanoparticles with low anisotropy support the use of prepared nanoparticles towards treatment of malignant tumour by thermal ablation.



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IN-SITU HIGH PRESSURE STUDIES ON NANOCRYSTALLINE MERCURY SULPHIDE

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ABSTRACT :

β -HgS nanoparticles play a vital role in many areas of science and technology. It has proven and promising application in the fields like electronic, optical and environmental remediation. Research has been employed for the remediation of mercury and β -HgS is a promising nanoparticle to remove the toxicity of the mercury from the contaminated environment. For this purpose β -HgS must be synthesized in various forms with high purity of controlled size and shape for stabilizing surface modification. The microwave assisted route is a novel method which is faster and energy efficient. This method is used for synthesizing metal sulphide. It is a fast, convenient, mild, energy – efficient and environmentally friendly route for synthesizing β -HgS. The prepared product was characterized by XRD, TEM and XPS. According to TEM observations the HgS nanoparticles are mostly spherical in shape with an average size of 15 – 20nm.

The nanomaterials are very sensitive to external parameters like pressure and temperature. The physical properties of materials depend strongly on the structure and interatomic distances. High pressure can vary these distances, which implies that we can study relations between structure and properties of the materials. Among II – VI semiconductors, β -HgS is semimetallic in nature and called as zero band gap semiconductors. The high pressure studies were carried out using a Mao-Bell type diamond anvil cell. The Rigaku 12 kW rotating anode X-ray generator with an energy dispersive X-ray diffraction system was employed. The sample was pressurized to various pressures up to 15 GPa. Generally HgS is observed under normal conditions both in the cinnabar phase (“ α ” or “red” form) and the metastable zincblende phase (“black” or “ β ” form). At high pressure it has been reported that the phase transformation from zinc blende to cinnabar phase takes place at 5.5 GPa to 14.5GPa and at 27 GPa it transforms into rock salt (NaCl). Based on the literature, the cubic phase transforms to distort NaCl at about 55 GPa. The above results have been reported for bulk HgS. No structural transition is obtained for nano sized HgS upto 15 GPa. Instead, we are able to notice the disappearance of some peaks. The energy and intensity of some peaks decreased on increasing the pressure. About 10 GPa, some peaks like (311) and (331) tend to diminish from vicinity. This confirms that as pressure is increased, the nanocrystalline phase of HgS transforms to the amorphous phase. According to the results obtained the transition pressure increases as the particle size is decreased.

Keywords: *Microwave heating, mercury sulphide, phase transition, high pressure XRD.*

Study of crystal surface with asymmetric X-Ray diffraction

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Crystallinity of the surface layer is an essential property for a potentially next generation electronics devices, such as: topological insulators, spin transistor etc. A perfect single crystal specimen even in an ultra-high vacuum conditions will have disturbed surface layer. For example in topological insulator the wave function of surface states is depend on the thickness of the top distorted layer and therefore it's characterization is needed for the explanation of the functional properties. Characterization of such layer with conventional X-ray techniques is complicated especially if there is no optical contrast between surface layer and crystal underneath and/or if the surface layer is amorphous.

We have explored the way to characterise the surface of single crystal using asymmetrical X-ray diffraction suggested in [1]. Estimation of thickness of an amorphous surface layer of single crystal performed via specular reflection near asymmetric non-coplanar diffraction. Adjusting via azimuthal scan near extremely asymmetrical diffraction condition one can expect intensity of two non collinear beams of specular reflection and diffraction to be at the same order of magnitude. While both this beams were induced by the same source of energy – incident beam. Thus diffraction will modulate specular reflectivity. In present study we use matrix formalism in dynamical theory described in [2]. Within that formalism, wave equation is treated with characteristic equation. In [2] this is polynomial equation of fourth order and therefore it generally has four roots and each root is a wave number. Then, wave equation is solving with the optical matrix composed of these roots.

Analysis of roots of characteristic equation shows that if angle between the crustal surface and either incidence or diffracted beam is close to the angle of total external reflection, only three out of four roots of the dispersion equations contribute to asymmetrical diffraction. The one root that has very small value can affect optical matrix conditioning and dramatically increase uncertainties in calculation procedure. We have modified the matrices form [2] to accommodate only three relevant roots of dispersion equation. We are going to present simulation of specular reflectivity and extremely asymmetric diffraction preformed with newly developed 3x3 matrix formalism. The sensitivity of X-ray reflectivity modulated with the in-plane diffraction to a thickness of the surface layer will be discussed.

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Arsenic incorporation by iron minerals applicable to natural attenuation of arsenic

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Iron minerals are present in various forms which are formed by both abiotic and biotic processes. Acid mine drainage often contains high iron as well as other metal(loid)s. Acid mine drainage is produced by mining and exposure of sulfur bearing minerals to atmosphere. When the acid mine drainage is discharged and environmental conditions change, dissolved iron and metal(loid)s chemically and biologically precipitate. Main precipitated iron minerals include ferrihydrite, schwertmannite and goethite. When these iron minerals precipitate, metal(loid)s can be incorporated. Incorporation of metal(loid)s in iron minerals involves adsorption and co-precipitation. In this study arsenic adsorption and co-precipitation by iron minerals were tested using synthesized ferrihydrite, schwertmannite and goethite. Arsenic was simultaneously added to the solution during the synthesis of iron minerals to test arsenic co-precipitation while arsenic was reacted with already synthesized iron minerals for adsorption. Synthesized iron minerals and arsenic incorporated iron minerals were characterized by scanning electron microscopy(SEM), X-ray diffraction(XRD) and X-ray absorption spectroscopy(XAS). Arsenic incorporation rate based on arsenic/iron ratio was the highest in co-precipitated ferrihydrite followed by schwertmannite. Arsenic removal rate by goethite was higher through adsorption than co-precipitation. Arsenic co-precipitation and adsorption by iron minerals were applied to elucidate mechanisms of arsenic natural attenuation in mine sediments. In mine sediments, iron minerals occurred as mainly poorly crystalline minerals such as ferrihydrite and schwertmannite with minor amount of goethite, which were confirmed by XRD and XAS. The mechanism of arsenic natural attenuation in mine sediments was mainly through arsenic co-precipitation by ferrihydrite and schwertmannite followed by arsenic adsorption by goethite evidenced by comparison of X-ray absorption near edge structure (XANES) of arsenic. Schwertmannite and ferrihydrite were formed in acid mine drainage and arsenic was incorporated in their structure during the formation of these iron minerals. Additionally, Schwertmannite and ferrihydrite might be transformed to goethite and arsenic was adsorbed onto the surface of goethite. Arsenic adsorption/incorporation by iron minerals implies that iron minerals in mine site naturally attenuate arsenic in mine sediments.

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Anti-biofouling property of adsorbed polymer nanolayers

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Over the past two decades, there have been booming research interests in anti-biofouling surfaces, which resist adsorption of biomolecules and attachment of microorganisms, for a variety of biomedical and biotechnological applications. Polymers have been essentially used to develop antifouling coatings against primary protein adsorption. Moreover, chemical end-grafting of polymer chains can be utilized to stabilize polymer coating under various environmental conditions. However, this “bottom-up” approach still suffers from significant limitations including substrate chemical specificity, complicated and expensive chemical protocols, and susceptibility to thermal or hydrolytic degradation. Hence, we need to develop a new rational design of anti-fouling polymer layers that realize necessary attributes for next-generation coating technologies. In this study, we report on the use of nanometer-thick polymer adsorbed layers on solid substrates as alternative antifouling films. Recently, we found that homopolymer melt chains on a solid surface favor an increase of the number of solid-segment contacts via the equilibration process, resulting in densely packed polymer “flattened layers” regardless of the magnitude of attractive solid-segment interactions¹⁻⁷. In addition, we have established the “top-down” approach to extract the lone flattened chains from polymer thin films using solvent leaching. Moreover, our recent results revealed that the densely packed flattened chains are impenetrable even for chemically identical polymer chains⁶. We characterized the film structure of the flattened polymer layers using X-ray reflectivity and atomic force microscopy. In addition, non-fouling experiments for the flattened layers using model proteins were performed. The details will be discussed in the presentation.

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Intrinsic Dynamic Difference Between Hydrogenated and Deuterated Lipids and Packing Effect on Their Transbilayer Movement

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The transbilayer movement of phospholipids, or so called lipid flip-flop, in cellular membranes is an area of significant biological importance, which helps to construct and maintain the membrane structures. The packing state of lipids in real systems, which is a consequence of multiple factors such as spontaneous curvature of lipid itself, negative charges on headgroup, and the interaction or incorporation of proteins or peptides into the membrane, is potential to cause defect sites within membrane. The defects would act as membrane channels which regulate many biological functions, including of lipid flip-flop. Our aim is to understand the effect of such defects, which are created by incorporation of unsaturated lipid or negatively-charged lipid into the membrane, on lipid flip-flop, and to answer the question as whether lipid flip-flop can be induced from only one side of the membrane bilayer. Unlike real cells which have protein incorporation into the membrane, so called flippase or floppase to accelerate lipid flip-flop, our interest is on protein-free bilayer where the flip-flop is a slow dynamics and can be characterized by neutron reflectometry. By mean of Langmuir-Blodgett/Schaefer deposition methods, it is possible to prepare successive adsorbed layers resulting in a final asymmetric composition. During preliminary neutron experiments, we also observed the slight difference in the intrinsic dynamics between hydrogenated and deuterated lipids, which will also be discussed in the presentation.

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GIXD measurements on monolayers at the water/air interface with hard and high energy X-rays at PETRA III

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Diffraction data of monolayers at the water/air interface in dependence of the surface pressure are important for the understanding of the structural ordering of molecules in 2D membranes according to the intermolecular interactions.

At PETRA III the High Resolution Diffraction Beamline P08 and the High Energy Materials Science Beamline P07 provide a setup for grazing incidence diffraction on liquid surfaces and interfaces. A Langmuir trough is available, too.

For simplicity the grazing incidence at P08 is realized by a mirror, while at P07 a secondary optic utilizing broad bandwidth crystals is employed which allows reflectivity measurements, too [1]. For both setups a fluorescence detector is available.

The impact of the photon energy will be discussed too, since P08 is usually operated at 15 keV and P07 at 60 keV for these types of measurements.

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MBE: Time Resolved Studies with High Energy Photon GIXD

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With recent developments on modern synchrotron radiation sources and new 2D detectors high energy x-rays (> 60 keV) become more and more interesting for studying the structure of surfaces, interfaces and ultra-thin films in situ and in operando.

Using high energy photons the Bragg angles become smaller and therefore a larger part of the q-space can be covered by a single detector image. Using a grazing incident geometry it is possible to obtain reciprocal space maps containing several crystal truncation rods with a simple azimuthal scan at a fixed detector position within very short time scales[1].

Here, we demonstrate how this method can be applied to diffraction measurements on epitaxial ultra-thin films. As a model case we use epitaxial iron oxide thin films on a MgO(001) substrate with thicknesses ranging from 5 up to 30 nm.

We will compare the data obtained at high energy photon PETRA III beamline P07 to the energies conventionally used for surface and thin film diffraction experiments (10 - 20 keV) taken at the high resolution diffraction PETRA III beamline P08.

The outline of the newly designed MBE-chamber and first data of in situ film growth in a prototype setup will be shown demonstrating the quality of the time resolved studies.

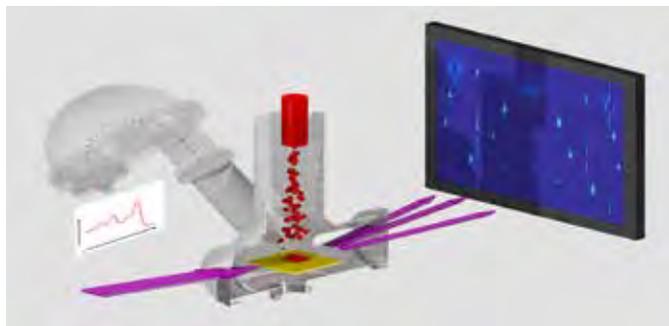


Figure 1: Sketch of newly designed MBE chamber for high energy X-rays

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Lysozyme at the solid – liquid interface - A high pressure X-ray reflectivity study

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Interactions between proteins and interfaces play an important role in nature. For example, in cells, proteins might adsorb at cell membranes, possibly causing conformational changes. Such changes are of high interest, as the function and possible aggregation of proteins is highly connected to their shape. Many human diseases are connected to such phenomena, for example the Alzheimer disease is linked to the aggregation of β -peptides[1]. Thus, it is important to understand the influence of interfaces on conformational changes of proteins. In the vicinity of highly hydrophobic interfaces, proteins tend to denature during the adsorption process due to strong hydrophobic interactions. The X-ray reflectivity technique gives the possibility to access the density profile of the protein layer *in-situ* with sub-Ångstrom resolution. By varying the hydrostatic pressure, the density of the water and with this the electron contrast between protein and water is changed, revealing further information on the system. In addition, it has been observed that pressure induces protein layer growth at interfaces, especially when denaturing co-solvents are present [2]. By using different denaturants under pressure, the mechanisms of protein adsorption and denaturation at interfaces can be investigated in detail.

In our study, we investigated lysozyme adsorption on OTS (Octadecyltrichlorosilane)-coated silicon wafers and the influence of the denaturant urea on the adsorbed lysozyme layer. Using our custom-built sample cell for X-ray reflectivity (XRR) measurements [2], we were able to apply pressures up to 5 kbar. The measurements were performed at the synchrotron light sources DELTA (Dortmund, Germany) and ESRF (Grenoble, France) using high energy X-ray radiation. Our results show that the lysozyme adsorbs in a dense layer at the interface. With increasing pressure, the hydrophobic gap is partially closed. This is in contrast to measurements of the same system without proteins. Also, radiation-induced denaturation of lysozyme was studied.

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Wetting/non-wetting transitions in FOSM-DMA-FOSM hydrogel triblock copolymer thin films

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Block copolymers form pathways for various applications due to their ability to self-assemble at nanoscales. In polymer thin films, the presence of polymer-substrate and polymer-air interfaces greatly affects the morphology of the films, which may dramatically change the surface properties of such films. We exploit these properties of BCPs and thin films in order to achieve a surface wettability gradient using an amphiphilic triblock copolymer. The polymer used, FOSM-DMA-FOSM¹ (FOSM: 2-(N-ethylperfluorooctane sulfonamido) ethyl methyl acrylate DMA: dimethyl acrylamide) is a physical network hydrogel consisting of hydrophobic and hydrophilic domains. The surface energy gradient in these films is achieved by solely changing the thickness of the thin films (fig: Water contact angle on FOSM-DMA-FOSM films with varying thickness). We use Atomic Force Microscopy (AFM), Grazing Incidence Small and Wide Angle X-ray scattering (GISAXS and GIWAXS), and X-ray Photoelectron Spectroscopy (XPS) to characterize these BCP films to obtain their molecular structure and orientation as a means to understand the underlying physics. It was observed that phase segregation and self-assembly of the BCP played a major role in surface structure of the films, leading to a gradient in surface wettability. As the material is a physical network hydrogel, it also acts as a smart material allowing hydrophobic to hydrophilic transitions.

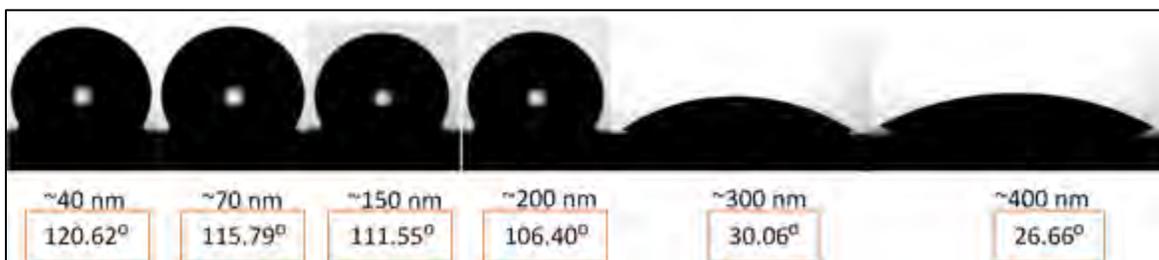


Fig: Water contact angle on as-cast FOSM-DMA-FOSM films of varying thickness

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Block copolymer adsorbed layers on solids

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Block copolymer thin films offer a simple and effective route to fabricate highly ordered periodic microdomain structures. The fundamental, yet unsolved question is whether these highly oriented microdomain structures persist even near an impenetrable solid wall. We here report adsorbed structures of polystyrene-block-poly (4-vinylpyridine) (PS-*block*-P4VP, $M_w=41,000$, weight fraction of PS=0.81) formed on planar silicon substrates. Perpendicularly aligned cylindrical microdomains were created by a solvent vapor annealing process¹ as a model and the strongly bound polymer layer onto the substrate surface was derived by solvent leaching with chloroform, a good solvent for the polymers, and thereafter characterized by using atomic force microscopy, scanning electron microscopy, grazing incidence small angle x-ray scattering, and x-ray reflectivity. The results showed that both PS and P4VP chains lie flat on the substrate, forming a heterogeneous 2-dimensional structure without long-range order. Moreover, a spin-coated PS-*block*-P4VP thin film annealed under vacuum at 190 °C ($>T_g$ of both blocks, but below the ODT temperature) showed a similar microscopic heterogeneous structure on the substrate, indicating the generality of the interfacial polymer structure. Details will be discussed in the poster.

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Hard x-ray diffraction imaging in Bragg geometry

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First order phase transitions (FOPT) are a fundamental physical paradigm; they are ubiquitous, heavily studied, and dynamic. The latter character poses a significant barrier to understanding fundamental characteristics of the many types of FOPTs as the natural instability makes rudimentary study difficult. The nucleation and growth process under variable conditions can elucidate areas of fundamental physics, chemistry and materials science. Studies suggest that lattice deformation induced by metal-ion doping might contribute to the properties of phase transition in VO₂ films in a system co-existence of both competing ferromagnetic and anti-ferromagnetic domains [1]. Previously, it has been found that a boundary region distinguished by spin disorder suppresses the dynamic nature of the FOPT. The unanswered question now pertains to the role of lateral mismatch induced strain. The open question asks what role this plays in the nucleation and growth behaviour of the transition process. The nucleation process begins generally from point defects, a multi-coherent length environment, including intra-domain and inter-domain length scales along side the intrinsic coherent topography will need to be teased apart to generate a strain propagation picture of both the domain boundary itself and its behaviour through the FOPT. This view will generate an intricate understanding applicable to many FOPT mechanisms and allow us to determine how to engineer and control phase transitions for applicable devices.

Previously, we have performed Bragg geometry ptychography on a Nb thin film at beamline 34-ID-C at Advanced Photon Source (APS, Argonne) with collaboration with Ian K. Robinson from University College London and Dr. Ross Harder from Argonne National Laboratory [2]. Here at Diamond Light Source, we are in the phase of commissioning Bragg-geometry ptychography at I13 coherence branch, and Prof. Ian Robinson's group has performed some preliminary experiments on Bragg coherent diffraction imaging (Bragg CDI), and the results obtained are promising. We are the first beamline that uses a robot diffractometer instead of a conventional 6-angle diffractometer for Bragg-geometry diffraction imaging experiments. We envisage Bragg-geometry CDI and ptychography will be fully operational in the near future at I13. [1] Correlation between thermal hysteresis width and broadening of metal-insulator transition in Cr- and Nb-doped VO₂ films, Kenichi Miyazaki, Keisuke Shibuya, Megumi Suzuki, Hiroyuki Wado and Akihito Sawa, *Japanese Journal of Applied Physics* **53**, (7) (2014). [2] Bragg-geometry ptychography in Niobium thin film, Nicolas Burdet, Xiaowen Shi, Xiaojing Huang, Jesse N Clark, Ross Harder, and Ian K, Robinson, in preparation for *IUCrJ* (2016)

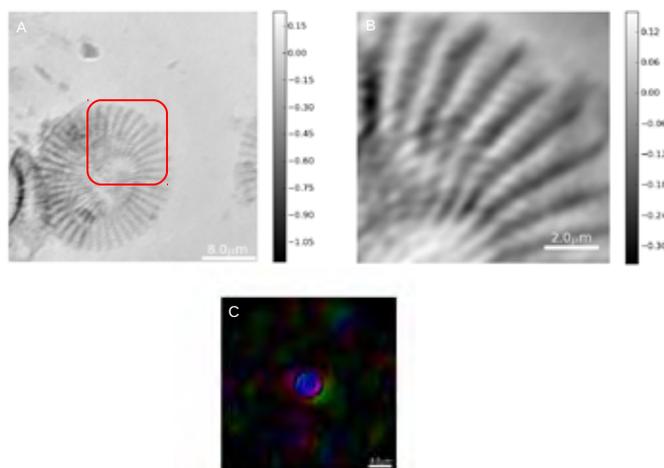


Figure 1
A: Reconstructed phase image of a Silica diatoms, B: Phase image of the area within the red square box in 1(A), C: Reconstructed complex probe image

Interfacial Phenomena in 3D Printing of Polymers

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3D printing is a rapid process that occurs in non-equilibrium conditions. Each layer is being deposited on top of the former layer in high rate and in variable temperatures. The structural strength of the printed items depends on the interlayer adhesion and interfacial phenomena. These phenomena correlate with the printing parameters as deposition rate, temperature and contact surface and their effect is different between polymers and printers. To date these interfacial phenomena were investigated under equilibrium conditions.

In this work we used technique of neutron reflectometry in order to investigate the interfacial chains diffusion in the process of polymer 3D printing. We spun cast a film of deuterated PMMA from toluene solution onto an HF etched 8 mm thick Si wafer. The sample was then annealed at $T=60^{\circ}\text{C}$ in a vacuum of 10-3 Torr and placed on the stage of a custom design UV 2048 printer (figure 1), where acrylic oligomer ink was used to print a polymer layer over the d-PMMA. The oligomer ink was cured immediately after injection with a Phoseon UV lamp (380-420 nm).

The samples were then studied at the NIST reflectometer, where the beam was reflected in the geometry shown in figure 2. The data shown below in figure 3 was then fit to obtain the parameters tabulated below: From this data we find that when the printing is done at room temperature, the interfacial width wit PMMA is only 3.0 nm. Varying the droplet size and the number of printed layers did not affect the interfacial width, but heating the substrate to 65C immediately increased the interfacial width outside the range of the reflectivity beam. These results indicate that the interlayer interfacial width between printed layers can be very small and hence the interfacial adhesion of the layer may be weak. Further studies are in progress now to determine the effects of printing on a heated stage.

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Figure 1: Sample in the 3D printer

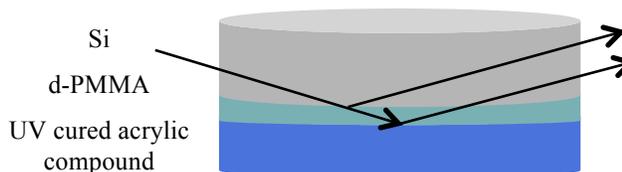


Figure 2: Layers of examined samples

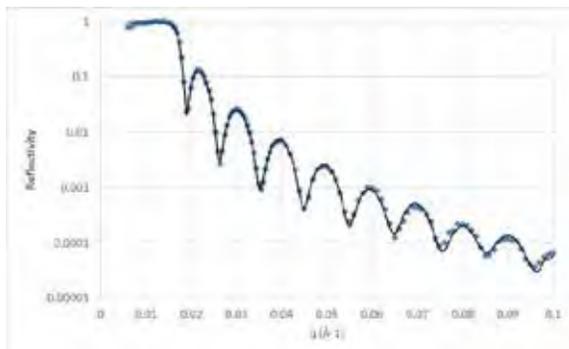


Figure 3: Reflectivity spectra from the interface of a spun-cast d-PMMA film in contact with 3D printed acrylic layer

	Thickness (nm)	Interlayer width (nm)
D-PMMA	60	3
UV cured printed layer	600	

SAXS Investigation of Microporosity of NbH Sintered Powder

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Compact structures obtained by vacuum sintering of niobium powder are widely used in microelectronics engineering as metal plates in oxide semiconductor capacitors.

This communication presents some results of scanning electron microscopy (SEM) study of the NbH sintered powder during its nitriding.

The sintered NbH was nitrided by bleeding gaseous nitrogen in a vacuum chamber when the specimen cooled after sintering, subsequently keeping the cooled specimen in a nitrogen atmosphere to complete gas absorption (vacuum level restoration).

The analysis of the changes in angular distributions and the small-angle X-ray scattering intensity level, as well as the integral parameters, scattering indicatrix asymptotics, and calculations of the submicrometre pore sizes and concentrations suggest the following conclusion, namely that the porous system is noted for nitriding, which differs from the initial system by the greater number of submicrometre pores formed in different dimensional fractions. This redistribution appears in a decrease of small submicrometre pores probably owing to the pores being blocked by the products of interaction of sintered powder particles and the gas phase. The contribution of small submicrometre pores, which are easily blocked while the capacitor system operates, can be ignored for the corresponding analysis of the process. This, nitriding assists in generating a porous system and stabilizing it, and facilitates oxide restoration in the surface electrolyte contact area.

Polarized Neutron Reflectometer “Sharaku“ with 2-D MWPC in J-PARC

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Polarized neutron reflectometry is one of the powerful methods to investigate various phenomena on the surfaces and interfaces of a variety of films with layered structures such as magnetic materials. The polarized neutron reflectometer SHARAKU [1], named after the famous Japanese ukiyo-e printer, was constructed at BL17 of the MLF in the beginning of 2012, and then we started the user program.

In this instrument, a two-dimensional position-sensitive neutron detection system consists of multi-wire proportional chamber (MWPC) with helium-3 gas and its data reduction software have been developed for the measurement of off-specular reflectivity and grazing incidence small-angle neutron scattering (GISANS). Each wire's signal is read out by amplifier-shaper-discriminator (ASD) individually to meet with demands for a fast counting response and high spatial resolution for the measurement at intense pulsed neutron sources. The multi-wire element used in the detector system comprises 128 anode wires, 128 cathode wires along y-axis, and 128 cathode strips along x-axis. The pitch between anode/cathode wires is 1.0 mm. The spatial resolution was 1.8 mm. The MWPC has been installed at the distance of 250 cm from a sample position.

An available neutron wavelength of the instrument is $0.24 < \lambda < 0.64$ nm for polarization analysis experiment. The detector covers $0.05 < q_z < 12.0$ nm⁻¹ for polarized neutron specular experiment and $0.002 < q_x < 0.01$ nm⁻¹ for off-specular neutron experiment. We report characterization results of 2-D MWPC system at BL17 and its applications to neutron reflectivity measurements.

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***In-operando* Electrochemical Study Epitaxial Thin Film V₂O₅ Electrodes: Results from X-ray Reflectivity**

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Energy storage is of great importance in our future [1]. However, fundamental scientific understanding of rechargeable batteries is far behind industrial standards today. Two open questions in basic science are: (1) How do the electroactive ions move through the active material [2]? This is particularly interesting for different ion sizes such as Li¹⁺ and Mg²⁺. (2) How is this affected by grain boundaries and defects?

In order to resolve these issues, we have defined *epitaxial thin film electrodes* as *our simple and well-defined model system*. We have chosen V₂O₅ as the active material, since it is a layered compound, and it is known to intercalate Li¹⁺ as well as Mg²⁺.

The surface normal reaction front, and therefore the ions' movement through the layers is investigated by means of *in-operando* XRD and XRR in a conventionally setup electrochemical half-cell (see schematic in Fig. 1). In this setup, we will probe the depth-dependent structure via XRD and the surface normal density profile via XRR *in-operando*. We are especially sensitive to the interfaces formed during ion intercalation and the formation of the solid electrolyte interface. As a result, we expect to gain insight into the ions' transport in the surface normal direction, i.e. through the layers. In particular, we will be able to distinguish between the rate limiting steps during this process, either reaction rate or ion ingress into the electrode. We will present recent XRR results conducted at Stanford Synchrotron Radiation Lightsource.

We expect that our results will significantly improve the atomic level understanding of the movement of electroactive ions through the active materials, thus gathering a fundamental understanding of dynamic processes in energy storage, an important missing piece our knowledge today.

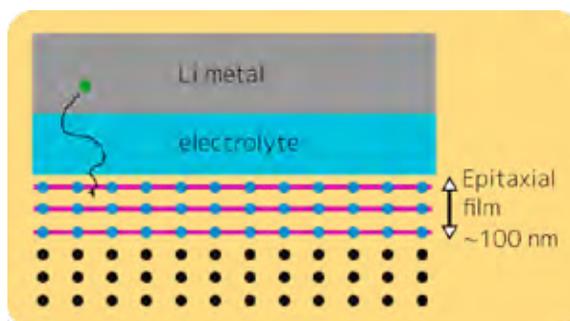


Fig 1.: Schematic representation of the experimental setups. Black markers correspond to the substrate material, blue to the V₂O₅ epitaxial thin films, green to the ions, and the magenta lines indicate the surface parallel layers.

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Nanoparticle Enlarged Interfacial Effect on Phase Transition of 1-Octadecanol/Silica Composites

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Motivated by the interest in an interfacial effect on crystallization behaviors and material properties of polymer nanocomposites, phase behaviors of a novel model system for polymer nanocomposite, 1-octadecanol/silica nanosphere composites ($C_{18}OH/SiO_2$), were studied by means of thermal analysis and wide-angle X-ray diffraction. Although a huge specific surface area of silica nanoparticles enlarges the surface–volume ratio of $C_{18}OH$ molecules, surface freezing phenomenon is not observed by DSC in the $C_{18}OH/SiO_2$ composites (as shown in Fig.1). While pure $C_{18}OH$ exhibits rotator RIV phase with molecules tilted with respect to the layer normal, the silica network favors and enhances untitled RII phase by disturbing the layering arrangement. Moreover, the confined $C_{18}OH$ shows a polycrystalline mixture of orthorhombic β form and monoclinic γ form. In the interfacial region, the slightly polar $C_{18}OH$ molecules interact with the silica surface through hydrogen bonding, thus enhancing the translational disorder along the long axes of molecules and disturbing the formation of hydrogen bond between adjacent molecules. In addition, the random connected interspace essentially favors the rotational and translational disorder of $C_{18}OH$ molecules. Altogether, the silica network, especially the silica surfaces, induces the stability of untitled RII phase and β phase with weakened interlayer coupling. It is demonstrated that the interfacial interaction between the $C_{18}OH$ molecules and the silica surface contributes to the peculiar phase transition behaviors of $C_{18}OH/SiO_2$ composites. The investigation of the model system of long-chain alcohol/nano- SiO_2 composites may help us to understand the complicated interfacial effect on phase behaviors and material properties of polymer nanocomposite systems.

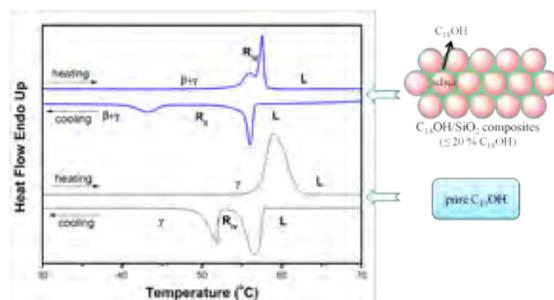


Fig. 1 DSC traces of pure $C_{18}OH$ and $C_{18}OH/SiO_2$ (350 nm) composites during heating and cooling processes. The percentages are for the mass ratio of $C_{18}OH$ in the composites.

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Solid-supported DMPC multilayers containing cholesterol at high hydrostatic pressure

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A lipid bilayer is the basic component of cell membranes, which separates the intracellular and extracellular region and regulates the mass transfer between both regions in all living organisms. Bilayers undergo pressure- and temperature-induced phase transitions. However, they need their high flexibility, which is given in the liquid phase, to fulfill their biological functionalities. In nature, membranes are highly complex systems that are interstratified by cholesterol and proteins. Adding cholesterol increases the stability of the membrane and reduces the lateral mobility of the lipid molecules. Thereby the phase boundaries of the system are shifted in comparison to pure lipid systems.

We present an *in situ* high pressure x-ray reflectometry (XRR) study on the structure of solid supported DMPC (like 1,2-dimyristoyl-sn-glycero-3-phosphocholine) multilayers containing cholesterol in different concentrations. The reflectivities were measured at the solid-liquid interface between silicon and an aqueous buffer solution in a high pressure XRR cell [1]. For this purpose, lipid layers were prepared on hydrophilized silicon wafers by spin coating. Their vertical structure was analyzed up to a maximum pressure of 5000 bar at temperatures of 20 and 37°C, revealing phase transitions from the fluid phase into different gel phases in the latter case.

Apart from that, we observed a pressure-change induced multilayer formation [2]. As is commonly known, water has an abrasive effect on lipid multilayers causing the formation of vesicles, we show that changing the pressure can reverse this process.

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External field control of self-assembled monolayer on Au(111)

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Self-assembled monolayers (SAMs) are used for adjusting the work function of metal electrodes in organic devices, because the energy level difference between the HOMO or LUMO and the work function affects the electron injection through the metal-organic interfaces. The controlling mechanisms of the work function are (1) electric double layer caused by the polarization of the SAM molecule, and (2) electrons spilled at the metal surfaces are pushed back inside the metal due to Pauli repulsion, resulting a change in dipole moment at the surface. Both mechanisms are strongly related to the surface structure.

Although the work function is controlled by the SAM formation, controlling the work function after the formation of SAMs is difficult. To achieve the surface switching, low-density SAMs are found to work [1,2]. Especially the method reported in ref. [2] is simple and stable, which are required for technological applications. However, the direct observation of the molecular switching has not been performed. Therefore, we performed an x-ray reflectometry measurement on the low-density SAM with applying external electric fields.

The reflectivity measurement was performed at BL13XU of the SPring-8, Japan with 10 keV x-ray. The sample structure is shown in Fig.1. Electric potentials of $\pm 1V$ were applied through the ionic liquid (IL) at room temperature. Before the measurements, the sample was cool down to 93K to reduce the radiation damage. The reflectivity change $I(Q)/I_0(Q)$ for the Au/IL interface and Au/SAM/IL interface were analyzed with software GenX [3]. Based on the analysis, we found the $\pm 10^\circ$ of molecular tilting induced by the external electric field.

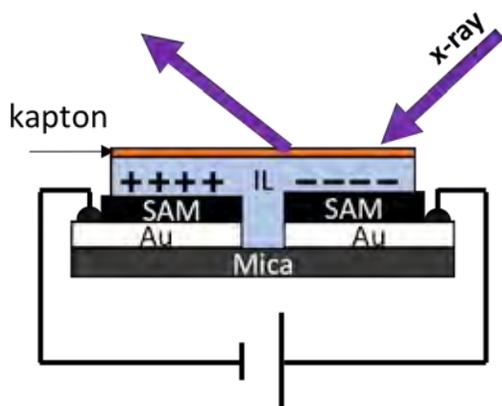


Fig. 1: Sample configuration

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Photoinduced dynamic phase competition probed by surface x-ray diffraction

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We show that the competition between the antiferromagnetic metallic phase and the charge- and orbital-ordered insulating phase at the reentrant phase boundary of a layered manganite, $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, can be manipulated using ultrafast optical excitation. For values of x close to 0.5, this material is an antiferromagnetic metal at low temperatures, a charge- and orbital-ordered insulator at moderate temperatures, and a paramagnetic metal above 220 K.

To investigate the possibility of non-thermal dynamic control of the metallic and charge- and orbital-ordered insulator phases, we excited an $x=0.505$ compound with ultrafast laser pulses and probed the structural response with x-ray diffraction. Performing the diffraction measurements in a grazing-incidence geometry was essential in order to match the penetration depths of the laser and x-ray light.

The time-dependent evolution of the Jahn-Teller superlattice reflection (3/4, 5/4, 6), which is sensitive to the formation of the charge and orbital order, was measured at different laser fluences. The laser-induced enhancement and reduction the Jahn-Teller reflection intensity reverses sign between earlier (~10 ns) and later (~150 ns) time delays during the relaxation after photo excitation as shown in Fig 1. This effect is consistent with a scenario whereby the laser excitation modulates the local competition between the metallic and the insulating phases.

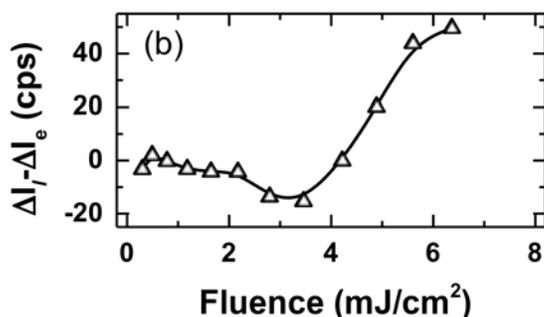


Fig. 1. The difference in intensity between the late and the early time-resolved signals.

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Resonant Soft X-ray Scattering for Soft Materials

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P-78

The structure of materials, the way in which atoms and molecules are organized at the nano- and mesoscale, determines their physical properties and functions. The complexity of material architecture, chemistry, and interactions among constituent materials, make it a challenging task to elucidate clear structure-property relationships. We need sharper tools in order to discover, understand, and control mesoscale phenomena and architectures. Over the past a few years, we have developed Resonant Soft X-ray Scattering (RSoXS) and constructed the first dedicated resonant soft x-ray scattering beamline at the Advanced Light Source, LBNL. RSoXS combines soft x-ray spectroscopy with x-ray scattering thus offers statistical information for 3D chemical morphology over a large length scale range from nanometers to micrometers. Using RSoXS to characterize multi-length scale soft materials with heterogeneous chemical structures, we have demonstrated that soft x-ray scattering is a unique complementary technique to conventional hard x-ray and neutron scattering. Its unique chemical sensitivity, large accessible size scale, molecular bond orientation sensitivity with polarized x-rays and high coherence have shown great potential for chemical/morphological structure characterization for many classes of materials. Recent RSoXS results on organic electronics, block copolymer thin films, and membrane structures, as well as some recent development of in-situ soft x-ray scattering with in-vacuum sample environment will be discussed.



Coherent Hard X-ray Scattering Beamline for Structure and Dynamics

Investigations at Liquid and Solid Interfaces

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The Coherent Hard X-ray Scattering (CHX) beamline [1], currently starting its user program at Brookhaven National Laboratories National Synchrotron Light Source II, is dedicated to experiments such as X-ray Photon Correlation Spectroscopy (XPCS) that exploit the extraordinary source brightness. The beamline's capabilities for measuring dynamics as well as for (simultaneous) structural characterization on solid and liquid interfaces will be described.

The beamline endstation instrumentation is designed to collect as much of the available scattering information as possible, allowing for covering simultaneously a Q-range corresponding to atomic sizes to hundreds of nanometers. The integrated endstation approach combines an 18 axes diffractometer, enabling horizontal and vertical scattering geometries, with a small angle scattering instrument with up to 16m sample-to-detector distance and in-vacuum detectors [Figure 1]. Grazing incidence small (GISAXS) and wide angle (GIWAXS/GIXD) scattering can be performed on systems at solid and liquid surfaces, such as polymer films, sputtered metallic films, or organic monolayers at the liquid-gas interface. Accessible time scales for dynamic measurements range from sub-microseconds (propagating capillary waves on liquid surfaces) to hundreds of seconds (e.g. relaxation in polymer melts). Taking advantage of the small X-ray beams needed for coherent scattering experiments (2-10 micrometer), 'single-shot' GIXD from organic monolayers at the liquid-gas interface has been demonstrated with a time resolution of tens of milliseconds. Complementary sample information such as electron density profiles perpendicular to the surface normal can be obtained at solid surfaces by regular X-ray Reflectivity (XR) and from diffuse scattering (GIXOS) [2] from thin films at the liquid-gas interface.

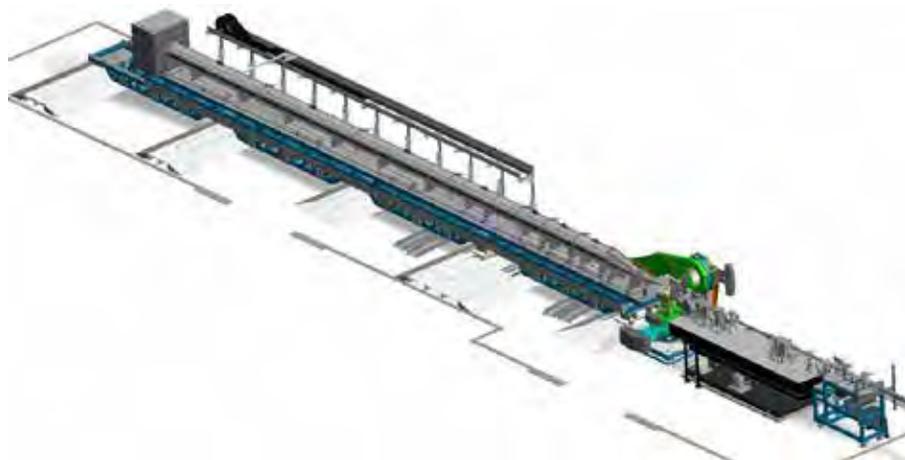


Figure 1: CAD model of the CHX endstation instrumentation.

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Ternary blend polymer solar cells with self-assembled structure for enhancing power conversion efficiency

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Bulk heterojunction (BHJ) polymer solar cells are an area of intense interest due to their advantages such as mechanical flexibility, low costs, and the easiness of the fabrication. The active layer is usually consisted of a polymer donor and acceptor material. The performance of polymer bulk heterojunction solar cell is highly dependent on the morphology of active layer. However, controlling the morphology of the active film to obtain the best performance of the device is extremely difficult since the optimal morphology of the active layer is not thermodynamically stable. Here we report a self-assembled structure formed by phase separation between poly[N-9''-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) and polystyrene (PS) for the active layer morphology optimization. Insulating polymer PS is used as processing additive to enhance the performance of solar cell devices by increasing the charge carriers mobility and crystallinity of PCDTBT/ Phenyl-C61-butyric acid methyl ester (PCBM) system. PS is also served as a template to confine PCBM at the interface between PS and PCDTBT. The aggregation behavior of PCBM between PS and PCDTBT is studied by neutron reflectivity at National Institute of Standards and Technology. The surface morphology is investigated with atomic force microscopy (AFM) and the columnar structure is studied by investigation of cross-section of the blend thin film of PCDTBT and PS under the transmission electron microscopy (TEM). The different morphological structures formed via phase segregation are correlated with the performance of the BHJ solar cells fabricated at the Brookhaven National Laboratory.

A simultaneous multiple angle-wavelength dispersive X-ray reflectometer applied to the dynamical study of soft matter interfaces

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The simultaneous multiple angle-wavelength dispersive X-ray reflectometer (DXR) has been developed for time-resolved X-ray reflectivity measurements. The apparatus is schematically shown in Fig. 1. A synchrotron white X-ray beam from a bending magnet is incident on the polychromator crystal. The polychromatic X-ray beam is focused onto the sample with incident angles α that change continuously between $\alpha(E_H)$ and $\alpha(E_L)$. The intensity distribution of the specularly reflected beam is measured by using a PILATUS 100K detector. A large range in reciprocal space can be observed with a single detector exposure, with no need to scan the sample, incident beam, or detector. Measurements with a time resolution between less than one second and several tens of seconds, depending on the sample and momentum transfer range Δq , are possible. Typical measurements are performed using a white synchrotron beam from a bending magnet source of the 6.5 GeV electron storage ring PF-AR at KEK to obtain the wavelength region of 0.561 - 0.648 Å (energy 22.1 - 19.1 keV) and the incident angles of 0 - 1.7 degree. The reflection of water surface is shown in Fig. 1 as an example.

In this presentation, we will show several applications for dynamical studies of soft matter interfaces.

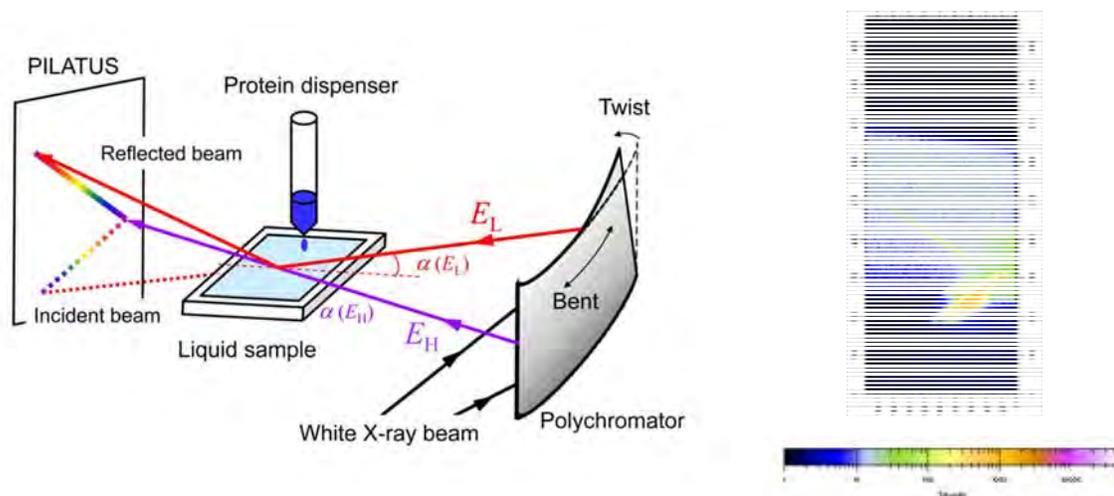


Figure 1. (left) Schematic figure of DXR combined with protein injection system. (right) A detector image of the X-ray beam reflected by water surface. The exposure time is 1 sec.

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Liquid-solid transition in colloidal system with added adsorptive polymer

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Understanding gelation and glass transitions is one of the greatest challenges in soft matter community. Colloidal systems with a depletion attraction has long been the most popular model systems to study gelation and glass transitions, where the added small solvent polymers or particles are not attracted to the surface of large colloidal particles. The physics mechanisms of gelation/glass transitions of these depletion attraction driven colloidal systems have been considered general mechanisms applicable to many other spherical colloidal systems including globular protein solutions. However, whether the findings from the depletion driven systems can be generalized to other spherical colloidal systems has not been carefully examined at all despite its importance. And therefore, this generalization may not be valid to other colloidal systems even though many researchers take this generalization as granted so far.

In this work, by tuning the attraction between small solvent particles and large colloidal particles (where the small particles can be strongly attracted to the surface of large colloidal particles) and investigating the gelation transition of our systems in a wide range of volume fractions, we conclusively demonstrate that the general physics mechanisms extracted from the depletion attraction systems failed to explain the gelation transitions in our systems. The formation of physical gels of our systems at the intermediate volume fraction follows closely with the percolation line that is in stark contrast to what are observed in widely studied gel systems driven by the depletion attraction in which the gelation transition follows basically gas-liquid transition line. Our results raise new questions that need to be carefully considered when efforts are devoted to develop general theory to explain the gelation phenomenon [1-4].

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Design of Soft Matter Interfaces beamline at NSLS-II

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We present the detailed design of the Soft Matter Interfaces (SMI) beamline, a long energy range canted in-vacuum undulator (IVU) beamline at NSLS-II. The SMI beamline will supply the multi-technique approach that is required to study all aspects of interfacial structure in soft matter, from crystalline solids to amorphous assemblies to liquid interfaces. The high brightness IVU source provides a small beam with minimal divergence, excellent energy tunability between 2.05 - 24 KeV, and extremely high photon flux. The optical beamline simulation was performed with Synchrotron Radiation Workshop (SRW) package which properly takes into account wavefront diffraction effects. Fully windowless, in-vacuum design will enable measurements at the K-edges of P, S, K, and Ca. SMI will provide a variable focusing which enables small angle scattering and grazing incidence geometries with high q resolution, or conversely micro-focusing with relaxed resolution [1].

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Thermoresponsive PNIPAM coatings for tissue engineering studied by neutron reflectometry

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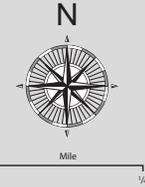
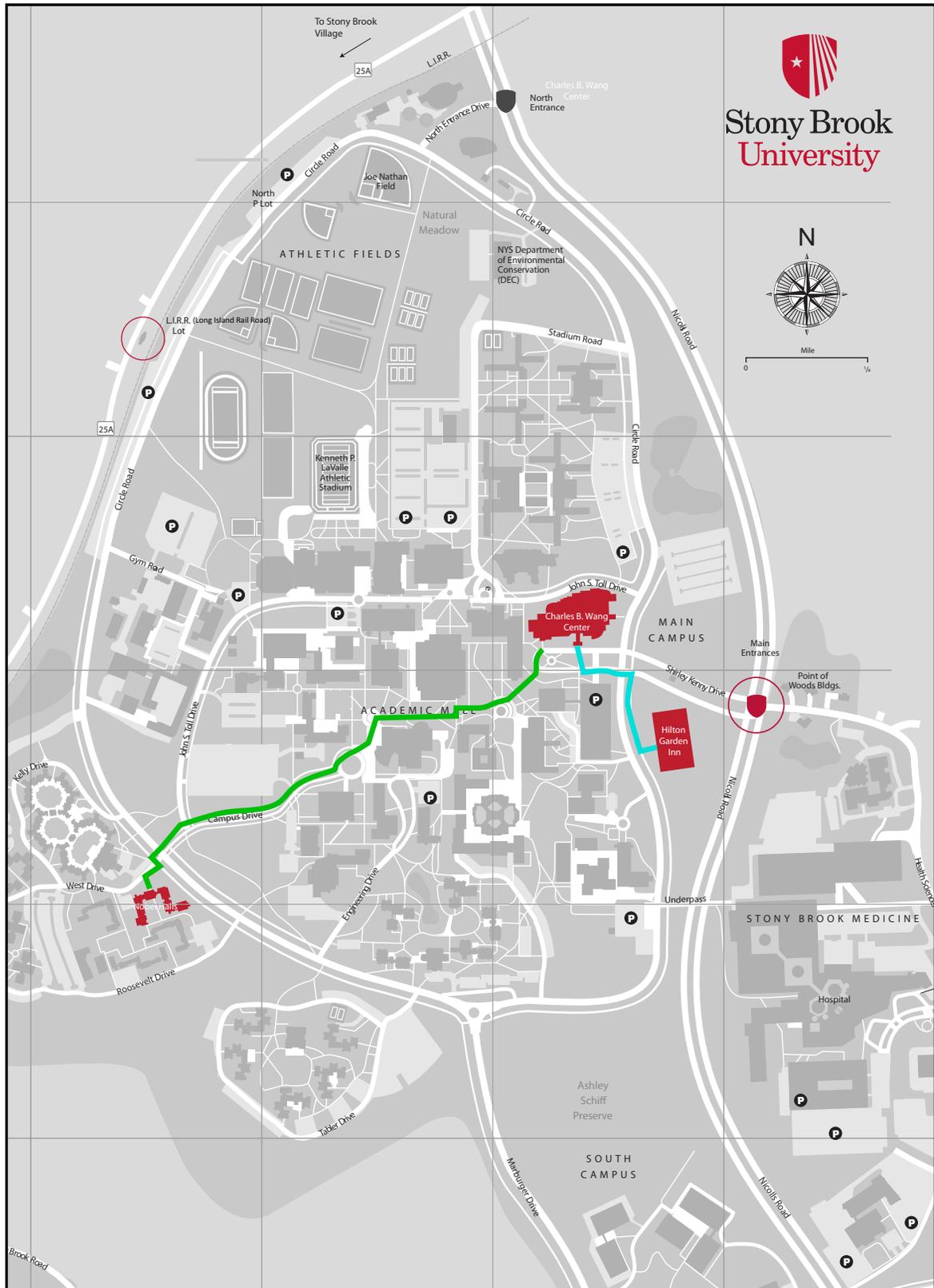
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Thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) has been widely used to form the basis of many novel drug delivery systems, tissue engineering scaffolds, and as a support/substrate for various biological and chemical applications. Here, we show how PNIPAM polymer surface coating atop a nanostructured linear diffraction grating can be used to controllably change the surface topography of 2D linear structures using temperature stimuli [1]. Neutron reflectometry and surface diffraction are utilized to examine the conformity of the polymer coating to the grating surface, its hydration profile, and its evolution in response to temperature variations. Current system demonstrates advanced performance in the effective alignment of cultured fibroblast cells and the easy release of the cells upon temperature change. Our study also revealed how the deposition of different lipid bilayers affects the properties of the underlying PNIPAM polymer. These results establish that the polymer-membrane interaction is critically mediated by the mechanics of the membrane, providing better insight into cultured cell-hydrogel interactions [2].

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Stony Brook Campus Map



 Hilton Garden Inn, Wang Center, Nobel Halls

 Walking route from Hilton to Wang

 Campus Entrance

 Walking route from Wang to Nobel Halls

