# SAS2022

XVIII INTERNATIONAL SMALL
ANGLE SCATTERING CONFERENCE

# ABSTRACT BOOK

CNPEM
ORGANIZAÇÃO SOCIAL DO MCTI

MINISTRY OF
SCIENCE, TECHNOLOGY
AND INNOVATIONS

## ORGANIZATION

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# Conference Agenda

## Date: Sunday, 11/Sept/2022

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|---|---|
| 3:00pm - 6:00pm | **Registration**<br>Location: **Foyer** |
| 4:00pm - 6:00pm | **Welcome cocktail**<br>Location: **Foyer** |

## Date: Monday, 12/Sept/2022

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|---|---|---|---|
| 8:30am - 9:10am | **SAS2022 Opening**<br>Location: **Campinas auditorium**<br>A1 Further Information on the Session | | |
| 9:10am - 10:00am | **Plenary 1: SAXS in the Era of Fourth-Generation Light Sources, Dr Narayanan Theyencheri, ESRF**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Harry Westfahl Junior** | | |
| 10:00am - 10:10am | **Break 1** | | |
| 10:10am - 10:50am | **Session 1a: Protein Structures, Assemblies and Dynamics 1**<br>Location: **Campinas auditorium**<br>Chair: **Prof. U-Ser Jeng** | **Session 1b: Colloids and Polymers 1**<br>Location: **Jatoba**<br>Chair: **Prof. Jon Otto Fossum** | **Session 1c: Magnetic Materials 1**<br>Location: **Paineiras**<br>Chair: **Dr. Antonio Augusto Malfatti-Gasperini** |
| 10:50am - 11:10am | **Coffee break 1**<br>Location: **Foyer** | | |
| 11:10am - 12:30pm | **Session 2a: Coherent Small Angle Scattering, Imaging 1**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Marios Georgiadis** | **Session 2b: Hybrid Materials and Biomaterials 1**<br>Location: **Paineiras**<br>Chair: **Dr. Leandro Barbosa** | **Session 2c: Modelling and Data Analysis 1**<br>Location: **Jatoba**<br>Chair: **Prof. Uri Raviv** |
| 12:30pm - 2:00pm | **Lunch Monday: Anton Paar sponsoring**<br>Location: **Jatoba** | | |
| 2:00pm - 2:50pm | **Plenary 2: Perspectives on SAXS tensor tomography, Marianne Liebi, PSI**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Carla Cristina Polo** | | |
| 2:50pm - 3:00pm | **Break 2** | | |
| 3:00pm - 4:20pm | **Session 3a: Coherent Small Angle Scattering, Imaging 2**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Carla Cristina Polo** | **Session 3b: Soft Matter and Self-Assembly 1**<br>Location: **Jatoba**<br>Chair: **Dr. Judith Elizabeth Houston** | **Session 3c: Modelling and Data Analysis 2**<br>Location: **Paineiras**<br>Chair: **Prof. Jochen S Hub** |
| 4:20pm - 4:40pm | **Coffee break 2**<br>Location: **Foyer** | | |
| 4:40pm - 6:00pm | **Session 4a: Protein Structures, Assemblies and Dynamics 2**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Paul David Butler** | **Session 4b: Colloids and Polymers 2**<br>Location: **Jatoba**<br>Chair: **Dr. Theyencheri Narayanan** | **Session 4c: Materials Science 1**<br>Location: **Paineiras**<br>Chair: **Dr. Rainer T. Lechner** |
| 6:00pm - 7:30pm | **On-Site Poster Session**<br>Location: **Campinas auditorium**<br>On-site poster presenters | | |

## Date: Tuesday, 13/Sept/2022

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|---|---|---|---|---|---|---|
| 7:55am<br>-<br>8:00am | **Online Poster Session Reminder: On-site poster authors are welcome to present in this online session** | | | | | |
| 8:00am<br>-<br>9:50am | **CanSAS satellite meeting 1**<br>Location: **Jatoba**<br>Chair: **Dr. Judith Elizabeth Houston**<br>Chair: **Dr. Andy James Smith**<br>A1 Further Information on the Session | **Online poster session 1: Protein Structures, Assemblies and Dynamics**<br>A1 Further Information on the Session | **Online poster session 2: Soft Matter and Self-assembly**<br>A1 Further Information on the Session | **Online poster session 3: Materials Science**<br>A1 Further Information on the Session | **Online poster session 4: Instrumentation, Data Format, Modelling and Beamlines**<br>A1 Further Information on the Session | **Online poster session 5: Colloids and Polymers, Hybrid Materials and Biomaterials**<br>A1 Further Information on the Session |
| 9:50am<br>-<br>10:10am | **Coffee break 3**<br>Location: **Foyer** | | | | | |
| 10:10am<br>-<br>11:00am | **Plenary 3: BioSANS for the Study of Membrane Protein, Dr Anne MARTEL, ILL, France**<br>Location: **Campinas auditorium**<br>Chair: **Prof. Jill Trewhella** | | | | | |
| 11:00am<br>-<br>11:10am | **Break 3** | | | | | |
| 11:10am<br>-<br>12:30pm | **Session 5a: Protein Structures, Assemblies and Dynamics 3**<br>Location: **Campinas auditorium**<br>Chair: **Prof. Jill Trewhella** | | **Session 5b: Dynamics, Kinetics, in situ and Time-Resolved 1**<br>Location: **Jatoba**<br>Chair: **Prof. Celso Valentim Santilli** | | **Session 5c: Interfaces, Surfaces and Grazing Incidence 1**<br>Location: **Paineiras**<br>Chair: **Dr. Paula C. Angelomé** | |
| 12:30pm<br>-<br>2:00pm | **Lunch Tuesday: Xenocs sponsoring**<br>Location: **Jatoba** | | | | | |
| 2:00pm<br>-<br>2:50pm | **Plenary 4: Recent Advances in Small-Angle Scattering and the Applications They Serve for Hard Materials, Prof Andrew Allen, NIST, USA**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Florian Meneau** | | | | | |
| 2:50pm<br>-<br>3:00pm | **Break 4** | | | | | |
| 3:00pm<br>-<br>4:20pm | **Session 6a: Materials Science 2**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Bernhard Schummer** | | **Session 6b: Instrumentation, Data Format and Beamlines 1**<br>Location: **Jatoba**<br>Chair: **Dr. Tomas Sigfrido Plivelic** | | **Session 6c: Colloids and Polymers 3**<br>Location: **Paineiras**<br>Chair: **Dr. Anjani Kumar Maurya** | |
| 4:20pm<br>-<br>4:40pm | **Coffee break 4**<br>Location: **Foyer** | | | | | |
| 4:40pm<br>-<br>6:20pm | **Session 7a: Magnetic Materials 2**<br>Location: **Jatoba**<br>Chair: **Dr. Viktor Petrenko**<br>Chair: **Prof. Andreas Michels** | | **Session 7b: Instrumentation, Data Format and Beamlines 2**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Javier Pérez** | | **Session 7c: Colloids and Polymers 4**<br>Location: **Paineiras**<br>Chair: **Dr. Christian Appel** | |
| 6:20pm<br>-<br>6:30pm | **Break to canSAS** | | | | | |
| 6:30pm<br>-<br>8:00pm | **CanSAS satellite meeting 2**<br>Location: **Jatoba**<br>Chair: **Dr. Judith Elizabeth Houston**<br>Chair: **Dr. Andy James Smith**<br>A1 Further Information on the Session | | | | | |

## Date: Wednesday, 14/Sept/2022

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|---|---|---|---|
| **8:30am<br>-<br>9:20am** | **Plenary 5: Microscopic mechanism behind the processing and functionality of polymer nanocomposites, Panchao Yin, South China University of Technology, Guangzhou, China**<br>Location: **Campinas auditorium**<br>Chair: **Prof. Watson Loh** | | |
| **9:20am<br>-<br>9:30am** | **Break 5** | | |
| **9:30am<br>-<br>10:50am** | **Session 8a: Colloids and Polymers 5**<br>Location: **Paineiras**<br>Chair: **Dr. Ryan Patrick Murphy** | **Session 8b: Coherent Small Angle Scattering, Imaging 3**<br>Location: **Campinas auditorium**<br>Chair: **Prof. Marianne Liebi** | **Session 8c: Materials Science 3**<br>Location: **Jatoba**<br>Chair: **Dr. Pablo Mota-Santiago** |
| **10:50am<br>-<br>11:10am** | **Coffee break 5** | | |
| **11:10am<br>-<br>12:50pm** | **Session 9a: Colloids and Polymers 6**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Ana Percebom** | **Session 9b: Coherent Small Angle Scattering, Imaging 4**<br>Location: **Jatoba**<br>Chair: **Dr. Jin Wang** | **Session 9c: Hybrid Materials and Biomaterials 2**<br>Location: **Paineiras**<br>Chair: **Prof. Renata C. Kaminski** |
| **12:50pm<br>-<br>2:20pm** | **Lunch Wednesday: AVS sponsoring**<br>Location: **Jatoba** | | |
| **2:30pm<br>-<br>5:30pm** | **FAZENDA TOZAN: VISIT**<br>Location: **Campinas auditorium**<br>A1 Further Information on the Session | **SIRIUS: VISIT**<br>Location: **Campinas auditorium**<br>A1 Further Information on the Session | |

## Date: Thursday, 15/Sept/2022

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|---|---|---|---|
| **8:30am**<br>**-**<br>**9:20am** | **Plenary 6: Dynamical properties of out-of-equilibrium materials studied with coherent X-rays, Dr Beatrice Ruta**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Aline Ribeiro Passos**<br>A1 Further Information on the Session | | |
| **9:20am**<br>**-**<br>**9:30am** | **Break 6** | | |
| **9:30am**<br>**-**<br>**10:50am** | **Session 10a: Protein Structures, Assemblies and Dynamics 4**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Guillaume Tresset** | **Session 10b: Dynamics, Kinetics, in situ and Time-Resolved 2**<br>Location: **Jatoba**<br>Chair: **Dr. Aline Ribeiro Passos** | **Session 10c: Instrumentation, Data Format and Beamlines 3**<br>Location: **Paineiras**<br>Chair: **Dr. Clement E. Blanchet** |
| **10:50am**<br>**-**<br>**11:10am** | **Coffee break 6**<br>Location: **Foyer** | | |
| **11:10am**<br>**-**<br>**12:50pm** | **Session 11a: Protein Structures, Assemblies and Dynamics 5**<br>Location: **Campinas auditorium**<br>Chair: **Barbara Bianca Gerbelli** | **Session 11b: Dynamics, Kinetics, in situ and Time-Resolved 3**<br>Location: **Jatoba**<br>Chair: **Prof. Aldo Craievich** | **Session 11c: Instrumentation, Data Format and Beamlines 4**<br>Location: **Paineiras**<br>Chair: **Dr. Mark Tully** |
| **12:50pm**<br>**-**<br>**2:20pm** | **Lunch Thursday: Dectris sponsoring**<br>Location: **Jatoba** | | |
| **2:30pm**<br>**-**<br>**3:30pm** | **Thursday: OPEN SAS meeting**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Jan Ilavsky** | | |
| **3:30pm**<br>**-**<br>**3:50pm** | **Coffee break 7**<br>Location: **Foyer** | | |
| **3:50pm**<br>**-**<br>**4:00pm** | **Official conference photo**<br>Location: **Foyer** | | |
| **4:00pm**<br>**-**<br>**5:00pm** | **Guinier lecture**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Jan Ilavsky** | | |
| **5:00pm**<br>**-**<br>**6:00pm** | **Awards, SAS2024 and SAS2027**<br>Location: **Campinas auditorium** | | |
| **7:00pm**<br>**-**<br>**10:00pm** | **Conference dinner** | | |

## Date: Friday, 16/Sept/2022

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|---|---|---|---|
| **8:30am<br>-<br>9:20am** | **Plenary 7: Soft Matter Systems Investigated by Small-Angle X-ray Scattering, Cristiano Oliveira, USP, Brasil**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Mateus Cardoso** | | |
| **9:20am<br>-<br>9:30am** | **Break 7** | | |
| **9:30am<br>-<br>10:50am** | **Session 12a: Soft Matter and Self-Assembly 2**<br>Location: **Campinas auditorium**<br>Chair: **Dr. François Boué** | **Session 12b: Modelling and Data Analysis 3**<br>Location: **Paineiras**<br>Chair: **Dr. Leandro Barbosa** | **Session 12c: Colloids and Polymers 7**<br>Location: **Jatoba**<br>Chair: **Dr. Andy James Smith** |
| **10:50am<br>-<br>11:10am** | **Coffee break 8**<br>Location: **Foyer** | | |
| **11:10am<br>-<br>12:50pm** | **Session 13a: Hybrid Materials and Biomaterials 3**<br>Location: **Paineiras**<br>Chair: **Dr. Charlotte Jennifer Chante Edwards-Gayle** | **Session 13b: Modelling and Data Analysis 4**<br>Location: **Campinas auditorium**<br>Chair: **Dr. Melissa Ann Graewert** | **Session 13c: Interfaces, Surfaces and Grazing Incidence 2**<br>Location: **Jatoba**<br>Chair: **Dr. Antonio Augusto Malfatti-Gasperini** |
| **12:50pm<br>-<br>2:20pm** | **Lunch Friday: Anton Paar**<br>Location: **Foyer** | | |
| **2:30pm<br>-<br>5:30pm** | **SIRIUS_2: VISIT**<br>Location: **Campinas auditorium**<br>A1 Further Information on the Session | | |

SAS2022
XVIII INTERNATIONAL SMALL
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# ORAL
ABSTRACTS

PLENARY 1

Chair: Dr. Harry Westfahl Junior

# P215 - SAXS IN THE ERA OF FOURTH-GENERATION LIGHT SOURCES

**NARAYANAN, Theyencheri**
*European Synchrotron Radiation Facility (ESRF), France*
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The advent of third-generation synchrotron sources in the mid-nineties led to significant broadening of the scope of small-angle X-ray scattering (SAXS) methods in the investigation of soft matter and biophysical systems. The high brilliance of these sources enabled time-resolved experiments in the millisecond range even with low contrast samples, and high angular resolution and spatially resolved measurements [1]. Indeed, parallel developments of advanced detectors, sample environments and most importantly new data analysis methods were pivotal in exploiting the source properties [2]. As a result, SAXS methods now allow simultaneous access to a broad range of size and time scales deciphering the structural information from sub-nm to micron size scales and kinetics down to the sub-millisecond time range in hierarchically organized systems [1]. This talk will present some representative applications ranging from soft matter self-assembly to cellular processes under thermodynamically [1] or physiologically pertinent states [3].

The fourth-generation sources such as the ESRF-Extremely Brilliant Source, Max IV, Sirius, APS-U, etc. offer even more exciting opportunities for SAXS and related methods [4]. The order of magnitude increases in the brightness and degree of coherence open new avenues for the investigation of soft matter and biological systems by scattering methods. In particular, the X-ray photon correlation spectroscopy (XPCS) has received a major boost. As a result, the equilibrium dynamics over a broader time and length scales has become accessible by this method. The improved beam properties together with the advanced pixel array detectors readily enhance the q-resolution of SAXS and ultra SAXS in the pinhole collimation. These new features will be illustrated by means of several examples such as the hierarchical self-assembly of amphiphilic systems, the emergence of active dynamics upon self-propulsion of colloids, etc. Indeed, the rapid onset of radiation damage is a significant challenge with vast majority of samples and appropriate protocols need to be adopted for circumventing this problem.

**Keywords**
Time-resolved SAXS, USAXS, XPCS, self-assembly, kinetics, dynamics

## References

[1] Narayanan, T. & Konovalov, O. Synchrotron scattering methods for nanomaterials and soft matter research. Materials, 13, 752 (2020). https://doi.org/10.3390/ma13030752

[2] Jeffries, C. M., Ilavsky, J., Martel, A., Hinrichs, S., Meyer, A., Pedersen, J. S., Sokolova, A. V. & Svergun, D. I. Small-angle X-ray and neutron scattering, Nat. Rev. Methods Primers, 1, 70, (2021). https://doi.org/10.1038/S43586-021-00064-9

[3] Brunello, E., Fusi, L., Ghisleni, A., Park-Holohan, S.-J., Ovejero, J. G., Narayanan, T. & Irving, M. Myosin filament-based regulation of the dynamics of contraction in heart muscle, PNAS, 117, 8177–8186 (2020). https://doi.org/10.1073/pnas.1920632117

[4] Narayanan, T., Sztucki, M., Zinn, T., Kieffer, J., Homs-Puron, A., Gorini, J., Van Vaerenbergh, P. & Boesecke, P. Performance of the time-resolved ultra-small-angle X-ray scattering beamline with the Extremely Brilliant Source. J. Appl. Cryst., 55, 98-111 (2022). https://doi.org/10.1107/S1600576721012693

SESSION 1A: PROTEIN STRUCTURES, ASSEMBLIES AND DYNAMICS 1
Chair: Prof. U-Ser Jeng

## P274 - BIOMOLECULAR SMALL-ANGLE SCATTERING: DATA REPRODUCIBILITY AND BENCHMARKING PREDICTIVE METHODS

**TREWHELLA, Jill**
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Through a process spanning more than a decade and a half, with consultation via open access reports and papers, the biomolecular Small-Angle Scattering (SAS) community worked to establish guidelines for SAS data quality and model validation (Trewhella et al. (2017) Acta Crystallographica D73, 710-728), which has been a major contributor to its maturation as a mainstream structural biology technique. Today, biomolecular SAS is well-positioned to achieve its full potential at the frontier of integrative structural biology, where different data types and computational methods are required to solve increasingly complex and dynamic structures, because the framework has been established to meet “best practice” standards for the field. The next phase of this work has been to undertake a round robin study to assess the reproducibility of biomolecular SAS data and provide consensus SAS profiles for benchmarking methods for SAS profile prediction from atomic coordinates. To this end 5 candidate proteins (RNaseA, lysozyme, xylanase, urate oxidase and xylose isomerase) were measured on 12 Small-Angle X-ray Scattering (SAXS) and 4 Small-Angle Neutron Scattering (SANS) instruments. In total, more than 150 SAXS data sets and more than 70 SANS data sets were submitted for evaluation. Measurements in batch mode and with in-line Size Exclusion Chromatography (SEC) were made using SAXS and SANS, in H2O and D2O buffers. The results of the study, which includes contributions from 50 international researchers from across the globe, will be presented.

**Keywords**
biomolecular small angle scattering, SAXS, SANS, structural biology, data reproducibility, benchmarking, small angle scattering profile prediction

SESSION 1A: PROTEIN STRUCTURES, ASSEMBLIES AND DYNAMICS 1
Chair: Prof. U-Ser Jeng

# P229 - HOW DO PLANTS SENSE TEMPERATURE - EARLY FLOWERING 3 FORMS ORDERED BIOMOLECULAR CONDENSATES

**HUTIN, Stephanie (1); COSTA, Luca (2); ZUBIETA, Chloe (1); TULLY, Mark (3)**
*1: Laboratoire Physiologie Cellulaire et Végétale (LPCV), CNRS, France; 2: Centre de Biologie Structurale (CBS), CNRS, France; 3: European Synchrotron Radiation Facilit (ESRF), France*
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Plants are exposed to frequent environmental changes and stress conditions, especially in the context of climate change and other anthropogenic activities. Increased average temperatures and prolonged periods of extreme heat due to global warming alter plant phenology and present a critical challenge for food security in the coming decades. Direct environmental sensing, especially of temperature changes, is essential for plant survival, but the mechanisms that plants use to monitor and respond to the environmental cues remain elusive. One important mechanism that allows a fast response to temperature stimuli is the formation of dynamic liquid-liquid phase separated (LLPS) states. LLPS allows for dynamic compartmentalization of macromolecules via the formation of biomolecular condensates as a function of the physicochemical surroundings. EARLY FLOWERING 3 (ELF3), a low-complex prion-like domains (PrD) containing protein, acts as a direct temperature sensor via LLPS[1,2].

Using biological small angle X-ray scattering (bioSAXS) in combination with other biophysical and structural techniques, we investigated the dilute and condensed phases of the thermosensor ELF3 with focus on the role of the PrD. We demonstrate that the length of polyQ repeats in the PrD correlates with thermal responsiveness in ELF3 by tuning the properties of the condensate as shown by scattering techniques and fluorescence and atomic force microscopies[3]. Furthermore, we demonstrate that the condensed phase assumes a semi-ordered structure as determined by small angle scattering, electron microscopy and X-ray diffraction. The ability of ELF3 to switch between active and inactive states through phase transition represents a novel thermosensory mechanism and here we describe the underlying structural, biochemistry and biophysics of this process.

**Keywords**
Liquid-Liquid phase separation, LLPS, SAXS, BM29

**References**

[1] Jung, Jae-Hoon et al. “A prion-like domain in ELF3 functions as a thermosensor in Arabidopsis.” Nature vol. 585,7824 (2020): 256-260. doi:10.1038/s41586-020-2644-7
[2] Silva, Catarina S et al. “Molecular mechanisms of Evening Complex activity in Arabidopsis.” Proceedings of the National Academy of Sciences of the United States of America vol. 117,12 (2020): 6901-6909. doi:10.1073/pnas.1920972117
[3] Hutin, Stephanie et al. ""The plant thermosensory protein EARLY FLOWERING 3 forms an ordered biomolecular condensate in vitro."" Nature Comms, in press

# P404 - DECODING THE MECHANISM OF AUTOXIDATION DECONSTRUCTION REACTION OF PLASTICS BY IN-SITU SIMULTANEOUS SAXS AND WAXS

**MAURYA, Anjani K. (1,2); ASUNDI, Arun S. (1,2); HESSE, Sarah A. (1,2); EBRAHIM, Amani M. (1,2); SULLIVAN, Kevin P. (2,3); PALUMBO, Chad T. (2,3); WERNER, Allison Z. (2,3); TAKACS, Christopher J. (1,2); BECKHAM, Gregg T. (2,3); SARANGI, Ritimukta (1,2); TASSONE, Christopher J. (1,2)**
*1: Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA; 2: Bio-Optimized Technologies to Keep Thermoplastics out of Landfills and the Environment (BOTTLE) Consortium, Golden, CO 80401, USA; 3: Renewable Resources and Enabling Sciences Center, National Renewable Energy Laboratory, Golden, CO, USA*
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The exponentially increasing production of plastics and their resistance to natural degradation in the environment is becoming one of the most pressing environmental issues of recent times. Therefore, efficient and cost-effective plastic deconstruction methods are required. Chemical deconstruction of mixed plastic waste offers a promising route to produce value-added chemicals and products. However, the selectivity and activity of these approaches are still limited by a lack of understanding of the reaction mechanisms. Hence, A fundamental understanding of the nature of the catalyst-substrate interface, the role of crystallinity, and the effect of solvents and catalysts on the substrate morphology (Figure 1) of the deconstruction reaction are needed which play key roles in the reaction kinetics.

In this contribution, we will describe our approach to in-situ and operando characterization of oxidative cleavage approaches. This reaction is naturally slow, the rate of polymer autoxidation can be significantly enhanced at elevated temperatures and in the presence of an appropriate solvent, catalyst, and initiator [1]. Autoxidation catalysts are multicomponent systems, consisting of Co and Mn organometallic complexes, Br or N-hydroxyphthalimide (NHPI) initiators, and aqueous or anhydrous acetic acid solvents. Small and wide-angle X-ray scattering (S/WAXS) are powerful techniques for in-situ probing of the multiscale structural changes in the polymer substrates during the deconstruction reaction. Here we describe the results from the in-situ characterization of polyethylene (PE) and polystyrene (PS) substrates by performing in-situ simultaneous SAXS and WAXS measurements at reaction relevant temperatures and pressure. Furthermore, the effect of solvents and catalyst components on the structure of polymer substrates will be discussed.

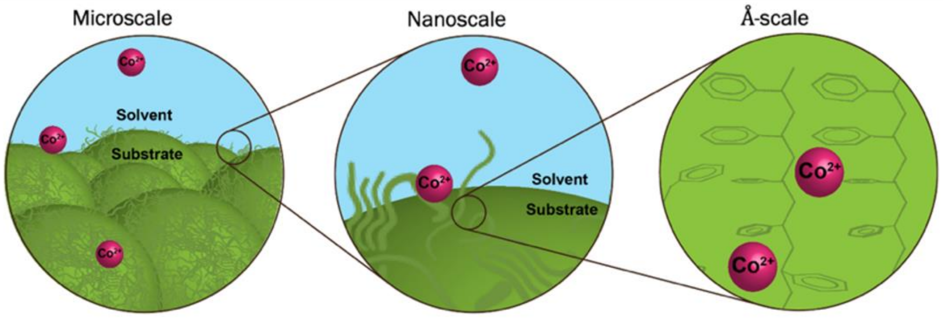

*Figure 1: Schematic of the multiscale structural interfaces in the autoxidation deconstruction reaction of polymer substrates.*

**Keywords**
Plastic Deconstruction, Autoxidation, Catalysis, in-situ SAXS and WAXS

## References

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SESSION 1B: COLLOIDS AND POLYMERS 1
Chair: Prof. Jon Otto Fossum

# P240 - CAPILLARY RHEOSAS: EXPLORING THE RHEOLOGY AND STRUCTURE OF COMPLEX FLUIDS UNDER EXTREME FLOWS AND CONFINEMENT WITH CAPILLARY RHEOMETRY AND SMALL-ANGLE SCATTERING

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Processing methods such as spraying, coating, and jetting produce extreme flow velocities of complex fluids within confined geometries. High shear rates and shear stresses within the fluid near the stationary wall can induce reversible or irreversible changes to the underlying fluid microstructure. To better understand and quantify these flow-induced changes, a capillary rheometer was developed to measure the viscosity of complex fluids at high shear rates and to enable simultaneous measurement of the fluid microstructure using small-angle scattering (SAS). Originally developed for small-angle neutron scattering, the same capillary setup and methodology was modified and expanded recently for x-ray scattering, which enables significantly lower count times, improved sample and shear rate throughput, higher shear rates up to 107 s-1, and extremely confined flows within capillaries down to 500 nm. This work will highlight and discuss the rheometer design criteria, recent rheometer upgrades, the advantages and limitations using either neutron or x-ray sources, and software control improvements. The structure-rheology relationships of different model systems will be discussed, including worm-like micelles, vesicles, polymers, proteins, silica nanoparticles, and larger colloidal crystals. By combining and expanding the measurement capabilities of capillary rheometry and scattering methods, new fundamental insights can be used to produce pharmaceuticals, coatings, lubricants, and fuel additives with improved flow-stability and rheological behavior.

**Keywords**
Rheology, Complex fluids, Soft matter, SANS, SAXS

SESSION 1C: MAGNETIC MATERIALS 1
Chair: Dr. Antonio Augusto Malfatti-Gasperini

# P117 - SIGNATURE OF DEFECT-INDUCED SYMMETRY BREAKING IN MAGNETIC NEUTRON SCATTERING

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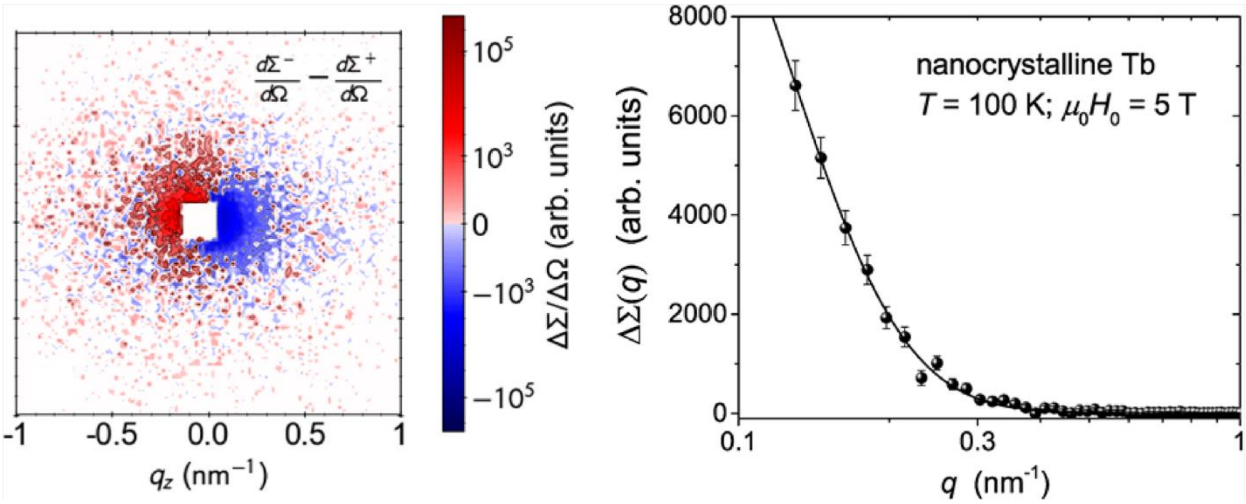
The antisymmetric Dzyaloshinskii-Moriya interaction (DMI) plays a decisive role for the stabilization and control of chirality of skyrmion textures in various magnetic systems exhibiting a noncentrosymmetric crystal structure. A less studied aspect of the DMI is that this interaction is believed to be operative in the vicinity of lattice imperfections in crystalline magnetic materials, due to the local structural inversion symmetry breaking. If this scenario leads to an effect of sizable magnitude, it implies that the DMI introduces chirality into a very large class of magnetic materials—defect-rich systems such as polycrystalline magnets. Here, we show experimentally that the microstructural-defectinduced DMI gives rise to a polarization-dependent asymmetric term in the small-angle neutron scattering (SANS) cross section of polycrystalline ferromagnets. The results are supported by theoretical predictions using the continuum theory of micromagnetics. This effect, conjectured already by Arrott in 1963, is demonstrated for nanocrystalline terbium and holmium (with a large grain-boundary density), and for mechanically-deformed microcrystalline cobalt (with a large dislocation density). Analysis of the scattering asymmetry allows one to determine the defect-induced DMI constant, D = 0.45±0.07 mJ/m2 for Tb at 100 K. Our study proves the generic relevance of the DMI for the magnetic microstructure of defect-rich ferromagnets.



(left) Experimental left-right asymmetry of the polarized difference SANS cross section of nanocrystalline Terbium. (right) Azimuthally-integrated data with fit (solid line) to theory prediction.

**Keywords**
magnetic SANS, polarized neutrons, micromagnetics, Dzyaloshinskii-Moriya interaction

SESSION 1C: MAGNETIC MATERIALS 1
Chair: Dr. Antonio Augusto Malfatti-Gasperini

# V269 - IMPACT OF ELECTRIC FIELD ON THE ASSEMBLY OF MAGNETIC NANOPARTICLES IN BULK AND AT INTERFACE

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It is well known, that properties of ferrofluids can be controlled by external magnetic field. However, inhomogeneous distribution of magnetic particles in non-polar ferrofluids was observed recently under external electric fields and formation of large aggregates was concluded in such systems. And it was also concluded, that electric fields, similar to magnetic fields, could be a driven force to induce the assembly of magnetic nanoparticles at the interface. The question of relaxation processes after switching off the field and returning the structure to its original state was considered according to the small-angle neutron scattering (SANS) for the bulk investigations and neutron reflectometry (NR) for interface studies.

Thus, it was shown by SANS that aggregation process depends on the magnitude of the DC electric field, and in alternating electric fields with a frequency of more than 800 mHz, aggregates are not formed at all. Also, the detected anisotropy of the SANS signal at the detector indicates the preferred orientation of the aggregates of magnetic particles in ferrofluids. Impact of temperature on such aggregation was also checked by SANS and it was concluded that with temperature increase above 60 °C, the aggregates formed in the electric field are destroyed. SANS with polarized neutrons was performed for detail study of the nuclear and magnetic structures in such systems.

Using specular neutron reflectometry, assembling of superparamagnetic nanoparticles of a dilute classical ferrofluid on a planar surface of the metal electrode (copper) was observed when an out-of-plane electric field is applied to the interface. Starting from only a wetting layer of magnetic nanoparticles on the electrode surface in the absence of the electric field, the evolution of the interface structure with the increase in the electric field strength is followed by analyzing the changes in the scattering length density depth profiles derived from neutrons reflectivity curves. At sufficiently strong electric field, the second adsorption layer is revealed which becomes even more saturated than the initial one. The reason of the observed effects is related to the polarization of the particles in the electric field and their interaction as dipoles.

**Keywords**
magnetic fluids, aggregation, self-assembly, SANS, NR

SESSION 2A: COHERENT SMALL ANGLE SCATTERING, IMAGING 1
Chair: Dr. Marios Georgiadis

# P412 - COHERENT DIFFRACTION IMAGING (CDI) AND MICRO-X-RAY FLUORESCENCE (μ-XRF) CHEMICAL IMAGING OF MICROAGGREGATES FROM A TROPICAL SOIL

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Highly weathered tropical soils are well known for progressively retaining applied phosphate into forms that are not readily available to plants. One proposed mechanism for this slowly reversible “phosphate fixation” phenomenon is diffusion of into micro- and nano-pores of soil aggregates, with natural organic matter potentially blocking some pores (Vermeiren et al., 2021). Moreover, biological recoverability of phosphate from these pore networks is poorly understood. The aim of this research was to characterize the physical structure of micro- and nano-pores of soil microaggregates along with their chemical composition. Isolated microaggregates of 10 – 40 µm were collected from a highly weathered soil in a forested area of São Paulo state. Subsamples were reacted with either 1 mM orthophosphate solution or deionized water (control). Computations using a simplified reactive diffusion equation predicted that aqueous phosphate at this concentration would fully diffuse into 30-µm diameter spherical microaggregates within 2 h, depending on porosity and adsorption characteristics of the composing minerals. The micro/nano-pore structure of three unique microaggregates were characterized by nano-tomography at the CATERETÊ coherent diffraction imaging (CDI) beamline at the Sirius synchrotron with ~80 nm resolution. Complementary micro-X-ray fluorescence (µ-XRF) elemental images were collected at the CARNAÚBA coherent X-ray nanoprobe beamline. Generally, 2D projections of CDI and µ-XRF structural and chemical images showed similarities of heterogeneous spatial features of the soil microaggregates analyzed. Images also revealed that the soil particles were microaggregates composed of smaller particles rather than mineral-coated quartz grains; with iron, titanium, and manganese being dominant elements along with trace elements. Tomographic reconstruction of CDI images of one microaggregate showed branching structures that we hypothesize are fungal hyphae. It is not clear whether any fungal hyphae invade intact microaggregates or are largely responsible for their formation and stabilization. In essence, our results illustrate the value of combining CDI with chemical imaging for studying heterogeneous soil micro- and nano-pore networks that potentially control changes in plant availability of phosphate and other soil nutrient elements.

## Keywords

soil, nano-tomography, aggregation, hierarchical structure

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SESSION 2A: COHERENT SMALL ANGLE SCATTERING, IMAGING 1
Chair: Dr. Marios Georgiadis

# P278 - REVEALING THE NANO-ARCHITECTURE DISSIMILARITIES OF GRASSES CELL WALL USING 3D COHERENT DIFFRACTIVE IMAGING

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Lignin is an aromatic polymer present in plant cell walls that represents the main bottleneck to the efficient conversion of polysaccharides into fermentable sugars to produce biofuels and bioproducts from plant biomass. As an alternative, genetic manipulations of the lignin biosynthetic pathway can generate plants with lower lignin levels or altered lignin structures, decreasing biomass recalcitrance. Therefore, the present study aims to explore the nano structure of Setaria viridis wild-type and transgenic cell (from plants with reduced lignin contents), employing coherent X-ray diffractive imaging (CXDI) at Cateretê beamline (Sirius, the 4th generation synchrotron source, Campinas, Brazil). We will show how the CXDI experiments performed in 3D ptychographic mode allows to study the tens of micrometers of S. viridis tissues and still obtain tens of nanometers resolution. At such length scales, the lignin content can be accurately quantified and characterized by image segmentation to further compare the transgenic lines with the wild-type plants. Finally, CXDI will allow a better understanding of grass cell wall strucutre aiming a rational engineering of grasses biomass for industrial applications.

**Keywords**
lignin, nano-tomography, plant cell wall

**Acknowledgements**
This work is supported by the São Paulo State funding agency (Fapesp 2020/13748-7 and 2021/06876-1).

# P434 - COHERENT SURFACE SCATTERING IMAGING IN DYNAMICAL SCATTERING REGIME AND HOLOGRAPHY IN GRAZING-INCIDENCE GEOMETRY

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From energy production and storage to dynamics in biomembranes and cells, from self-assembled hierarchical structures to fluid flow in confined geometries, natural and man-made processes around us exhibit structure and dynamics at surfaces and interfaces on nanoscopic to macroscopic length scales. For decades, surface x-ray scattering techniques have always been powerful tools for probing surface structures, due to their capabilities of probing buried interfacial structures and adapting in situ environments. In grazing-incident reflection geometry, x-ray coherent surface scattering imaging promises the reconstruction of mesoscale structures at surfaces and interfaces with nanometer resolution. The reflective surface breaks the symmetry encountered in conventional transmission coherent diffractive imaging and provides the momentum transfer in the off-the-plane direction so that three-dimensional (3D) reconstruction become possible. In addition, multiple scattering occurs close to the surface critical angles where dynamical scattering and holography are created to unveil the 3D structure in a single coherent-speckle pattern. As a result, we observed a set of unique coherent scattering fringes and speckle patterns collected with the reflection geometry with hard x-rays, which is extremely sensitive to the out-of-plane structure. With a simple surface pattern supported by the substrate, the scattering resembles Lloyd's mirror interference, suggesting that the x-rays are scattered multiple times. In the process of understanding and simulating the unique interference patterns, we first discovered the deficiency of the existing x-ray dynamical scattering theory that treats surface structure in grazing-incidence geometry for incoherent scattering. To overcome the problem, we develop a finite-element or grid-based distorted wave Born approximation (DWBA) by taking the heterogeneity of the sample and the coherence of the x-rays into consideration. The simulation reproduces the scattering pattern that matches the experiment data quantitatively in the dynamical scattering domain as seen in Figure 1. The most significant implication of the surface scattering holography method is the sensitive correlation between the multiple-scattering interference patterns and the 3D structure in a single scattering pattern (at a single incidence angle). The powerful technique, facilitated by the next-generation x-ray sources with high coherent flux, for visualizing the evolution of biological cells and membranes in an aqueous environment, thin-film and quantum dot growth at surfaces and interfaces, assembly of planner polymer nanocomposites, and structural analysis of 3D micro/nanoscale electronic circuits.

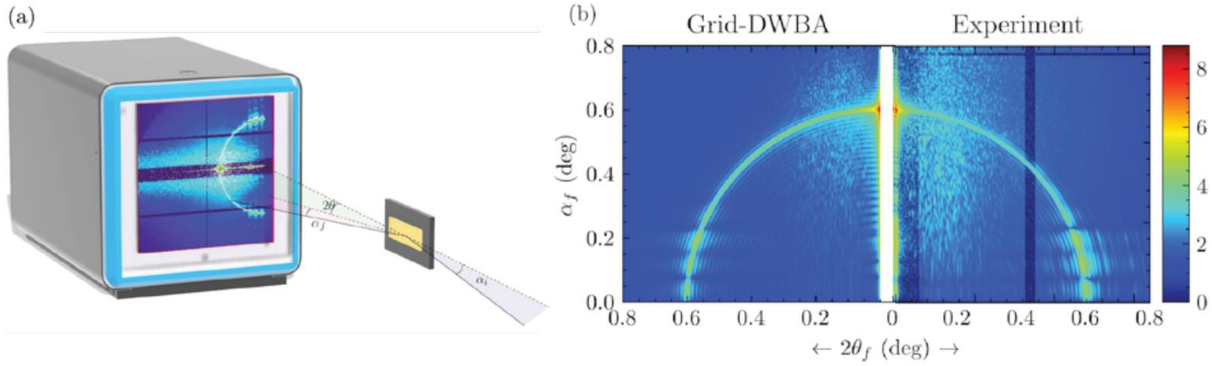

***Figure 1.*** *X-ray coherent surface scattering imaging and holography of a flat-silicon substrate supported gold single-bar pattern. a) scattering geometry (not to scale), b) finite-element or grid approach to solve multiple-scattering ($\alpha_f < 0.4°$) where the holographic patterns dominate: simulation (left) and experimental data (right).*

**Keywords**
coherent surface scattering imaging, dynamical scattering, grazing incidence, surfaces and interfaces

**Acknowledgements:**
This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. We also acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities.

SESSION 2A: COHERENT SMALL ANGLE SCATTERING, IMAGING 1
Chair: Dr. Marios Georgiadis

# V152 - 3D IMAGING OF THE POROUS POLYMERIC MEMBRANES IN NANOSCALE-RESOLUTION BY X-RAY PTYCHOGRAPHY COHERENT DIFFRACTIVE IMAGING

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The porosity and complex morphology of porous materials and membranes drive their applications in challenging separations varying from biomolecules purification to catalysts recovery in the chemical industry, gas and vapor separation in oil refineries, pollutant particle filtration for air purification, as well as their applications as biological scaffolds or as templates for nanomaterials. Imaging the structures is essential for the characterization and further progress of porous systems for separation membranes and other applications. Due to the complexity of the structures, the classical 2D microscopy images provide only a restrict information. A 3D image with high-resolution provides information about the material morphology, the structure functioning and its formation mechanism. Such can be obtained with use of electron microscopy techniques. However, the main drawback of electron microscopy for 3D imaging of porous polymeric materials is the need of high vacuum. That is where the x-ray-based imaging methods can have a great advantage as non-destructive characterization tool, which can be applied in air, water or other environments. The high penetration depth of hard x-rays allows the 3D analysis without the ultramicrotomy step required for electron microscope.

The combination of Sirius high photon coherent flux and Cateretê beamline capabilities to perform coherent X-ray imaging generated 3D images down to ~ 30 nm resolution. Such imaging, performed in the non-vacuum environment, is much closer to live-operation conditions. The 3D high-resolution image reconstruction of a representative membrane volume enables a much more comprehensive representation of the porous systems, allows to calculate the porosity and model the pore network, help to better understand transport phenomena, and guide future developments of industrial separations and biomedical systems.

**Keywords**
Membrane, Ptychography, Imaging

## SESSION 2B: HYBRID MATERIALS AND BIOMATERIALS 1
Chair: Dr. Leandro Barbosa

# V176 - NERVE FIBERS AND MYELIN ASSEMBLY IN A BRAIN SECTION RETRIEVED BY SANS

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The structural connectivity of the brain has been addressed by various imaging techniques such as diffusion weighted magnetic resonance imaging (DWMRI) or specific microscopic approaches based on histological staining or label-free using polarized light (e.g., three-dimensional Polarized Light Imaging (3D-PLI), Optical Coherence Tomography (OCT)). These methods are sensitive to different properties of the fiber enwrapping myelin sheaths i.e. the distribution of myelin basic protein (histology), the apparent diffusion coefficient of water molecules restricted in their movements by the myelin sheath (DWMRI), and the birefringence of the oriented myelin lipid bilayers (3D-PLI, OCT). We show that the orientation and distribution of nerve fibers as well as myelin in thin brain sections can be determined using scanning small angle neutron scattering (sSANS). Neutrons are scattered from the fiber assembly causing anisotropic diffuse small-angle scattering and Bragg peaks related to the highly ordered periodic myelin multilayer structure. The scattering anisotropy, intensity, and angular position of the Bragg peaks can be mapped across the entire brain section. This enables mapping of the fiber and myelin distribution and their orientation in a thin brain section, which was validated by 3D-PLI. The experiments became possible by optimizing the neutron beam collimation to highest flux and enhancing the myelin contrast by deuteration. This method is very sensitive to small microstructures of biological tissue and can directly extract information on the average fiber orientation and even myelin membrane thickness. The present results pave the way toward bio- imaging for detecting structural aberrations causing neurological diseases in future.

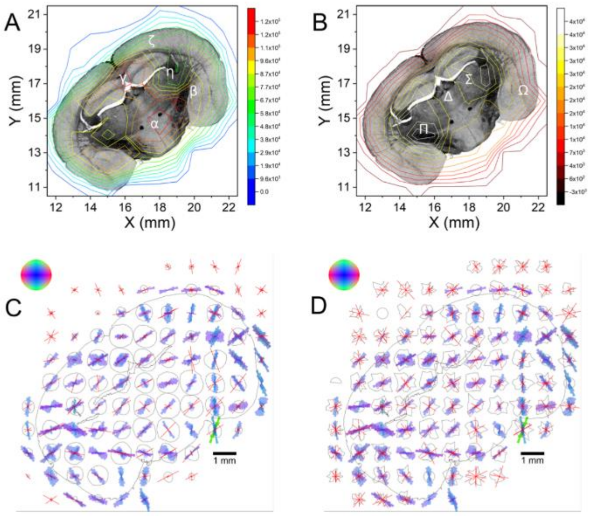

Figure 1: The map of a mouse brain obtained from scanning SANS: From the (A,C) Porod scattering and the (B,D) myelin correlation peak.

**Keywords**
SANS, brain, myelin, axons, orientation

SESSION 2B: HYBRID MATERIALS AND BIOMATERIALS 1
Chair: Dr. Leandro Barbosa

# V367 - SAXS: A VIEW ON THE LIPID-BASED NANOSTRUCTURED CARRIERS (NLC) DESIGNED FOR THE DELIVERY OF DOCETAXEL

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Skin cancer is the most common type of cancer in the world, being responsible for a death toll of two people per hour only in the United States [1,2]. The usual treatment for skin cancers is surgical excision, which causes discomfort for the patient, risk of metastatic spread during surgery and the aggravating fact that melanoma is recurrent in the elderly, who have more sensitive skin and in some cases are unable to undergo surgery[1,2]. Nanotechnology can make a promising contribution to the development of new clinical cancer treatments .The main antineoplastic agents, such as docetaxel, have limitations such as low water solubility, tissue toxicity and rapid degradation [3] . Such challenges can be overcome with the use of nanocarriers, as in the case of nanostructured lipid carriers (NLC). We developed a nanostructured hybrid system [3] composed of NLC incorporating docetaxel (DTX, 0.5%) adsorbed on a biopolymeric matrix of xanthan-chitosan gum (3:1%) containing the anesthetic lidocaine (LDC, 2%) to be an innovative drug delivery system (DDS) for the treatment of melanoma. The applicability of nanostructured lipid carriers (NLC) in drug delivery allows increasing the bioavailability of pharmacologic active compounds. Our aim in this study is to observe the structural organization of lipid-based drug delivery systems: NLC containing the anti-cancer drug docetaxel. SAXS measurements give structural details on the organization of excipients and drugs inside the NLC that will help us to select the best formulation aiming the treatment of melanoma. In order to probe the structural organization of the NLC, preliminary Small Angle Neutron Scattering (SANS) experiments were collected at the Helmholtz Zentrum-Berlin, V16-VSANS, Germany measurements with NLC containing or not DTX. Preliminary results showed changes in structure of the nanocarrier when the antineoplastic drug (DTX 0.5%) was encapsulated. SANS curves suggested the formation of two distinct hydrophobic clusters which are related to the correlation lengths model (equation 1) used to fit the scattering curves. The measurements were performed at P12 at PETRAIII (small angle X-ray scattering) in order to measure the structure of the following formulations: NLC (without docetaxel), NLC-DTX (with docetaxel), pure hydrogel chitosan+xanthan Hydrogelcontrol (withouth lidocaine), Hydrogel with lidocaine, NLC (without docetaxel) mixed with Hydrogel(control) (withouth lidocaine), NLC (without docetaxel) mixed Hydrogel with lidocaine, NLC-DTX (with docetaxel) mixed Hydrogel with lidocaine., for temperature range from 25°C (storage temperature), to 40°C (fever temperature) and also to observe the dynamics of the systems through the temperature in order to identify possible phase transitions temperature. First results show: (i) the formation of structure organization of solid lipid inside the NLC, that changes as a function of temperature disappering around 38 °C; (ii) the effect of docetaxel in the NLC; (iii) the remain crystalinity of the drug (docetaxel); (iv) the effect of the hydrogel structural shape with the influence of lidocaine and (v) the effect of hydrogel in the NLC systems.

**Keywords**
SAXS, Lipid-based nanostructured carriers (NLC), Docetaxel, Lidocaine.

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SESSION 2B: HYBRID MATERIALS AND BIOMATERIALS 1
Chair: Dr. Leandro Barbosa

## V282 - SOLUTION SMALL-ANGLE SCATTERING FOR DRUG DEVELOPMENT AND FORMULATIONS

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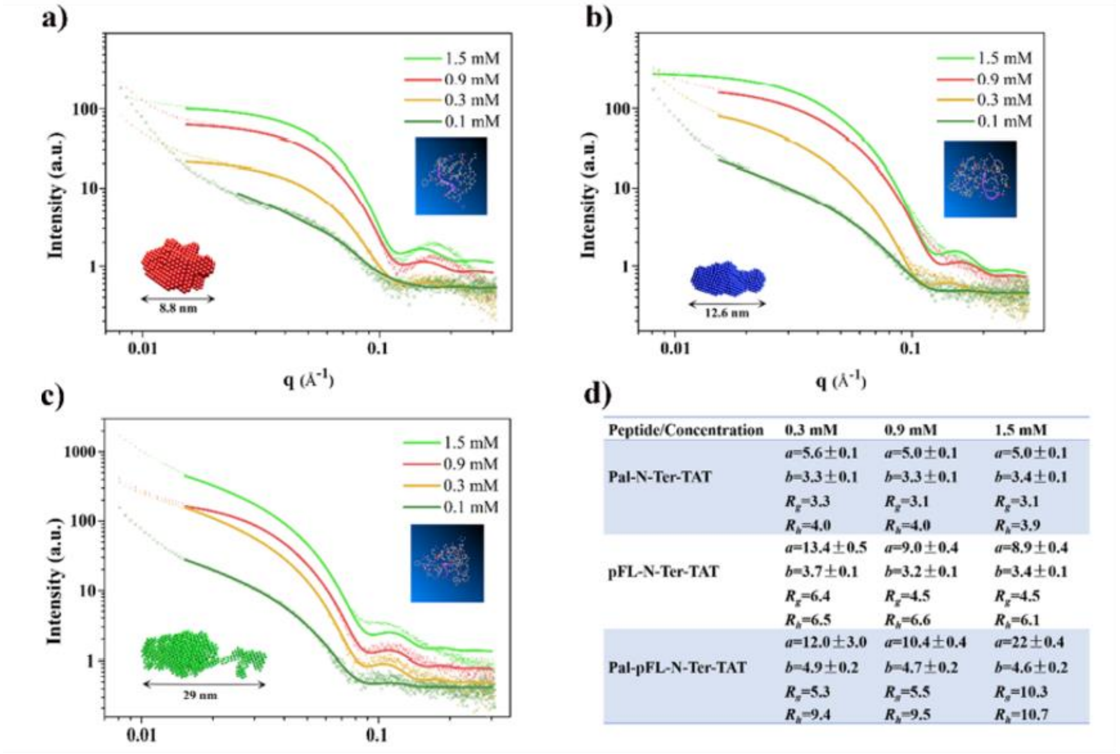
Drug development consists different stages and has challenges in both the formulation safety and stability before entering the market. Small-angle X-ray scattering (SAXS) is practical to study the structure of soft matters in solution, which can provide detailed structural information at the length scale of nanometers. The recent advances in both hardware technology and in novel data-analysis approaches significantly increased the popularity of SAXS in drug development, especially in drug formulation, making it a fast and robust scientific tool for structural biologists. As the first biological small-angle X-ray scattering (BioSAXS) synchrotron beamline in China, the BL19U2 beamline is a powerful tool to characterize the micro-structure of soft matters with high-throughput screening capabilities. Here we discuss the basic principles of SAXS and the diverse applications of this method in characterizing pharmaceutical materials. Examples include screening therapeutic monoclonal antibodies formulation, drug liquid-crystalline mesophase identification, solid dispersions formulation optimization, and protein-based drug development[1],[2]. In considering the challenges of drug development for SAXS measurements, we have performed a comprehensive upgrade on BL19U2 beamline in Shanghai Synchrotron Radiation Facility[3],[4], including optics, electronics, sample environments and the data acquisition system, which are devoted exclusively to the requirements of structural biology for drug development. In summary, the unique and rapid characterization from SAXS contributes to shorter time-to-market and a better understanding of structural properties for new drugs and vaccines development, that is considered as a versatile analytical technique for new drugs structural characterization.



| Peptide/Concentration | 0.3 mM | 0.9 mM | 1.5 mM |
|---|---|---|---|
| Pal-N-Ter-TAT | $a$=5.6±0.1 | $a$=5.0±0.1 | $a$=5.0±0.1 |
| | $b$=3.3±0.1 | $b$=3.3±0.1 | $b$=3.4±0.1 |
| | $R_g$=3.3 | $R_g$=3.1 | $R_g$=3.1 |
| | $R_h$=4.0 | $R_h$=4.0 | $R_h$=3.9 |
| pFL-N-Ter-TAT | $a$=13.4±0.5 | $a$=9.0±0.4 | $a$=8.9±0.4 |
| | $b$=3.7±0.1 | $b$=3.2±0.1 | $b$=3.4±0.1 |
| | $R_g$=6.4 | $R_g$=4.5 | $R_g$=4.5 |
| | $R_h$=6.5 | $R_h$=6.6 | $R_h$=6.1 |
| Pal-pFL-N-Ter-TAT | $a$=12.0±3.0 | $a$=10.4±0.4 | $a$=22±0.4 |
| | $b$=4.9±0.2 | $b$=4.7±0.2 | $b$=4.6±0.2 |
| | $R_g$=5.3 | $R_g$=5.5 | $R_g$=10.3 |
| | $R_h$=9.4 | $R_h$=9.5 | $R_h$=10.7 |

**Keywords**
Solution SAS, Drug discovery, High-throughput, Dynamics

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SESSION 2B: HYBRID MATERIALS AND BIOMATERIALS 1
Chair: Dr. Leandro Barbosa

# V-143 WHAT SAXS CAN TELL ABOUT MAGNETIC-NANOPARTICLE CELL INTERACTIONS

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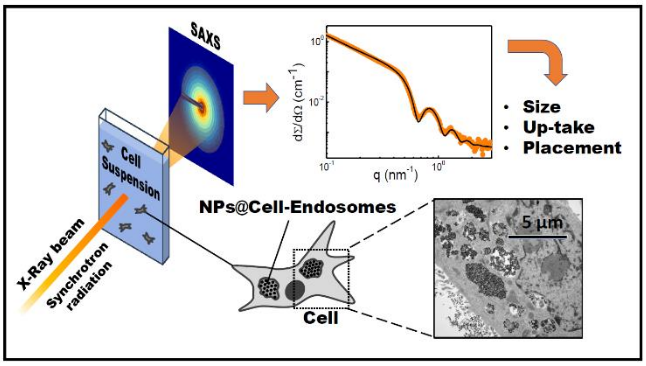
Magnetic iron oxide nanoparticles (NPs) are under analysis for several medical applications. The most relevant are diagnosis, cancer therapy and tissue regeneration. Once incorporated in the body the NPs responds to various intended and non-intended stimuli like pH variations, drag forces, light and magnetic field applications and chemically interact with molecules and proteins. The intended stimuli are used to make the NPs exert therapeutic actions such as magnetic hyperthermia and photo plasmonic hyperthermia. The non-intended stimuli are related to the interaction of the NPs with different biological environments and specially with cells where they get internalized, confined in cell endosomes, and may later be dissolved and release iron ions which may integrate to metabolic pathways or induce toxicity. In this context, access to detailed information on cells loaded with nanoparticles with nanoscale precision is of a long-standing interest in many areas of nanomedicine. Thus, designing a single experiment able to provide statistical mean data from a large number of living unsectioned cells concerning information on the nanoparticle size and aggregation inside cell endosomes and accurate nanoparticle cell up-take is of paramount importance. Small-angle X-ray scattering (SAXS) is a valuable tool to achieve such relevant data. Experiments were carried out in cultures of B16F0 murine melanoma and A549 human lung adenocarcinoma cell lines loaded with various iron oxide nanostructures displaying distinctive structural characteristics. Five systems of water-dispersible magnetic NPs of different size, polydispersity and morphology were analyzed, namely, nearly monodisperse NPs with 11 and 13 nm mean size coated with meso-2,3-dimercaptosuccinic acid, more polydisperse 6 nm colloids coated with citric acid and two nanoflowers (NF) systems of 24 and 27 nm in size resulting from the aggregation of 8 nm NPs. Up-take was determined for each system in B16F0 cells. We will show that SAXS pattern provides high resolution information on nanoparticles disposition inside endosomes of the cytoplasm through the structure factor analysis, on nanoparticles size and dispersity after their incorporation by the cell and on up-take quantification from the extrapolation of the intensity in absolute scale to null scattering vector. We will also report on the cell culture preparation to reach sensitivity for the observation of NPs inside cell endosomes carrying out SAXS with a high brightness synchrotron source. Our results show that SAXS can become a valuable tool for analyzing NPs in cells and tissues.



**Keywords**
SAXS, magnetic nanoparticles, nanoflowers, iron oxide, cells, uptake, biomedical applications

## P317 - SAXS AS A TOOL FOR STRUCTURAL MODELING OF MOLECULAR CHAPERONES

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Macromolecular chaperones are proteins that are part of the Protein Quality Control (PQC) of the cell by preventing and fixing protein misfolding of client proteins, and also by solubilizing aggregates. Pathologies related to these issues are associated with neurodegenerative diseases, such as Parkinson and Alzheimer, and also to some types of cancer. Small-Angle X-Ray Scattering (SAXS) is a well established technique to study this type of system, and since the 1990's it has become increasingly popular due to new analysis and modeling methodologies, which are still being developed to this day. In this study, we present applications of some of these SAXS methodologies for two main families of molecular chaperones: Hsp70 (HSPA8) and Hsp90 (AaHsp90), also showing results from a co-chaperone that acts on both of these families (AaSGT). Herein, we illustrate how these analyses were performed, which advances were important for obtaining these results and how other techniques corroborate or highlight limitations in the presented modeling approaches. We have performed Guinier, Kratky and p(r) analyses, and have modeled the proteins both by using beads as dummy atoms, and partial PDB structures as rigid bodies by means of software from the ATSAS suite. For HSPA8 we have obtained results compatible with it being a monomer with a flexible linker between its two domains, indicating that it alternates basically between an open and a closed conformation, as expected from the current model for Hsp70 family members. For AaHsp90, on the other hand, we have found that it is less flexible than other Hsp90 members, maintaining an open and highly elongated conformation while keeping its chaperone function. This observation is compatible with Hsp90s from other organisms that have different open/closed conformation equilibria. For the co-chaperone AaSGT we compared two different constructs of this protein, verifying initially the importance of the C-terminus for its function by comparing a wild type protein with a mutant missing the C-terminal region . We have found that beyond this functional difference there is also a structural facet: both constructs have strikingly different scattering profiles, impling in quite different models and topologies for each protein. The wild type is more elongated and disordered than the mutant, indicating that the C-terminus' disorder is important for protein function.

**Keywords**
Protein Folding, Molecular Chaperones, Hsp90, Hsp70, SGT

SESSION 2C: MODELLING AND DATA ANALYSIS 1
Chair: Prof. Uri Raviv

# P202 - LARGELY MODEL FREE INDIRECT FOURIER TRANSFORMATION OF SCATTERING CURVES OF INTERACTING PARTICLES

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The Indirect Fourier Transformation (IFT) is a well-established technique to evaluate small angle scattering data. The classical approach corresponds to a model free transformation of the scattering curve into its real space analogue. The real space curve therefore contains inter- and intra-particle contributions unless interaction effects are weak and can be neglected. However, if interaction effects cannot be neglected a separation of form and structure factor effects can be achieved by assuming a model for one of these effects and calculating the largely model free IFT to get the largely model free real space analogue of the other effect [1,2]. A new technique that allows to calculate IFTs of both form and structure factor effects in a largely model free way will be presented in this contribution. Such a calculation is possible, if the particles do not overlap, and by using restraints imposed by physics on the real space functions. An iterative approach is used, where IFTs of the form factor and of the structure factor are calculated in an alternating sequence and where the result of the previous IFT is used as a model for the factor that is currently not determined by the IFT. The process is repeated until a consistent picture of real space curves for form and structure factor is obtained.

**Keywords**
form factor, structure factor, indirect Fourier transformation

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# V181 - SCRUTINIZING THE HYDRATION SHELL OF PROTEINS FROM SAXS AND MD SIMULATIONS: EFFECTS OF WATER MODELS, FORCE FIELDS AND TEMPERATURE

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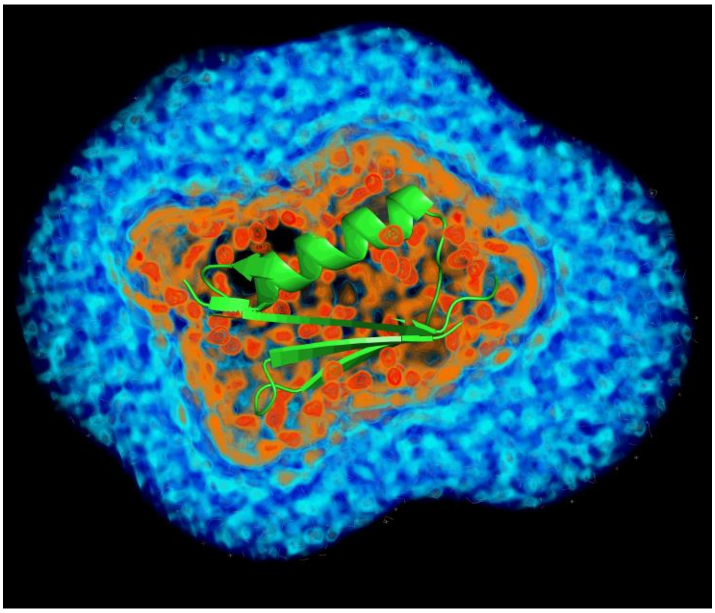
Proteins in solution are surrounded by a hydration shell consisting of several hydration layers, formed by the water molecules near the protein surface. Because the hydration shell influences the structure and activity of a protein, it may be considered as a functionally relevant part of the protein. However, the structure of the hydration shell remains poorly understood. Small-angle scattering (SAS) in solution using X-rays (SAXS) or neutrons (SANS) in principle provides information on the hydration shell, since both the radius of gyration (Rg) and the zero-angle scattering (I0) depend on the hydration shell contrast relative to the bulk solvent. Here, we used MD simulations and explicit-solvent SAXS/SANS calculations to investigate how variations of the hydration shell manifest in variations of Rg and I0. SAXS/SANS curves were computed for several proteins (xylanase, lysozyme, GB3 domain, and RnaseA), protein force fields, water models and temperatures. Our calculations reveal that different proteins exhibit different hydration layer contrasts. In addition, the water model significantly influences the hydration layer. Specifically, recent water models with increases dispersion interactions impose increased Rg and I0 as compared to a standard TIP3P model. On top of that, the temperature also has a decisive influence on the hydration shell and thus on the Rg and I0. Together, our calculations provide a novel route for comparing hydration layers between simulation and experiments, for validating water models, and, thereby, for scrutinizing the hydration layer of proteins.



**Keywords**
molecular dynamics simulation, hydration shell, radius of gyration, zero scattering intensity, SAXS and SANS

SESSION 2C: MODELLING AND DATA ANALYSIS 1
Chair: Prof. Uri Raviv

# V204 - A DATABASE OF CALCULATED SAXS, HYDRODYNAMIC AND SPECTROSCOPIC PARAMETERS FOR THE ALPHAFOLD PREDICTED PROTEIN STRUCTURES

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Following recent spectacular advances in AI-based 3D structure predictions from protein sequences, the AlphaFold (AF) consortium has made available a database for the entire human and other organisms' proteomes (https://alphafold.ebi.ac.uk). However, apart from simple cases of highly homologous sequences, or clearly recognized folding classes, how to rapidly ascertain a predicted structure's reliability should be considered. While shape-sensitive hydrodynamic parameters such as the translational diffusion and sedimentation coefficients (Dt(20,w), s(20,w)), and the intrinsic viscosity ([η]) can assess the overall likeliness of a conformation, SAXS yields the pair-wise distance distribution function p(r) vs. r, providing a direct structure correspondence. On this basis, we have calculated from the entire AF database containing >1,000,000 structures the corresponding Dt(20,w), s(20,w), [η], p(r) vs. r, and other parameters, using the extensively validated UltraScan SOlution MOdeler (US-SOMO) suite1 (http://somo.aucsolutions.com), and placed them in the US-SOMO-AF novel public domain database2 (https://somo.genapp.rocks/somoaf). Circular dichroism (CD) spectra were also computed using the SESCA program3. Some of AF's drawbacks were mitigated, such as generating whenever possible a protein's mature form (resulting in ~110,000 curated entries, a sizeable amount). Others, like the AF current availability of single-chain structures only, or the absence of prosthetic groups, limit their present direct applicability. Tests were conducted to verify the discriminatory capability of the calculated parameters. In particular, for SAXS eight p(r) vs. r datasets were chosen from the SASBDB database (https://www.sasbdb.org/) and compared with those calculated on the corresponding AF entries (for two, also a PDB structure was available). As shown in Figure 1 (panels a-f), both good accord (panels c and f) or noticeable differences (panels a.b,d,e) were observed. In addition, in Figure 1, panel g, the effects of partial flexibility are shown by the p(r) vs. r computed on 100 conformations generated by a discrete molecular dynamics (DMD) run on the AF-predicted UniProt O88338 structure (starting conformation shown in inset). These results confirm the major role that SAXS could provide in rapidly assessing the reliability of AF-predicted protein structures, and, coupled with the CD and hydrodynamic calculations, support the usefulness of the novel US-SOMO-AF database.

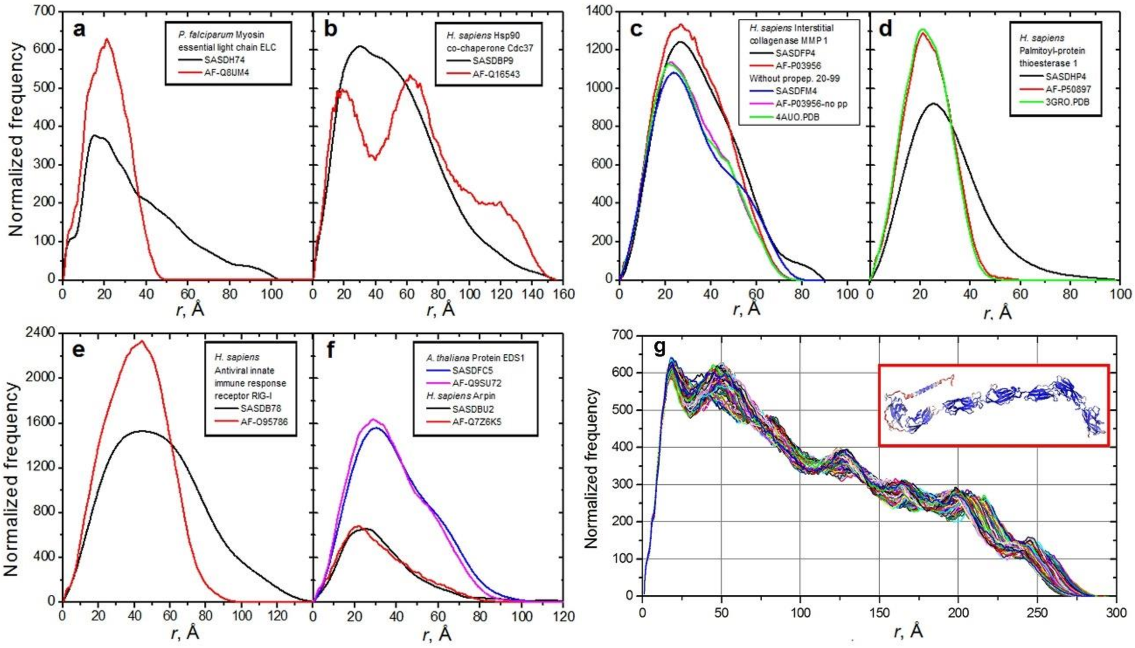

Figure 1 - Panels **a-f**, $p(r)$ vs. $r$ curves SAXS-derived and calculated from AF and RCSB PDB structures. Protein source and names, SASBDB, AF (UniProt) and RCSB PDB accession numbers for each entry are indicated in the boxes within each panel. In all panels the experimentally-derived and the AF-calculated $p(r)$ vs. $r$ are black and red lines, respectively. Additional SAXS-derived and AF calculated $p(r)$ vs. $r$ present in panels **c** and **f** are blue and magenta lines, respectively. Additional PDB calculated $p(r)$ vs. $r$ (green lines) are present in panels **c** and **d**.
Panel **g**, Calculated $p(r)$ vs. $r$ curves for the DMD-generated 100 conformations of the AF-predicted O88338 structure. (adapted from Brookes & Rocco, *Sci. Rep.*, in press (2022). (https://doi.org/10.1038/s41598-022-10607-z)

## Keywords

AlphaFold, SAXS, Hydrodynamics, Databases, Protein Structure

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PLENARY 2
Chair: Dr. Carla Cristina Polo

# P441 - PERSPECTIVES ON SAXS TENSOR TOMOGRAPHY

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SAXS tensor tomography (SASTT) allows to reconstruct the full 3D reciprocal-space map in a three-dimensional object from scattering patterns assembled around two rotation axis [1,2,3]. The method has since its introduction in 2015 been implemented at several beamlines worldwide, and development on both experimental as well as algorithm side is ongoing. The perspective of SASTT at new generation sources with increased brilliance, as well as with detector and acquisition schemes developing, the measurement time needed for this photon hungry measurements with a million or more scattering pattern per sample can be tremendously reduced. The perspective of measuring a sample within an hour is enabling this method for life science samples where enough statistics is crucial. On the algorithm side improvements on robustness and speed of the reconstruction have been achieved. While the previous work has mostly focused on relatively simple symmetries, recent work using a complete spherical harmonic basis enables the method to work with more complex symmetries at relatively low computational cost.

**Keywords**
SASTT, tensor tomography

SESSION 3A: COHERENT SMALL ANGLE SCATTERING, IMAGING 2
Chair: Dr. Carla Cristina Polo

# P183 - EVALUATION OF THE REGENERATED BONE IN CRITICAL SIZE DEFECTS USING SAXS IMAGING

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The healing process in large bone defects is a frequent source of problems for orthopaedic surgery which remain unsolved. Bioengineered bone grafts and scaffolds are an alternative in which achieving a continuous interphase between the host bone and the graft is still a major issue. Bioinspired composite scaffolds that resemble the nanostructure of bone are especially interesting as they offer a viable environment for cells to migrate, differentiate and regenerate tissue. One such example is PLGA fibres in combination with amorphous calcium-phosphates nanoparticles (aCaPs), which lead to enhanced osteoconductivity and biocompatibility [1]. The use of aligned fibres [2] and cell-seeded scaffolds [3] have been proven to be effective in improving the migration and proliferation of cells. In this work biocompatible 3D PLGA/aCaP scaffolds with oriented and aligned fibres, containing only extracellular matrix, or seeded with adipose-derived mesenchymal stromal cells, were tested in a mouse model for critical size bone defects.

Small-angle X-ray scattering (SAXS) has become a key method for studying the anisotropic nanostructure of bone as an arrangement of mineralized collagen fibrils [4]. By raster scanning, a macroscopic sample with a microbeam and measuring a scattering pattern at each point the distribution of nanostructural heterogeneities of complex structures were mapped with micrometric spatial resolution. To assess the integration and quality of regenerated bone growth in such scaffolds scanning SAXS and SAXS tensor tomography (SASTT) were used. With these techniques, we studied the anisotropic nanostructure of the newly regenerated bone in comparison with the native tissue, which was possible thanks to the use of synchrotron radiation at the cSAXS beamline at the Swiss Light Source (Paul Scherrer Institute, Switzerland).

Scaffolds with aligned fibres showed a higher degree of osseointegration and bone growth in vivo, with nanostructural orientations similar to those of the native bone. In contrast, scaffolds with randomly oriented fibres resulted in regenerated bone with a rounded callus with orientation perpendicular to the femur long axis and new bone formation generated disconnected islands of poorly aligned tissue, reminiscent of pseudo-arthrosis. These differences were particularly clear through 2D scanning SAXS and SAXS tensor tomography, which allowed analysis of changes in the nanostructure over macroscopic distances of 2-3 mm. The superiority of aligned scaffolds was also highlighted by the observation of the gap filled with newly formed bone. Those areas were found to have a higher mineral thickness than the random ones, which indicates an ongoing regeneration process. Finally, the performance of aligned decellularized scaffolds was very similar to the ones seeded with cells. This observation suggests that an appropriate amount of orientation in the extracellular matrix is sufficient to promote bone regeneration and migration of endogenous cells from the native bone into the scaffold.

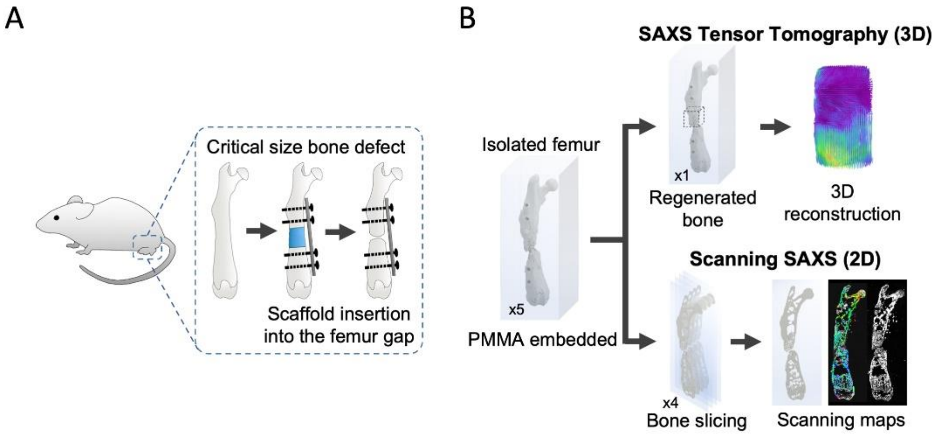

Figure 1: Description of the experimental procedure. A) Scaffolds with aligned and randomly oriented fibers were tested in vivo in 5 mice femurs with a critical size defect. The bones were extracted after 7 weeks and embedded in PMMA. B) The isolated femurs were sliced (x4) for scanning SAXS or the regenerated area extracted (x1) to be measured in SAXS tensor tomography.

**Keywords**

Scanning SAXS, Tensor Tomography, Bone Regeneration, Biomaterials

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SESSION 3A: COHERENT SMALL ANGLE SCATTERING, IMAGING 2
Chair: Dr. Carla Cristina Polo

# P255 - COMPLEX NEURONAL ORIENTATIONS IN VERVET AND HUMAN BRAINS ASSESSED WITH SMALL-ANGLE X-RAY SCATTERING, LIGHT SCATTERING, AND DIFFUSION MRI

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Great efforts in neuroscience go towards generating a detailed neuronal connectivity network model of the brain. This requires accurate and detailed mapping of neuronal orientations and tracts, with high-resolution and specificity. Particularly challenging are brain regions containing densely packed neurons with multiple fiber crossings. Diffusion MRI (dMRI) is currently used for assessing neuron orientations in vivo. However, its signal is non-specific, and with resolutions reaching ~100µm ex vivo, it probes thousands of neurons per voxel.

X-ray scattering can retrieve 3D neuronal orientations with specificity, in sections using 3D scanning SAXS (3D-sSAXS) [1] or tomographically using tensor tomography [2], due to the ~17nm periodicity of myelin, the layered membrane insulating neuronal axons. Measuring scattering patterns for all sample points requires raster-scanning, with a pencil-beam.

Scattered Light Imaging (SLI) [3] uses a reverse setup: illuminating histological sections under different angles enables measuring scattered light form the whole sample [4], with micrometer resolution. While X-ray scattering probes myelinated neurons (layer periodicity ~nm), optical scattering is sensitive to nerve fibers (diameters ~µm).

Here, we use 3D-sSAXS and SLI to probe neuronal orientations in vervet and human brain samples, at the particularly challenging region of corona radiata, with multiple fiber crossings. Human sample 3D-sSAXS results are compared to dMRI.

60µm-thick vervet monkey brain sections were mounted on glass slides. A ~17×11mm2 region was measured with SLI [3] (3µm resolution) and SLI scatterometry [4]. For 3D-sSAXS [2], the same sections were placed in-between coverslips, and a ~19×11mm2 region containing the SLI-scanned region was X-ray-scanned at beamline 4-2 of Stanford Synchrotron Radiation Lightsource (beam-diameter=100µm). SAXS results were rigidly registered to SLI for comparison.

A corona radiata-containing specimen from the human brain was extracted and dMRI-scanned in a Bruker 11.7T scanner (200µm voxels). 80µm-thick vibratome sections were placed in-between coverslips, and a ~28×20mm2 region was X-ray scanned (beam-diameter=150µm). MRI results were registered to SAXS, first manually (to identify the virtual MRI plane), then using 2D rigid registration.

We reconstructed multiple neuronal orientations per voxel with both SAXS and SLI in the vervet corona radiata, and found a high qualitative and quantitative correspondence between the two methods, Figure (top). Both primary and (where detected) secondary direction per voxel were in agreement, with median difference <0.05o and <0.5o respectively. The out-of-plane angle in SLI was also experimentally confirmed by SAXS for the first time.

In the human corona radiata, SAXS and dMRI gave similar neuronal orientations, Figure (bottom), with more unspecific crossings derived with dMRI, possibly corresponding to false-positive orientations.

Overall, we demonstrate a combined X-ray and light scattering approach towards providing ground-truth neuronal orientations in the most challenging primate brain region, with high-specificity and high-resolution. This hitherto unavailable information is necessary to validate dMRI-derived orientations and disambiguate complex fiber arrangements, towards a comprehensive brain connectivity network model.

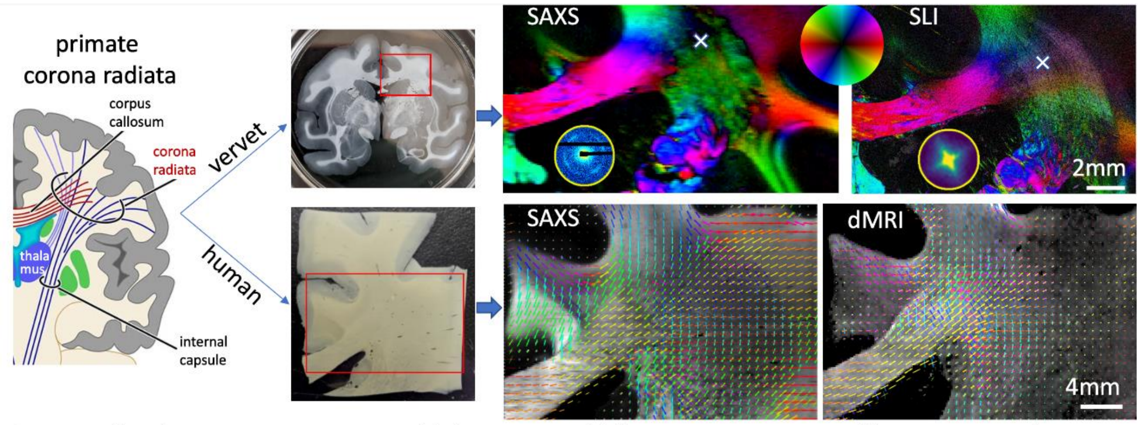

**Figure**. Small-angle X-ray scattering, scattered light imaging and diffusion MRI in a vervet and human corona radiata. **Top**: Neuronal orientations in vervet brain with SAXS and SLI, encoded with colorwheel. Sample point with crossing fibers in corona radiata highlighted with **X**, and corresponding X-ray and light scattering patterns in inset. **Bottom**: Neuronal orientations in human brain with SAXS and diffusion MRI, depicted with lines, with overlayed lines showing neuronal crossings.

## Keywords

scanning Small-Angle X-ray scattering, scattered light imaging, neuronal orientations, brain

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SESSION 3A: COHERENT SMALL ANGLE SCATTERING, IMAGING 2
Chair: Dr. Carla Cristina Polo

# P213 - 3D COLLAGEN FIBRIL ORIENTATION MAP ON DECIPHERING BREAST CANCER METASTASIS PROGRESS

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Breast cancer is the leading cause of cancer death in women worldwide [1]. In these patients, more than 90% of breast cancer-related deaths are caused not by the primary tumor, but by their metastases at distant sites. Metastasis is an extraordinarily complex process, entailing tumor cells to acquire a set of features that allow them to develop new foci of the disease. Systemic changes in the microenvironment between the cancer cells and the host stroma play an important role in supporting the growth and progression of the tumor by degrading, re-depositing, cross-linking and stiffening collagen fibrils. Although the knowledge of breast carcinogenesis is being progressively elucidated with 2D cell-culture experiments, they are not able to reproduce the real physiological pattern of the tumor microenvironment where the surroundings cells are equally as important as the tumor cell itself. Small-angle X-ray scattering has been successfully exploited to observe the organization of collagen fibrils in breast tissues [3]. To probe the remodeling of collagen fibrils in breast tumor in a volume-resolved way, it was exploited the potential of the Small-angle X-ray Scattering Tensor Tomography (SASTT) in providing six-dimension images. Therefore, this study aimed to provide the basis to help in deciphering the mystery organ-specific metastasis.

The SASTT experiment was carried out at the SAXSMAT P62 beamline at the PETRA III storage ring in Hamburg, Germany. The SAXSMAT beamline has dedicated instrumentation to perform such an experiment. It was used a 12.4 keV monochromatic beam focused to have 20 x 20 µm2 at the sample position to scan horizontally and vertically at several rotations and tilt angles with 50 ms exposure time. The region of interest of the freeze-dried breast tumor samples was selected and cut in a cylindrical shape with 1mm-diameter and 1.5 mm height and placed on top of the tomographic stage system. A two-dimensional single-photon counting detector, Eiger2-9M ®DECTRIS, positioned at 3854 mm from the sample was used to record the photons scattered at small-angle, covering a q-range between 0.06 nm-1 and 1.95 nm-1. An in-house python-based pipeline data processing and reconstruction was used to average each of the 2,034,900 SAXS patterns and further reconstruct it.

A higher degree of content and orientation of the collagen fibrils was observed in the SASTT images at tumor region previously indicated by an expert breast pathologist as a metastatic area. The orientation of the collagen fibrils to the tumor boundary can be an important sign of how the invasion of tumor cells into the stroma and migration toward the blood or lymphatic stream to a secondary organ is triggered.

**Keywords**
Collagen, Breast Cancer, SAXS, WAXS

SESSION 3A: COHERENT SMALL ANGLE SCATTERING, IMAGING 2
Chair: Dr. Carla Cristina Polo

## P205 - THE CHAMELEON TONGUE - AMONG THE FASTEST ON EARTH: UNVEILING THE COMPLEX TISSUE ARRANGEMENT BY MULTI-MODAL X-RAY IMAGING

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With their independently rotating eyes, colour change abilities and long extensile tongue that projects out of their mouth, chameleons have fascinated scientists and naturalists for centuries. Their tongue used for hunting smaller prey is a unique, complex array of bone elastic elements and muscles that can be extended up to 6 times its length at rest and up to twice their body length. The mechanism for tongue ejection is similar to pulling the string of a bow and shooting an arrow. Before the tongue is lunched, muscle action loads elastic elements; aka pulling the string; the tongue projection is triggered by the recoil of elastic elements loaded by the muscle action, aka shooting the arrow.

Composed of highly elastic elements, the tongue is projected at 5.8 ms-1 and can sustain acceleration up to 500 ms-2. The large mechanical power transferred during tongue extension makes it the fastest recorded biological tissue. Such acceleration is not only the resultant of loaded muscle action but sustained by a complex array of thin collagen fibres and sheaths forming helical clockwise and anticlockwise, parallel and angularly inter-connected collagen fibres along with the tongue position. We use a correlative imaging approach using histology, microCT, birefringence microscopy and SAXS tensor tomography to reveal a complex arrangement of collagen material of various densities and calcification levels in and around the entoglossal, the basal part of the chameleon tongue.

SAXS tensor tomography reveals the oriented collagen and mineral nanostructure in the transition regions from the entoglossal process and accelerator muscle, linking the nanostructural arrangement of muscle and collagenous tissues to the macroscopic robustness and explosiveness of the chameleon tongue. Due to the helical structures crossing each other within the tissues, we aim to push the limit of SAXS tensor tomography by extracting multiple orientations from voxel. Understanding these specific tissues' structures and roles could serve as a basis for the future development of simultaneously firm and flexible fibres for robotic or tissue engineering.

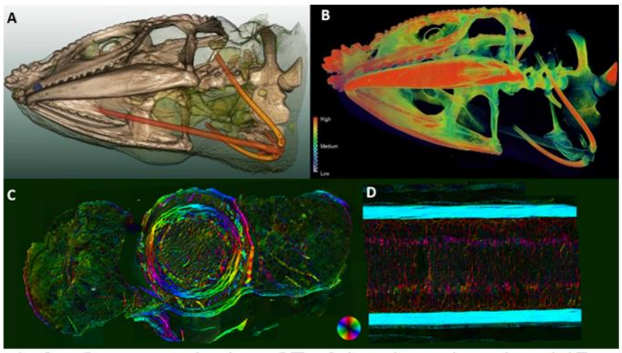

Figure 1: **A** - Segmented micro CT of the chameleon head (*Furcifer pardalis*). The entoglossal process represented in orange. **B** – Electron density of the chameleon head showing low values for the basal part of the entoglossal process. **C** – Birefringence microscopy of *Furcifer pardalis* entoglossal cross-section and **D** – longitudinal section. The Colour code represents the primary tissue orientation.

## Keywords

SAXS Tensor tomography, micro CT, scanning SAXS, Chameleon

SESSION 3B: SOFT MATTER AND SELF-ASSEMBLY 1
Chair: Dr. Judith Elizabeth Houston

## P222 - CONNECTING LIQUID RESONANT SOFT X-RAY SCATTERING AND SMALL-ANGLE NEUTRON SCATTERING FOR GREATER-THAN-SUM-OF-PARTS MEASUREMENT OF MESOSCALE STRUCTURE WITH CHEMICAL SPECIFICITY

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Resonant soft x-ray scattering (RSoXS) is an emerging, hybrid technique that promises to offer new insights into mesoscale structure with chemical specificity and the ability to probe molecular orientation. It does this by coupling SAXS with low-energy (285 eV at the carbon K-alpha edge) x-ray spectroscopy. RSoXS was originally developed and has been applied to great effect in thin films of organic semiconductors. Recently, our team has developed the first quantitative fitting engine for RSoXS data using GPU-accelerated forward simulation of real-space morphologies and applied this software to measure the orientation distribution in polymer-grafted nanoparticles, reverse osmosis water membranes, and several other families of industrial materials.

The promise of RSoXS as a label-free alternative to SANS has not been fully realized, however, largely due to its inability to study liquid samples, or indeed practically any sample without significant structure factor contributions. This limitation arises because of the very feature that makes RSoXS unique: at the low photon energy used for organic molecules, a typical absorption length is about 500 nm. RSoXS measurements are, therefore, overwhelmingly conducted on thin films and typically on highly concentrated samples due to the extremely small probe volume. The design of the NIST RSoXS beamline at the National Synchrotron Light Source-II addresses this issue by incorporating a TEM port holder in the chamber; the sample thicknesses required for electron beam transparency are similar to those required for soft x-rays. We have procured a commercial TEM liquid cell capable of encapsulating a 500 nm film of flowing liquid between two thin silicon nitride membranes.

This talk will describe the commissioning of the cell, the first RSoXS measurements of dilute biomolecules in solution, and our recent efforts to combine solution RSoXS with solution SANS measurements to obtain a greater-than-sum-of-the-parts characterization of the sample. We will discuss the future extension of the liquid RSoXS technique to the study of electrochemically active thin films in the hydrated state, and how measurements of pure form factor scattering enabled by the liquid sample environment and combined SANS-RSoXS experiments will enable quantitative understanding of the underpinnings of the RSoXS measurement.

**Keywords**
soft x-ray scattering, RSoXS, SANS, liquid measurements, soft matter

SESSION 3B: SOFT MATTER AND SELF-ASSEMBLY 1
Chair: Dr. Judith Elizabeth Houston

# P128 - LOCALIZATION OF DYE MOLECULES IN SURFACTANT ASSEMBLIES VIA SANS CONTRAST VARIATION

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Organic azo dyes are interesting building blocks in supramolecular chemistry. Analysis of such supramolecular assemblies can take advantage of the response of the dyestuff spectrum to changes in their chemical environment. This property is often used to monitor alterations in a solution state by means of simple UV/vis-spectroscopy.1 Frequently studied systems are dye/surfactant-solutions with the dye being used as a model solute to investigate solubilization phenomena.1

Up until now, little attention has been paid to the morphology of dye/surfactant assemblies in solution.2 In addition to that, the localization of dye in a surfactant micelle, which is relevant in practical application, was often inferred from changes in dye absorption only.1

Small-angle neutron scattering (SANS) with the technique of contrast variation permits both, the elucidation of assembly morphology and the unambiguous localization of dye molecules within surfactant micelles.

We studied the interaction between the commercial, anionic azo dye Blue and the cationic surfactant dodecyltrimethylammoniumbromide (DTAB) in an alkaline buffer solution. Aqueous solutions of Blue and DTAB phase-separate above a Blue:DTAB ratio of 1:2.5. Below this ratio, stable solutions are formed. In this 1-phase region, the absorption spectrum of Blue depends on the concentration of DTAB (Fig. 1, left). To better understand underlying mechanisms, the morphology of assemblies in the 1-phase region was studied with SANS. Moving from the precipitation threshold to the surfactant-rich side leads to a shrinking of assembly size and a reduction in its anisotropy from flexible cylinders at a 1:3-ratio to oblate ellipsoids at a 1:6-ratio. This is indicated in Fig. 1, right. SANS contrast variation was performed by matching DTAB to the solvent and observing the scattering signal arising from Blue only. Resulting SANS-curves were evaluated with core-shell models. For all sample compositions, we unambiguously located Blue on a surface-layer of the dye-surfactant micelle, forming its shell.

This work demonstrates the feasibility of SANS contrast variation for dye/surfactant-systems and shows morphological changes in dye/surfactant micelles close to a precipitation threshold. Findings are related to observations from UV/vis-spectroscopic investigations.

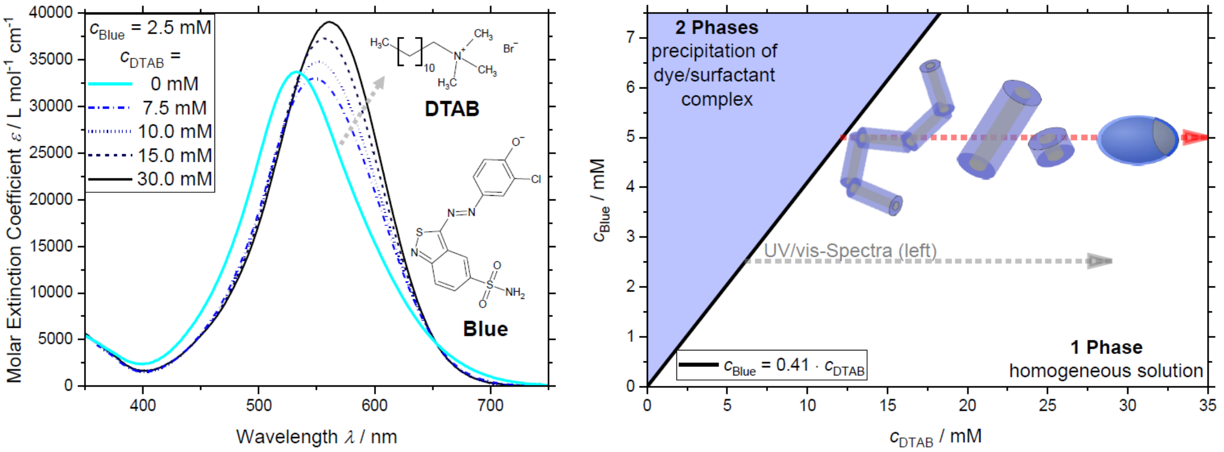

Figure 1: Left: Change of Blue UV/vis-spectrum upon addition of surfactant DTAB. Right: Phase behavior of aqueous solutions of Blue and DTAB. Changes in aggregate morphology with increasing DTAB/Blue-ratio are indicated and

were determined with SANS. The location of the dye on the outside of the aggregate was determined by contrast variation.

**Keywords**
SANS, contrast variation, surfactant, dye, assembly

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SESSION 3B: SOFT MATTER AND SELF-ASSEMBLY 1
Chair: Dr. Judith Elizabeth Houston

## V236 - SOFT X-RAY SCATTERING FOR MOLECULAR ORIENTATION IN THIN BLOCK COPOLYMER FILMS

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Block Copolymers (BCPs) have become increasingly technologically relevant due to their ability to pattern a variety of morphologies at length scales between 5-100 nm. In particular, they have become increasingly important to the semiconductor industry, where BCP lithography acts as a complementary patterning technology to improve the cost effectiveness of optical and extreme ultraviolet (EVU) lithography. As patterning technologies shift to smaller length scales BCPs with stronger interaction parameters are necessary to reach the desired length scales. In these systems scaling theories predict a stretching of the polymer chains due to the stronger interactions between the components. However, measuring the changes in chain conformation and the molecular orientation distribution in amorphous soft matter is an ongoing challenge.

In this work we will utilize resonant soft X-ray scattering to interrogate molecular orientation in block copolymer films. In the soft X-ray spectral region (defined as ~ 100 eV – 3000 eV) there are a number of atomic absorption edges including carbon, nitrogen and oxygen. Near these absorption edges the refractive index (and therefore the contrast) between different materials changes based on the material chemistry and the wavelength of the X-rays. Additionally, when there are preferentially oriented molecular dipoles in the material the relative angle between the polarization of the incident beam and those dipoles also influences the local contrast. As a result, soft X-rays become sensitive to the molecular orientation distribution in a sample. Measurements on a series of vertically oriented lamellae of polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA) show evidence of anisotropy in the scattering profile induced by interactions with the soft X-ray beam. The scattering anisotropy is localized to energy regions sensitive to the aromatic rings in PS and the carbonyl bonds in PMMA, providing evidence that this originates from preferential orientations of the polymer chains within the films. Utilizing a recently developed GPU based simulation platform we fit the scattering pattern using a data fusion approach, integrating real-space images to enable fitting of the scattering anisotropy. The result of the fitting is a molecular anisotropy profile for both the PS and PMMA chains The results will be discussed in context with theoretical predictions for chain orientation in BCPs.

**Keywords**
Block Copolymers, Soft X-rays, Molecular Orientation, Thin Films

SESSION 3B: SOFT MATTER AND SELF-ASSEMBLY 1
Chair: Dr. Judith Elizabeth Houston

# V368 - NANODOMAINS IN TERNARY PHASE DIAGRAMS: ULTRA-FLEXIBLE MICROEMULSIONS AND THE OUZO EFFECT

**PRÉVOST, Sylvain (1); KIRCKL, Sebastian (2,3); MARČELJA, Stjepan (4); KUNZ, Werner (3); ZEMB, Thomas (2); GRILLO, Isabelle (1)**
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Liquid mixtures without surfactants but with solvotropes can form spontaneous nano-sized domains. Such concentration fluctuations are reminiscent from critical phenomena, but extend beyond the narrow region immediately adjacent to plait points. This phenomenon is in fact already widely utilised in many domains, from phase separation to perfumes, passing by chemical syntheses. Such ultra-soft assemblies are best probed with scattering techniques, and the possibility offered by H/D isotopic labelling render neutrons unique to unveil their static and dynamic features. Combining SANS and SAXS, we show that the Ouzo effect obtained by crossing the biphasic region of some mixtures and resulting in large droplets with potentially long life-time are composed of two ternary solutions that are both structured at the nanometer-scale. Our experiments suggest to revisit phase diagrams with a new angle on mesoscopic organization.

**Keywords**
critical point, ternary phase diagrams, microemulsions, surfactant-free, mesoscopic fluctuations

SESSION 3C: MODELLING AND DATA ANALYSIS 2
Chair: Prof. Jochen S Hub

## P239 - IMPROVEMENTS IN SMALL-ANGLE X-RAY SCATTERING DATA MODELING OF MESOPOROUS MATERIAL SBA-15

**TAN, Xiangyin (1); OSELIERO FILHO, Pedro Leonidas (2); FANTINI, Márcia Carvalho de Abreu (2); OLIVEIRA, Cristiano Luis Pinto de (2); BORDALLO, Heloísa Nunes (1,3)**
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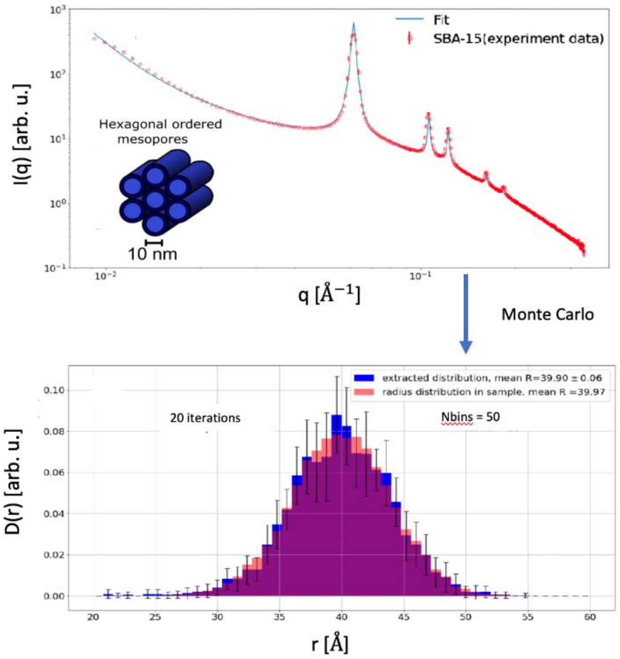
Ordered mesoporous silica (OMS) materials, such as SBA-15, have pores in the size range 2 - 50 nm (the so-called ""mesopores""), highly ordered. Among the many applications, they are used as carrier of drugs, enzymes and, more recently, vaccines [1], in which the desired material is loaded into the mesopores. In this sense, it is crucial to characterize in advance their size, shape, size distribution and spatial ordering of the mesopores. Among the experimental techniques used to this end, small-angle X-ray scattering (SAXS) is probably the most suitable and convenient one, since the experiments are non-invasive, easy to perform, fast and reproducible. However, advanced analysis through data modeling is needed in order to retrieve ""hidden"" structural information contained in the experimental curves, like the size distribution of mesopores, cited before. Most of the models currently available, with no exception, assume an analytical expression for the size distribution of the mesopores (gaussian, lognormal, Schulz-Zimm, etc.), which, besides realistic, corresponds to a strong constraint in the modeling and makes impossible to correctly describe, for instance, bimodal-like distributions. Moreover, from the experimental point of view, it is common the need for increase the diameter of the mesopores in order to fit different sizes of biomolecules. This is done in general by adding a swelling agent in the synthesis of SBA-15 that disturbs not only the 2D-hexagonal ordering of mesopores [2] but potentially their size distribution. In this context, the aim of the present work is to improve one of the state-of-art models used for SAS data modeling of SBA-15 [3] by introducing the Monte Carlo (MC) method in order to retrieve the mesopores size distribution in a free modeling approach. Differently from the application of MC to polydisperse spheres, as in spherical nanoparticles, here we are dealing with lots of other parameters that have to be also optimized in the fitting, making this study [4] very interesting, useful and, of course, challenging. Because MC takes longer processing times, it will also be discussed strategies to speed up the calculations.



## Keywords

SBA-15, SAXS, Monte Carlo, data modeling, size distribution

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## Acknowledgements

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## P170 - DATA PROCESSING AT LOKI SANS BEAMLINE

**POTRZEBOWSKI, Wojciech; NIELSEN, Torben; HOUSTON, Judith; HOLM ROD, Thomas**
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LOKI is a Small Angle Neutron Scattering (SANS) instrument currently under construction at the European Spallation Source ERIC (ESS) in Lund, Sweden.

It is primarily suited for studies of soft matter materials. LOKI's high flux combined with small beam size will greatly improve the study of weakly scattering samples.

LOKI will also provide a flexible sample area with the potential to integrate multiple simultaneous techniques during data collection.

The flexible sample environment together with advanced detector setup and the easy usability of instrument sets high demand for data processing. Here we present the data processing pipeline for the LOKI beamline, with primary focus on data reduction and data analysis components.

Data reduction will be performed using an in-house developed software package called scipp [1], while data analysis will be primarily served through SasView software tool [2].

We will present the latest functionality of the packages and discuss future directions.

We will also discuss integration of these software tools with the entire data processing pipeline for Live Data Processing and its potential impact on future experiments.

### Keywords

SasView, scipp, data analysis, data reduction, live data analysis

### References

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## SESSION 3C: MODELLING AND DATA ANALYSIS 2
Chair: Prof. Jochen S Hub

# V327 - A COMPUTATIONAL MODEL FOR INTERPOLYELECTROLYTE COMPLEXES

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Advances in modern polymer science allow to create evermore complex self-assembled structures, which are driven mostly by using electrostatic and hydrophobic forces. An example of such a system are multicompartment interpolyelectrolyte complexes (MIPECs) to be obtained by combining appropriate copolymers of opposite charge and which are stabilized by a hydrophilic corona. These water-soluble colloids of 50-200 nm size combine different solubilisation properties, functionalities, and variable mesoscopic structure that make them interesting for example in the field of drug delivery. The structure of the MIPECs have been already studied e.g. by Small Angle Neutron Scattering (SANS). However, a detailed description of the architecture and appropriate modeling of the data is still missing. In this talk, we will present a computational model which can describe the existing SANS data and offer further structural insights from the model parameters. This top-down, coarse-grained model presents micelles of hydrophobic chains as spherical particles confined into a spherical region composed of the IPEC. This simplistic model allowed us to use Molecular Dynamics (MD) simulations to rapidly sample the configurations of the system. The obtained scattering intensities revealed the lack of a fractal behavior and the confinement shape. Moreover, we will show that by considering a third different Scattering Length Density (SLD) we can realistically model the scattering contribution of the confined region and obtain a realistic model of our system. This structural model then was tested on experimental SANS data obtained from complexes of oppositely charged microemulsion droplets and polyelectrolytes.

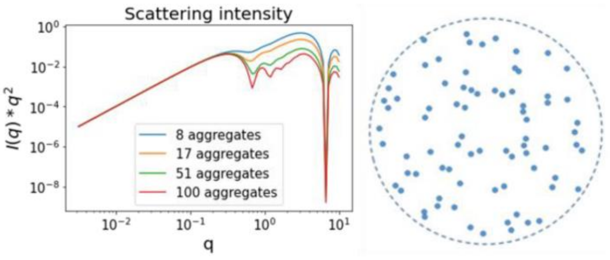

***Figure 1.*** *At left, the scattering intensity is plotted (normalized with $I(q=0) = 1$). At right, a 2D representation of the system is depicted.*

**Keywords**
Polymer Micelles, Modeling, Molecular Dynamics, Neutron Scattering, Coarse-Graining

### References

An important contribution on the routine to calculate the scattering intensity is given by Dr. Sergei Grudining, which we deeply acknowledge. The funding of the PhD project support “Structure and Dynamics of MIPECs of Dual Polarity” by the ILL and TU Berlin is also gratefully acknowledged (Project no. : 191_24).

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## SESSION 3C: MODELLING AND DATA ANALYSIS 2

Chair: Prof. Jochen S Hub

# V209 - EOM 3.0: ENHANCED ENSEMBLE DESCRIPTIONS OF UNSTRUCTURED BIOMOLECULAR SYSTEMS

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Unstructured biological macromolecules are in general poorly described by single conformational models. Intrinsically Disordered Proteins (IDPs) and Intrinsically Disordered Regions of proteins (IDRs) are better explained as ensembles of models that seek to map out the conformational space accessible to such systems. The Ensemble Optimisation Method (EOM) is one such approach that has been used routinely for the SAXS driven analysis of flexible and unstructured biological systems since its introduction as part of the ATSAS suite of programs in 2007 [[1]-[2]].

Here we report a significant enhancement of the underlying strategy of ensemble generation and conformational selection procedures of EOM. The model generation routine RANCH has been completely re-envisioned to facilitate major improvements. For example, in the configuration of input, allowing for the construction of simple, e.g. single unstructured peptide and nucleotide polymers and very complex, e.g. multi-chain proteins with and without symmetry, fixed and randomized interface definitions, non-protein components, including glycosylation and lipids. Databases of protein backbone dihedral and bond angles have been updated and made user accessible to provide an improved built-in definition of allowable conformations, as well as allowing for user-defined angular probability maps. As a direct consequence, this also facilitates data-driven secondary-structure assignment of protein sequences, eg. provided by NMR chemical shifts.

The new EOM 3.0 streamlines the data flow between related applications by employing FFMAKER to convert generated models to calculated scattering intensities for analysis methods which also simplifies input from data sources other than RANCH. This well defined data exchange format further opens the door for alternative data analysis methods. Besides the traditional genetic algorithm (GAJOE) for ensemble selection, the new EOM provides a secondary method to judge and optimize ensembles, based on the non-linear least squares approach. Here we compare the two methods.

Overall, these enhancements provide a significantly improved user experience.

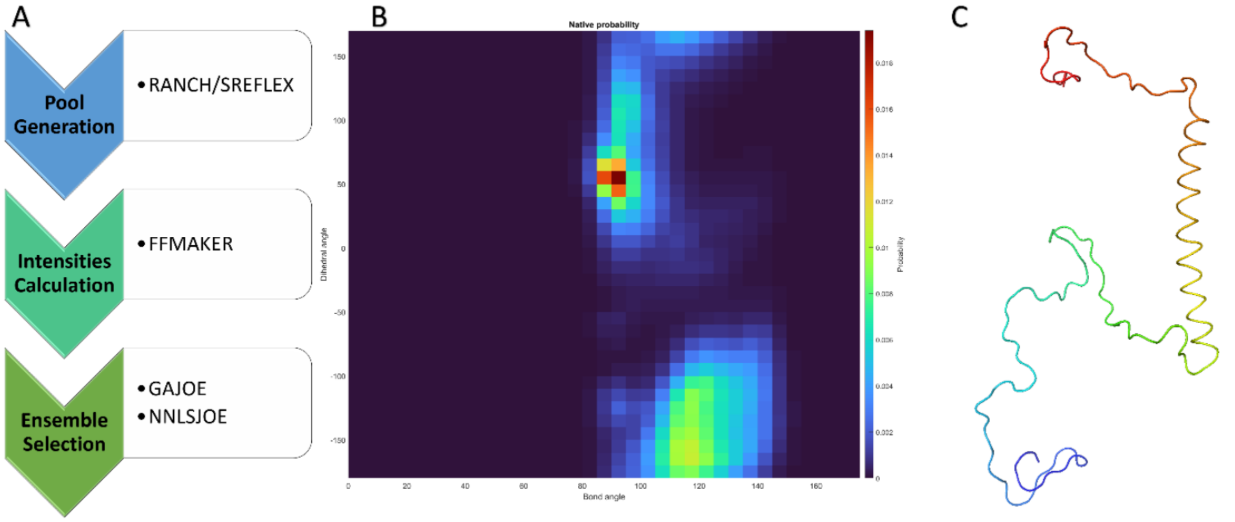

**Figure 1.** (A) Program flow for EOM 3.0. (B) Native/coil secondary structure probability map of dihedral and bond angles for 45,514 protein entries with sequence homology less than 90%. (C) PyMol visualization of a native/coil resulting model for a 224 AA sequence, with a helical (AA 161-194) region.

**Keywords**
IDPs, IDRs, disorder, proteins, SAXS

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## P226 - SELF-ASSEMBLY KINETIC PATHWAYS OF HEPATITIS B VIRUS CAPSIDS IN THE PRESENCE OR NOT OF ANTIVIRALS

**KRA, Kalouna (1,2); CHEVREUIL, Maelenn (1,2); GARGOWITSCH, Laetitia (1); LECOQ, Lauriane (3); WANG, Shishan (3); DEGROUARD, Jéril (1); NHIRI, Naïma (4); JACQUET, Eric (4); ZINN, Thomas (5); PEREZ, Javier (6); FIEULAINE, Sonia (2); BRESSANELLI, Stéphane (2); TRESSET, Guillaume (1)**

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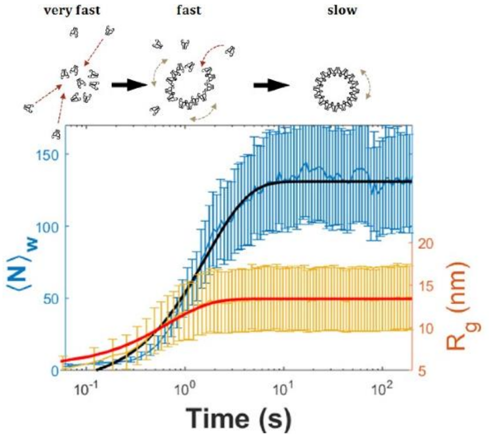
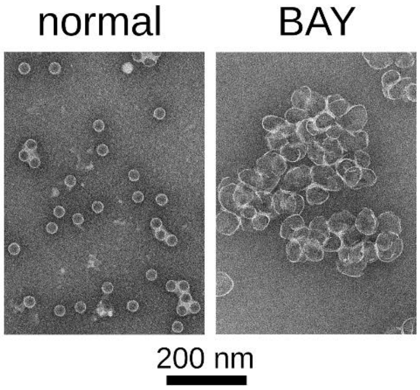
Worldwide, about 240 million people suffer from a hepatitis B infection causing in some cases liver cancer and cirrhosis. Hepatitis B virus (HBV) is an enveloped, DNA virus, the capsid of which contains 120 dimers of the capsid protein arrayed on an icosahedral lattice. The 149 N-terminal residues (Cp149) of the capsid protein can self-assemble in vitro into empty capsids (diameter ~34 nm), thus providing a valuable tool for elucidating the kinetic pathways using state-of-the-art techniques such as time-resolved small-angle X-ray scattering (TR-SAXS) with synchrotron source.

We first investigate the assembly and disassembly processes of dimeric Cp149 capsid proteins, hereafter called subunits, by rapidly quenching the system initially at equilibrium through a change of ionic strength or chaotropicity.1 TR-SAXS data are collected on the ID02 beamline of the European Synchrotron Radiation Facility (France). Along the assembly pathway, the classical nucleation-growth mechanism (less than one second) is followed by a slow relaxation phase (several minutes) during which capsid-like metastable species self-organize into ordered shells. By contrast, the disassembly proceeds through fractal-branched clusters of subunits that eventually vanish over a long time scale (several hours). These findings confirm the nonsymmetrical nature of the kinetic pathways leading to either assembly or disassembly of HBV capsids.

Capsid assembly modulators (CpAMs) are antiviral molecules currently in clinical trials, known to yield malformed HBV capsids during assembly. Our motivation is then to elucidate the effects of two generic types of CpAMs, namely, BAY 41-4109 and JNJ-632, on the kinetic pathways, and to better determine the morphologies of the intermediate species. TR-SAXS data obtained on the SWING beamline at the synchrotron SOLEIL (France) reveal that CpAMs lead to large, polydisperse end-products comprising up to 150 subunits on average in the presence of JNJ, and most probably more for BAY. The time scales with JNJ are shorter than without CpAMs, however, we observe a very long time scale (several days) with BAY. Cryotransmission electron microscopy shows species larger than normal capsids, mostly not closed. Notice that the scattering patterns at high q-values are unchanged in the presence of CpAMs indicating that the local arrangement of subunits is preserved. We hypothesize that CpAMs enhances the subunit-subunit interaction energy and lowers locally the spontaneous curvature of the shells. As a result, the growth is kinetically trapped due to the rapid depletion of subunits and the shells are partially formed.

Ongoing work includes modeling of the kinetics using bayesian inference with a Hamiltonian Monte Carlo method applied to TR-SAXS data, and structure determination of the end-products by 2D class averaging of electron micrographs. We expect to establish models for the self-assembly kinetic pathways in the presence of antivirals, which can ultimately help design new drugs to combat viral infection and prevent pandemics.





## Keywords

virus, self-assembly, time-resolved, antiviral

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## P196 - STUDY OF THE INTERACTION BETWEEN MODEL VESICLE LIPID MEMBRANES AND SARS-COV-2 RECEPTOR-BINDING DOMAIN (RBD) AND SPIKE PROTEINS

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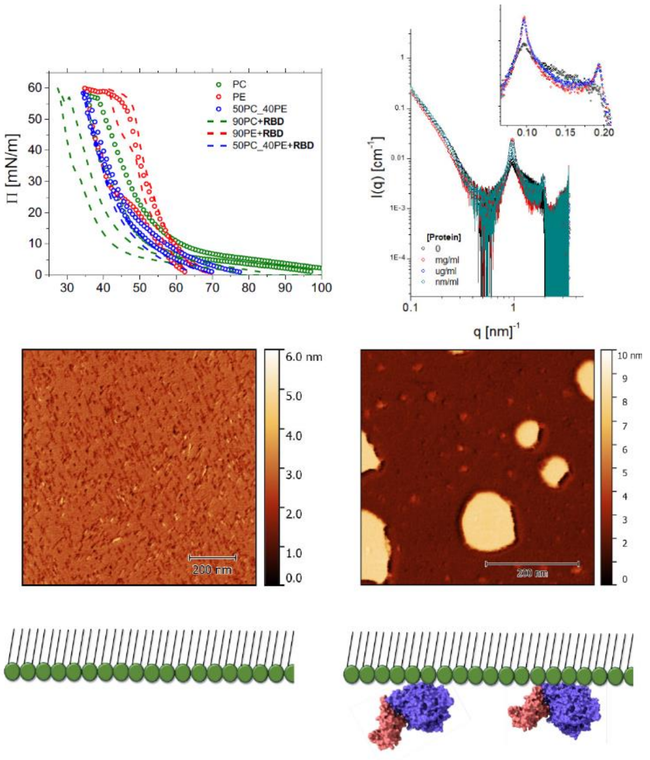
The incorporation of proteins, peptides to lipid bilayers affect their mechanical properties as well as their three-dimensional organization. It has been shown that proteins, at low concentrations, are adsorbed at interfaces with little disturbing effects on membrane elasticity. A new coronavirus, SARS-CoV-2, has been identified as the pathogen of coronavirus disease 2019 (COVID-19). The COVID-19 outbreak has spread around the world and has become a public health emergency of international interest. This has stimulated intense research interest. In addition to promoting lung dysfunction, the virus can also infect other human tissues such as the small intestine, kidneys, heart, thyroid, testicle and adipose tissue[1,2]. How are complex biochemical and biophysical processes, the interaction between model lipid membranes and proteins associated with severe acute respiratory syndrome (SARS) associated with the SARS-CoV-2 coronavirus has been shown to be unpredictable. Thus, in this work we propose to better understand the interfacial interaction of model membranes with different composition with the envelope membrane of Sars-CoV-2 (DPPC, DPPE and cholesterol) with receptor-binding domain (RBD) via the study of Langmuir and Langmuir-Blodgett (LB) films and small angle X-ray scattering (SAXS). Interactions will be studied with membranes which comprise mostly the key lipid components of the mammalian cell membrane (DPPC), blood cells (DPPC and cholesterol), bacteria membrane (DPPE). For all composition studied, we observed of the presence of protein changes the profile of surface pressure of monolayers and the principal changes in the surface pressure occur in the liquid condensed phase. Changes in this region are important because the natural surface pressure of bilayers is present there ($\Pi$=30mN/m), indicating in this situation high changes happen in the membrane in the presence of the proteins. Also fitting the SAXS data we obtained some structural structural and thermodynamic parameters of the membrane as lamellar periodicity, membrane thickness, Caillé parameter. We observed some changes in those parameters in the presence of COVID proteins.



## Keywords

SAXS, Spike protein, Lipids membrane, RBD protein, Langmuir trough

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## Acknowledgements

This work is supported by Fundação de Amparo à Pesquisa do Estado de São Paulo (process numbers 2018/05888-3).

## P224 - STUDYING POLYDISPERSITY IN BIOPHARMACEUTICAL FORMULATIONS WITH SMALL ANGLE X-RAY SCATTERING (SAXS)

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Small angle X-ray scattering (SAXS) is a universal and powerful method to analyze proteins and other macromolecules in solution over a broad range of conditions. As a high-through put method, it has become highly attractive for the pharmaceutical industry. SAXS provides direct insights in the quaternary state and structural responses to the effects of buffer composition, to interactions with other macromolecules or small ligands.

Here, I present structural investigations on formulation studies that profit from SAXS including Covid-19 related therapeutics. First, we will take a look at disease-related antibodies and show how the application of SAXS can be used to study their oligomeric composition (1-3). We will highlight the vast possibilities to use SAXS for antibody characterization and stability assays. In addition, new modes of SAXS data collection such as ion exchange chromatography coupled to SAXS with the parallel collection of multi-angle laser light scattering will be discussed.

**Keywords**
biological solution scattering, pharmaceutical research, polydispersity

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# P232 - UNVEILING THE BINDING STRUCTURES AND COMPOSITION OF AMYLOID MODIFIER SERF1A WITH HUNTINGTON PEPTIDES USING COMBINED SAXS, NMR, AND OPTICAL SPECTROSCOPIES

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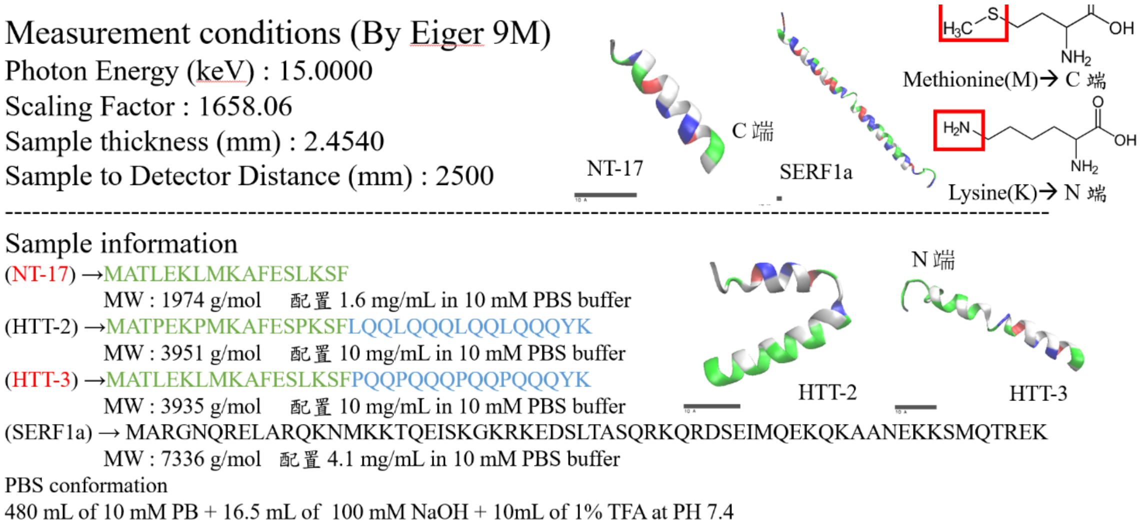
In Huntington disease (HD), one of the many neurodegenerative disorders, abnormal expansion occurs in huntingtin (Htt) exon 1, resulting in fibrillization of Htt polyglutamine (PolyQ). An amyloid modifier SERF1a was recently found to participate in the fibrillization process of Htt; the molecular mechanism is, however, elusive. In this research, interactions of SERF1a with several synthetic Htt peptides modified from Htt (for carrying respectively coiled coil enhancing or disrupting sequences) are studied using combined SAXS, NMR, and several optical spectroscopies including circular dichroism, UV-vis absorption, refractometry. Isothermal titration calorimetry (ITC) is further used to reveal a general binding ratio 1:2 of SERF1a to the Htt peptides. The partially coiled coil structure of SERF1a is reconstructed from the combined NMR and SAXS data; whereas the structures of the Htt peptides are reconstructed from combined molecular simulation and SAXS data analysis. On the basis of the two individual structural models obtained, the binding structure of SERF1a with two Htt peptides is reconstructed from Rosetta molecular simulation confined with the corresponding SAXS data of the mixtures of SERF1a and Htt peptides. From the binding complex binding structure retrieved, a possible binding mechanism of SERF1a and the Htt peptide is proposed.



Measurement conditions (By Eiger 9M)
Photon Energy (keV) : 15.0000
Scaling Factor : 1658.06
Sample thickness (mm) : 2.4540
Sample to Detector Distance (mm) : 2500

Sample information
(NT-17) →MATLEKLMKAFESLKSF
MW : 1974 g/mol 配置 1.6 mg/mL in 10 mM PBS buffer
(HTT-2) →MATPEKPMKAFESPKSFLQQLQQQLQQLQQQYK
MW : 3951 g/mol 配置 10 mg/mL in 10 mM PBS buffer
(HTT-3) →MATLEKLMKAFESLKSFPQQPQQQPQQPQQQYK
MW : 3935 g/mol 配置 10 mg/mL in 10 mM PBS buffer
(SERF1a) → MARGNQRELARQKNMKKTQEISKGKRKEDSLTASQRKQRDSEIMQEKQKAANEKKSMQTREK
MW : 7336 g/mol 配置 4.1 mg/mL in 10 mM PBS buffer
PBS conformation
480 mL of 10 mM PB + 16.5 mL of 100 mM NaOH + 10mL of 1% TFA at PH 7.4

**Keywords**
Huntington disease, Polyglutamine, Solution SAXS, Molecular structural simulation, Binding structures

# P175 - MECHANISTIC INSIGHTS INTO LIQUID WATER SATURATION IN FUEL CELL CATALYST LAYERS USING OPERANDO SMALL ANGLE X-RAY SCATTERING

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It is essential to properly regulate the water content in the polymer electrolyte fuel cells (PEFC) as local oxygen transport resistance depends on the local water distribution. Excess water retention in the pores results in blockage of the reactant gas diffusion to the active sites of the electrochemical reaction, thus reducing performance and efficiency. At the same time, proper hydration of the ionomer in the membrane and the catalyst layer is needed for better performance.

Various measurement techniques suitable with the length scale of PEFC components have been explored to address the PEFC water management challenge. For the gas diffusion layer (GDL), technological advances have permitted operando water saturation quantification and elucidation of its mechanism with X-ray tomography with few microns resolution 1-4. Furthermore, sub-voxel information contained in the X-ray tomography data has demonstrated accurate water quantification in the nano-porous microporous layer (MPL)5. However, in the nanoscale regime of the catalyst layer, the quantification of water and the pore-filling mechanism remains nontrivial. Studies involving imaging techniques dedicated to understand the water management in the catalyst layer have been carried out albeit with the limited spatial resolution6. Nevertheless, the pore-scale information has remained unresolved.

Small angle X-ray scattering (SAXS) technique is proposed as a non-destructive diagnostic tool to investigate the catalyst layer saturation under operating conditions. SAXS is well suited for diagnosing the presence of liquid water during operando experiments because of its sensitivity to electron density contrast, nanoscale observation window, high temporal resolution and adequate spatial resolution to distinguish the components in PEFCs. Herein, SAXS intensity profiles measured at cSAXS, Swiss Light Source, Paul Scherrer Institut, Switzerland, with a recently developed SAXS-compatible operando PEFC (Figure 1 middle and right) are interpreted using representative morphology models and assuming different water filling mechanisms (Figure 1 middle and left). The presentation will provide insights into the wetting phenomena in the catalyst layer of PEFC during operation using a representative morphology modelling approach.

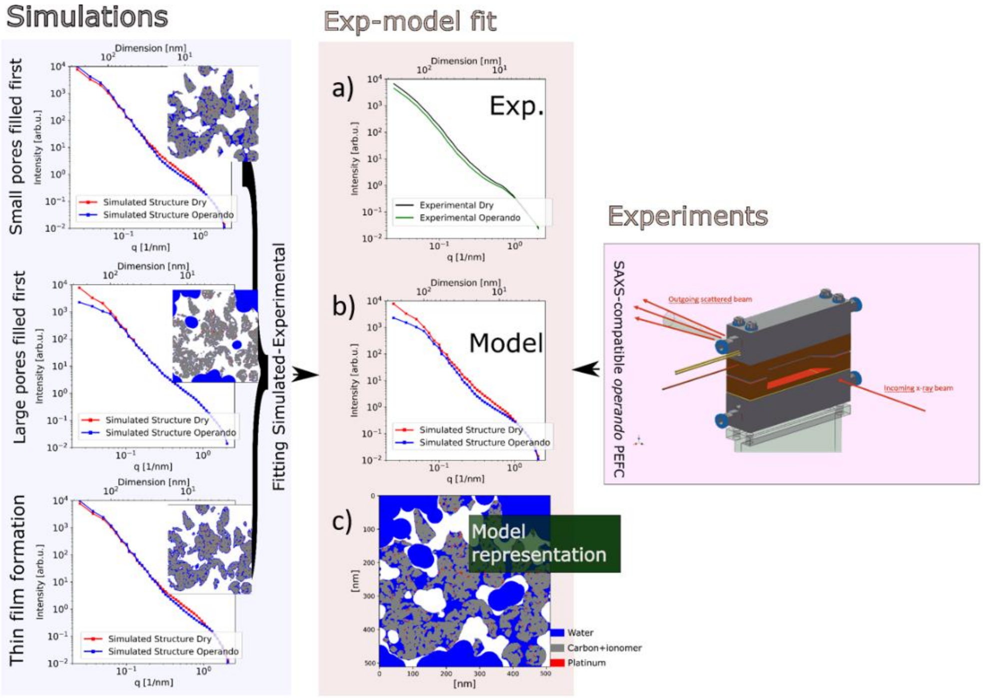

Figure 1 Left: Numerical SAXS intensity profiles derived from representative morphology model in different wetting scenarios. Cross section of 3D model used is shown as inset. Middle: a) Representative experimental *operando* SAXS data of partially saturated catalyst layer at constant voltage 100 mV fitted with the different wetting scenarios, b) the numerical SAXS best fit from the model, c) cross section of 3D model representation from the fit. Right: Schematic design of SAXS-compatible *operando* PEFC used for the experiment.

**Keywords**
PEFC catalyst layer, water management, representative morphology model, numerical scattering

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# V325 - EXTENDED Q-RANGE SMALL-ANGLE-NEUTRON SCATTERING TO UNDERSTAND THE MORPHOLOGY OF PROTON-EXCHANGE MEMBRANES: THE CASE OF THE FUNCTIONALIZED SYNDIOTACTIC-POLYSTYRENE MODEL SYSTEM

**SCHIAVONE, Maria-Maddalena (1); LAMPARELLI, David Hermann (2); DANIEL, Christophe (2); GOLLA, Manohar (2); ZHAO, Yue (3); IWASE, Hiroki (4); ARIMA-OSONOI, Hiroshi (5); TAKATA, Shin-ichi (5); SZENTMIKLOSI, Laszlo (6); MAROTI, Boglarka (6); ALLGAIER, Jürgen (7); RADULESCU, Aurel (1)**

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To design new proton exchange membranes (PEM) one should not only consider the molecular polymer architecture, but also understand the microstructure of membranes in terms of microphase separation of hydrophilic ionic material that promotes proton conductivity from the hydrophobic regions that provide the mechanical strength and limit the dimensional changes of the membrane during swelling. The proton conduction in PEMs depends on water and is determined by the water behavior at different length scales between the molecular level and the mesoscale as a function of the hydration level and temperature conditions. In addition, membrane stability and mechanical strength depend on the preservation of the crystalline regions under such conditions. To assess the link between conductivity / mechanical stability and morphology, the structural levels between a few Å (crystal structure) and the mesoscopic scale (hundreds of nm) should be characterized under relevant conditions for application. Small-angle neutron scattering (SANS) over an extended Q range with contrast variation is a unique method for such a detailed analysis. Syndiotactic polystyrene (sPS) is a semi-crystalline polymer that presents several crystalline forms with polymer chains arranged in either the trans-planar or helical conformation. Particularly, δ- and ε-phases are formed by crystallization from solution, representing co-crystals of s-PS with low molecular mass guest molecules (clathrates). These forms have a great potential for application when different guest molecules can be loaded and exchanged in the cavities formed between the helices of the crystalline regions, for fluorescent materials (with chromophore invited molecules), optical memories (with photo-reactive guest molecules), non- linear optical materials (with polar guests) and chiropractic memories (with chiral guest molecules). On the other hand, given the recent developments, which enable a controlled sulfonation of only the amorphous phase, preserving thus the crystallinity of the material, and an improved resistance to oxidation decomposition when fullerenes are added, the sulfonated syndiotactic polystyrene (s-sPS) may become a good potential candidate for some PEM applications, as it presents a high proton conductivity comparable to Nafion, high chemical and thermomechanical stability, and a low cost. We report here a microstructural investigation on s-sPS and s-sPS / fullerene membranes at different levels of hydration and temperature using the contrast-variation SANS technique, supplemented with XRD, FTIR, UV-Vis and optical microscopy. The uni-axial and as-cast films containing the δ-form sPS were functionalized in different degrees, which were determined by prompt-gneutron activation analysis. The use of uni-axially deformed films allowed the identification and characterization of different structural levels that extend over a wide range of lengths, which are formed and evolve in both dry and hydrated state. The neutron scattering length density of the crystalline regions was varied using the guest exchange procedure between toluene isotopologues incorporated in the sPS lattice, while the scattering properties of

the hydrated amorphous regions were varied using different H2O / D2O mixtures. A direct understanding of hydrated regions and pathways was possible following the analysis of the relationship between the morphology of hydrated domains obtained by SANS and proton conductivity measured under different conditions.

**Keywords**

semi-crystalline polymers, proton-exchange membranes, SANS, extended Q-range, contrast variation

SESSION 4B: COLLOIDS AND POLYMERS 2
Chair: Dr. Theyencheri Narayanan

## V227 - NON-DESTRUCTIVE INVESTIGATIONS OF GRAPHITIZED POROUS SILICON FOR CHARGE STORAGE DEVICES

**ROMANITAN, Cosmin (1); BRATOSIN, Irina (1); KUSKO, Mihaela (1); CULITA, Daniela (2); RADOI, Antonio (1); VARASTEANU, Pericle (1); TUTUNARU, Oana (1)**
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Porous silicon based supercapacitor electrodes with different pore morphologies were obtained using an electrochemical etching process where both the anodization current and the etching time were varied, followed by functionalization of the internal surface area. The challenge for conformal modification of the ultra-high internal surface of nanoporous silicon was tackled by electrochemical polymerisation of 2,6-dihydroxynaphthalene using cyclic voltammetry or potentiometry. In this way, an assembly of interconnected networks of graphene strongly adhering to nanoporous silicon matrix was resulted [1].

Since the storage ability of the composite electrodes is closely related to structural parameters, a non-destructive characterization becomes mandatory [2.3]. For that reason, different X-ray based methods, such as high-resolution X-ray diffraction (HRXRD), X-ray reflectivity (XRR), total external reflection (TER) or Small-Angle X-ray Scattering (SAXS) were successfully applied. Thus, the unit cell parameter and lattice strain of the porous silicon lattice in the absence/presence of the carbon polymer was obtained by HRXRD [1]. Recently, high-resolution X-ray diffraction techniques allowed us to elaborate a novel non-destructive formalism to get the static Debye-Waller distribution along the z-axis, further used for porosity depth gradient determination [5]. XRR and TER curves were used for surface porosity determination, while X-ray reciprocal space maps (RSMs) were used for the determination of the mean porosity in the whole volume [4]. In addition, the specific surface area, an essential aspect in the context of the charge storage devices, was estimated from SAXS measurements. The obtained results showed that the specific surface area ranges typically between 80 m2/g and 200 m2/g in our porous silicon and the graphitization of the porous silicon modifies the specific surface area (SSA) and increases the active sites for charge storage. The results were correlated with BET absorption-desorption isotherms and the overestimation of the SSA from SAXS was attributed to the inaccessibility of N molecules in narrow/close pores. At the same time, Guinier law in the low-q range brings information related to the pores/characteristic sizes, while the Porod region is related to the surface morphology.

Next, the correlation of the microstructure with the standard electrochemical measurements of the assembled supercapacitors allowed us to achieve the input data for a rational design of the next generation of charge storage electrodes.

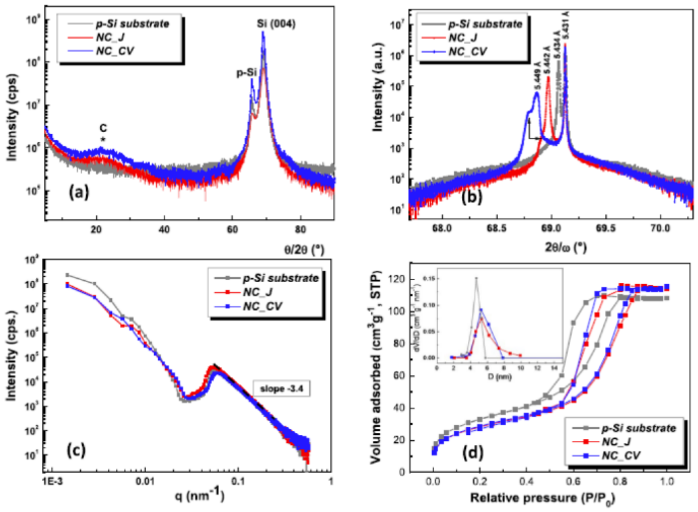

**Figure 1.** X-ray diffraction analyses: (**a**) *θ/2θ* wide angle X-ray diffraction; (**b**) *2θ/ω* scans for (004) Bragg reflections; (**c**) small angle X-ray scattering; and (**d**) N2 adsorption/desorption isotherms for *NC_CV* and *NC_ J* samples in comparison with *p-Si substrate*. The figures are reproduced from (Romanitan et al., *Sci Rep* **8,** 9654 (2018).

**Keywords**
porous silicon; supercapacitors; SAXS curves

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**Acknowledgments**

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# V300 - X-RAY SCATTERING AND ABSORPTION STUDIES OF POLYMER ELECTROLYTE FUEL CELL CATHODE ELECTROCATALYSTS

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Synchrotron-based X-ray techniques are particularly useful for probing the effects of electrode preparation process and the fuel cell operating conditions on the degradation of high surface area carbon-supported platinum and platinum-alloy nano-particle electrocatalysts. These studies have mainly utilized ex situ microcopy techniques or in situ evaluation of electrochemically-active surface area and electrocatalytic activity. We have used X-ray scattering and X-ray absorption spectroscopy (XAS) techniques to determine the key mechanistic steps in the degradation of Pt and Pt alloy nano-particle electrocatalysts in aqueous and MEA environments and to correlate the effects of the electrode preparation process on the final electrode structure towards optimization of the performance of the state-of-the-art Pt alloy/C based MEAs.

**Keywords**
Polymer Electrolyte Fuel Cell, Electrocatalysts, USAXS

## SESSION 4C: MATERIALS SCIENCE 1

Chair: Dr. Rainer T. Lechner

# P177 - SIZE EFFECTS ON SURFACE CHEMISTRY AND RAMAN SPECTRA OF SUB-5 NM OXIDIZED HIGH-PRESSURE HIGH-TEMPERATURE AND DETONATION NANODIAMONDS

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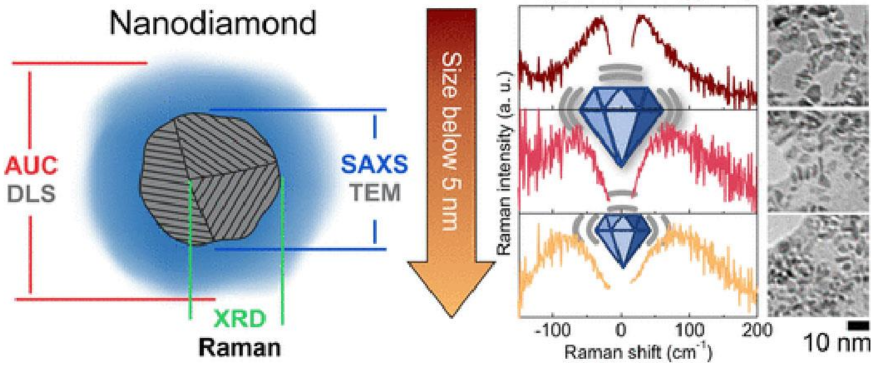
Materials with very small dimensions are of major importance for fundamental science as well as innovative applications. Ultrasmall nanoparticulate materials with core sizes in the 1 nm to 3 nm range bridge the gap between single molecules and classical, larger-sized nanomaterials [1]. In this size region, interesting phenomena such as quantum size effects [2], structural transformations or phononconfinement effects take place. Here, we investigate the effects of size on the surface chemistry, microscopic structure, and Raman scattering of high-pressure high-temperature (HPHT) and detonation nanodiamonds (DNDs) down between 2nm to 3nm [3]. Annealing in air and ultracentrifugation was used to control the size and surface chemistry of the NDs, resulting in three fractions of oxidized HPHT NDs and DNDs. The particle size and particle size distribution (PSD) of those fractions was analyzed by dynamic light scattering, analytical ultracentrifugation, small-angle X-ray scattering (SAXS), X-ray diffraction, and transmission electron microscopy as complementary techniques. SAXS is the only technique, which is capable to provide statistically relevant data of the samples in liquid without being affected by the ND hydration shell. All the tree fractions of both HPHT O-NDs and size-reduced oxidized DNDs (SR O-DNDs) as well as the commercial single-digit DNDs (SD DND ref.) were measured in vacuum using a custom-built sample cell with a quartz capillary having 10 μm thin walls with a flexible SAXS system developed by Fraunhofer Development Center X-ray Technology especially for low contrast samples in liquids. Based on the obtained PSD, we identify size-dependent and synthesis-dependent differences of ND properties. The analysis revealed a similar PSD of the smallest fractions with mode sizes down to the 2nm to 3nm range for both HPHT O-NDs and SR O-DNDs. This enabled a detailed comparison of HPHT O-NDs with SR O-DNDs in the sub-5 nm region and some discrimination between the effects of size and structural defects on their spectroscopic response. Comprehensive comparison of detonation and pure monocrystalline HPHT NDs reveals effects of diamond core size and defects, chemical and temperature (in)stability, and limitations of current phonon confinement models. In addition, low-frequency Raman scattering in the 20 cm−1 to 200 cm−1 range is experimentally observed. The size dependence of this signal for both HPHT NDs and DNDs suggests that, it may correspond to confined acoustic vibrational, “breathing-like” modes of NDs.



**Keywords**

high-pressure high-temperature, detonation, nanodiamonds, SAXS, phonon-confinement

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SESSION 4C: MATERIALS SCIENCE 1
Chair: Dr. Rainer T. Lechner

# P357 - ON THE USAGE OF ASAXS TO ANALYZE STRUCTURE AND COMPOSITION OF SIZE-TUNABLE NI–CU CORE–SHELL NANOPARTICLES FOR APPLICATION IN CATALYSIS

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Tailor-made mono- and bi-metallic nanoparticles (NPs) are on great interest in e.g. catalysis, as sensor materials, and analytical assays. A facile and efficient methodology is developed for the solvothermal synthesis of size-tunable, stable, and uniform NiCu core–shell NPs for various application in catalysis [1]. Their diameter can be tuned in a range from about 6 nm to 30 nm and the Ni:Cu ratio is adjustable in a wide range from 1:1 to 30:1. The NPs are structurally characterized by a method combination of complementary methods: transmission electron microscopy, anomalous small-angle X-ray scattering (ASAXS), X-ray absorption fine structure, and X-ray photoelectron spectroscopy.

Here, we focus on the ASAXS method and its ability to analyze nanostructure details and their compositions at once.

The X-ray K-absorption edges of the two elements Ni and Cu are nearby (8333 eV and 8979 eV). Consequently, the strong variation of the anomalous scattering behavior in the energy range between 8 keV to 9 keV is used for this special ASAXS investigation.

ASAXS excluded the hypothesis of a bimetallic core-shell structure and evidenced a core-shell-shell nanostructure. The outer shell having the lowest electron density is found to be NiO while the inner core is Cu and Ni alloyed. That was proved to be valid for all particle sizes and Ni:Cu ratios. The inner shell is pure Ni.

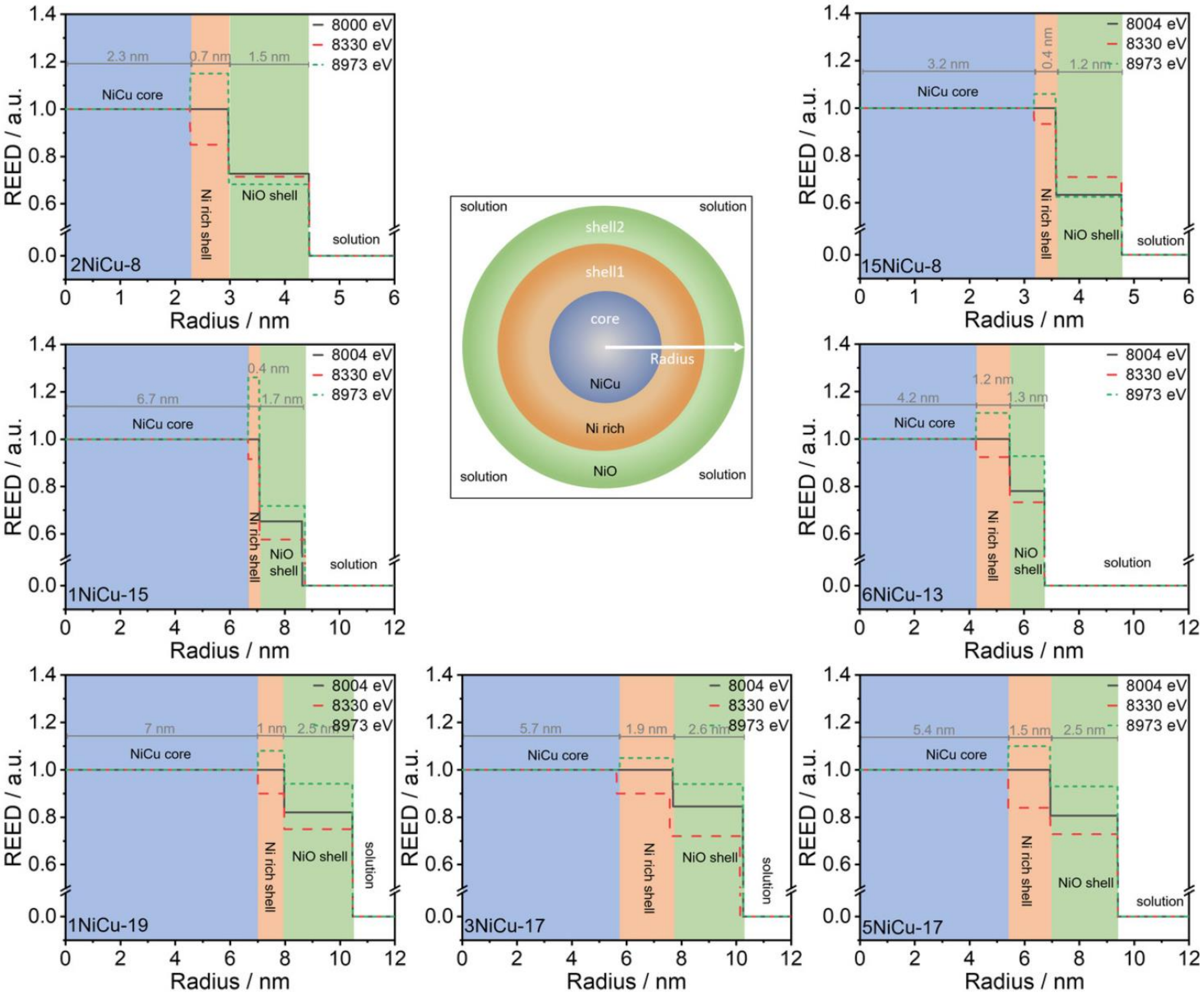

Figure1:

The resulting structural models of 7 core-shell-shell nanoparticles of different sizes and different Ni:Cu ratios are shown. The calculated relative effective electron density (REED) profiles of the NiCu NPs are sketched for three particularly X-ray energies. The areas of the NPs are indicated by blue for the NiCu alloyed core, orange for the inner Ni dominated shell, and green for the outer NiO shell.

**Keywords**
ASAXS, metallic nanoparticles, analysis method, catalysis

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SESSION 4C: MATERIALS SCIENCE 1

Chair: Dr. Rainer T. Lechner

## P169 - PROBING THE STACKING PROPERTIES OF CESIUM LEAD HALIDE PEROVSKITE NANOPLATES WITH SAXS

**MORAL, Raphael Fernando (1); MALFATTI-GASPERINI, Antônio Augusto Malfatti (2); BONATO, Luiz Gustavo (1); OLIVEIRA, Cristiano Luis Pinto de (3); NOGUEIRA, Ana Flávia (1)**
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Cesium lead halide perovskite nanoplates (PNPs) have been extensively investigated in recent years for their outstanding optical properties. These nanoplates can self-assemble into stacks in the solid state, forming superlattices. These stacks are hundreds of nanometers long and can even form a superstructure of adjacent stacks. Considering this self-assemble ability, we sought to understand whether or not these PNPs stack in suspension in organic solvents such as hexane, decane, dodecane, and hexadecane. For this purpose, we probed different compositions of PNPs using SAXS and WAXS measurements in different conditions.

Our preliminary results show that this self-assemble in solution depends on the quality of the solvent: hexane shows little or no stacking, while hexadecane shows strong stacking scattering in SAXS. With these SAXS curves we could determine the space between the nanoplates, finding a common distance of about 5 nm for all samples ($CsPbBr_3$ or $CsPbI_3$) in all solvents. These findings agree with HAADF-STEM images. In addition, our results suggests that PNPs with narrow thickness distribution self-assemble into stacks more easily than PNPs with broad size distribution. Finally, a parallelepiped form factor offered a good fit to the data, yielding consistent morphology and aspect ratio of the PNPs.

The information provided by the combination of SAXS and TEM on these superstructures enables the engineering of promising nanostructured platforms for optoelectronic applications. In addition, the precise measurement of the distances, both in solids superstructures and in colloidal suspensions, allows us to evaluate the efficiency of Föster resonant energy transfer FRET between nanoplates. The efficiency of FRET process is critical to understand charge carriers' dynamics in devices and the optical behavior of these PNPs in suspensions in organic solvents.

**Keywords**
Perovskite nanoplates, self-assemble, stacking, SAXS, superstructure

SESSION 4C: MATERIALS SCIENCE 1
Chair: Dr. Rainer T. Lechner

# V416 - MICROSTRUCTURE CHARACTERIZATION OF PEFC CATALYST INKS AND ELECTRODES USING IN SITU ULTRA SMALL ANGLE X-RAY SCATTERING

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Catalyst layers of a polymer electrolyte fuel cell (PEFC) are typically prepared by first dispersing a catalyst powder, comprised of platinum or platinum alloy nanoparticles supported on carbon blacks, with ionomer in solvent followed by extensive mixing using a variety of methods. The purpose of the ink mixing and processing procedure it to break up large agglomerates of the catalyzed carbon powder (>10 µm) and form a uniform dispersion. This study uses the in-situ measurement of ultra-small angle X-ray scattering (USAXS) combined with SAXS to study the catalyst agglomerate size distribution during ink mixing/processing for efficient coating of catalyst layers while optimizing cell performance and lifetime and minimizing ink processing time and cost. The sonicated catalyst ink is circulated through a thin-walled capillary tube situated in the beamline using a peristaltic pump. The effects of catalyst ink composition and processing variables on catalyst agglomerate size and ink properties are evaluated using different solvents, ionomer-carbon ratios, support types, and sonication time. The proper ink composition and sonication method that facilitate the break-up of carbon agglomerates with the minimum amount of time are determined. This presentation will also describe the results of in-situ/ex-situ X-ray scattering studies of the evolution of the cathode catalyst layer during the ink drying process to determine the impact of solvent removal rates and solvent identity on the structural evolution of cathode electrodes.

**Keywords**
PEFC, catalyst, X-ray scattering

CANSAS SATELLITE MEETING 1
Chair: Dr. Judith Elizabeth Houston, Dr. Andy James Smith

## P445 - SIMULATION OF MAGNETIC SANS PATTERNS USING SASVIEW: CHIRAL MAGNETIC STRUCTURES IN EXPERIMENT AND THEORY

**Tim Snow**
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A session to open discussions on multi-probe data analysis and fusion, multi-detector data analysis and fusion as well as the robust co-refinement of SAXS and SANS data.

**Keywords**
Multi-probe, Multi-detector, SAXS, SANS, Data fitting

# V446 - POLARISED TIME-OF-FLIGHT-SANS AT ISIS: CURRENT STATUS AND FUTURE CHALLENGES

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Polarized neutron scattering is a powerful technique for investigating the structure and dynamics of condensed matter, in particular magnetic materials and superconductors. The spin of the neutron provides SANS a unique sensitivity to study magnetism and magnetic materials at the nanoscale.

This contribution will show a selection of recent results on magnetic materials from the TOF SANS instruments Larmor and ZOOM at ISIS, UK. Special attention is paid to the ongoing developments to improve data analysis and to employ polarized neutron techniques on TOF instruments, e.g. polarisation analysis.

**Keywords**
polarised neutrons, magnetic materials, CanSAS

CANSAS SATELLITE MEETING 1
Chair: Dr. Judith Elizabeth Houston, Dr. Andy James Smith

# P449 - GENERIC DESCRIPTION OF SAS RESOLUTION FUNCTION

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The numerical convolutions of the appropriate functions for fixed wavelength SANS gives improved Q resolution functions that are slightly flatter in the peak and broader in the tails than the classic Mildner & Carpenter approach. However, in time-of-flight SANS the resolution curves from all the wavelengths contributing to a particular Q value are averaged together, weighted by the number of neutrons detected at each wavelength. Since the resolution width is inversely proportional to wavelength this often gives a curve that is noticeably sharper in the peak and broader in the tails than a simple Gaussian. In either type of SANS measurement a more detailed description of Q resolution smearing within fitting programs such as SasView will need generic resolution functions of arbitrary shape. The generic resolution function was subject of discussion at CanSAS workshop in March 2021 and efforts have been for devising data format and using arbitrary function in SasView. The summary of these activities will be provided in the presentation.

**Keywords**
Modelling and Data Analysis

CANSAS SATELLITE MEETING 1
Chair: Dr. Judith Elizabeth Houston, Dr. Andy James Smith

## P285 - MONOCHROMATIC SANS INSTRUMENT AT THE TU DELFT REACTOR

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The TU Delft in the Netherlands operates a small 2.3MW research reactor, we are in the process of upgrading and adding a hydrogen cold source which will increase significantly our cold neutron flux. With this flux gain we are in the process of updating and upgrading a monochromatic SANS instrument. The detector will have a new 60x60cm 3He detector, velocity selector and a range of sample environment options.
The instrument is currently in commisioning and is expected to be operational at the end of the year.
I will present the status of the instrument, expected performance and also an overview of the expected science that we hope to use the instrument for. Furthermore I will detail how this will be available to the community. I will also briefly discuss the overlap with our spin echo SANS (SESANS) instrument which allows for the probing of larger structures up to the 10's microns.

**Keywords**
monochromatic, SANS, neutron

CANSAS SATELLITE MEETING 1

Chair: Dr. Judith Elizabeth Houston, Dr. Andy James Smith

## V444 - SIMULATION OF MAGNETIC SANS PATTERNS USING SASVIEW: CHIRAL MAGNETIC STRUCTURES IN EXPERIMENT AND THEORY

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No Text.

**Keywords**
SasView, Magnetic chirality, Magnetic SANS

PLENARY3

Chair: Prof. Jill Trewhella

# P363 - BIOSANS FOR THE STUDY OF MEMBRANE PROTEIN

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An adequate membrane-mimicking environment is of first importance for the function of membrane protein. In recent years, several tools have been improved or developed to purify membrane protein in physiological-like conditions and enable their functional and structural study. I would like to present here the instrumental improvements that, together with adapted membrane mimicks and complementary techniques, allow us to probe the shape and dynamics of membrane protein in solution.

Using the example of the ABC transporter BmrA, I will show how SEC-SANS, together with invisible detergents or nanodiscs, provide the optimal experimental conditions to record low resolution structure and dynamics information on membrane protein. In combination with Cryo-Electron microscopy, H/D-exchange-mass spectroscopy and computing simulations, it reveals the conformational landscapes explored by BmrA through its enzymatique cycle. These tools are ideally suited for the study of protein-lipid interdependence.

**Keywords**

membrane protein, structure in solution

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SESSION 5A: PROTEIN STRUCTURES, ASSEMBLIES AND DYNAMICS 3
Chair: Prof. Jill Trewhella

## P189 - THE HYDRATION LAYER EFFECT ON SAXS DATA OF INTRINSICALLY DISORDERED PROTEINS STRONGLY DEPENDS ON PEPTIDE CONFORMATION, AMINO ACIDS SEQUENCE, AND FORCE FIELDS

**FISCHBACH, Tobias; HERMANN, Markus; HUB, Jochen S**
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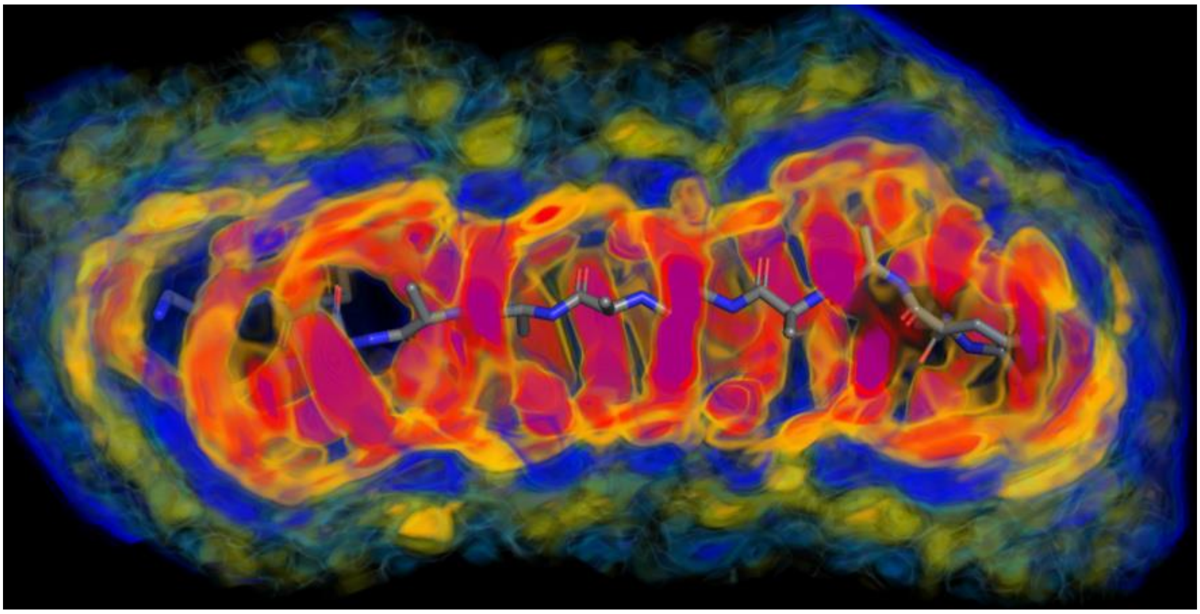
Intrinsically disordered proteins (IDPs) are key players in signal transduction and, therefore, in health and disease. SAXS provides unique structural information on IDPs; however, translating SAXS signals into atomistic ensembles is challenging owing to the low information content of the data. In addition, it is poorly understood how the hydration layer of IDPs is controlled by peptide conformation and composition and, thereby, how the hydration layer influences the SAXS signals.

We first present a method for obtaining atomistic ensembles of IDPs by coupling all-atom molecular dynamics (MD) simulations on-the-fly to experimental SAXS data. The data is integrated into the simulations with only a minimal bias, thereby following Jaynes's maximum entropy principle. Using explicit-solvent SAXS predictions, we investigate how the hydration layer of IDPs influences the radius of gyration Rg and the forward scattering I(0) as detected by SAXS experiments. We find that the hydration layer effect on Rg and I(0) strongly depends on the peptide conformation and amino acid sequence, and, to a lower extend, on the applied water model. To clarify how the amino acids composition affects the hydration layer, we present a hydration layer contrast score for the 20 common amino acids. Together, explicit-solvent simulations provide are a valuable tool to interpret SAXS data of IDPs and to obtain an atomistic view on the hydration layer of biomolecules.



**Keywords**
intrinsically disordered proteins, molecular dynamics simulations, explicit solvent, hydration layer, SAXS-driven MD

## P366 - USING SANS TECHNIQUE FOR IMPROVEMENT OF THE METHODOLOGICAL STRATEGIES TO FUNCTIONALIZE ANTIBODIES

**TREMARIN, Beatriz (1); YOKAICHIYA, Fabiano (1); KELLERMANN, Guinther (1); FRANCO, Margareth K.K.D. (2); SCHMIDT, Christian (3); STORSBERG, Joachim (3)**
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Antibodies have played an essential role in Jawed vertebrates protecting them against invading pathogens. The application of antibodies in clinics and biomedical sciences requires functionalization strategies able to retain the reactivity of native antibody. Currently one applies trial and error to achieve antibody functionalization. In this work, we propose the use of small-angle neutron scattering (SANS) and mathematical modeling of antibody and antibody-antigen super-complexes as a more general method to identify which processes successfully lead to antibody functionalization. We expect our effort will help to refine such versatile tools and improve their production. For this research we have used as antibody pure goat anti rabbit immunoglobulin, and for the antigen, pure Horseradish Peroxidase. GNOM and DAMMIF programs of the ATSAS package were applied in SANS curves to determine the pair distribution function and the overall shape of the macromolecules, respectively. The results show remarkable differences in the conformation of antibody and the complex structures. The antibody has a globular structure with a radius of gyration around 33 Å, and the complex display an elongated cylindrical shape with radius of gyration around 63 Å. The molecular weights of antibody and complex determined from SANS curves using the MoW program were 52 kDa and 96 kDa, respectively. SANS measurements of these macromolecules at different temperatures in 25-40oC range, indicate no changes in size or shape of the antibody-antigen complex. This study shows how the scattering techniques can provide useful information about the conformation of the antibody and antibody-antigen formation and help to shed light in the understanding the physical, chemical, and structural changes related to antibody functionalization with useful applications in immunological system.

**Keywords**
SANS, Antibodies, Antigen.

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SESSION 5A: PROTEIN STRUCTURES, ASSEMBLIES AND DYNAMICS 3
Chair: Prof. Jill Trewhella

# V173 - TOWARDS A COMPREHENSIVE PICTURE OF TEMPERATURE-RESPONSIVE ELASTIN-LIKE PEPTIDES

**MOROZOVA, Tatiana (1); MATSARSKAIA, Olga (1); WEHBE, Zeina (1); WALDIE, Sarah (2); GARCIA, Nicolas A. (3); KOZA, Michael M. (1); MOULIN, Martine (1); LAUX, Valerie (1); HAERTLEIN, Michael (1); FORSYTH, Trevor (1); BARRAT, Jean-Louis (1); ROOSEN-RUNGE, Felix (2)**
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Elastin-like peptides (ELPs) are biomolecules mimicking the hydrophobic repeat units of elastin, a protein providing elasticity to biological tissues such as lung, ligaments and blood vessels. ELPs undergo a hydrophobic collapse upon crossing a lower critical solution temperature (LCST). Due to their stimulus-responsive properties, ELPs are of interest for a broad range of applications including advanced biomaterials, protein purification and drug delivery. While the hydrophobic collapse is believed to be key for the elastic properties of elastin, a comprehensive mechanistic characterisation of the static and dynamic aspects of the collapse has not yet been obtained. In particular, the dynamical state within the collapsed hydrophobic domains of elastin is debated (fluid-like structure vs. a more specific stacking). By combining SANS, QENS, molecular dynamics simulations and selective deuteration, we investigate the temperature response of selectively deuterated ELPs. Neutron data indicate differences in the behaviour of short and long ELPs, and, in agreement with simulations, a shift towards more compact ELP structures with increasing temperature is observed. Using our results, we aim at establishing a framework for the investigation of stimulus-responsive molecules and materials.

**Keywords**
thermoresponsive peptides, elastin-like peptides, SANS, QENS, molecular dynamics

# V210 - INTERACTION OF PROHIBITIN WITH THE INNER MITOCHONDRIAL MEMBRANE

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Prohibitins (PHB) are highly conserved heterodimeric proteins composed of two subunits PHB1 and PHB2 arranging to make a multimeric ring at the inner mitochondrial membrane [1]. They play a crucial role in premature cellular aging, tumor suppression, cell cycle regulation, apoptosis, and mitochondrial homeostasis via their function in the intermembrane space (IMS) of mitochondria (between the inner and outer membranes).

Despite the essential role of this complex, little is known regarding its molecular structure and arrangement within the membrane. Initial reports suggest that the formation of the prohibitin complex is influenced by the action of cardiolipin (CL), which is involved in maintaining a particular shape and curvature of the inner mitochondrial membrane [2].

The two main aims of this project are to (i) characterize the interaction between the N-terminal helices of PHB (NT-PHBx) with the membrane and establish a possible synergy of the two PHB homologues, and (ii) understand the role of cardiolipin in this interaction.

To answer these questions, we employ both interface and bulk techniques on simplified model systems, using synthetic peptides corresponding to the transmembrane domains of PHB (NT-PHB, 20-24 residues long), and synthetic or natural mixtures of lipids. As interfacial techniques exploring the solid/liquid interface, we apply Neutron and X-ray Reflectometry (NR, XR) and Quartz-crystal microbalance with dissipation monitoring (QCM-D). As bulk techniques applied to extruded liposomes we employ Small-Angle Scattering by X-rays and Neutrons (SAXS, SANS), as well as Dynamic and Static Light Scattering (DLS, SLS).

NR and QCM-D preliminary results suggested a higher tendency of NT-PHB1 of insertion into the membrane in presence of CL, while NT-PHB2 is able to remove lipid from the bilayer in absence of CL. Due to the amphipathic character, NT-PHB2 seems to puncture the membrane.

SANS is employed to evaluate the in solution structure, studying the effect of the peptides on the vesicles, focusing on the liposomes. Preliminary SANS results show that the peptide induces fusion of the vesicles, from multilamellar to unilamellar vesicles, indicating a tendency of the peptides to disrupt the membrane.

**Keywords**
Lipid-Protein interaction, Prohibitin, Cardiolipin, SANS

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https://doi.org/10.1038/s42003-019-0471-x

## P362 - DETERMINATION OF MEMBRANE WATER PERMEABILITY THROUGH STRESS FREE TIME-RESOLVED SANS

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The lipid bilayer, the basic unit of biological membranes, is an essentially impermeable barrier. Because of this, the environment inside the cell can be significantly different from the environment surrounding it such as pH, ion compositions and concentrations. Since several cellular functions require the fast transport of large or charged molecules through the membrane, the cell membrane contains assisting proteins that specifically transport them across the membrane. Permeation is then either mediated by membrane transport proteins or happens via passive diffusion. Due to the structure of the membrane, we could imagine that passive transport is limited to small molecules. Even water that can passively go through a biological membrane, may do so slowly for certain functions, so the cell also has active water transporters, such as aquaporin, to move water through faster. The energy required to move water across the lipid bilayer passively as well as its intrinsic mechanism is still debated.

Here we focus on passive water permeation through model membranes. Although several techniques have been used to measure water permeation such as NMR, fluorescence, and micropipetting, they all rely on a rapid change of the osmotic pressure of the solution surrounding the vesicles. Here we take advantage of contrast between H2O and D2O to investigate, through time resolved SANS, the membrane permeability of different lipid membranes.

The principle is to follow the scattering intensity of a hydrogenated vesicle solution, initially prepared in H2O, when diluted with D2O. The resulting changes in scattering would be a result of the intake of D2O into the vesicle’s interior without any induced stress on the membrane. Our result will be compared to previously reported results in the literature and discussed through theoretical and computational approaches in order to determine the important parameters governing permeability through membranes.

**Keywords**
membrane permeation, SANS, kinetic, time resolved

SESSION 5B: DYNAMICS, KINETICS, IN SITU TIME-RESOLVED 1
Chair: Prof. Celso Valentim Santilli

# P225 - IN-SITU SAXS INVESTIGATION OF THE CALCINATION PROCESS DURING SYNTHESIS OF SOFT TEMPLATED CARBONS WITH ORDERED CYLINDRICAL MESOPOROSITY

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Meso- and microporous carbon materials show versatile applicability in fields such as hydrogen storage via cryo-adsorption, separation of energy dense CO2/CH4 mixtures due to selective adsorption, and electrochemical energy storage in supercapacitor technology [1]. Such carbon materials with hierarchically structured pores can for instance be produced via a soft templating carbon (STC) route, which is schematically depicted in Figure 1. During STC synthesis, interaction of the precursor and the copolymer leads to the formation of rod like micelles that self-organize on a two dimensional hexagonal lattice and act as a soft template for the mesopore space. After the sol–gel process and subsequent drying of the polymer surrounding the hexagonally arranged rod-like micelles, a calcination step at elevated temperatures (250–350 °C) in a nitrogen/oxygen atmosphere is necessary, to remove the surfactant micelles and thereby create accessible mesoporosity. The resulting polymer structure with cylindrical mesopores, ordered on a 2D hexagonal lattice, is subsequently carbonized and can additionally be activated to introduce microporosity within the mesoporous skeleton [2]. The efficiency of the calcination step to remove the surfactant strongly influences the characteristics of the resulting porous network, and thus, plays a key role in modeling the structural properties required for specific applications. Ideal calcination reliably removes the surfactant and gives way to mesopore space, while at the same time being gentle enough to preserve the intended hexagonal pore structure, leading to application adjusted hierarchically structured carbon. Finding ideal calcination parameters, however, proves to be challenging [1–3].

In this study, we therefore present time resolved in-situ small angle X-ray scattering (SAXS) of the STC precursor material upon calcination using synchrotron radiation. The observed shift of Bragg peaks associated with the periodically arranged (surfactant-filled) mesopore space towards higher q-values indicates shrinkage of the structure. This allows us to describe the mesopore lattice parameter as a function of the holding time and temperature and to estimate suitable timescales for each calcination temperature. Relative peak height progression are used to elucidate form factor effects and the loss of higher order Bragg reflexes upon calcination indicate changes in the mesopore structure and a reduction of the quality of the mesopore arrangement. Moreover, first estimations of the in-situ progression of the specific surface area are discussed. Summarizing, the presented results deepen the understanding of the processes at play upon surfactant removal in STC synthesis and elucidate the influence of the applied temperature, the ratio of nitrogen and oxygen in the calcination atmosphere and the isothermal holding time on the resulting carbon precursor material, which could contribute to the improvement of the synthesis of STCs and as a result lead to materials with application adjusted pore size distribution and tailored porous properties.

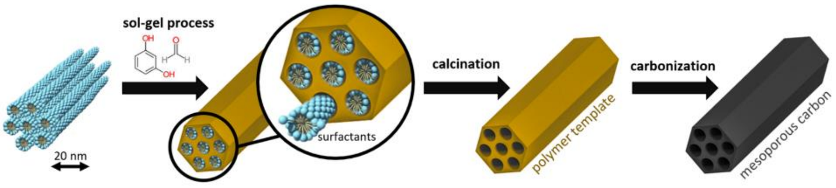

*Figure 1: Schematic representation of the ideal soft-templated carbon (STC) synthesis route.*

**Keywords**
soft templated carbon, calcination, STC, mesoporosity

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# V302 - TYPICAL THREE-LAYER ORTHOTROPIC ORGANIZATION OF CARTILAGE ACHIEVED BY FRONTAL ULTRAFILTRATION UNDER ULTRASOUND WAVES OF CELLULOSE NANOCRYSTALS SUSPENSIONS, PROBED BY IN SITU TIME RESOLVED SAXS.

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The focus of this work is to study by in situ time-resolved SAXS, the combined effects of transmembrane pressure and ultrasound waves on the dynamical structural organization and orientation of cellulose nanocrystals (CNCs), with the aim of developing orthotropic multilayered cellulosic structures.

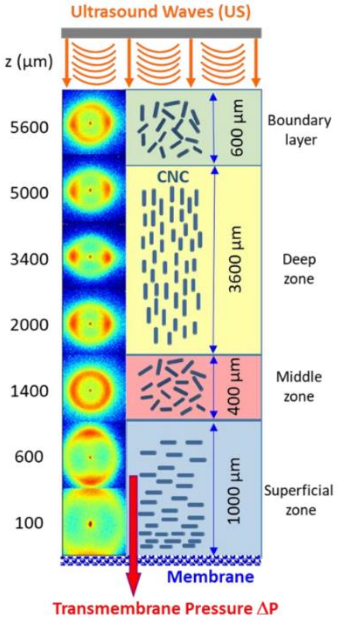
A dedicated SAXS channel-type (frontal ultrafiltration / ultrasound) (FU / US) cell was implemented at the European Synchrotron Radiation Facility (ID02 TRUSAXS beamline) to simultaneously generate an US-induced vertical acoustic radiation force at the top of the channel and simultaneously a transmembrane pressure force at the bottom of the channel near the membrane surface (Fig.1).

Recently, we were able to evidence the ability of the ultrafiltration processes to develop well-defined layered structures of CNCs [1-3]. Furthermore, we discovered by using ultrasound waves, it was possible to align the CNCs along the wave propagation direction [4].

In this work, thanks to FU/US set-up and in situ SAXS, typical multilayer orthotropic structuring that mimic the articular cartilage organization, was achieved in one single FU/US processing on CNC suspensions (Fig. 2). The three continuous structured layers (superficial, middle, and deep) regions representative of the multizonal material cartilage [5] was realized starting from an initial CNC suspension at C = 10 wt % and reaching equilibrium in a few tens of minutes.

The first layer (1000 µm-thick) pertaining to the superficial zone was composed of tightly packed CNCs with their directors aligned parallel to the membrane surface, and a concentration gradient reaching up to 48 wt% at the membrane surface (Fig. 3). The second intermediate layer (400 µm-thick) corresponding to the isotropic middle transitional zone of the cartilage, was located at the intersection where the vertical acoustic radiation force balanced the transmembrane pressure forces, inducing an isotropic orientation of the CNCs at a constant concentration of 13.5 wt%. The third layer (3600 µm-thick) associated to the deep region with objects arranged perpendicular to the articular surfaces, was located below the ultrasonic blade, where the ultrasound waves induced an alignment of the CNCs with their directors aligned perpendicular to the membrane surface, along the ultrasonic wave direction of propagation at a constant concentration of 13.5 wt%. In the vicinity of the ultrasonic blade a boundary layer (600 µm-thick) was highlighted with a global orientation of CNCs along the acoustic radiation and some fluctuations of the orientations at short time scale (1 s).

From the 2D SAXS patterns, the anisotropy PCA were calculated in the (0.071-0.368) nm-1 q-range. It allowed to follow the time dependent evolutions of the anisotropy levels of CNCs orientations inside the differents zones as a function of time and distance Z from the membrane surface (Fig. 3).



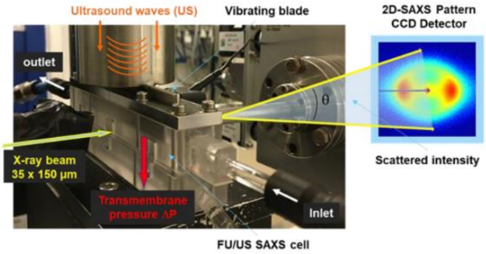


Fig. 1 : Ultrafiltration/Ultrasound-SAXS cell on ID02

Fig. 2: Typical orthotropic organization of cartilage achieved by FU under US. 2D-SAXS patterns at t = 88 min.

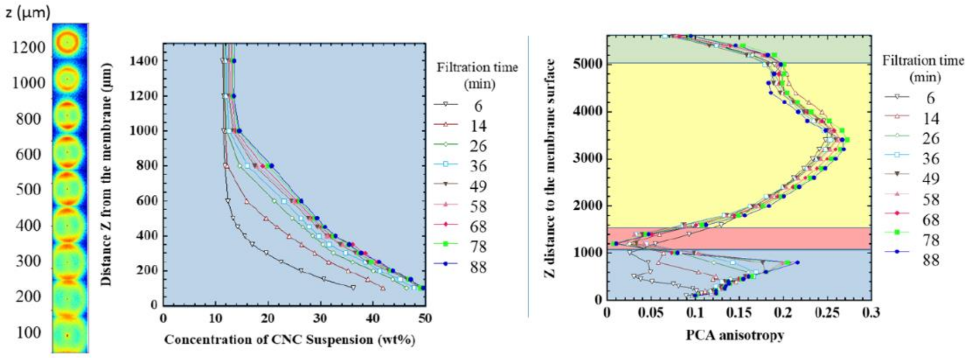


Fig. 3: Concentration profiles and PCA anisotropy of CNCs suspensions during FU/US process inside different zones. $C_{initial}$ = 10 wt%, $\Delta P = 1.2 \times 10^5$ Pa, Acoustic Pressure = 297 kPa

**Keywords**
Cellulose, Ultrafiltration, Ultrasound, Orthotropic, Cartilage

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## SESSION 5B: DYNAMICS, KINETICS, IN SITU TIME-RESOLVED 1

Chair: Prof. Celso Valentim Santilli

# V372 - REAL-TIME OBSERVATION OF NUCLEATION AND GROWTH OF PVP STABILIZED AG NANOPARTICLES: INSIGHT EFFECT OF POLYMER CHAIN

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Metal nanoparticles remain the interest of research due to their widespread applications in photonics, microelectronics, and biotechnology, because of their size-dependent localized properties [1,2]. The efforts have been constructed to precisely control the size and shape of the nanoparticles [3-6]. In the last decade, numerous research activities have been made to understand the nucleation and growth of the nanoparticles[7-9], however, a comprehensive understanding of the effect of surfactant on the nanoparticle's core growth and its relative interaction is still a challenge. Therefore, we investigate the reaction dynamics and growth kinetics of the Ag nanoparticles under the effect of variable chain-length surfactant polymer using time-resolved small-angle X-ray scattering at the Austrian-SAXS beamline of Elettra Sincrotrone Trieste, Italy. In order to study the pure interaction between the metal-core and the polymer, we adopt the radiation-induced synthesis using water radiolysis to avoid the external chemical reducing agent[4-6]. In this presentation, we will describe the step-by-step reaction dynamics and kinetics of the metal nanoparticles. The insight into the mechanism of the reaction of polymer stabilized Ag nanoparticles will be demonstrated.

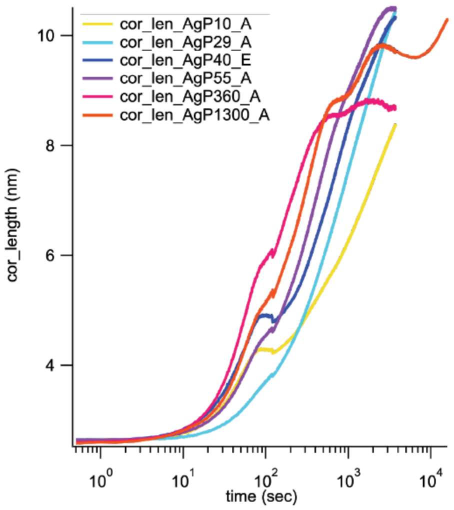

Figure1: Correlation length of the variable chain-length capped Ag-nanoparticles as a function of time.

## Keywords

Polymer capped Nanoparticles, Nucleation and growth mechanism, time-resolved SAXS

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SESSION 5C: INTERFACES, SURFACES AND GRAZING INCIDENCE 1
Chair: Dr. Paula C. Angelomé

# V391 - IN SITU GISAXS AND ELECTROCHEMISTRY: CHARCATERIZATION OF FUEL CELL CATALYSTS AND ELECTROCHEMICAL DEALLOYING

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Electrochemistry has a considerable technological impact on energy materials, such as fuel cells, supercapacitors and batteries, or on dealloying processes for the generation of nanoporosity. In situ analysis at the nanoscale with GISAXS is essential to provide a complete understanding of the fundamental processes responsible for reduced lifetime and performances in energy applications, on one hand, and responsible for the structure evolution during dealloying, on the other hand.

Here we present the development of an electrochemical cell to be able to conduct such type of investigations[1]. The capability of the cell will be demonstrated on the recent results obtained on PtNi catalyst layers of fuel cells during electrochemical cyclic voltammetry [2, 3] as well as on the dealloying of binary systems AgAu and CoPd [4]. In both topics, the GISAXS results provide valuable insights in the processes involved, like Ostwald ripening or coalescence.

At the end, an outlook will be given to current projects related to biology and battery research.

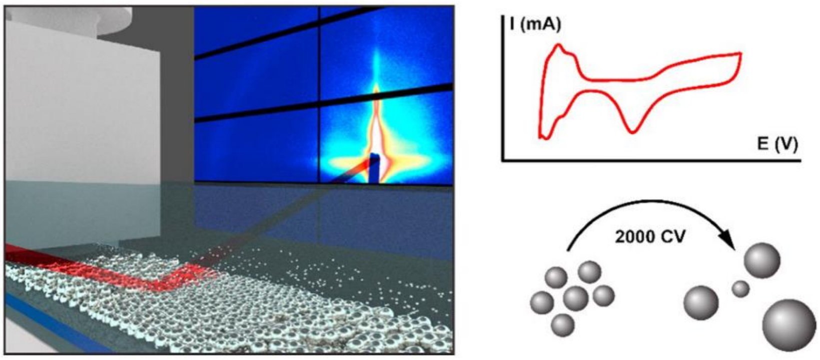

Fig. 1 Electrochemical Cell with GISAXS pattern of a Pt film (left) during cyclic voltammetry protocol (right, top), which causes the growth of Pt particles after 2000 cycles due to Ostwald ripening (right, bottom).

**Keywords**
electrochemistry, GISAXS, fuel cells, dealloying, ostwald ripening, coarsening

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SESSION 5C: INTERFACES, SURFACES AND GRAZING INCIDENCE 1
Chair: Dr. Paula C. Angelomé

# P321 - IN OPERANDO MONITORING TEMPLATED ELECTRODEPOSITION OF PT FILMS WITH HEXAGONAL PORE STRUCTURE BY SYNCHROTRON GISAXS

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Liquid crystal (LC) templated electrodeposition is a facile and versatile method to electrodeposit metal films with highly structured mesopores. These mesopores are essential to increase surface area for electrocatalysis and sensing. Previous studies showed that LC templating allowed to tailor pore size[1,2], shape[3,4], and orientation[5] of the pores in the deposited film. Generally, these studies suggest that the pores in the film inherit the structure of the LC template.

However, little is known about the interplay between the kinetics of the templated deposition, i.e. the transition from the structure of the LC template to the resulting film. A better understanding of this interplay requires in operando monitoring structural changes during the templated electrodeposition process.

In this work, we characterized the surface structure of Au substrates during templated electrodeposition of Pt with in operando Grazing Incidence Small Angle X-Ray Scattering (GISAXS).

We were able to identify a series of structural changes at the film surface: Initially, a nucleation burst of Pt coincides with a loss of preferential alignment of the LC. The morphology of the nucleated Pt corresponds to the substrate. At later stages of deposition, the morphology of the Pt film changes, and vertically aligned pores form. These findings potentially lead to more effective electrodeposition routines and films with higher accessible surface area.

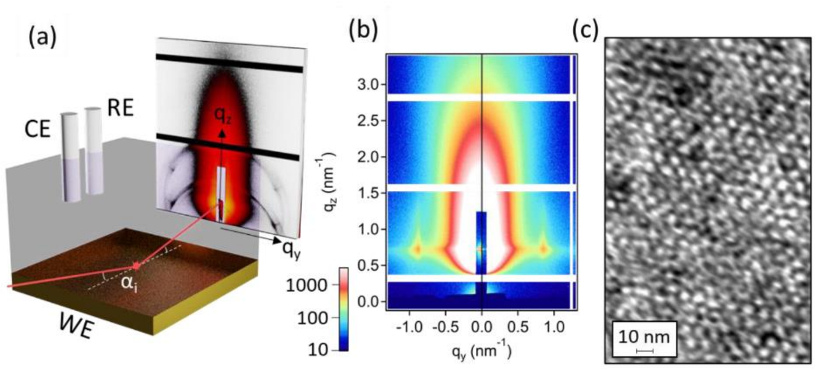

Figure 1: *Operando* GISAXS experiment during templated electrodeposition of Pt films: (a)Schematic experimental setup, (b) GISAXS pattern of mesoporous Pt film after deposition and removal of electrolyte. Vertical streaks at $q_y=\pm0.9\text{nm}^{-1}$ indicate vertical preferential alignment of the pores in the Pt film. (c)TEM image of mesoporous Pt film showing hexagonal pore structure.

## Keywords

Electrochemical Deposition, Liquid Crystal, Soft template

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## SESSION 5C: INTERFACES, SURFACES AND GRAZING INCIDENCE 1

Chair: Dr. Paula C. Angelomé

# P167 - SPONTANEOUS SURFACE ADSORPTION OF AQUEOUS GRAPHENE OXIDE BY SYNERGY WITH SURFACTANTS

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Finding new materials and systems that can stabilise interfaces in the forms of emulsions, foams and more is of continuous interest and importance in the field of colloid science. Conventionally, molecular surfactants have fulfilled this purpose, as their amphiphilic nature drives them to locate at interfaces and reduce interfacial tension. However, surfactant-stabilised emulsions (and foams) are only kinetically stable, and phase separation tends to occur within days or even hours. Pickering or particle-stabilised emulsions are viable alternatives for overcoming this issue, as the energy barrier for effecting their desorption from the interface (leading to destabiliation of the system) is much higher than for surfactants, giving longer lifetimes.

Graphene oxide (GO) is an emerging colloidal 2D nanomaterial that could serve as such a Pickering stabiliser. GO has an extraordinarily high surface area and is easily dispersed in aqueous environments. However, as a pure aqueous dispersion, GO sheets do not spontaneously adsorb at the air–water interface due to their high negative surface potential (– 60 mV) and hydrophilic functionality. However, when incorporated with surfactant molecules at optimal ratios and loadings, GO sheets can spontaneously be driven to the surface. It is hypothesised that the surfactant molecules experience favourable attractive interactions with the surfaces of GO sheets, resulting in co-assembly that serves to render the sheets surface active e.

This spontaneous adsorption of graphene oxide (GO) sheets and surfactants at the air–water interface is explored using X-ray reflectivity (XRR) measurements performed at the Australian Centre for Neutron Scattering, Lucas Heights, Australia. Addition of too much surfactant appears to inhibit GO surface adsorption by saturating the interface, and low loadings of GO/surfactant composites (even at optimal ratios) do not show significant adsorption indicating a partitioning effect. Lastly, surfactant chemistry is also a key factor dictating adsorption capacity of GO, with the greatest effects observed for nonionic and zwitterionic surfactants and GO (Fig 1.).

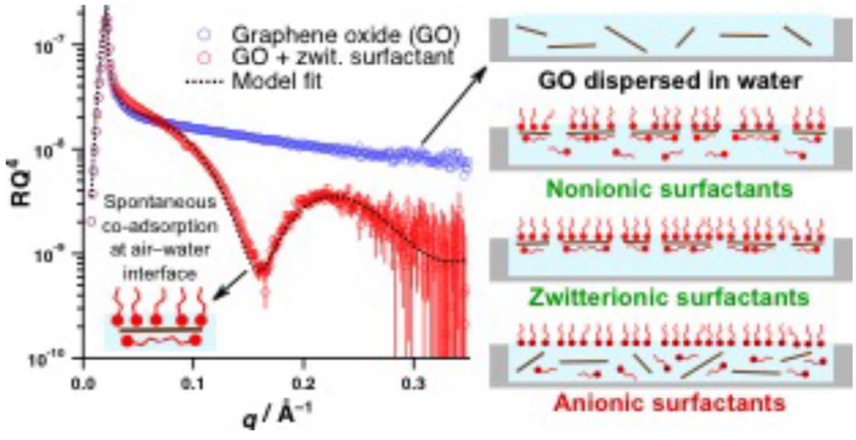

Fig.1 – XRR patterns measured of the air-water interface from a solution with pure aqueous GO sheets and aqueous GO sheets with zwitterionic surfactant. The schematics on the right illustrate the surface activities for the various GO/surfactant composites analysed.

**Keywords**
Graphene, surfactants, adsorption

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# V299 - LATEST RESULTS ON THE COMBINATION OF SMALL ANGLE X-RAY SCATTERING AND DEEP X-RAY LITHOGRAPHY FOR INTERDISCIPLINARY RESEARCH

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Interdisciplinarity is becoming fundamental in the combination of microfabrication and characterization techniques both aimed at the construction of new micro/nanodevices and at the development of novel materials. In this communication, we underline the advantages obtained combining Small Angle X-ray Scattering (SAXS) for investigation and Deep X-ray Lithography (DXRL) for microfabrication. SAXS is a standard method for structural characterization at the nanoscale. Its strength also relies in its excellent in situ capabilities. DXRL is a lithographic technique that induces changes in materials due to the effect of high energy X-rays (3–20 keV). It gives patterns with high resolution and penetration depth leading to high aspect ratio, vertical sidewalls, and optical quality surfaces. It allows producing microcomponents for micromechanics, microoptics, microfluidics, microelectronics. DXRL can also be employed in the irradiation of novel materials and in the study of the related structural and functional changes. We will present the latest results from the research performed at the Austrian SAXS beamline and at the DXRL beamline at Elettra- Sincrotrone Trieste (Italy). We will first describe our recent activity on mesoporous materials. After the investigation of their structure and correspondent mechanical properties upon irradiation [1] we proceed to a practical application: their use as active sample holders to deliver fluids through the pores [2]. We will then report on the structural changes induced by X-rays on the precursor of cellulose TMSC (Trimethylsilyl cellulose), and on its application as double tone resist for the fabrication of (bio)microfluidic devices [3]. We will show the microstructuring of noble metal xerogels that are subsequently thermally converted into the corresponding metals [4]. Finally, we will present the direct patterning of Metal Organic Frameworks (MOFs) to obtain a methanol vapour sensor [5], opening the possibility to fabricate microdevices composed of tailored MOFs.

**Keywords**
SAXS, Deep X-ray Lithography, functional materials, radiation assisted synthesis and processing of materials, interdisciplinarity

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PLENARY 4

# P126 - RECENT ADVANCES IN SMALL-ANGLE SCATTERING AND THE APPLICATIONS THEY SERVE FOR HARD MATERIALS

Chair: Dr. Florian Meneau

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Major innovations in small-angle X-ray and neutron scattering (SAXS and SANS) at major X-ray and neutron facilities offer a wide range of new characterization tools for researching materials phenomena and processes relevant to advanced applications.

The new generation of diffraction-limited storage rings, incorporating multi-bend achromat (MBA) concepts, dramatically decrease electron beam emittance in the ring, and significantly increase X-ray brilliance over previous 3rd generation sources. For most synchrotron based SAXS, the main result is intense X-ray incident beams that are more compact in the horizontal plane, allowing significantly improved sample spatial resolution, faster run times, and better time resolution. For sufficiently small incident beams, a few tens of micrometers in diameter, such sources offer a new era for coherent-beam SAXS methods such as X-ray photon correlation spectroscopy (XPCS) studies of particle or other material dynamics [1]. Meanwhile, X-ray free-electron laser (XFEL) sources, providing extremely bright, fully coherent, X-ray pulses of 100 femtoseconds or less, now support SAXS studies of material processes where entire SAXS datasets can be collected in a single pulse [2].

SANS facilities continue to evolve at both reactor-based steady-state and pulsed spallation neutron sources. Developments in neutron optics and multiple detector carriages now enable data collection in a few minutes for materials characterization over nanometer-to-micrometer scale ranges [3]. This significantly opens up real-time studies of material processes acting over extended length scales, e.g., reactions in hierarchical systems or rheological SANS (rheoSANS) investigations of particle slurries and suspensions [4] (Fig. 1). At pulsed neutron sources SANS can be increasingly integrated with total scattering (TS) studies of local ordering in complex materials, or with neutron diffraction (ND) for engineering materials and alloys [5]. Meanwhile, polarized SANS and spin echo SANS (SESANS) are becoming established in investigating exotic magnetic ordering phenomena in materials, e.g., skyrmions.

At both X-ray and neutron facilities, increasingly advanced coherent imaging modes have been developed, some exploited in parallel with SAXS and SANS to establish a more quantitative visualization of complex material microstructures. Many of the above innovations have also led to corresponding developments for grazing incidence studies of 2D surface morphologies, thin films and coatings.

Some of these developments will be reviewed and discussed with regard to state-of-art studies directed at hard matter applications, and future prospects highlighted.

**Keywords**
materials characterization, operando, instrumentation, processing

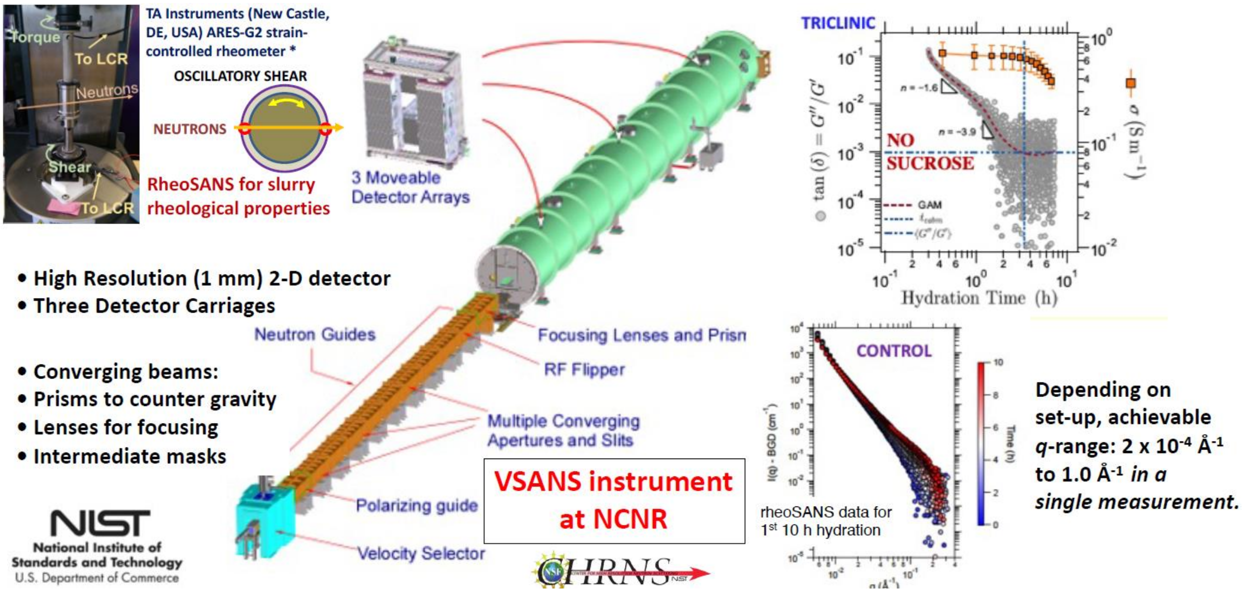

Fig. 1. NIST VSANS at NIST Center for Neutron Research (NCNR) with small-amplitude oscillatory shear (SAOS) cell, example real-time data for hydrating cement, rheology data for shear moduli: G', G'' and electrical conductivity, σ.

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SESSION 6A: MATERIALS SCIENCE 2
Chair: Dr. Bernhard Schummer

## V220 - THE NSOFT AUTONOMOUS FORMULATION LABORATORY: X-RAY AND NEUTRON SCATTERING FOR INDUSTRIAL FORMULATION DISCOVERY

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While scattering methods (SAXS, SANS, WAXS) are workhorse techniques for characterizing model macromolecular formulations, they have not been widely used to characterize real products, largely because the large number of components (10-100) often precludes rational mapping between component fractions, structure, and product stability. Multimodal characterization and machine learning (ML) tools promise to greatly reduce the expense of exploring the stability boundaries of a particular, desirable phase in highly multicomponent products. Here we describe the development of the Autonomous Formulation Laboratory, a highly adaptable platform capable of autonomously synthesizing and characterizing liquid mixtures with varying composition and chemistry using x-ray and neutron scattering in addition to a suite of secondary measurements such as optical imaging, UV-vis-NIR and capillary rheometry. We will highlight our efforts in deploying an active-learning agent which controls all aspects of the AFL including sample composition choice, sample preparation, characterization, and analysis. Using our agent, we can resolve phase boundaries at high resolution with as much as a 95% reduction in measurement time compared to a naïve grid search.

**Keywords**
Autonomous Experiments, Machine Learning, Artificial Intelligence, Formulations

SESSION 6A: MATERIALS SCIENCE 2
Chair: Dr. Bernhard Schummer

# P219 - DEVELOPMENT OF SERIAL X-RAY SCATTERING MEASUREMENTS FOR STRUCTURAL ANALYSIS OF CARBON FIBRE FILAMENTS

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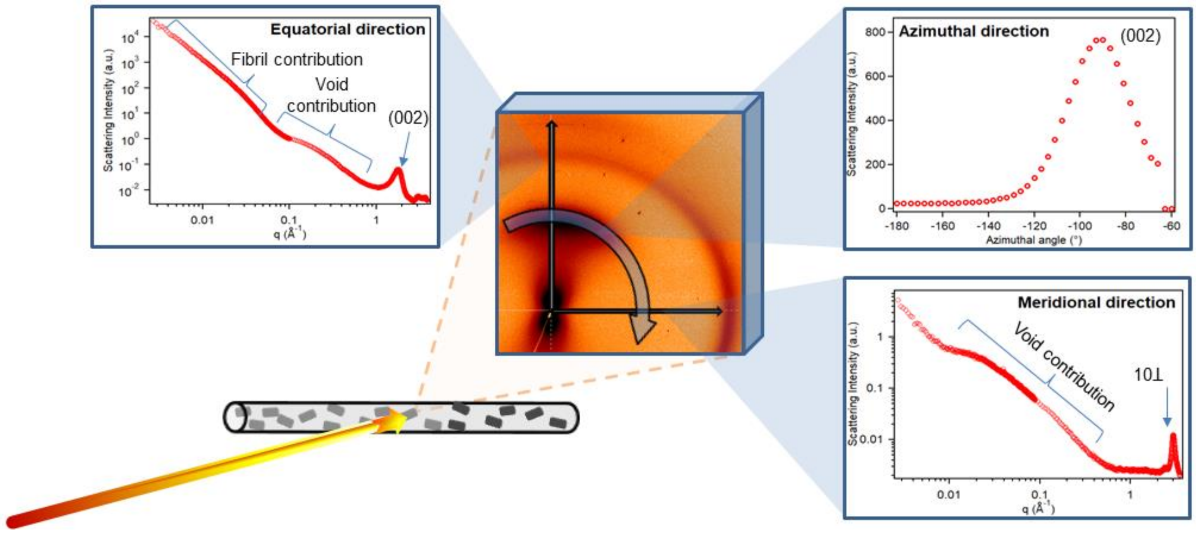
A new methodology for the optimization of X-ray scattering measurements of carbon fibre (CF) filaments has been developed at the small- and wide-angle X-ray scattering (SAXS/WAXS) beamline at the Australian Synchrotron. The new characterisation procedure - referred to as monofilament serial SAXS/WAXS scattering – is a fully automated protocol to measure with high accuracy the microstructural heterogeneity along the axis of individual fibre filaments. The underpinning measurement routine ensures the scattering cross section is maintained while scans are acquired along several millimetres of the fibre at a step resolution of ~250mm. This serial measurement approach is enabled by installation of a new ultra-high vacuum (UHV) experimental environment available on the SAXS/WAXS beamline. These in-vacuum measurements ensure maximum sensitivity and greatly reduced acquisition time due to very low levels of background scattering. The methodology is complemented by rapid detector positioning for fast access to SAXS/WAXS measurements without modifying the experimental conditions. In this work, a SAXS/WAXS study is presented of the microstructure and evolution, from PAN-precursor to standard grade CFs, along the seven different processing stages in the carbonisation line at Carbon Nexus of Deakin University for better understanding of the processing parameters on the CFs structure. Furthermore, the microstructure of the manufactured CFs was benchmarked with a known industry standard such as the Toray T300. The results showed that less structural disorder in the Nexus CFs lead to a similar tensile strength but higher modulus than the T300. Also, a smaller void diameter appears to compensate for the impact of higher void content on the tensile strength of the Nexus CF.



**Keywords**
Carbon Fibre, Polyacrylonitrile (PAN), Microstructure, Mechanical properties

SESSION 6A: MATERIALS SCIENCE 2
Chair: Dr. Bernhard Schummer

## V221 - SYNCHROTRON SCATTERING METHODS FOR SOFT MATERIALS INDUSTRIAL RESEARCH AND DEVELOPMENT

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Consumer products based on soft matter technology very often exhibit macroscopic properties, which are strongly dependent on their micro- and nano-structures extending over multiple size scales. Synchrotron Small-Angle X-ray Scattering (SAXS) techniques pro-vide complementary information to electron and optical microscopy and help researchers to gain better insight into the structural details of a given specimen from atomic or molecular to micron scales. Typical systems investigated span over a wide range of soft materials such as polymers, liquid crystals, colloids, surfactants, etc., related (noncrystalline) biological systems such as proteins, nucleic acids, membranes, tissues, bones, and multi-component mix-tures like detergents, food ingredients, pharmaceuticals, etc. Modern synchrotron SAXS instruments cover more than four or-ders of magnitude in length scales, corresponding to real-space dimension from the µm down to the Angstroms facilitating the investi-gation of hierarchical structures. Furthermore, the high photon flux and collimation enable time-re-solved ex-periments down to millisecond range, even with dilute samples and often high angular resolution. The scattering techniques can be combined with various sample envi-ronments (e.g., in-situ rheology, rapid mixing, varying temperature, humidity or pressure) for probing in-situ real-time structural dynamics, crystallization/dissolution kinetics, or out-of-equilibrium dynamics. Sub-micron beams enable high real-space spatial resolution studies of heterogenous specimens.

The European Synchrotron Radiation Facility (ESRF) operates a suit of advanced instruments with a wide range of sample environ-ments mimicking industrial processing conditions and operated by a dedicated staff of experts. Industrially relevant research is supported both through collaborations / partnerships with industry, as well as through fast and flexible access via proprietary experiments. For the investigation of complex multi-component systems, the available techniques can also be combined.

This contribution will illustrate the state-of-the-art performance of the following synchrotron scattering techniques by recent examples of industrial relevance. New possibilities offered by the ESRF EBS (Extremely Brilliant Source) Upgrade in 2019/2020 will be discussed.

- The Small-Angle, Ultra Small-Angle and Wide-Angle X-ray Scattering (SAXS/USAXS/WAXS) instrument at ESRF combines the three techniques in a unique instrument, covering a wide scattering vector (q) range of 10-3 nm-1 ≤ q ≤ 50 nm-1 using 1 Å X-ray wave-length. The high angular resolution is achieved by a combination of high degree of collimation, long sample-to-detector distance (~31 m) and high-resolution detector. In addition, for an appropriate system, it is possible to probe equilibrium dynamics over these time and length scales by X-ray Photon Correlation Spectroscopy (XPCS), and out-of-equilibrium dynamics by combined rheology and SAXS (Rheo-SAXS) and rapid mixing techniques. XPCS is complementary to dynamic light scattering and suitable for turbid samples
- Scanning micro-/nano-beam SAXS/WAXS and single micro-crystal/fibre diffraction (µXRD) allows the local nanostructure of very small objects to be mapped, like micro-specimens of composite materials, micromechanical parts, polymer fibers, microfluidics and biological specimens with an X-ray beam of 200 nm to 2µm size.

**Keywords**
(ultra) small-angle X-ray scattering; micro-/nano-diffraction; out-of-equilibrium dynamics, in-situ studies, industrial applications

# V413 - SMALL ANGLE SCATTERING FOR MANUFACTURING

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Advanced manufacturing is an engine to the goal of economic growth and receives increasing attention from industrial, academic, and governmental bodies. Compared with conventional manufacturing, advanced manufacturing integrates new innovative technologies in both products and processes. In other words, the outcome of advanced manufacturing is often process-driven. Hence, time-resolved measurements are required to understand the material's response to processing conditions,

Advanced engineering materials produced by advanced manufacturing frequently have hierarchical structures. Synchrotron-based small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) provide a unique window to peer into the dynamically driven phase transformation and microstructural evolution. In recent years, in a collaboration between the National Institute of Standards and Technology and the Argonne National Laboratory, both in the United States, we have investigated some of the most challenging questions faced by advanced manufacturing, including additive manufacturing of metals and advanced processing of ceramics. In this talk, we will use examples to highlight the significant values of kinetics datasets in understanding these complicated manufacturing processes, not just as experimental evidence to elucidate the unconventional transformations but also as critical validation data to benchmark and validate the modeling predictions to accelerate the product development and certification of these advanced engineering materials.

## Keywords

advanced manufacturing, additive manufacturing of metals, kinetics, processing, ceramics

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SESSION 6B: INSTRUMENTATION, DATA, FORMAT AND BEAMLINES 1
Chair: Dr. Tomas Sigfrido Plivelic

# P133 - TOWARDS 6 DECADES OF SIZES - NEXT GENERATION USAXS INSTRUMENT AT APS-U

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APS USAXS instrument has been available to user community for over 22 years and during this time its users published over 650 journal publications and theses. While this instrument has yet to find serious synchrotron based following, multiple commercial devices are currently available and provide similar capabilities, albeit at much longer data collection times and lower X-ray energies. APS upgrade, planned for 2023/2024, will result, among others, in major increase in brightness and reduction in X-ray divergence, offering capabilities which will enable major performance improvements of our next generation APS USAXS. This new device, planned to be installed and commissioned in fall of this year, will extend the low Q range to below 3e-5 [1/A] with possibility to reduce this low Q range even lower in the future. X-ray energy range will be extended to approximately 10 – 30 keV. This will allow study of materials (such as metal alloys) that are hard to perform using commercial USAXS lab source devices. In combination with improved SAXS and diffraction (WAXS) devices, next generation USAXS-SAXS-WAXS will offer up to 6 decades of scatter size characterization. Taking advantage of higher X-ray flux of new APS, data collection times will decrease by at least factor of 2 to less than 90 seconds for full data set; faster data collection is important for in-situ time-resolved studies (such as temperature dependent studies). Overall, next generation USAXS will provide world-unique facility with combined capabilities of USANS instrument for low-q range, SAXS instrument for medium Qs, and powder diffraction device on high-q/WAXS, with penetration capabilities comparable with neutrons for many materials but much shorter times. This new instrument will be available to general user community after APS-U and commissioning, likely by the end of 2024. This talk will present design of the new device, preliminary results obtained on existing instrument, and planned capabilities which user community should find useful to understand.

**Keywords**
Ultra-Small X-ray Scattering Instrument, USAXS

SESSION 6B: INSTRUMENTATION, DATA, FORMAT AND BEAMLINES 1
Chair: Dr. Tomas Sigfrido Plivelic

# P218 - LOW DIVERGENCE MICROFOCUS SAXS AT BEAMLINE I22, DIAMOND LIGHT SOURCE

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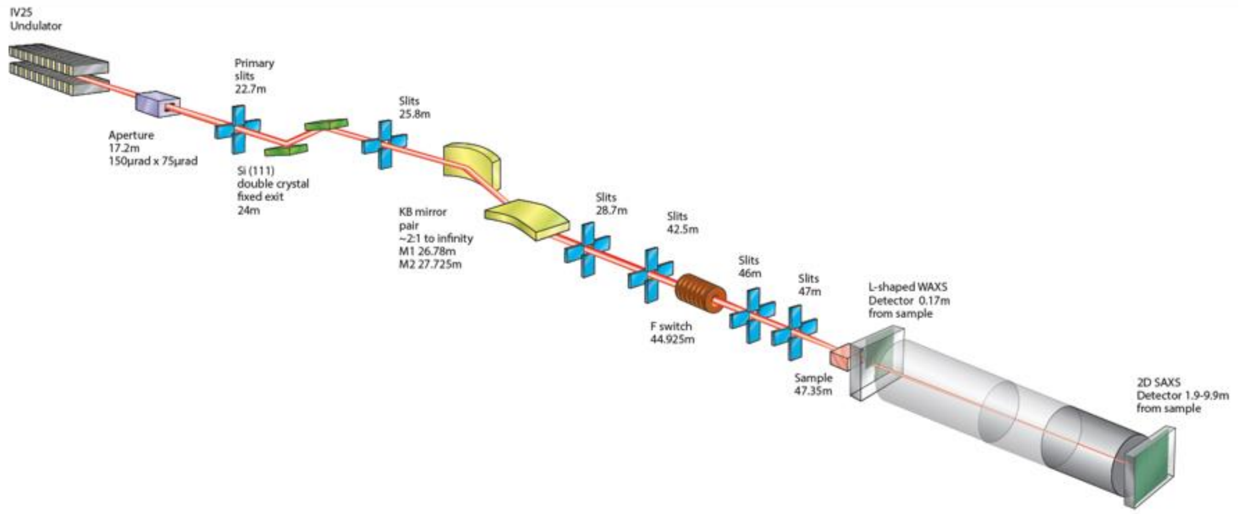
Many samples that one would wish to study with SAXS could benefit from using a smaller beam as a probe. This may be because the sample is physically small, or there may be spatial inhomogeneity of the structural features one wishes to probe. The ability to dictate probe size is a very useful addition to a SAXS beamline's repertoire. Particularly with the advent of techniques such as Gi-SAXS, SAXS Tomography, and SAXS Tensor Tomography.

Small beams can be achieved, quite simply, by restricting the beam size with slits, but this comes with a severe flux penalty for achieving the smallest beams. More sophisticated schemes, utilising focussing optics, can be envisioned and each has attendant pluses and minuses to the approach.

Since 2009, beamline I22 at Diamond has had a microfocus capability, around which has built a succesful programme of research into atmospheric pollutants4-5, soft matter and biomaterials1-3, including bone and other soft tissues

In 2018 the facility was upgraded to provide what we now think is the best compromise between usability, flux, beam size, and beam divergence.

This talk will describe both iterations of the facility. We will enumerate the various tensions between the competing priorities, why the various design decisions were made, and show some science examples.



**Keywords**
Microfocus, Divergence, Data Quality

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# V137 - THE NEW SMALL ANGLE X-RAY SCATTERING BEAMLINE FOR MATERIALS RESEARCH AT PETRA III (SAXSMAT – P62)

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To expand the SAXS capabilities at the PETRA III storage ring at DESY a new dedicated SAXS beamline has been built in the last years and is now in regular user operation. The new SAXSMAT beamline P62 is dedicated to perform combined small- and wide-angle X-ray scattering mainly in transmission mode. The beamline is focusing on the following key techniques: anomalous SAXS, SAXS computed tomography (SAXS/WAXS Tensor Tomography1 or SAXS/WAXS Invariant Tomography2), and combined SAXS/WAXS techniques for in-situ and operando studies. The beamline aims at in-situ and operando characterization of structural and functional materials (soft- and hard condensed matter), and catalytic and electrochemical processes by a combination of SAXS/WAXS, and multi-probe imaging techniques. Furthermore, X-ray energy scans comparable to EXAFS can be done within a couple of minutes as well. This feature is needed to explore the anomalous scattering contribution in different fields of science.

The SAXS-instrument is based on a 13m long and 1m diameter evacuated tube system in which the SAXS detector (in vacuum Eiger2 X 9M) can be continuously moved along the beam direction. In front of the SAXS-tube, a specially designed cone allows the installation of a WAXS detector (Eiger 2X 4M-DESY) for simultaneous SAXS/WAXS measurements. The sample area is an open space that allows the installation of different kinds of sample environments setups either from P62 or from the users. A small vacuum sample chamber is available for low scattering samples. A large helium-filled chamber with high-resolution nano-positioners is available for SAXS-tensor tomography. Both sample environments are designed such that combined SAXS/WAXS measurements with lower background scattering can be performed.

Within this contribution the following topics will be presented:

Current status and performance of the SAXSMAT beamline

Showcase for anomalous SAXS/WAXS to determine an organic surfactant layer on top of metallic nanoparticles

Showcase for SAXS tensor tomography to obtain a 3D representative model in real space describing the nanostructure

Showcase for in-situ synthesis study of the formation of ZnO particles

## Keywords

SAXS/WAXS, ASAXS, SAXS-CT, SAXS-TT

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## V293 - DESIGN AND PERFORMANCE OF THE RESONANT SOFT X-RAY SCATTERING STATION AT NSLS-II

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A polarized resonant soft x-ray scattering (RSoXS) station for soft matter characterization was recently built by the national institute of standards and technology (NIST) at the national synchrotron light source-II (NSLS-II). The RSoXS station is located within the spectroscopy soft and tender (SST-1) beamline suite at NSLS-II located in Brookhaven National Laboratory, New York. The RSoXS station was designed for measurements of soft matter in both in situ and vacuum sample environments. The beamline features a novel optical design and the station includes a dual detector setup, two sample manipulators and compatibility with sample holders designed for transition electron microscopy (TEM). We will cover the performance of the beamline and measurement station, including energy resolution and degree of variable polarization, the higher harmonic content and suppression methods, the extent and mitigation of the carbon absorption dip on optics, and the experimental and data management system.

**Keywords**
Beamline, Soft X-rays, RSoXS, resonant scattering

SESSION 6C: COLLOIDS AND POLYMERS 3
Chair: Dr. Anjani Kumar Maurya

## P244 - WHAT DO COSMETICS, PETROLEUM, AND NANOCATALYSTS HAVE IN COMMON IN LIGHT OF SAXS?

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Physical chemistry of colloids is a field where fundamental science often meets applications. We can transpose the knowledge of concepts and phenomena between different areas, such as cosmetics, oil production, catalysis, diagnostics, and displays. It has allowed our group to research different fields by comprehending phenomena at the nanoscale and their relationship with the macroscopic properties. For that, structural characterization of the colloids is essential, and SAXS has been the main tool.

Most cosmetics are formed by colloids, from emulsions (very common) to nanoparticles (still a challenge), and we have used SAXS to characterize several of them. Lamellar liquid crystals generally stabilize emulsions from moisturizers and hair conditioners. However, the stabilization mechanism was not fully described before. So, we used SAXS to study the formed structures, revealing several kinds of organization, which depend on the method of homogenization, and directly affect the stability and rheological properties.

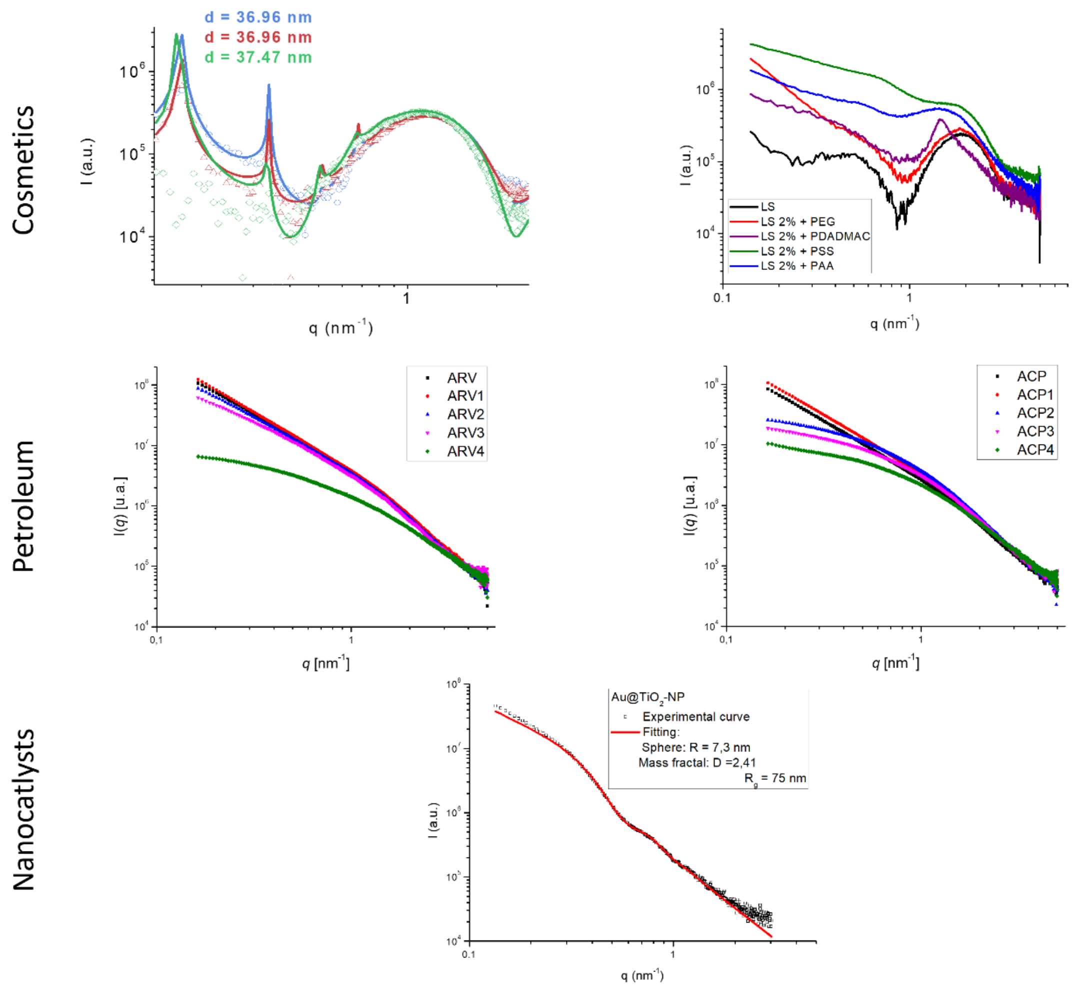
Liquid crystals dispersed as micro- or nanoparticles can also be used as a vehicle for oily ingredients. We have prepared soft particles (using only surfactants, polymers, and fatty alcohols) with a liquid-crystalline core capable of uptake and slowly releasing oily ingredients in cosmetics, such as sunscreens and insect repellents. The core structure was elucidated by SAXS, which allowed the correlation between the choice of molecules and the uptake capacity and stability.1

The growing consumer demand for biobased and biodegradable ingredients is making the industry replace some of the most common surfactants used in cosmetics. Stereamidopropyldimethylamine and sodium lauryl sarcosinate are two of the main substitutes. However, their interaction with other ingredients present in the formulations was still scarcely studied, making it difficult to control products final properties. We used SAXS to elucidate the assemblies formed by these surfactants in the presence of different organic acids and polymers, to understand and control their effects on the formulation.

The study of colloids has contributed significantly to the progress of petroleum field, mainly for fuels and lubricating oils. However, the colloidal research on crude oil is still incipient. The asphaltenes aggregates are still a problem for oil production, and we used SAXS to characterize the colloids formed by different fractions of them. We obtained the aggregates dimension and degree of organization, and distinguished which were the problematic fractions.2

Finally, we also used SAXS to characterize inorganic nanoparticles prepared for photocatalysis. Janus nanoparticles formed by a gold core and a semi-shell of titania promoted the water photolysis to obtain hydrogen as a green fuel. SAXS was necessary to confirm the structure and dimensions observed by microscopy and mainly to determine titania fractality, which is essential for catalytic properties.

These results show SAXS can elucidate various colloidal structures present in applications, making possible the correlation with the physicochemical properties. This understanding is vital for controlling the properties and transposing the knowledge between the different areas.



Examples of SAXS results of diferente samples classified by field of application.

**Keywords**
Colloids, Surfactants, Polymers, Cosmetics, Petroleum

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SESSION 6C: COLLOIDS AND POLYMERS 3
Chair: Dr. Anjani Kumar Maurya

# P348 - THE EVOLUTION OF EQUILIBRIUM NAPSS / DTAB SUPRAMOLECULAR STRUCTURE IN DILUTE AQUEOUS SOLUTION WITH INCREASING SURFACTANT BINDING

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In the past decades comprehensive research has been carried out in order to understand the behaviour of complexes of oppositely charged polymer polyelectrolytes and surfactants (P/S). A general feature of P/S system is that they self-assemble into supramolecular structures above a certain surfactant concentration, the critical aggregation concentration (cac). There are several studies aiming at describing the structural and phase properties of P/S systems. In the literature, two main topics have been investigated: i), the structure of the precipitate in the equilibrium two-phase region, and ii) the structural evolution of the complexes as a function of the polymer/surfactant ratio. In the phase-separation region, examples of hexagonal, lamellar, and cubic structure have been identified. At the same time, there is little information about the structure of the complexes in the one-phase region and only a few studies have been published dealing with the effect of surfactant concentration on the morphology of P/S aggregates. Despite that one of the most investigated P/S systems is the dodecyl trimethylammonium bromide (DTAB)/ sodium polystyrene sulfonate (NaPSS) mixture, structural information about this system is practically not available in the literature.

In our study we prepared several 17 kDa NaPSS/DTAB samples with increasing DTAB and constant NaPSS concentrations in the equilibrium one-phase region and we also prepared stoichiometric NaPSS/DTAB precipitate. Since in the recent decades, it has been clearly shown that the high charge density P/S mixtures are prone for formation of kinetically arrested non-equilibrium aggregates, we used a novel sample preparation method to facilitate the formation of the equilibrium non-aggregated P/S complexes in the entire investigated surfactant concentration range. We measured the binding isotherm and simultaneously, we performed small-angle X-ray scattering measurements and performed data modelling with least-square fitting method on absolute scale. We showed that by increasing the binding ratio the formed complexes exhibit an elongated to spherical transition which ends with well-defined precipitate with hexagonally closed packed structure with spherical particles at the crystal lattice points. We also showed that the addition of indifferent electrolyte (NaCl) changes the structural behavior of the system and yields amorphous structure. Summarizing, we have now connected the binding isotherm to the evolution of the structural features of complexes in the equilibrium one phase region and to the structure of the phase separated stoichiometric precipitate.

**Keywords**
polyelectrolyte, surfactant, SAXS, structure

SESSION 6C: COLLOIDS AND POLYMERS 3
Chair: Dr. Anjani Kumar Maurya

## P254 - DIRECTING CYCLODEXTRIN-SURFACTANT INCLUSION COMPLEXES SELF-ASSEMBLY

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Cyclodextrins (CD) are a class of cyclic oligosaccharides formed by α-(1-4) linked D-glucopyranoses units. The shape and the presence of a cavity in their molecules provide remarkable physicochemical properties and the unique ability to form inclusion complexes with a variety of molecules, such as drugs, polymers, and surfactants. Cyclodextrin-surfactants host-guest complexes are a flourishing research field due to the availability and diversity of surfactants and their tendency to self-organize into highly ordered structures1. Among the surfactants available to integrate the complexes, the polyoxyethylene alkyl ether carboxylic acids (CiEjCH2COOH) are particularly interesting candidates due to their pH and temperature responsiveness 2.

CD-surfactant inclusion complexes can spontaneously assemble into complex designs of different shapes and orders of magnitude as a result of a balance of forces. One of many challenges is controlling and directing the self-assembly process to obtain the desired structures linked to their function-oriented potential. Different strategies to control it have been investigated based on the response to external stimuli, such as light, pH, and temperature, or the addition of another component to the system as, for example, polymers.3

In this work, we use a thermodynamic and structural approach to characterize the morphology of the assemblies arising from the inclusion complexation of α-CD and β-CD with the polyoxyethylene alkyl carboxylic acids C12E5CH2COOH and C12E10CH2COOH in aqueous solutions. Small-angle neutron scattering (SANS) experiments revealed a spontaneous assembly of the inclusion complexes into highly ordered structures. In a multi-level assembly order, it was possible to tune the structures by exploring the components' concentration, cyclodextrin-to-surfactant ratio, and the pH responsiveness of the surfactants. The formation of well-layered hollow cylinders was verified for the most concentrated systems at high pH, with ionized surfactant molecules, whereas crystalline platelet structures were observed at low pH. In addition, the analysis allowed unveiling the effect of the number of ethylene oxides in the surfactants and the CD cavity size on the morphology of the aggregates. Many other techniques have been used for a comprehensive structural characterization of the supramolecular aggregates, particularly differential scanning calorimetry and optical and cryo-electron microscopy. Furthermore, the addition of chitosan to the system revealed a novel parameter for the self-assembly control. The polymer addition affects the specific inclusion complexation forces, long-range electrostatic interactions, and dispersion forces within the supramolecular aggregates, influencing the CD-CD hydrogen bonding network.

### Keywords

Surfactants, Cyclodextrin, Inclusion complexes, Self-assembly, Chitosan

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## V129 - COMBINING LIGHT AND SMALL ANGLE X-RAY SCATTERING TO ASSESS STRUCTURE AND MORPHOLOGICAL TRANSITIONS OF COACERVATE MICELLES

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Complex coacervate relates to an aqueous liquid-liquid phase separation typically from mixture of oppositely charged polyelectrolytes solutions. The process produces a polymer-rich coacervate phase in equilibrium with a polymer-poor supernatant. The coacervate can be constrained to colloidal dimensions if a charged-neutral diblock copolymer is used. These nanometric aggregates are called complex coacervate core micelles (C3Ms). Their structure consists of a highly hydrated core composed by the the oppositely charged polymers surrounded by the shell formed by the neutral and water-soluble block. Previous studies demonstrated that the nature of their stability remains unclear. In the present study, C3Ms formed by a charged-neutral diblock copolymer, poly(acrylamide)-b-poly(acrylic acid), and an oppositely-charged homopolymer, poly(diallyldimethylammonium chloride), were thoroughly investigated. Dynamic light scattering and small-angle X-ray scattering measurements suggest that in some conditions the investigated structures are probably in equilibrium condition, because the aggregates did not show any significant pathway dependence nor were affected by aging. However, the stability and structure of the C3Ms can vary depending on several parameters, such as the shell density and the ionic strength. Herein, we observed that by reducing the shell density in the system, the size of the aggregate increases, maintaining their globular shape. On the other hand, a morphological change with large clusters formation was observed at higher ionic strengths. Based on these results, the boundaries of thermodynamic and kinetic regimes were defined, and can contribute to clarify fundamental aspects of this important self-assembly structure.Thermodynamic

**Keywords**
polyelectrolyte, coacervate micelles, morphological transition, thermodynamic stability

## SESSION 7A MAGNETIC MATERIALS 2

Chair: Dr. Viktor Petrenko, Prof. Andreas Michels

# V253 - DIRECTED NANOPARTICLE ASSEMBLY PROBED AT THE RECENTLY INSTALLED MAGNETIC SAMPLE ENVIRONMENT AT COSAXS, MAX IV

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Self-assembly of nanoparticles is a common route to produce mesostructured materials with high crystallographic order, i.e. mesocrystals [1]. The emergent properties of the assembled arrays can be tuned by the choice of nanoparticle size, material, and shape. Self-assembly of superparamagnetic iron oxide nanocubes, which allow for the formation of linear structures under the influence of an external magnetic field [2][3], is a fast process that requires high photon flux at synchrotron facilities to be studied in real-time. However, the availability of high and easily controllable magnetic fields in combination with synchrotron radiation allowing for time-resolved scattering experiments is sparse. We have thus developed and installed a magnetic sample environment at the CoSAXS beamline at MAX IV Laboratory (Lund, Sweden), which allows for fields of up to 3.5 T and simultaneous SAXS and WAXS measurements with 10 ms time-resolution (Figure 1). We show that an external magnetic field directed the fast formation of linear assemblies in nanoparticle dispersions almost instantaneously after applying the field, continuous growth was detected over time, suggesting that adjacent nanoparticles initially form small chains that grow both in length and width over time. Linear assemblies have shown to have strongly anisotropic magnetic properties, making them promising candidates for biomedical applications such as hyperthermia treatment [4].

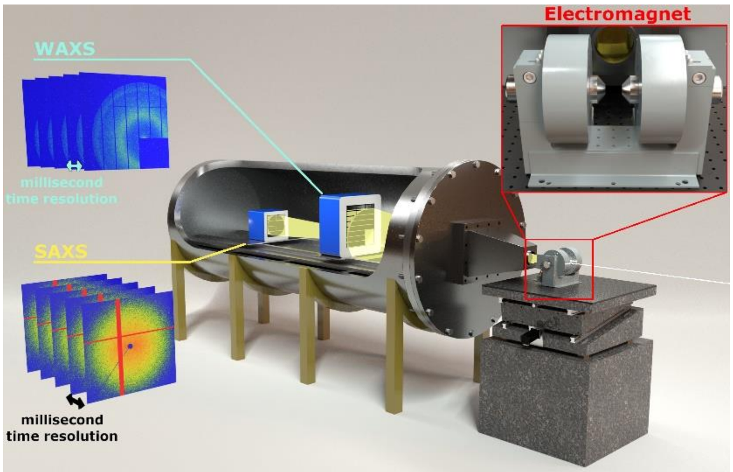

**Figure 1: Instrumental setup consisting of an electromagnet for simultaneous fast time-resolution SAXS and WAXS measurements.**

**Keywords**
Self-assembly, magnet, nanoparticle

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## SESSION 7A MAGNETIC MATERIALS 2

Chair: Dr. Viktor Petrenko, Prof. Andreas Michels

# V122 - MAGNETIC NEUTRON SCATTERING FROM SPHERICAL NANOPARTICLES WITH SURFACE ANISOTROPY: ATOMISTIC SIMULATIONS

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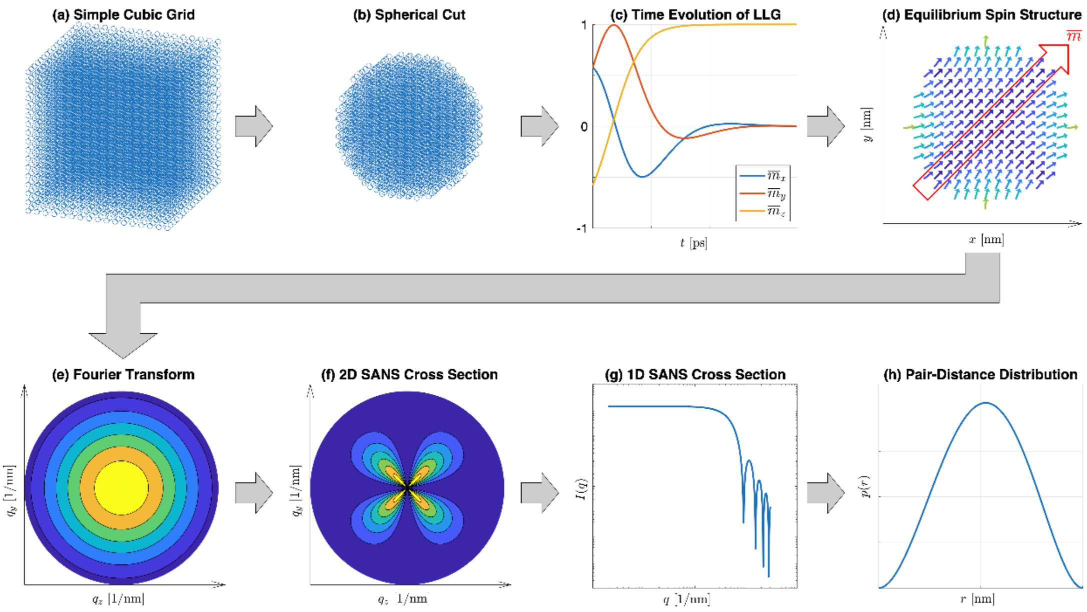
We consider a dilute ensemble of randomly-oriented spherical nanomagnets and investigate its magnetization structure and ensuing neutron-scattering response by numerically solving the Landau-Lifshitz-Gilbert equation. Taking into account the isotropic exchange interaction, an external magnetic field, a uniaxial magnetic anisotropy for the particle core, and in particular the Neel surface anisotropy, we compute the magnetic small-angle neutron scattering cross section and pair-distance distribution function from the obtained equilibrium spin structures. The numerical results are compared to the well-known analytical expressions for uniformly magnetized particles and provide guidance to the experimentalist. Moreover, the (directed) Neel surface anisotropy is compared to a random surface anisotropy and the effect of a particle-size distribution function is modeled.



**Keywords**
Magnetic Small-Angle Neutron Scattering, Magnetic Nanoparticles, Surface Anisotropy, Atomistic Simulations

**Acknowledgements**
This work was financially supported by the National Research Fund of Luxembourg (AFR Grant No. 15639149).

SESSION 7A MAGNETIC MATERIALS 2
Chair: Dr. Viktor Petrenko, Prof. Andreas Michels

# V120 - MICROMAGNETIC SIMULATION OF NEUTRON SCATTERING FROM NANOPARTICLES: EFFECT OF VACANCY-TYPE LATTICE DEFECTS

**SINAGA, Evelyn P (1); ADAMS, Michael P (1); BERSWEILER, Mathias (1); VIVAS, Laura G (1); HASDEO, Eddwi Hesky (1); LELIAERT, Jonathan (2); BENDER, Philipp (4); HONECKER, Dirk (3); MICHELS, Andreas (1)**
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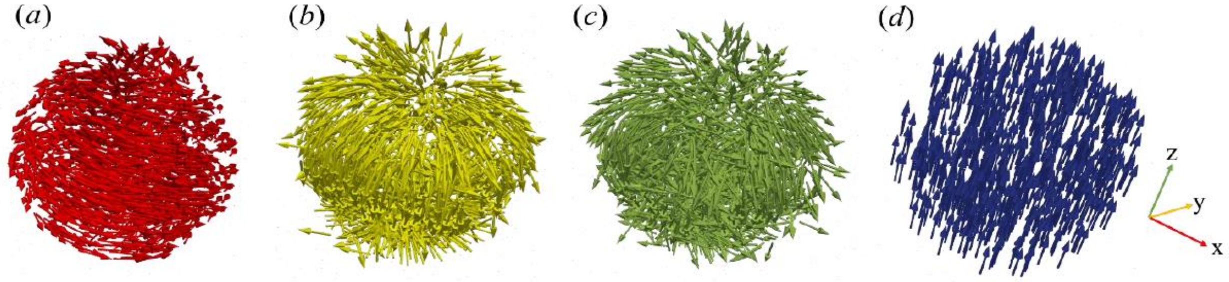
We employ micromagnetic continuum simulations to model the effect of vacancy-type lattice imperfections on the magnetic small-angle neutron scattering cross section and the related pair-distance distribution function of magnetic nanoparticles. Our expression for the magnetic energy takes into account the isotropic exchange interaction, the magnetocrystalline anisotropy, the magnetodipolar interaction, and an externally applied magnetic field. The signatures of the defects and the role of the dipolar energy are highlighted and the effect of a particle-size distribution is studied. The results serve as a guideline to the experimentalist.



Remanent state spin structures of 40-nm-sized iron spheres with defect concentrations of (a) xd = 0%, (b) xd = 5%, (c) xd = 15% and (d) xd = 0% without taking into account the magnetodipolar interaction in the energy minimization.

**Keywords**
micromagnetic simulation, continuum model, nanoparticles

**Acknowledgements**
This work was financially supported by the National Research Fund of Luxembourg (PRIDE MASSENA Grant and AFR Grant No. 15639149).

SESSION 7A MAGNETIC MATERIALS 2
Chair: Dr. Viktor Petrenko, Prof. Andreas Michels

## V121 - RESOLVING THE COMPLEX SPIN STRUCTURE IN FE-BASED SOFT MAGNETIC NANOCRYSTALLINE MATERIAL BY MAGNETIC SMALL-ANGLE NEUTRON SCATTERING

**BERSWEILER, Mathias (1); ADAMS, Michael P. (1); PERAL, Inma (1); KOHLBRECHER, Joachim (2); SUZUKI, Kiyonori (3); MICHELS, Andreas (1)**

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Small-angle neutron scattering (SANS) is one of the most important techniques for microstructure determination, being utilized in a wide range of scientific disciplines, e.g., material science, physics, chemistry and biology. The reason for its great significance is that conventional SANS is probably the only technique, which is able to investigate structural inhomogeneities in the bulk of materials and on a mesoscopic length scale of roughly 1 to 300 nm (Michels, 2021). Moreover, the exploitation of the spin degree of freedom of the neutron provides SANS with a unique sensitivity to study magnetism and magnetic materials at the nanoscale. Magnetic SANS ideally complements more real-space and surface-sensitive magnetic imaging techniques, e.g., Lorentz transmission electron microscopy, electron holography, magnetic force microscopy, Kerr microscopy, or spin-polarized scanning tunneling microscopy. Recent progress regarding the theoretical understanding of magnetic SANS allows one to disclose the interplay between the microstructure and magnetic properties, and/or to quantitatively analyze the magnetic interactions e.g. in nanoparticles systems, bulk ferromagnetic or nanocrystalline materials. The present work will focus on our recent results obtained in ultrafine-grained nanocrystalline materials (Bersweiler et al., 2022). In particular, we will demonstrate the unique ability of magnetic SANS to quantitatively analyze the magnetic interactions, namely the exchange-stiffness constant and the strength and spatial structure of the magnetic anisotropy and magnetostatic fields in (Fe0.7Ni0.3)86B14 alloy. This particular compound is a promising HiB-NANOPERM-type soft magnetic nanocrystalline material, which exhibits an ultrafine-grained microstructure with an average particle size as small as 4 nm and an extremely small coercive field of ~ 4.9 µT (Li et al., 2020). The neutron data analysis based on the micromagnetic SANS theory yields an exchange-stiffness constant of Aex = (10 ± 1) ´ 10-12 J/m, a value that is 2-3 times larger than those reported previously for similar alloys (Honecker et al., 2013). The large value of Aex together with the small grain size and low anisotropy is believed to be responsible for the extreme magnetic softness of this alloy. Furthermore, the magnitude of the extracted anisotropy-field and longitudinal magnetization scattering functions allow us to conclude that the magnetization jumps at internal particle-matrix interfaces, and the ensuing dipolar stray fields, are the main source of the spin-disorder in this material.

**Keywords**
magnetic small-angle neutron scattering, micromagnetic theory, soft magnetic materials, nanocrystalline alloys, magnetic structures

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## Acknowledgements

This work was financially supported by the National Research Fund of Luxembourg (AFR grant No. 15639149 and CORE grant SANS4NCC).

SESSION 7B: INSTRUMENTATION, DATA FORMAT AND BEAMLINES 2
Chair: Dr. Javier Pérez

# P151 - NEW OPPORTUNITIES ON BIOMOLECULAR SOLUTION STRUCTURAL STUDIES WITH THE BIOLOGICAL SMALL- AND WIDE-ANGLE X-RAY SCATTERING BEAMLINE 13A AT TPS

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Fast and rich developments recently in the instrumentation and data analysis of synchrotron small-angle X-ray scattering (SAXS) on biomolecules in solution have made biological SAXS (BioSAXS) a mature and popular tool in structural biology. Here, we report an advanced beamline developed at the beamline 13A of the 3.0 GeV Taiwan Photon Source, Hsinchu, for biological small- and wide-angle X-ray scattering (SAXS-WAXS or SWAXS). The undulator beamline is characterized with a high photon flux up to 4X1014 photons/s and a wide X-ray energy range 4 - 23 keV, for time- or energy-resolved SWAXS. The endstaton features with an in-vacuum SWAXS detecting system comprising two mobile area detectors of Eiger X 9M/1M and an online size-exclusion chromatography system incorporated with several optical probes including UV-vis absorption spectrometer and refractometer. The instrumentation and automation allow simultaneous SAXS-WAXS data collection and data reduction for high throughput biomolecular conformation and composition determinations. The performance of the endstation is illustrated with the SWAXS data collected for several model proteins in solution, covering the scattering vector q across three orders of magnitude. The crystal-model fittings to the data in the q-range ~ 0.005 – 2.0 Å-1 indicate high similarity of the solution structures of the proteins to their crystalline forms, except for some subtle hydration-dependent local details. We discuss the possible new horizons of such SWAXS capability in studying time-resolved and correlated local and global structures of biomolecules in solution.

**Keywords**
SAXS and WAXS; online size exclusion chromatography, integrated UV-Vis absorption, and refractometer, biomolecular solution scattering

SESSION 7B: INSTRUMENTATION, DATA FORMAT AND BEAMLINES 2
Chair: Dr. Javier Pérez

# P415 - UPGRADES AND DEVELOPMENTS ON SOLUTION SCATTERING BEAMLINE B21

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B21 is a small-angle X-ray scattering (SAXS) beamline with a bending magnet source in the 3 GeV storage ring at the Diamond Light Source Ltd synchrotron in the UK. The beamline utilizes a double multi-layer monochromator and a toroidal focusing optic to deliver 2 × 1012 photons per second to a 34 × 40 µm (FWHM) focal spot at the in-vacuum Eiger 4M (Dectris) detector. A high-performance liquid chromatography system and a liquid-handling robot make it possible to load solution samples into a temperature-controlled in-vacuum sample cell with a high level of automation. Alternatively, a range of viscous or solid materials may be loaded manually using a range of custom sample cells. A default scattering vector range from 0.0026 to 0.34 Å-1 and low instrument background make B21 convenient for measuring a wide range of biological macromolecules. The beamline has run a full user programme since 2013.

While B21 has mostly been targetted towards catering to the structural biology community with an EMBL style sample loading platform and a dual pump HPLC system. In recent years we have developed a mail-in program and have been expanding to broaden our capabilities to facilitate the broader soft condensed matter community. We have modified our sample environment so that solid or viscous samples such as gels, cubic phase lipids etc can be measured. These are pre-loaded into capillaries or into well in custom 3D printed sticks and the beamline now offers a mail-in service where these samples can be sent in. We have also developed facilities for in situ illumination of samples allowing us to choose wavelengths of light from the UV-VIS region for in situ illumination of light activated samples during SAXS measurements. In this presentation I will describe these developments and give some examples of science applications.

**Keywords**
SAXS, synchrotron, beamline, biosaxs

# P192 - BIOSAXS AT EMBL HAMBURG IN CORONA TIMES: BEAMLINE OPERATION AND SCIENTIFIC PROJECTS

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The last two years of pandemics with lasting lockdowns and travel restrictions were challenging for the international and mobile user community of large-scale scientific facilities. Synchrotron beamlines were urged to develop new ways to work under these conditions, in particular for experiments aiming at better describing the virus and developing therapeutics or vaccines against Covid-19.

BioSAXS is a key method in biophysics and structural biology and is one of the synchrotron techniques helping in the fight against the SARS-CoV-2 virus1,2,3,4,5. The P12 beamline of EMBL Hamburg, located on the PETRA III ring, is dedicated to biological solution scattering. It is equipped with an automatic sample changer for high throughput studies and a SEC-SAXS setup for online purification. Further experimental possibilities allow for wide-angle scattering (WAXS), anomalous scattering (ASAXS), and time-resolved SAXS (TR-SAXS).

Here, we shall present the response of the P12 team to the current pandemic. We shall describe the beamline automation that allowed a smooth transition from on-site visits to a full remote/mail-in mode, and discuss the pros and cons of this way of operation.

We shall also specifically highlight the Covid-related projects at P12. In particular, the receptor-binding domain (RBD) domain of the viral spike protein was measured in presence of synthetic nanobodies that could neutralize the virus1. Nsp7 and nsp8 are proteins of SARS-CoV-2, that assemble into oligomers and are involved in the replication of the virus. The stoichiometry and topology of Nsp7+8 complexes were determined using SAXS and mass spectrometry for seven different members of the coronavirus family2. SAXS has also been particularly useful to study and characterize the lipid nanoparticles employed to package nucleic acids in mRNA vaccine used against Covid3,4,5.

**Keywords**
SARS-CoV2, mRNA vaccine, BioSAXS, automation

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SESSION 7B: INSTRUMENTATION, DATA FORMAT AND BEAMLINES 2
Chair: Dr. Javier Pérez

# P159 - LANTHANIDE-CAGED COMPOUNDS AS EFFICIENT TOOLS FOR SAXS CONTRAST VARIATION

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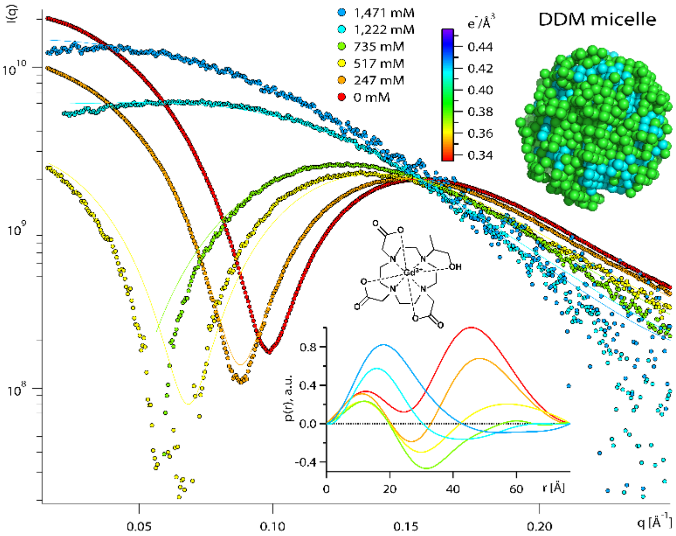
Small angle X-ray scattering (SAXS) is increasingly used to extract structural information from a multitude of soft matter and biology systems in aqueous solution, including polymers, detergents, lipids, colloids, proteins and RNA/DNA.

When SAXS data are recorded at multiple contrasts, i.e. at different electron densities of the solvent, the internal electron density profile of solubilized molecular systems can be probed. However, contrast variation SAXS has been limited by the range of electron densities available by conventional agents such as sugars, glycerol and salt, and by the fact that several soft matter and biology systems are modified in their presence.

Here we present a pioneering SAXS contrast variation study using lanthanide-caged compounds as novel and efficient tools to modify the solvent electron density and obtain information on the internal structure of complex biomolecular systems in solution. We present results from DDM micelles, from a small monomeric protein (lysozyme), a large oligomeric protein complex (Protease 1), and a protein-RNA complex (aIF2-tRNA). In all cases, the lanthanide-caged complexes reached higher electron densities than control experiments with sugar, and were inert towards the biomolecular system studied, i.e. its structural integrity was preserved. A detailed analysis of the internal structure of the DDM micelles and the protein-RNA complex was therefore possible.

Beyond an analysis of the internal structures of solubilized biomoleculecular assemblies, the SAXS contrast variation series allow equally to propose models for the interaction of contrast agents with macromolecules, as well as the interparticle interactions between isolated contrast molecules.

In conclusion, lanthanide-based compounds represent a novel and promising class of molecules for SAXS contrast variation experiments. We discuss potential applications to soft matter and biology systems, as well as strategies to alter their physico-chemical properties specifically with the aim to improve their contrast agent properties. Finally, the complementarity of this approach with solvent contrast variation and deuteration in small angle neutron scattering (SANS) is discussed.



**Keywords**
SAXS, contrast variation, electron density, biomacromolecular assembly

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SESSION 7B: INSTRUMENTATION, DATA FORMAT AND BEAMLINES 2
Chair: Dr. Javier Pérez

## V135 - SAMPLE MINIMIZING CO-FLOW CELL FOR TIME-RESOLVED SOLUTION SCATTERING AT BIOCARS 14-ID BEAMLINE AT THE ADVANCED PHOTON SOURCE

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Time-resolved crystallography provides atomic resolution structures of intermediates. However, large functional structural changes may not be accessible due to crystal packing forces. In addition, structural dynamics in the crystal may differ from the dynamics in the solution environment [1]. X-Rays solution scattering can probe a wider range of structural dynamics in molecules, albeit with much less structural resolution. In pump-probe time-resolved solution scattering, the reaction in a molecule is triggered by an external short stimulus (PUMP), afterword X-Ray scattering of the molecule is probed by a short X-Rays pulse (PROBE). Then the sample volume is refreshed and the process is repeated. A complete time-resolved experiment typically involves collecting scattering data at a number of time delays between pump and probe pulses. However, for non-reversible reactions or reactions with slow initial-state recovery, when experiments are conducted with standard 0.5mm-1mm diameter capillary flow cell, the sample consumption for the complete experiment can be as high as several hundred milligrams of protein, unsustainable value for research lab produced proteins.

At BioCARS we adopted and redesigned cytometry-style sheath flow device, initially introduced by Nigel Kirby and collaborators [2]. The cell was originally developed to decrease radiation damage of the samples during static SAXS measurements. In partnership with Kusel Design (Australia), we developed a robust flowcell, which was integrated into the BoCARS sample environment. In this setup, the flow cell can accept laser pump beams in both orthogonal and collinear (with X-Ray beam) configurations. The sample is injected through the adjustable needle in the center of the capillary filled with the matching buffer. By varying sample and buffer flow rates one can achieve different sample core/buffer sheath size ratio. In standard capillary flow cell measurements, the rate of the liquid replenishment at the capillary walls approaches zero in a laminar flow regime. Protein at the capillary walls therefore suffers radiation damage. In the co-flow cell, only the sheath buffer is in the contact with the capillary wall. This eliminates one of the main contributions of the protein radiation damage in solution scattering experiments [3].

Using a co-flow cell configuration where sample core diameter was 300μm in a 600μm capillary, we collected time-resolved data for photoactive yellow protein. We show that for the similar quality of the time-resolved data achieved in the standard flow cell experiments, the co-flow time-resolved experiment required 5-20 times less sample quantity. Singular Value Decomposition, Global Analysis and Kinetic Analysis of the data in both experiments show closely matching scattering fingerprints from intermediates, concentration time courses, and similar protein dynamics.

**Keywords**
Time-Resolved Solution Scattering, Sample Minimizing, Photoactive Yellow Protein

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SESSION 7C: COLLOIDS AND POLYMERS 4
Chair: Dr. Christian Appel

# V390 - EFFECTS OF IONIC STRENGTH ON THE THERMORESPONSIVE ASSEMBLY OF AMPHIPHILIC GRAFT COPOLYMER, POLY(ETHYLENE GLYCOL)-GRAFT-(POLY(VINYL CAPROLACTAM)-CO-POLY(VINYL ACETATE))

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We report the effect of the addition of potassium chloride on the thermoresponsive assembly of an amphiphilic graft copolymer, poly(ethylene glycol)-graft-(poly(vinyl caprolactam)-co-poly(vinyl acetate)) (commercial name Soluplus®). This polymer has received attention due to is biomedical applications as a solubalizer for drugs with poor water solubility and due to the change in its rheological properties close to body temperature. Our group has previously explored the change in physical and structural properties as this thickening process occurs. Additionally, prior research has shown the addition of salts to aqueous Soluplus® solutions has effects on the rheological properties. Here we explore the effect of ionic strength on the formation of micelles and the gelation process. Preliminary SAXS shows, in low concentration samples (<10 wt%), the addition of KCl does not affect the nanoscale structure of Soluplus®. Conversely, at higher concentrations of Soluplus®, the addition of salt can disrupt the formation of nanoscale structures.

**Keywords**
Soluplus®, Thermoresponsive polymer, Rheology, SAXS

SESSION 7C: COLLOIDS AND POLYMERS 4

Chair: Dr. Christian Appel

# V356 - SAXS/WAXS STUDY OF CROSSLINKED SINGLE-ION CONDUCTING SILICA-PEO HYBRID ELECTROLYTES FOR LITHIUM METAL BATTERIES

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Hybrid electrolytes present the potential of combining the advantages of inorganic and polymer electrolytes while overcoming their disadvantages in lithium (Li) metal based batteries [1,2]. We designed a new hybrid electrolyte which is an organic crosslinked PEO network ensuring ionic motion and inorganic (SiO1.5) crosslinking site reinforcing the mechanical properties with highly delocalized TFSI anions grafted onto the inorganic sites resulting in a homogenous crosslinked organic-inorganic hybrid material by one-pot synthesis (Figure a). Different electrolytes were prepared by varying the inorganic/PEO ratios and salt content (EO/Li ratio). The HySI electrolytes are denoted HySI_a where a is the weight fraction of grafted TFSI anions and Li cations.

SAXS/WAXS studies were performed to determine the local structure of the HySI hybrid electrolytes for various content of silica and TFSI anions (Figure b). These electrolytes contain PEO chains, grafted TFSI anions, and silica crosslinkers (APTES). The two main scatterers from SAXS point of view are this S atom from TFSI and Si from APTES, compared to the C, H, O atoms from PEO.

At 25 °C, the crystalline structure of PEO dominates the scattering profiles with lamellar phase peaks at low q and two crystalline peaks at very large q* (1.35 and 1.64 Å-1) (not shown). Above the melting temperature at T=60°C, with disappearance of crystalline peaks of PEO, the remaining scattering profile show two main scattering features. (i) At the lowest q, a scattering decay like q-a with a in between 3 and 4 and (ii) A correlation peak at ~0.26 Å-1, except for the salt-free sample (HySI_0), demonstrating that the peak stems from the presence of grafted anions. An ad-hoc model of two power laws to describe the low and intermediate q range and a Lorentzian to quantify the evolution of correlation peak was designed to fit the scattering profiles (Figure b). The detailed analysis reveals many insights on hybrid electrolyte (HySI) inner structure and its evolution with varying TFSI salt content. The main results are (i) the electrolyte structure at mesoscopic scale does not evolve upon PEO crystallization and melting, this demonstrates the high mechanical strength of the solid electrolyte. (ii) The influence of the silica content in the hybrid materials has little influence on its structure. (iii) The silica crosslinked nodes are distributed unevenly within the materials at large scale and the sample displays locally a spatial phase separation (iv) The grafted TFSI anions induces the structuration at a local scale with a given characteristic size. (v) TFSI molecules are rather homogenously distributed within the TFSI-rich domains. These detailed structural informations are correlated to the electrochemical behavior of the HySI electrolyte.

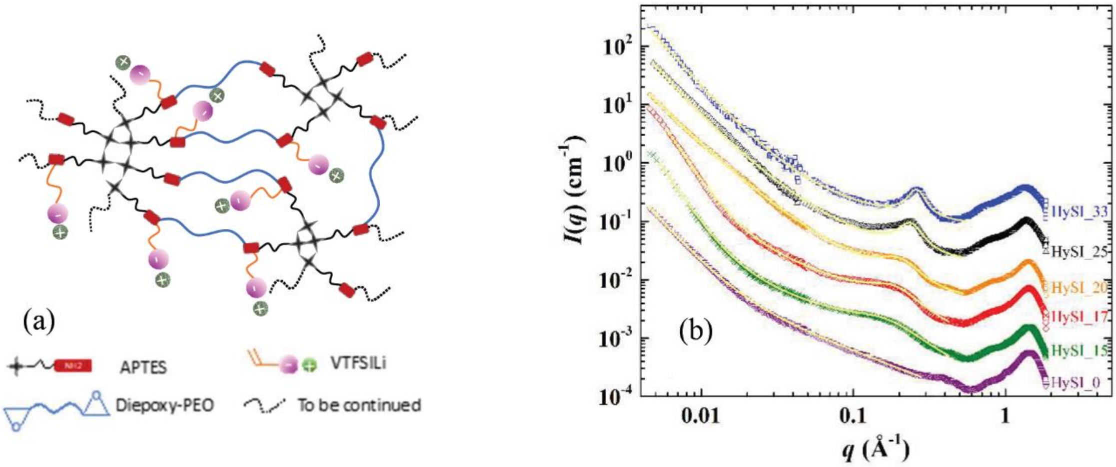

**Figure.** a) Chemical Structure of Silica-PEO hybrid (HySI) electrolyte. (b) SAXS/WAXS scattering curves recorded at 60 °C for the HySI_$w_{\mathrm{VSTFSILi}}$ electrolytes with $w_{\mathrm{VSTFSILI}}$ of (▽) 0, (×) 15, (◇) 17, (○) 20, (△) 25, and (□) 33. The curves are shifted in intensity for clarity. The yellow continuous lines are the fit curves from the *ad-hoc* model with two power laws to describe the low and intermediate q range and a Lorentzian to find the peak position and width.

**Keywords**
Hybrid electrolytes, Lithium Metal Batteries, Single Ion Hybrid Electrolytes, SAXS

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SESSION 7C: COLLOIDS AND POLYMERS 4
Chair: Dr. Christian Appel

## V373 - THE POLYELECTROLYTE TO NEUTRAL POLYMER TRANSITION AS SEEN BY SMALL ANGLE SCATTERING

***LOPEZ, Carlos (1)**; **WATANABE, Takaichi (2); RICHTERING, Walter (1)***
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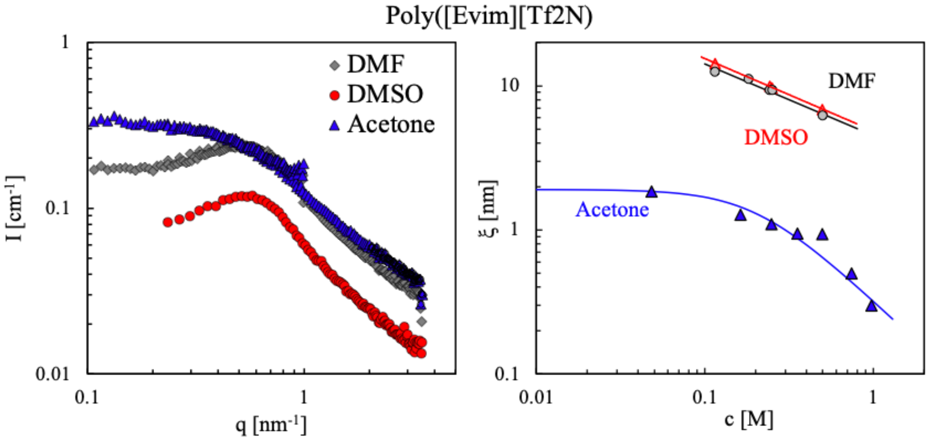
Polyelectrolytes are polymers bearing ionic groups along their backbone. When dissolved in polar media, counterions dissociate from the backbone. The strong electrostatic repulsion between like-charged chains means that polyelectrolyte solutions are strongly correlated systems, and display very different structural and rheological behaviour from those of neutral polymers.

Here, we investigate the structural properties of several polyelectrolyte systems in media of varying dielectric permittivity and polarity using SANS and SAXS. Polystyrene sulfonate (PSS) with tetrabutyl ammonium counterions is found to be soluble in a wide array of organic solvents. When the dielectric constant of the solvent media is high, a clear peak is observed in the structure factor, which scales as q* ˜ c1/2 as expected by various theories. As the solvent permittivity is lowered, chains first collapse into pearl-necklace structures, and the peak position scales as q* ˜ c1/3. Such structures are only partially collapsed and retain many typical polyelectrolyte properties. When the dielectric constant is lowered further, chains fully collapse into globules which can be modelled using ellipsoidal form factors. The absence of a peak in the structure factor signals weak electrostatic interactions between particles.

We also studied a polymerised (ionic liquid) (PIL) with hydrophobic counterions in DMF, DMSO and acetone. In the first two solvents, a peak is observed in their scattering function, as expected for strongly charged polyelectrolytes. In acetone, by contrast, the PIL behaves as a neutral polymer and its scattering signal in semidilute solution is well-described by an Ornstein-Zernike function. The very different behaviour observed for these systems cannot be explained by differences in the dielectric constant of the solvent media and the relative affinity between counterions, polymer backbone and solvent must be considered instead.



**Keywords**
Polyelectrolyte, SANS, SAXS, Polymer, Ions

PLENARY 5

Chair: Prof. Watson Loh

# V442 - MICROSCOPIC MECHANISM BEHIND THE PROCESSING AND FUNCTIONALITY OF POLYMER NANOCOMPOSITES

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We are interested in the studies of the microscopic mechanism and theory in the synthesis-structure-property relation of polymer nanocomposites via the using of X-ray and neutron scattering techniques. As the general issue of material science research, the unclear inherent structure-property relation of the polymer nanocomposites resulting from their multi-component, hierarchical structures is aimed to be resolved. We applied polymer-molecular cluster composites with well-defined structures as model systems and studied the materials comprehensively with the extraction of experimental data in both temporal and spatial dimensions. X-ray and neutron scattering techniques with complementary contrast for material characterization are developed for the research on fine structures of amorphous material systems. This helped break the limit for the research on solutions and non-crystalline sample systems and brought in the capability in quantifying the hierarchical structures and dynamics from chain segments to single chain/molecular cluster to co-assemblies of multiple units. The reaction kinetics, solution dynamics and structure-property relation can be obtained and the previous theories on ‘reducing agents-controlled synthesis of clusters’ and ‘static property of metal-organic polyhedron’ were revised. The research can finally lead to the concept of material-by-design with required hierarchical structures and dynamics. The decoupling of multi-functionalities can be achieved, facilitating the precise design of materials with the effective integration of ion conduction, gas transportation and promising mechanical properties as well as transformative topological explosion-proof materials.

**Keywords**
small angle scattering; neutron scattering; polymer nanocomposite; molecular cluster; nanoconfinement; dynamics

SESSION 8A: COLLOIDS AND POLYMERS 5
Chair: Dr. Ryan Patrick Murphy

# V388 - EXPLORING THE INTERNAL STRUCTURE OF TUNABLE POLYMERIC NANOPARTICLES SYNTHETIZED BY EMULSION PROCESSES

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Polymeric nano and microparticles with inner nanoheterogeneities (e.g. core-shell, segregated nanodomains, etc) have attracted much attention in many fields such as biomedicine, catalysis, electronics, among others.[1-2] The diameter of these particles ranges from several nanometers to several micrometers depending on the application. Moreover, the possibility to functionalize their internal structures plays a significant role in the abovementioned applications, e.g for drug delivery, to be able to transport a compound inside the nanoparticle. For this reason, synthesis of polymeric nanoparticles of different sizes with tunable domains is of great importance.[3]

In this context, we studied the size, shape, hierarchical organization, and internal structure of polymeric nanoparticles possessing replaceable groups. Three different emulsion polymerization processes were studied in order to compare the effectiveness of each. As main monomers, 2-Hydroxyethyl Methacrylate (HEMA) and pentafluorophenyl methacrylate (PFMA) were chosen. On the one hand, HEMA is a monomer widely used in biomedical applications because it provides great biocompatibility. On the other hand, PFMA due to its lipophilic nature is nano segregated within the nanoparticles (as we will demonstrate along this work) and provide leaving groups which offers the possibility of tuning these nanodomains with functionalities.

The polymeric nanoparticles were synthesized by batch process and semi-continuous process in (a) an oil-in-water (O/W) microemulsion, (b) conventional emulsion and (c) semi-continuous emulsion system stabilized by the surfactant sodium dodecyl sulfate (SDS), using different amounts of HEMA and PFMA depending on the formulation.

In order to understand the influence of HEMA/PFMA ratio and type of polymerization process selected on the structure of the polymeric nanoparticles DLS, ζ-potential and SAXS experiments were performed. Two general trends were observed: a) the higher the content of HEMA, the bigger the obtained nanoparticles and b) for the same formulation, the sizes of nanoparticles varied with the method as microemulsion < emulsion < semi-continuous.

The inner structure of the nanoparticles was explored by means of SAXS. Several different models were tested, including core-shell spheres and multilevel Beaucage or Hammouda models,[4-5] among others. It was ruled out that the nanoparticles containing mixed monomers do not possess a core-shell structure. Instead, they can be modeled as big spheroids (50-200 nm) containing small nanodomains segregated inside (2-10 nm). A detailed discussion on SAXS analysis will be presented in the conference

**Keywords**
polymeric nanoparticle, tunable polymer, emulsion polymerization

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SESSION 8A: COLLOIDS AND POLYMERS 5
Chair: Dr. Ryan Patrick Murphy

# V193 - MULTISCALE STRUCTURE OF POLY(IONIC LIQUID)S IN BULK AND SOLUTIONS BY SMALL ANGLE NEUTRON SCATTERING

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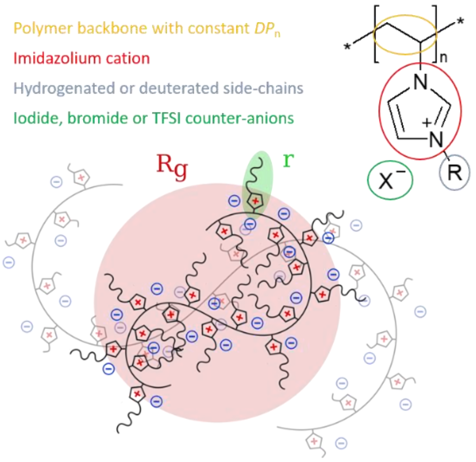
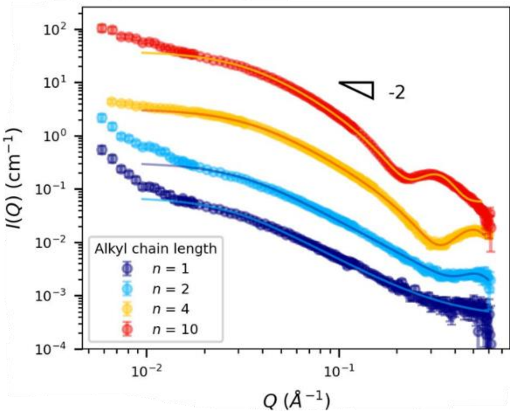
Poly(Ionic Liquid) (PIL) refer to a special type of polyelectrolyte in which each monomer unit is composed of an ionic liquid (IL). They have recently drawn significant attention since they present a unique combination of the properties of ILs (e.g. high thermal, chemical, electrochemical stabilities, interfacial adsorption and enhanced ionic conductivity. . . ) with those of polymer materials (e.g. processability, viscoelasticity, adhesion, film-forming properties, and broad macromolecular design...). ILs show a local phase separation which confers the bulk with either a globular or a sponge-like structure in which the ionic domain organizes in channels across the bulk [1].

On a polymer physicist point of view, the main difference between an ideal polymer melt and PILs stems from the presence of counter-ions and local interactions between IL monomer units due to their amphiphilic nature. The structure of bulk Poly(n-alkyl)vinylimidazolium PIL with varying side chain length n and counter-ion was determined by small angle neutron scattering (SANS). The considerable differences in behavior between melts and solutions originates from modulated electrostatic repulsions, either dominant for short side chains or screened by the counter-ions and long side chains. These interactions shape the conformation of the PIL chains but also the overall bulk structure. These considerations are precious insights for future applications of these polymers, particularly by exploiting their viscoelastic properties which deviate from those of ideal polymer chains.





**Keywords**
SANS, Poly(ionic liquids), polymer, Ionic liquid

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SESSION 8A: COLLOIDS AND POLYMERS 5
Chair: Dr. Ryan Patrick Murphy

# V347 - THE DESALTING/SALTING PATHWAY: A ROUTE TO FORM METASTABLE AGGREGATES WITH TUNEABLE MORPHOLOGIES AND LIFETIMES

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We present a new way of formulating colloidal complexes from aqueous mixtures of nanoparticles (γ-Fe2O3 nanoparticles coated with PAA2k) and polyelectrolytes (PDADMAC) of opposite charges. This method allows to obtain non-equilibrium metastable complexes with adjustable morphologies and lifetimes. Our strategy is based on the existence of a critical salinity Icrit (NH4Cl) from which the electrostatic interactions are sufficiently screened so that the complexation between the species no longer operates. The idea is to start from a homogeneous dormant mixture produced at Inominal salinity (Inominal =1M NH4Cl) much higher than Icrit(=0.62 M NH4Cl), to desalting this solution to a salinity Itarget lower than Icrit in order to initiate the formation of complexes. The mixture is then allowed to stand for a determined duration ttarget before resalting it again to its nominal value. We have demonstrated that complexes remain in solution after the last resalting step, with a characteristic lifetime varying from a few seconds to several days.

SAXS, DLS and Optical microscopy is performed to understand the overall size and internal morphology of complexes at different values of Itarget. Kinetics of dissolution of complexes after resalting step is also analyzed by time resolved SAXS and DLS experiments (not shown here). Figure b show the SAXS scattering profiles of these complexes after desalting at different Itarget. The low q of Scattering profile represents the typical porod scattering (q-4) of hard surfaces, whereas high q represents the correlation peak of nanoparticle aggregates in complexes. The high q correlation peak broadens and shift towards low q for different Itarget, as Itarget is close to Icrit. The evolution in SAXS scattering curves are fitted by Hard sphere (Percus-Yevick) structure factor model to estimate the volume fraction of nanoparticles in the complexes (not shown here).

The detailed analysis reveals that the lifetimes of such complexes after the resalting step depends on Itarget: the closer Itarget to Icrit is, the more difficult it is to dissolve the aggregates. Such peculiar behavior is driven by the inner structure of the complexes that are formed after desalting. When Itarget is far below Icrit, strong electrostatic interactions induce the formation of dense, compact and frozen aggregates. Such aggregates can only poorly reorganize further on with time, which makes their dissolution upon resalting almost reversible. Conversely, when Itarget is close to Icrit more open aggregates are formed due to weaker electrostatic interactions upon desalting. The system can thus rearrange with time to lower its free energy and reach more stable out-of-equilibrium states, which are very difficult to dissociate back upon resalting, even at very high ionic strength.

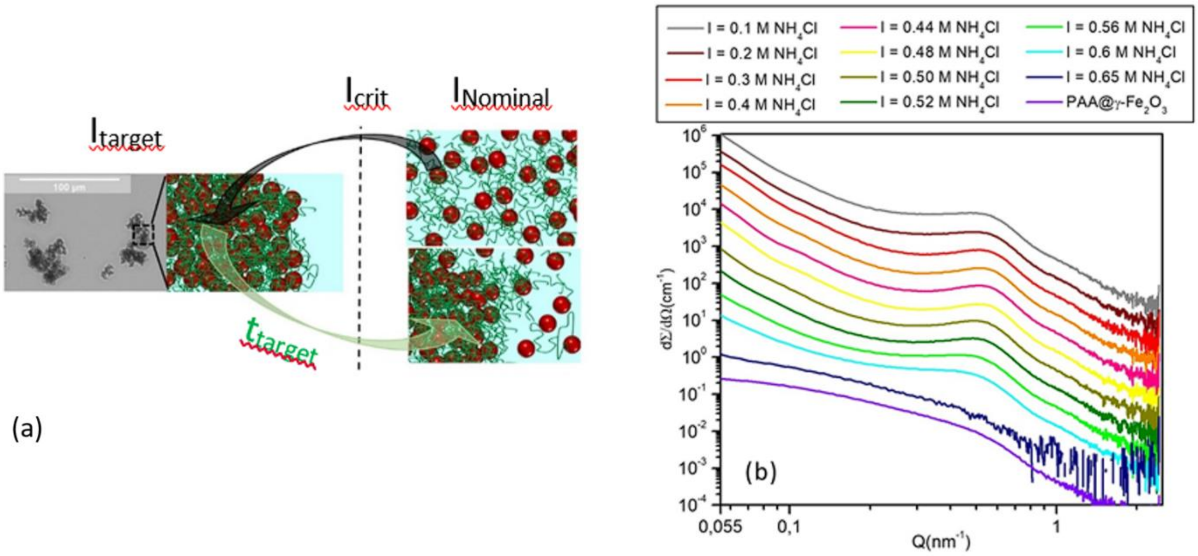

Figure (a) Scheme of desalting and resalting of the PAA@γ-$Fe_2O_3$ nanoparticles/PDADMAC complexes. (b) SAXS scattering curves of the PAA@γ-$Fe_2O_3$ nanoparticles/PDADMAC system upon desalting from 1M $NH_4Cl$ at different $I_{target}$. The scattering curves are also compared with the form factor of pure PAA@γ-$Fe_2O_3$ nanoparticles.

**Keywords**
Nanoparticle-polyelectrolyte complexes, time-resolved SAXS, Non-equilibrium assemblies, tunable delivery

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SESSION 8A: COLLOIDS AND POLYMERS 5
Chair: Dr. Ryan Patrick Murphy

## V414 - STRUCTURAL ORIENTATION, ELONGATION AND RELAXATION OF THREE-ARM STAR POLYMERS EXPOSED TO EXTENSIONAL FLOW

**MORTENSEN, Kell (1); KIRKENSGAARD, Jacob (1); ALMDAL, Kristoffer (2); HASSAGER, Ole (2); GARVEY, Christopher (3); HUANG, Qian (2); BORGER, Anine (1)**
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We present structural studies of the deformation [1] and successive relaxation of a polystyrene star polymer exposed to high-rate extensional flow [2]. The three-armed polystyrene star polymer has short deuterated segments at the end of each arm to highlight the structure in the SANS study. The form factor of the three-armed star molecules is in in the relaxed state in perfect agreement with that of the random phase approximation of Gaussian chains, and appears in the SANS pattern with the characteristic correlation ring. During the steady-state flow, the scattering pattern transforms into two sets of independent correlations peaks, reflecting the structure of a polymer confined in a fully oriented, slightly stretched three-armed tube, the three arms being parallel or anti-parallel to the direction of flow. Upon cessation of flow, the relaxation constitutes three distinct regimes. In a first regime, the perpendicular correlation peaks disappear, signifying disruption of the virtual tube. In a second regime, broad scattering arcs emerge, reflecting relaxation from highly aligned chains to more relaxed, still anisotropic form. New entanglements dominate the last relaxation regime where the scattering pattern evolves to a successively elliptical and circular pattern, reflecting relaxation via reptation.

**Keywords**
Polymer, Stretched, Flow

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SESSION 8B: COHERENT SMALL ANGLE SCATTERING IMAGING 3
Chair: Prof. Marianne Liebi

# P238 - MULTISCALE CHARACTERIZATION OF A POLYMER ELECTROLYTE FUEL CELL CATALYST USING SCANNING SMALL ANGLE X-RAY SCATTERING AND PTYCHOGRAPHIC X-RAY NANO TOMOGRAPHY

**APPEL, Christian (1); IHLI, Johannes (1); HOLLER, Mirko (1); GAO, Zirui (1); KOHLBRECHER, Joachim (1); ETZOLD, Bastian J. M. (2); GUIZAR SICAIROS, Manuel (1); LIEBI, Marianne (1)**
*1: Paul Scherrer Institut, 5232 Villigen PSI, Switzerland; 2: Technical University of Darmstadt, Department of Chemistry, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, 64287 Darmstadt, Germany*
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The development of many future applications, e.g. in the energy and transportation sector, rely on the technological development of advanced composite materials tailor-made for specific applications. One good example are polymer electrolyte fuel cells (PEFCs), in which the important electrochemical reaction takes place in a nanocomposite catalyst layer. Its hierarchical structure ranging from single nanometre to millimetres plays a crucial role in the transport of gaseous and liquid reactants to the catalytically active sites which affects their efficiency. Therefore, tools for multiscale characterization of the catalyst structure are needed to assess the catalyst in its pristine state and ideally also under realistic working conditions, i.e. elevated temperatures and humid environment.

In this study, we utilize scanning Small Angle X-ray Scattering (sSAXS) combined with Ptychographic X-ray Computed nano-Tomography (PXCT) to probe the catalyst structure of different compositions on multiple length scales. From sSAXS we obtain information on the nanostructure, i.e. few Å to few hundreds of nm, statistically averaged over the spatial resolution of the x-ray beam, i.e. few tens of µm, scanned over macroscopic areas[1] of the catalyst layer. This data is complemented with simultaneous scanning X-ray Fluorescence (XRF) measurements from which we can obtain correlative chemical information. In a second set of experiments, PXCT measurements with the OMNY end-station[2] were performed on ~20 µm sized pillars extracted and milled out from the same catalyst samples that were measured in the sSAXS experiments using a focussed ion beam, to directly correlative both measurements. PXCT measurements of the µ-pillars provide tomographic reconstructions of the electron density distribution in 3D with a spatial resolution down to 20 nm. X-ray experiments were performed at the cSAXS beamline of the Swiss Light Source (SLS), Paul-Scherrer-Institute, Switzerland.

Figure 1 shows exemplarily results on one of the catalyst samples. The nanostructure of the catalyst layer comprises of three compounds, a carbon support, a proton conducting ionomer (polymer structure) and ~3 nm large Pt nanoparticles. In the isotropic 1D scattering curves in Figure 1C, characteristic scattering signals for each of them can be identified and used to create 2D images to illustrate nanoscale features on macroscopic length scales as shown in 1B at the example of the ionomer backbone spacing. Results from PXCT measurements as shown in 1E/F are able to directly visualize the 3D electron density distribution, thus pore and material distribution above 20 nm. Future analysis of the data aims to correlatively combine results from both techniques using morphological models for the SAXS data. These morphological models can be validated by the 3D electron density from PXCT, chemical maps from scanning XRF as well as complementary SANS measurements on the catalysts. By comparing results from the analysis of different compositions of the catalyst layers, we hope to better understand the relation between structure and performance in these nanocomposite materials.

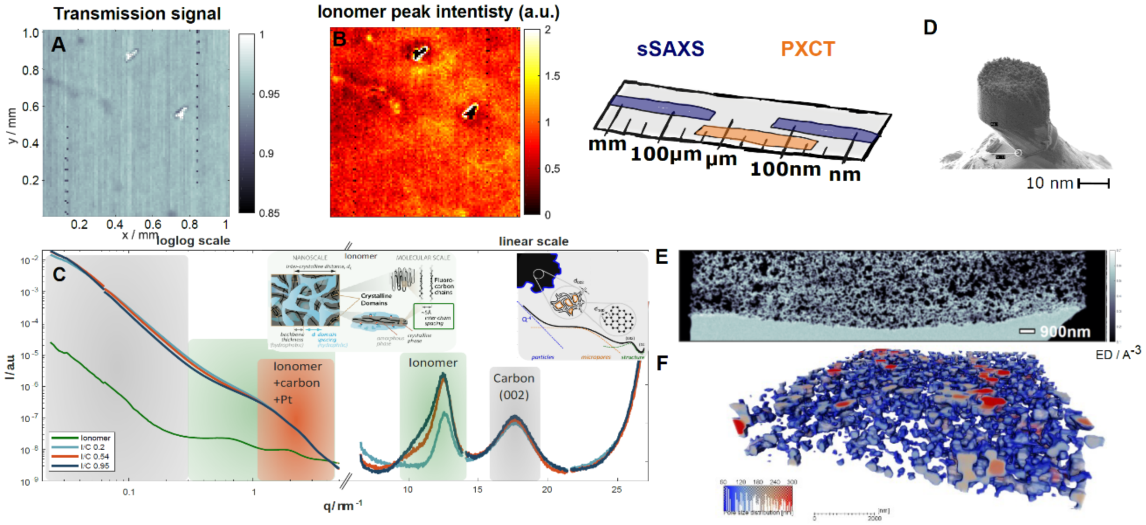

**Figure 1:** A,B,C show results from sSAXS experiments and D, E, F from PXCT measurements
A - normalized sample transmission from catalyst layer (1x1mm2)
B - Scattering map of the integrated ionomer peak intensity around q~12.4nm-1
C - Representative SAXS and WAXS curves for the sample. Highlighted features in the image correspond to the carbon support, the ionomer (polymer component - binder) and the catalytic sites within the nanocomposite catalyst
D - FIB-milled μ-pillar as prepared for the PXCT measurements
E - Tomographic slice through reconstructed 3D electron density distribution showing a cut through the catalyst coated membrane with the nanporous catalyst being the upper layer
F - Rendered pore network from subvolume within the catalyst layer

## Keywords

SAXS, XRF, PXCT, FuelCell, Imaging

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SESSION 8B: COHERENT SMALL ANGLE SCATTERING IMAGING 3
Chair: Prof. Marianne Liebi

## P234 - A PTYCHOGRAPHIC X-RAY COMPUTED TOMOGRAPHY SET-UP ON THE SWING BEAMLINE

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Far field Ptychographic X-ray Computed Tomography (PXCT) is a scanning technique that exploits the diffraction from a coherent X-ray beam to produce 3D maps of the sample electronic density in absolute units (e-/Å3). It is particularly adapted to the characterization of inhomogeneous materials where small variations of the local density are scientifically significant (porous/hierarchical materials, cements, micro-fossils, bio-mineral structures, teeth, bones, plants cell walls, …). Photon detection with high angular resolution, together with a good signal to noise ratio, is essential to resolve the speckles produced by the diffraction of the coherent beam: the higher the angular resolution is, the larger the coherent beam on the sample can be (up to 5 µm currently), and the smaller is the number of steps needed to scan the sample. A SAXS beamline is then well adapted for that imaging technique, since high angular resolution in the diffraction patterns can be obtained with a large sample-to-detector distance. An ambient temperature nanoprobe end-station has recently been commissioned on the general SAXS/WAXS beamline (SWING) at Synchrotron SOLEIL for PXCT imaging [3] and was opened to external users in February 2022. The set-up has been designed to be portable and capable of handling sample-sizes of a few tens of micrometer size. All positioning stages are comprised of piezo-driven actuators, of which dynamic control is done using a SOLEIL PowerBrick motion controller. Interferometry feedback is synchroneously acquired for reconstruction purposes.

The first reconstructed imaging results include 2D-images measured from a Siemens star, with an estimated resolution better than 19 nm, and 3D- images from a porous Silica sample with a 3D estimated resolution of 40 nm.

**Keywords**
coherent imaging, ptychography, far-field diffraction, tomography

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PowerBrick[1] motion controller
[1] DeltaTau plateform from Faraday motion https://www.faradaymotioncontrols.co.uk/

# P283 - DIFFRACTION PATTERN REFINEMENT FOR IMAGE PROCESSING AT CATERETÊ BEAMLINE

**CARVALHO, Julia Carina; TONIN, Yuri Rossi; FERRAZ, Paola; MIQUELES, Eduardo Xavier**
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In this work, we present part of the imaging commissioning system developed by the scientific computing group in order to support Cateretê (CAT) beamline in their imaging goals. Ptychography, being one of the available techniques at CAT, is a scanning lensless imaging process that increases reconstruction robustness by redundancy of information through a set of diffraction patterns, which are obtained from different overlapping regions of the object measured by a detector. Often, the detector raw values present aberrations due to dead pixels, saturation and pixel response calibration issues that affect the ptychography reconstruction. Therefore, we have to include some refinement techniques applied on measured data to pre-process diffraction patterns and deal with the sensitivity to detector pixel values, since these patterns are a measurement of the Fourier reciprocal space. This is done by a series of necessary data corrections including masking of pixel values, centralization of frequency values and binning to successfully obtain ptychographic reconstructions. Images in the reciprocal space are obtained after restoration, a process that reprojects pixels from the detector (Pimega540D) device in order to form a virtual image, from which ptychographic, XPCS or plane wave CDI can benefit. In this work we explain in detail the consequences of choosing wrong values for each one of the parameters in the process of preparing a large sequence of images for one of these imaging techniques. A high-performance computing approach for preparing a sequence of images is presented, using Jupyter-notebooks, in order to improve user experience for Cateretê users through processing queues from Tepui facility. Finally, the resolution on the two-dimensional ptychographic images is compared to standard techniques like Fourier-ring correlation in order to provide a robust imaging system.

**Keywords**
Imaging, pre-processing, ptychography, diffraction pattern

SESSION 8B: COHERENT SMALL ANGLE SCATTERING IMAGING 3
Chair: Prof. Marianne Liebi

# V421 - COHERENT SURFACE SCATTERING IMAGING WITH NANOMETER RESOLUTION FOR 3D MESOSCALE STRUCTURES AT SURFACES AND INTERFACES

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Coherent surface scattering imaging (CSSI) is a recently developed high-resolution non-destructive X-ray imaging technique for imaging supported nanostructures at surfaces and buried interfaces. Unlike conventional coherent imaging techniques in transmission geometry such as CDI and ptychography, CSSI operates in grazing-angle geometry and can probe non-periodic nano-features in thin-film based 3D systems, such as the growth of thin films and quantum dots, dendrites developing in lithium batteries, etc. A one-of-a-kind CSSI beamline is being developed as a featured beamline for the APS Upgrade to an MBA source. The beamline design is based on incorporating grazing-incident geometry with small-angle coherent X-ray imaging. The achievable spatial resolution is a few nanometers in all three dimensions, thanks to the cutting edge wavefront preserving X-ray optics for 2-D focusing, the high-precision motion-decoupled nanopositioning stages for surface alignment and scanning, and the state-of-the-art in vacuum detector system for sufficient imaging oversampling in a reflection geometry.

In this talk, I will present the progress of the design and construction of the dedicated CSSI beamline, as well as the CSSI methodology development from the perspectives of the instrumentation requirements and the dynamical-scattering based reconstruction algorithms.

Precise control of the sample alignment and position manipulation is very critical for CSSI, due to the reflection geometry of the CSSI at grazing angles. The freedoms of being able to independently position the in-plane and out-of-plane scattering angles, as well as the interception of the sample surface with the incident probe, can only be achieved by an appropriate stacking of high-precision linear and angular stages so as to eliminate the motion couplings required for CSSI sample alignment and scanning. We have developed a sample manipulation prototype that consists of a sample alignment stage assembly and a data acquisition stage assembly. The two assemblies can independently take care of the sample alignment and CSSI scans with designed resolution and accuracy.

Another critical aspect of CSSI is imaging reconstruction theory and algorithm. Conventional coherent X-ray imaging techniques such as CDI and ptychography assume homogenous electric field illumination on the entire sample and ignore multiple scattering effects. Hence, the kinematical-approximation based reconstruction algorithms via simple forward and backward Fourier transforms are thus valid for the iterative phase retrieval processes. In contrast, scattering at grazing geometry must be handled in the framework of dynamical scattering theory due to the substantial interference between the reflection of X-rays from the supporting surface or substrate with the object of interest. We thus developed a coherent forward surface scattering theory based on the distorted-wave Born approximation (DWBA). Also, a new reconstruction algorithm has been developed to deal with the complex backward transformation in CSSI and will be discussed in the talk.

**Keywords**
coherent imaging, small angle scattering, grazing-incidence

## P252 - UNDERSTANDING THE DIFFERENCE BETWEEN SAXS AND SANS SIGNALS FROM NANOPOROUS CARBON SURFACES

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Activated nanoporous carbon materials have attracted significant interest in recent years due to their vast applicability in some of the most challenging technological fields of modern humankind, such as electrochemical energy storage or hydrogen storage. Those applications require very small pore sizes in the sub-Nanometer range, in connection with high specific surface area and high pore volume. Activated carbons can be synthesized from a variety of different precursors, such as from biological waste residues (wood chips, coconut shells, etc.) or from cotton fibers [1]. Activation to introduce microporosity is either achieved chemically, using strong chemical agents (i.e. acids, bases or salts), or by physical activation using oxidizing gasses (CO2, O2, or H2O steam) at temperatures up to 1000 ºC or by a combination of both. Depending on the type of precursor material and activation process, functional groups containing hydrogen (H), hydroxides (-OH), oxygen (O) and nitrogen (N) may be present in the nanoporous carbon structure. A versatile technique for investigating the pores structure of nanoporous carbons is small-angle scattering of X-rays (SAXS) neutrons (SANS). Differences in the recorded signal between SAXS and SANS of the same sample material can be explained by different scattering contrasts for X-rays and neutrons, the latter being particularly sensitive to hydrogen. In the scope of this work, we have investigated ultra-microporous (i.e. pore sizes < 0.7 nm) viscose-based activated carbon cloth (ACC) [2], with both, SAXS and SANS. Surface groups containing hydrogen, originating from the precursors or the activation process are assumed to be responsible for significant changes in the shape of the scattering signal. We present a simple model that first determines the size distribution of spherical pores from SAXS by Indirect Fourier Transformation (IFT) [3], and subsequently, the SANS data are described by the introduction of a thin layer of different scattering contrast within the pores. The model allows the contrast and thickness of the added layer to be determined, and in combination with information on the surface chemistry within the sample based on X-ray photoelectron spectroscopy, information on the type and density of surface functional groups can be achieved.

**Keywords**
nanoporous carbons, small-angle X-ray scattering, small-angle neutron scattering, surface chemistry

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SESSION 8C: MATERIALS SCIENCE 3
Chair: Dr. Pablo Mota-Santiago

## P155 - SMALL-ANGLE X-RAY SCATTERING FOR THE DETERMINATION OF THE SPECIFIC SURFACE AREA OF MATERIALS

**KEILBACH, Andreas (1); EHMANN, Heike M. A. (1); SCHERDEL, Christian (2); REICHENAUER, Gudrun (2); SCHLUMBERGER, Carola (3); THOMMES, Matthias (3)**
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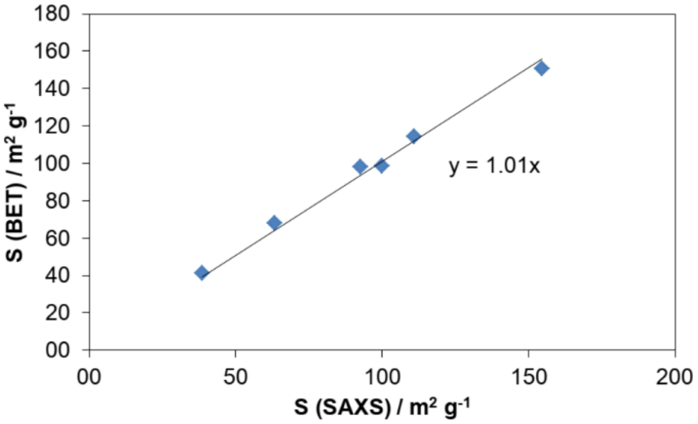
The reliable measurement of the specific surface area of many modern materials – porous or non-porous – is of vital importance both in research and industry. To date, the most commonly used method for the determination of the specific surface area of any material is based on the BET (Brunauer-Emmet-Teller) method that relies on the physisorption of gas molecules at the sample surface. The BET method has a number of limitations and challenges, e. g., time-consuming sample preparation/measurement and that the size and effective cross-section of the adsorptive molecules that cover the sample surface is not always known. Small-angle X-ray scattering (SAXS) has good potential to overcome these limitations. In this contribution we will present SAXS as an alternative and complimentary approach for reliable and fast surface area assessment and compare it to the established BET method. The results for the specific surface area obtained from SAXS measurements showed excellent agreement to those obtained from Argon 87 K physisorption experiments. This allowed for the first time an experimental cross-validation of the validity of BET surface areas obtained from Argon over those where Nitrogen (which may overestimate specific surface areas of silicas and other oxides in the order of >20 %) was used as the adsorptive. For the assessment of the specific surface area by SAXS it could be shown that no outgassing is required, resulting in significantly shorter overall sample preparation and measurement times. Also, the risk of irreversibly altering the nature of the sample by high-temperature treatment during the outgassing procedure can be completely avoided.

This fundamental study can be considered a major step in enabling SAXS for reliable surface area assessment for applications both in nanoporous materials development and quality control, thus boosting SAXS for surface area determination as a complimentary method to gas adsorption, but in particular for materials, where the application adsorption is restricted or not possible at all, as for instance in materials, where sorption causes a change in the state of the adsorbent such as present in various pharmaceutical materials and polymers (swelling/deformation).



**Keywords**
specific surface area, BET

SESSION 8C: MATERIALS SCIENCE 3
Chair: Dr. Pablo Mota-Santiago

# V191 - SPECIFIC ANALYSIS OF HIGHLY ABSORBING NANOPOROUS POWDER BY SMALL-ANGLE X-RAY SCATTERING

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The characterization of nanoporous powders of highly absorbing compounds by Small-angle X-ray scattering involves overcoming several difficulties before quantitative information related to the porous texture such as the specific surface and the porous volume can be derived. In this work, we first calculated the predominance of the grain facets reflectivity and scattering from the bulk of a grain having the density of ThO2, a highly absorbing material. We have characterized microporous ThO2 powder having micrometric grain size, in which the scattering signal is predominant using a high resolution synchrotron instrument in order to minimize the absorption effect and cover a wider q range, and compared with the results using a laboratory X-ray source. Concerning the absorption problem existing with a laboratory X-ray source, we proposed a new and robust experimental method to correctly determine the scattering intensity in absolute scale of the highly absorbing granular samples. This method allows to calculate accurately the porous volume and the specific surface using the Porod's law and the invariant without using a synchrotron instrument. This last result opens new perspectives for the characterization of the volume and the surface of highly absorbing actinide oxide powders.

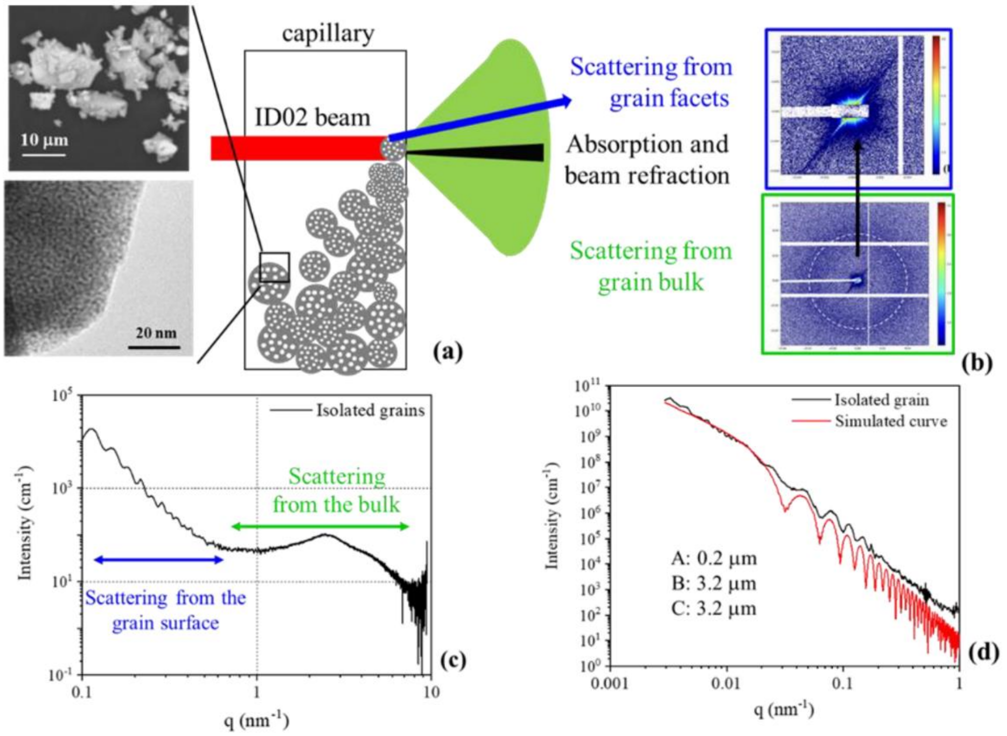

**Figure 1.** (a) Schematic illustration of the experiments and images of the powder and of a part of a grain obtained by scanning and transmission electron microscopies respectively; (b) 2D SAXS pattern of the isolated grains; (c) Azimuthally averaged 1D SAXS pattern

## Keywords

Small Angle X-ray scattering, highly absorbing porous powder, reflectivity and scattering contribution, absolute scattering intensity

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SESSION 8C: MATERIALS SCIENCE 3
Chair: Dr. Pablo Mota-Santiago

# V318 - TRACEABLE NANOPARTICLE CHARACTERIZATION WITH SAXS

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SAXS is a widely applied method to characterize nanoparticles and allows to retrieve information about the size, concentration, shape and inner structure of the particles. Traceability to the SI system of units means that the result of a measurement is directly related to an SI unit via an unbroken chain of comparisons, each having stated uncertainties. In practice this allows us to derive not only a value for the measurands, but also a reliable uncertainty estimate.

We have implemented traceable SAXS measurements at the four-crystal monochromator beamline of PTB [1] at the synchrotron radiation facility BESSY II in Berlin using the HZB SAXS setup [2]. Traceability for the size determination of solid spherical particles is well established at this beamline [3] and has been extended to spherical particles with an inner structure [4].

This talk details the recent advances towards traceability for concentration determination. For suspensions of spherical particles, traceable concentration measurements can be achieved by evaluating the intensity of the scattering signal. This requires knowledge of the effective electron density difference between the particles and the suspending medium [5]. We have achieved traceable measurements by a combination of different approaches based on tabulated data, analytical centrifugation and contrast matching, depending on the material of the particles. Figure 1 displays expected limits for the concentration determination using these approaches. An ISO standard for particle concentration measurements using SAXS is currently being prepared taking these results into account.

As a further extension, this talk will present the analysis of nanoparticles with non-spherical shape. In the framework of the EMPIR nPSize project [6], the traceability chain of various shape descriptors for particles of different shapes, such as cuboids and truncated bipyramids, has been investigated. By applying Debye's scatterig formula to a randomly distributed point cloud of elementary scatterers, the SAXS data for complex shapes can be analysed [7]. Figure 2 shows the determination of the minor axis for truncated bipyramids from scattering data using this approach [8].

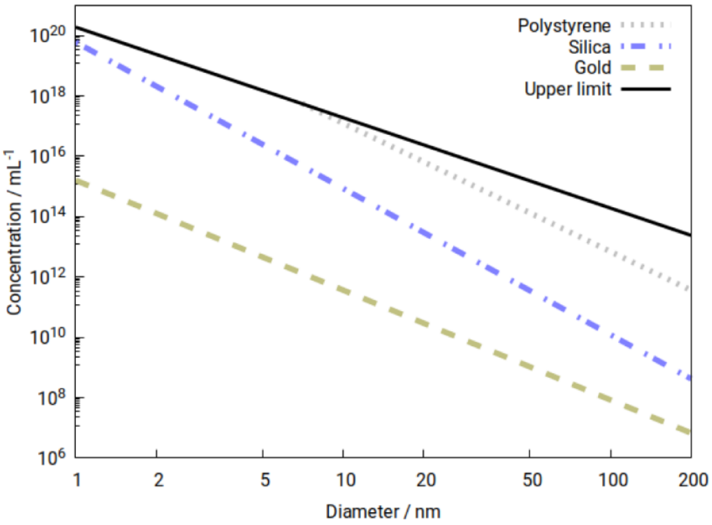

Figure 1. Limits for the concentration determination of nanoparticle suspensions for various materials.

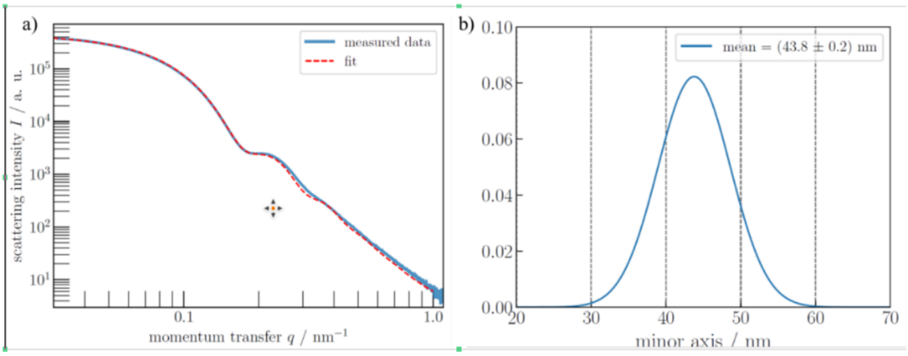

Figure 2. (a) Measured scattering curve for truncated bipyramidal $TiO_2$ particles and model fit assuming a fixed aspect ratio
(b) Number-weighted distribution of the minor axis

**Keywords**

Nanoparticles, Traceability, Concentration

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SESSION 9A: COLLOIDS AND POLYMERS 6
Chair: Dr. Ana Percebom

# P178 - PROBING THE LOCAL BULK MODULUS OF SOFT COMPRESSIBLE OBJECTS USING SMALL-ANGLE NEUTRON SCATTERING

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An object's bulk modulus quantifies its resistance to an isotropic compression. For soft deformable colloids the bulk modulus must be known to predict their response to crowding. Here, we will present a new approach to obtain partially-deuterated, high molecular weight polyethylene glycol (dPEG), which is used to exert osmotic stress on soft objects [1]. In this study, microgels were used as a model system for soft compressible spheres and their bulk modulus is determined by means of small-angle neutron scattering with contrast matching. By partial deuteration the scattering length density of the dPEG was matched in pure heavy water. Consequently, no contribution of the osmotic stress polymer is measured during the scattering experiments, and the form factor of the microgels was directly measured. Furthermore, in addition to the total radius, the variation of the different parts of the microgels can be also measured as a function of the external osmotic stress. Therefore, using this method the different elasticity along a single particle, such as viruses, can be determined directly.

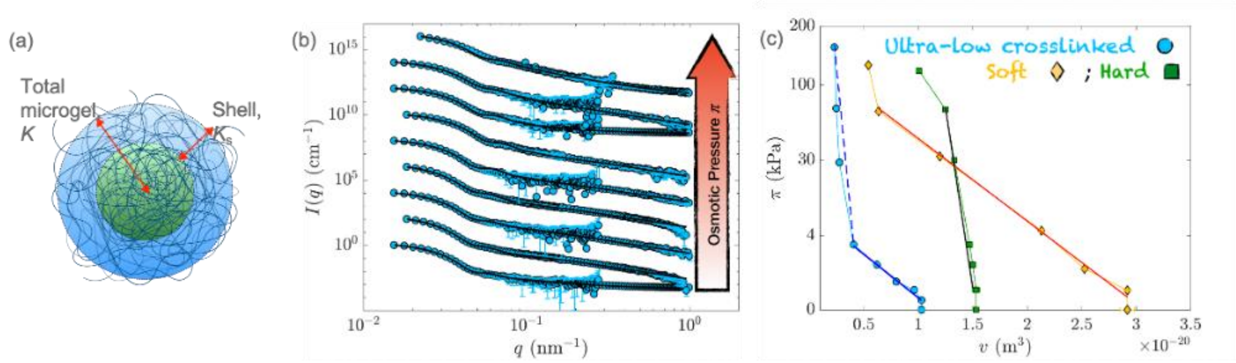

Figure 1. (a) Sketch of a nanogel. (b) SANS data of ultra-low crosslinked nanogels with increasing concentration of dPEG (osmotic pressure). (c) Osmotic pressure of suspensions of different nanogels, π, vs. nanogel volume, v. The local slope (straight lines), gives the bulk modulus.

## Keywords

Microgels, Bulk modulus, contrast matching

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SESSION 9A: COLLOIDS AND POLYMERS 6
Chair: Dr. Ana Percebom

# P179 - PHASE BEHAVIOR AND STRUCTURE OF ULTRA-SOFT SPHERES IN TWO- AND THREE DIMENSIONS

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In our recent publications [1-4], we explored the phase behavior of super-soft spheres using solutions of ultra-low crosslinked poly(N -isopropylacrylamide) based microgels as a model system.
We used SANS with contrast variation to directly access the microgel bulk modulus showing that is one order of magnitude smaller than for regular microgels. In bulk, the samples show a liquid-to-crystal transition at higher volume fraction with respect to both hard spheres and stiffer microgels. Furthermore, stable body centered cubic (bcc) crystals are observed in addition to the expected face centered cubic (fcc) crystals. Small-angle X-ray and neutron scattering with contrast variation allow the characterization of both the microgel-to-microgel distance, and the architecture of single microgels in crowded solutions. The measurements reveal that the stable bcc crystals depend on the interplay between the collapse and the interpenetration of the external shell of the ultra-low crosslinked microgels [1]. This peculiar phase behavior is due to strong defamations of the particles that we determine combining small-angle neutron scattering with contrast variation data and computer simulations [2,3].
Then we confine them at liquid-liquid interface [4]. Atomic force measurements are used to study their phase behavior. In addition, neutron reflectivity and interfacial rheology are used to both their vertical extension and the visco-elastic properties of the monolayer [5]. Once confined at interfaces, these ultra-soft spheres show a behavior in between flexible macromolecules and hard particle.

**Keywords**
nanogels, compressibility, SANS, neutron reflectivity, crystallisation

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## P273 - MONITORING PLANT PROTEIN DIGESTION BY SMALL ANGLE SCATTERING

**BOUÉ, François (1); NAPIERAJ, Maja (1); LUTTON, Evelyne (2); PEREZ, Javier (3); BRULET, Annie (1)**
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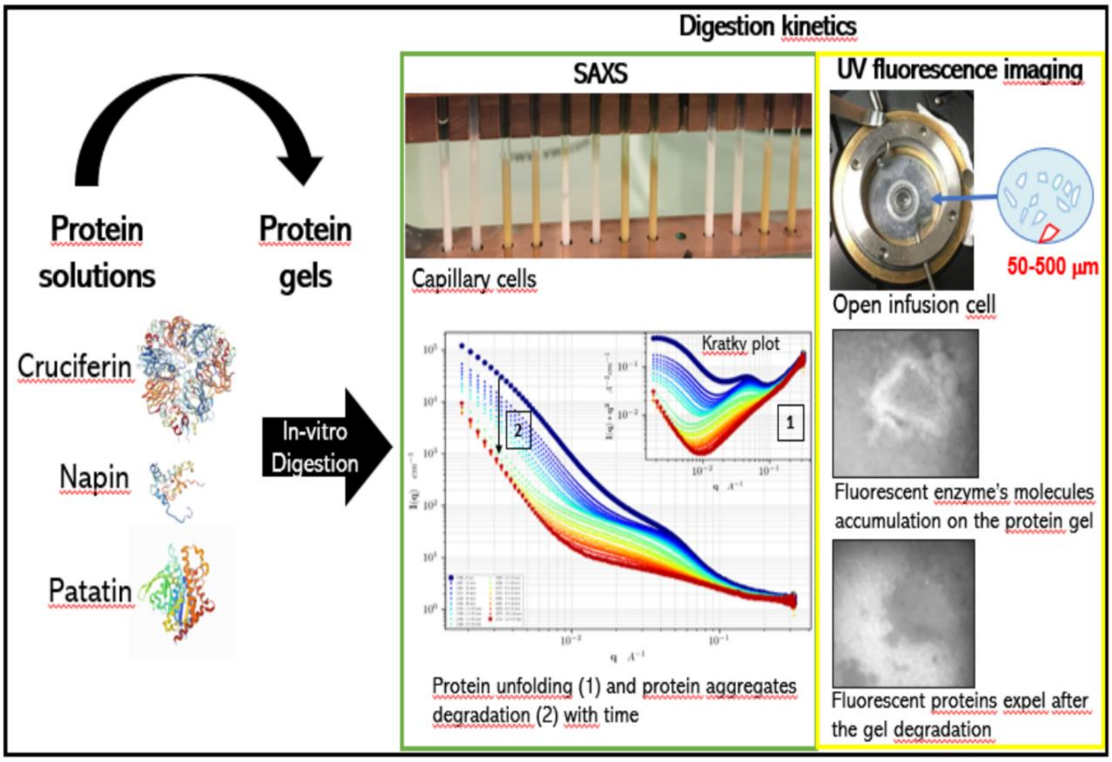
Proteins are crucial macronutrients, but they also structure food. They can form structures at multiple spatial scales, in particular in gels. Here they are prepared by heating a model isolate of cruciferin and napin from canola seeds, environmentally sustainable.

To obtain structural information on digestion mechanisms, a multilength and multitime scale monitoring was developed in vitro for gastric and intestinal steps (following Infogest protocol), using several techniques. Coupling them lead us to face the problem of the intrinsic heterogeneity of samples during digestion. This was easy with UV microscopy, which showed progressive diffusion-reaction inside a 50-200 microns gel piece with apparent external erosion of the gel [1] (Figure, right). Conversely, we had to make samples homogeneous (by initial imbibition at 4 °C of enzymatic juice) for rheology to follow the deconstruction of network connectivity [2]. The same constraint held for Small Angle Scattering of Neutrons[2], except for Neutron Dark Field Imaging (ICON, PSI), which gave scattering information (at micron scale), with a gradient with a few mm resolution.

In this paper we show that using the narrow beam of synchrotron SAXS, we could monitor sample heterogeneity together with getting information at the 1-100 nm scale. Proteins are gelled in a capillary, and gastric or intestinal juice poured on top and let diffuse at 37 °C. As illustrated in the Figure, by vertical scanning (0.15 mm) of the gel, we collect data as a function of both time t and depth z (spatial progression). Applying, to this large set of (z, t) couples, automatic fitting (by evolutionary algorithms) of the correlation size and of the apparent exponent at high Q related to unfolding, we observe how z and t variations are combined in this diffusion-reaction enzymatic process.

Satisfyingly, heating at different pH leads to clear differences in initial gel structures, and in their evolution under digestion. It can follow complex paths : e.g., when heating at high pH proteins remain compact before that digestion unfolds them, while at lower pH heating unfolds proteins, which re-aggregate under digestion. At the smallest Qs, we monitor the vanishing of the aggregate arrangement, which remains to be connected with the modulus evolution.

This rather fine characterization of protein gels digestion illustrates how it can proceed through successive rearrangements, but not obligatorily along the simplest deconstruction trend. It can be applied to different proteins (like dairy gels studied formerly by SAXS), and other foods. This could then be complemented by going back to SANS to use neutron contrast matching for multi-ingredients food.



Left: X-ray vertical scanning of capillaries with enzymatic juice on top of a colza protein gel.
Right: UV fluorescence microscopy imaging of digestion of such gel.

**Keywords**
SAXS-SANS-Food-Digestion-Kinetics-Protein unfolding/aggregation

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SESSION 9A: COLLOIDS AND POLYMERS 6
Chair: Dr. Ana Percebom

# P418 - SHEAR INFLUENCE ON COLLOIDAL CLUSTER GROWTH: A SANS AND USANS STUDY

**GARVEY, Christopher J. (1); MUNZY, Chris D. (2); DE CAMPO, Liliana (3); SOKOLOVA, Anna (3); REHM, Christine (3); HANLEY, Howard J. M. (4)**
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A structural understanding of the effects of steady state shear on colloidal gelation has largely been inferred from oscillatory rheological studies1, an essentially perturbative approach, and complementary computer simulation2. In this study we examine directly the structural evolution of a gelling system in situ in a simple shear field (Couette flow) using neutron scattering over an extended range of scattering vectors, 3x10-4 nm-1 < q < 3.1x10-1 nm-1. This range of scattering vectors contains information about the individual nano-scale sol particles and the network formed by the gelling particles. Two instruments at the Australian Centre for Neutron Scattering (Lucas Heights, Australia) were utilized: conventional pinhole SANS (BILBY3); and slit smeared intensity from a Bonse-Hart USANS (KOOKABURRA4). Gelation was initiated from a model system of silica nanoparticles where a slight adjustment of the pH modulated interparticle interactions. In the absence of shear we observe that the sol rapidly increases in viscosity until flow is arrested, in the case of an applied shear we observe that viscosity rapidly increases until it reaches a maximum, and then viscosity decreases. Scattering curves at constant shear rate were modelled to yield the growth and volume fraction of clusters. Derived structural parameters were used to calculate viscosities from a simple theoretical model5 which gives excellent agreement with measured viscosities.

**Keywords**
gelation, shear, viscosity

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## SESSION 9A: COLLOIDS AND POLYMERS 6

Chair: Dr. Ana Percebom

# V372 - REAL-TIME OBSERVATION OF NUCLEATION AND GROWTH OF PVP STABILIZED AG NANOPARTICLES: INSIGHT EFFECT OF POLYMER CHAIN

**BHARTI, Amardeep (1)**; **AMENITSCH, Heinz (2)**; **MARMIROLI, Benedetta (2)**; **BERNSTORFF, Sigrid (1)**

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Metal nanoparticles remain the interest of research due to their widespread applications in photonics, microelectronics, and biotechnology, because of their size-dependent localized properties [1,2]. The efforts have been constructed to precisely control the size and shape of the nanoparticles [3-6]. In the last decade, numerous research activities have been made to understand the nucleation and growth of the nanoparticles[7-9], however, a comprehensive understanding of the effect of surfactant on the nanoparticle's core growth and its relative interaction is still a challenge. Therefore, we investigate the reaction dynamics and growth kinetics of the Ag nanoparticles under the effect of variable chain-length surfactant polymer using time-resolved small-angle X-ray scattering at the Austrian-SAXS beamline of Elettra Sincrotrone Trieste, Italy. In order to study the pure interaction between the metal-core and the polymer, we adopt the radiation-induced synthesis using water radiolysis to avoid the external chemical reducing agent[4-6]. In this presentation, we will describe the step-by-step reaction dynamics and kinetics of the metal nanoparticles. The insight into the mechanism of the reaction of polymer stabilized Ag nanoparticles will be demonstrated.

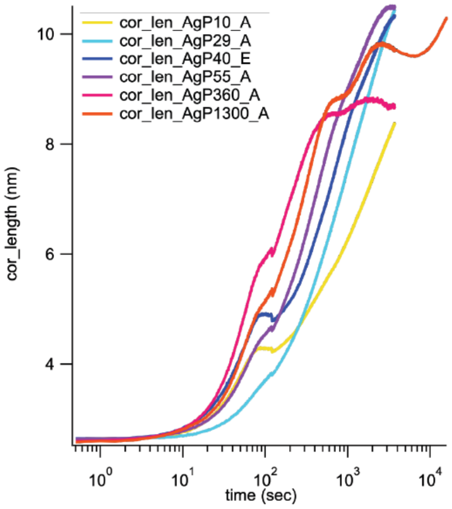

Figure1: Correlation length of the variable chain-length capped Ag-nanoparticles as a function of time.

**Keywords**

Polymer capped Nanoparticles, Nucleation and growth mechanism, time-resolved SAXS

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SESSION 9B: COHERENT SMALL ANGLE SCATTERING, IMAGING 4
Chair: Dr. Jin Wang

# P259 - QUANTIFYING MYELIN LEVELS AND NEURONAL ORIENTATIONS IN MOUSE AND HUMAN BRAIN USING SAXS TENSOR TOMOGRAPHY

**GEORGIADIS, Marios (1); GAO, Zirui (2); GUIZAR-SICAIROS, Manuel (2); LIEBI, Marianne (2,3); RAJKOVIC, Ivan (4); WEISS, Thomas M. (4); YANG, Lin (5); BUNK, Oliver (2); ZEINEH, Michael (1)**

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Myelin constitutes 50-60% v/v of our brain; it insulates neuronal axons, enabling fast and efficient signal transmission, while its disintegration is associated with multiple neurological/neurodegenerative diseases. Myelin quantification however remains a challenge, with MRI methods being unspecific, and microscopy methods destructive. The recently developed small-angle X-ray scattering tensor tomography (SAXS-TT)1-2 enables directly probing myelin non-destructively, due to the ~17nm periodicity of myelin layers. We applied SAXS-TT on mouse brains and human brain samples, quantifying myelin levels and neuronal orientations. We compared mouse results to MRI metrics, 2D and 3D histology. We also studied dysmyelinated (shiverer), control and treated mice. Further, we selectively imaged central and peripheral nervous system (CNS/PNS) myelin, exploiting minute nanostructure periodicity differences. Finally, we demonstrated the method in a human visual cortex sample.

A paraformaldehyde-fixed mouse brain was MRI-scanned, placed in a Kapton tube, in agarose gel, and SAXS-TT-scanned in cSAXS (Swiss Light Source), Fig. 1A. One hemisphere was subsequently serially-sectioned for myelin histology, the other underwent confocal imaging. Three mouse brains (control, dysmyelinated/shiverer and treated), and a human brain visual cortex sample were similarly prepared and SAXS-TT-scanned in LiX (National Synchrotron Light Source-II) and in 4-2 (Stanford Synchrotron Radiation Lightsource), respectively. SAXS-TT reconstructions used the iterative reconstruction tensor tomography algorithm3, on i) the anisotropic scattering signal at q-values of the 2nd (and most prominent) myelin peak of CNS or PNS myelin, and ii) the anisotropic myelin-specific signal, corresponding to the peak after background subtraction. Method details are in 4.

Our analysis provided tensor-tomographic reconstruction of the myelin-sensitive (Fig. 1B) and myelin-specific (Fig. 1C) signal across the mouse brain, resulting in brain-wide myelin maps (Fig. 1D). SAXS-TT-derived myelin levels highly correlated with myelin histology, while magnetization transfer MRI was the most myelin-sensitive MRI contrast. Moreover, neuronal orientations were reconstructed for each voxel (Fig. 1E), correlating highly with confocal microscopy-derived orientations. By separately reconstructing the central and peripheral myelin signal, we yielded both CNS and PNS myelin maps, showing for the first time in 3D the “ball-socket” connection of the trigeminal nerve to the brain (Fig. 1F). Comparing dysmyelinated and treated myelin levels to controls, we showed minute levels in dysmyelinated, and higher levels, similar to controls, in periventricular regions of treated mice (Fig. 1G). Finally, we demonstrated SAXS-TT on human samples, reconstructing myelin levels in the human cortex specimen, highlighting the line of Gennari, a thin line of myelinated neurons in the cortex.

Overall, we showed SAXS-TT as a non-invasive, myelin-specific imaging method, that can be used as a gold-standard for quantitative myelin level and neuronal orientation investigations in the mouse and human nervous system.

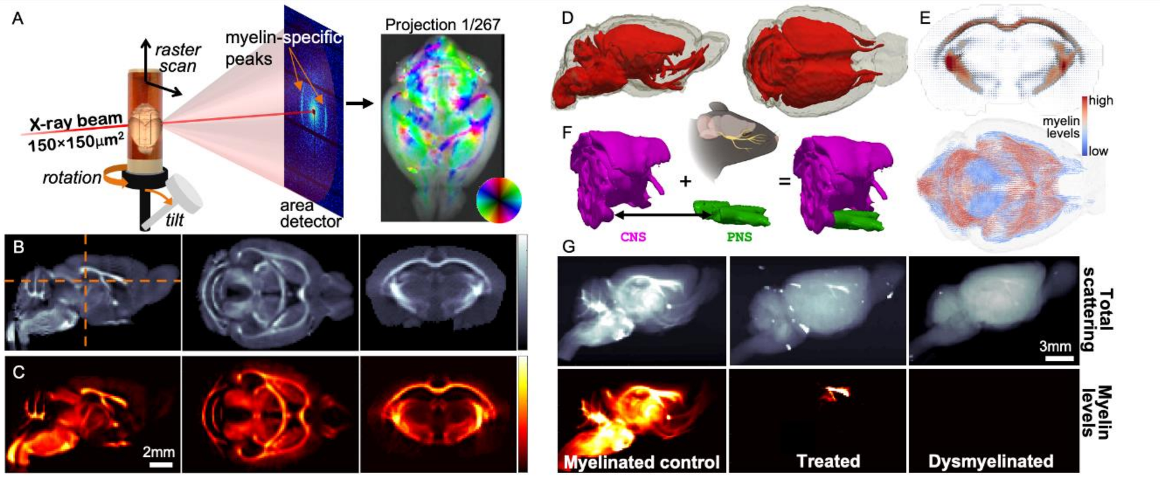

***Figure 1**. SAXS-TT in mouse brain. **A)** SAXS-TT experimental setup and one projection (signal orientation encoded by colorwheel). **B)** Sagittal, axial, and coronal virtual slices of tensor-reconstructed reciprocal space-map intensity at myelin peak q-values. **C)** Same virtual slices depicting the myelin-specific signal. **D)** 3D myelin distribution map of highly myelinated areas. **E)** Reconstructed neuronal orientations represented by ellipsoids (coronal slice - top), and by lines (top view of 3D map - bottom), color-encoded by myelin levels per voxel. **F)** Central and peripheral nervous system (CNS-PNS) 3D myelin maps, showing the ball-socket CNS-PNS fit at the trigeminal nucleus (trigeminal nerve in yellow in mouse head sketch). **G)** Side projection of mean scattering intensity at myelin peak (top) for control, dysmyelinated and treated mouse brains, and with isolated myelin-specific signal (bottom).*

## Keywords

SAXS tensor tomography, mouse and human brain, myelin levels, neuronal orientations

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## Acknowledgements

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## SESSION 9B: COHERENT SMALL ANGLE SCATTERING, IMAGING 4
Chair: Dr. Jin Wang

# P134 - HIERARCHICAL POROUS SCAFFOLDS FOR CULTURING COMPLEX TISSUES: THE SCATTERING OF FOAMS

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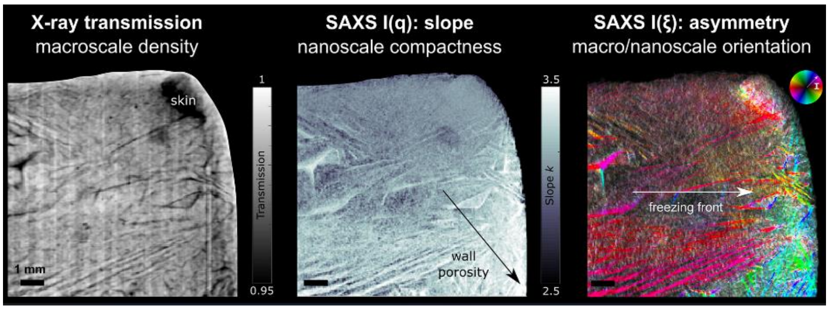
In materials science, structure spans over different length-scales, and determines the macroscopic properties and functionalities of hierarchical materials. Similarly, the structural hierarchy of soft biological tissues define their function and performance. During growth, cells can interact, and adapt to their 3D environment, but are incapable of self-assembling over the macroscopic length-scales of complex tissues. Consequently, cells during in vitro culture are guided towards their macroscale assembly by 3D scaffolds that mimic the extracellular matrix (ECM) with appropriate structural, mechanical and chemical signaling at the nanoscale. Porous structures, such as foams, that can trap cells in their porosity, are exploited for bone-mimetics, but are rarely considered for soft tissue engineering, where hydrogels are the norm. However, hydrogels' structure is mainly isotropic, and the trapped cells only grow into small aggregates without hierarchy. Therefore, we optimize the 3D porous scaffolds, as a foam structure to enable the growth of complex soft tissues by tuning their formulation, processing and structuring at the nano- and mesoscale. These foams will support 3D cell culture of complex tissues, such as skeletal muscle, focusing primarily on ideal tissue structure rather than on functionality, being fundamental in the fields of medical, pharmaceutical, biological and even food sciences, due to the current rise of artificial meat.

Structural characterization correlates the material composition and organization to its macroscopic properties. Here, we combine small X-ray and neutron scattering to investigate ultraporous and lightweight biopolymer-based foams using cellulose nanofibrils (CNFs), as building blocks. We collect spatially resolved maps at the macroscale (info on foam density and porosity), at the nanoscale (info on foam structural compactness, orientation of the foam walls, and packing state), and at the molecular scale (info cellulose on crystallite dimensions and protein conformation). Specifically, we compare the impact of freeze–thawing–drying (FTD) fabrication steps, such as static/stirred freezing and thawing in ethanol/water, on foam structural hierarchy spanning from the molecular to the millimeter scale. As such, we demonstrate the potential of small angle scattering for hierarchical characterization of biopolymer foams [1].

Furthermore, we investigate the development and structure of freezing fronts of CNF suspensions in real time with neutron imaging. When freeze-dried, CNF suspensions form high-porosity foams, which often have regions of different densities, resulting in structural inhomogeneities and defects. Understanding how the freezing front advances in the presence of particles, and how it influences the porosity and structure of the foam is necessary for prescriptive analysis of freeze-drying, as it dictates not only the structure of the foam, but also the freezing velocity, time, and overall energy consumption of the process. By using "fractional freezing", we differentiate the solidified freezing front from the remaining liquid solution, using the contrast of hydrogenated solutes in deuterium oxide. These findings serve as a basis for the development of predictive models for the structures produced by freeze-drying, which are then employed for cell scaffolding.



**Keywords**
celulose, SANS, SAXS, imaging, scaffolding, foam

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SESSION 9B: COHERENT SMALL ANGLE SCATTERING, IMAGING 4
Chair: Dr. Jin Wang

## P248 - SAXS TOMOGRAPHY OF NEXT GENERATION BATTERIES

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With the increasing electrification and implementation of renewable energy sources, more efficient and affordable energy storage technologies are needed. Lithium-ion batteries (LIBs) hold a dominant position on the market but have issues with cost effectiveness, scarcity, and an uneven geographical distribution of lithium1,2. Sodium-ion batteries (SIBs) have been identified as a promising alternative to LIBs as sodium both has a higher abundance and a substantially lower cost. The sodium-ion-battery technology also has a strong analogy to the lithium-ion battery, simplifying the implementation and development. However, the graphite electrodes used in Li-ion batteries cannot be used for Na-ion batteries as sodium ions do not intercalate into graphite at ambient pressure. Developing a suitable anode material remains a major challenge and hinders the commercialization of SIBs1. One alternative to graphite which have emerged as a promising anode material for SIBs is hard carbon. Hard carbon has a disordered, amorphous like structure with regions of a few stacked graphene layers as depicted in Figure 13. The nanoporosity and the stacked graphene layers give a characteristic scattering pattern in SAXS/WAXS with a pronounced plateau region around 10-1 Å-1 and a broad carbon peak around 1.7 Å-1 (Fig.1).

In this contribution, we present a study of the sodiation mechanisms in the hard carbon structure using spatially resolved small- and wide-angle x-ray scattering (SAXS/WAXS). Today there is a general view that hard carbon involves three types of storage sites, intercalation between graphene layers, insertion into nanopores, and adsorption on edge and defects, but there is currently an intense debate about which sodiation mechanism dominates the kinetics of sodium ion insertion2. These storage mechanisms can be efficiently studied with x-ray scattering by evaluating changes in the nanostructure of the hard carbon electrode at various degrees of sodiation. To do this, we have adapted a method for quantifying changes in interlayer spacing and size of stacked graphene layers and for characterizing the nanoporosity by Guinier analysis, where changes in shape and volume indicate sodium insertion into pores.

With scanning SAXS/WAXS and SAXS/WAXS tomography, performed at the cSAXS beamline at the Swiss Light Source, we investigate how the degree of sodiation depends on charge rate and position in the electrode by spatially resolving inhomogeneities in 3D in hard carbon electrodes during different steps of sodiation. For this we built a custom-made capillary cell to have the full hard carbon electrode in the field of view to directly be able to correlate structural and electrochemical data. This provides us with a unique tool to connect the nanostructure of sodiated hard carbon to the macroscopic length scales of a full electrode to understand the kinetic limitations of sodiation.

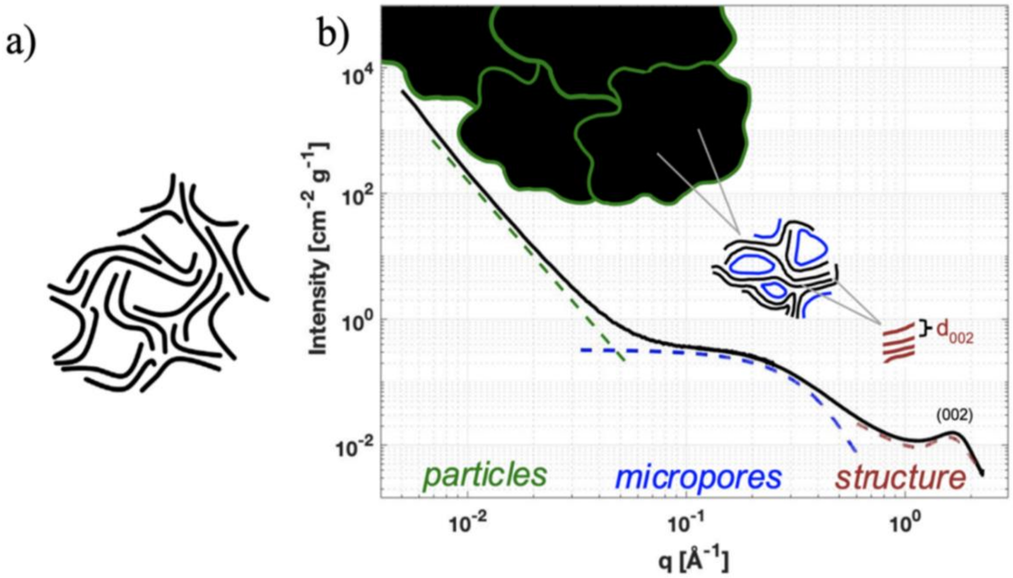

**Figure 1:**
a) Schematic over the hard carbon structure and b) corresponding characteristic scattering pattern.

**Keywords**
Hard Carbon, Sodium-ion-batteries, SAXS, SAXS tomography

## SESSION 9B: COHERENT SMALL ANGLE SCATTERING, IMAGING 4
Chair: Dr. Jin Wang

# V153 - MICROMAGNETIC RESPONSE FUNCTIONS FOR SMALL-ANGLE NEUTRON SCATTERING BY SPATIALLY INHOMOGENEOUS FERROMAGNETS WITH A NONZERO AVERAGE UNIAXIAL ANISOTROPY

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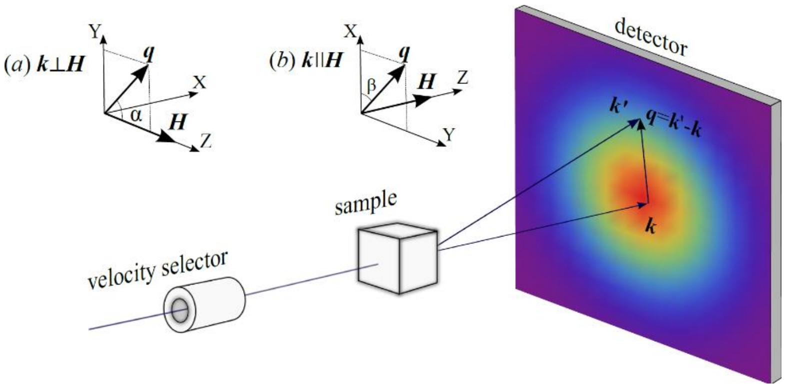
Magnetic small-angle neutron scattering (SANS) is a powerful tool for analyzing microstructure of magnetic materials. A lot of recent development have happened in the micromagnetic theory of SANS, combining the laws of magnetic texture formation (micromagnetics) with the neutron scattering theory. The micromagnetic SANS theory [1] claimed a lot of recent successes, describing the intricate details of the spin misalignment SANS cross sections and their dependence on the magnitude of the externally applied magnetic field. Yet, so far the micromagnetic SANS theory was based on the assumption that the considered magnetic material is statistically isotropic. It can have a local randomly fluctuating (both in magnitude and the direction) anisotropy, but this must average to zero. There is a wide class of materials, falling under these assumptions (most notably the metallic glasses, or materials, consisting of small randomly-oriented grains), but also there are many examples materials, which have global (non-zero on average) anisotropy.

In this talk we present an extension [2] of classical micromagnetic SANS theory to globally anisotropic magnets. We derive and compile a list of the micromagnetic SANS response functions for different mutual orientations of the direction of the global anisotropy, the external field and the wave-vector of the incident neutron beam. Some of these expressions are tested here using the existing data of magnetic-field-annealed Vitroperm alloy and plastically-deformed Ni, allowing to determine the corresponding global uniaxial anisotropy quality factors.



**Keywords**
SANS, micromagnetics, anisotropy

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SESSION 9B: COHERENT SMALL ANGLE SCATTERING, IMAGING 4
Chair: Dr. Jin Wang

## V295 - ANALYSIS OF NANOPARTICLE ASSEMBLIES IN REAL AND RECIPROCAL SPACE

**LEE, Byeongdu (1); ZHENG, Cindy Y (2); YAO, Yudong (1); DENG, Junjing (1); SEIFERT, Soenke (1); MIRKIN, Chad A. (2)**
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The rise of 4th generation synchrotron radiation sources has given small angle x-ray scattering (SAXS) community a great opportunity. Particularly, in the nanoparticle assembly studies, scattering data from a coherent light source can be collected and analyzed in both real and reciprocal spaces, where the real space imaging may enable visualizing various defects of the assemblies while the scattering data provides statistically averaged but higher resolution information. In this presentation, we will present our recent study on a directed self-assembly using combined scanning electron microscopy (SEM), ptychography x-ray imaging, and micro-SAXS.[1] The real space images obtained from ptychography measurements reveal various defects of the crystalline assembly including line and edge dislocations. On the other hand, micro-SAXS measurement enables fast and large-scale evaluation of the structures and lower resolution imaging with scattering contrast. Applied are also tomographic reconstruction and 3D reciprocal space mapping, which are complimentary to each other and share the same measurement geometry.

**Keywords**
DNA, assembly, mapping, ptychography, crystal

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SESSION 9C: HYBRID MATERIALS AND BIOMATERIALS 2
Chair: Prof. Renata C. Kaminski

## P344 - SMALL-ANGLE X-RAY SCATTERING LOOKING INSIDE THE PROTEIN CORONA

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The lack of fundamental understanding of physicochemical processes that occur when nanoparticles are injected into the bloodstream has hampered meaningful advances in nanoparticles-based precision medicine. Inside the body, nanoparticles (NPs) non-specifically adsorb blood proteins (forming the so-called protein corona) which end up masking the outermost surface of the engineered NPs and represent one of the main mistargeting reasons. Furthermore, the protein corona is prone to induce NPs aggregation, limiting their ultimate application since the overall surface area is drastically changed, reducing their biological outcome. Also, the surface charge and composition (dictated by the protein corona), as well as the size and shape of particles or aggregates, are intimately correlated to undesirable coagulation disorders and immune responses. Although many reports have tried to draw a correlation between protein corona and NPs aggregation, the amount of information is still sparse, and the correlation between them is not obvious. In parallel, mimicking NPs in natural medical environments is challenging, and only a very few and low informative number of techniques can finely probe these structures when in blood. Further, the complexity related to the ionic strength of the media and the vast span in concentration ranges of all components are bottlenecks that limit consistent and rational nanoparticle-based medical development.

Here we first report an innovative experimental design that spans over an extensive protein-to-particle concentration range and provides an entire picture that considers protein corona formation and NPs partial or massive aggregation states close to natural medical conditions. Silica nanoparticles of ~ 25 nm were first synthesized and later incubated in buffers at distinct ionic strengths with either bovine albumin serum, bovine $\gamma$-globulin, chicken egg lysozyme, fetal bovine serum, or human plasma. These complex mixtures of nanoparticles and proteins were then in-depth investigated by Small-Angle X-ray Scattering (SAXS) technique which was complemented by Dynamic Light Scattering (DLS) with Cryo-Transmission Electron Microscopy (Cryo-TEM) techniques. The approach described here was able to finely map protein corona formation and its NPs aggregation induction in a concentration-dependent fashion as required for a rational understanding of sustainable and effective systems for medical use.

In parallel, we also present new strategies to closely look at the protein corona, which relies on obtaining trustable binding parameters for the unprecedented visualization and size estimation of unstained hard and soft coronas in aggregation-free model systems. The first new strategy relies on the SAXS technique to follow the protein adsorption on silica nanoparticles and estimate binding parameters based on a model-free approach without being affected by non-bounded proteins. The second meaningful advance relies on visualizing unstained soft and hard protein coronas by core-loss energy filtering TEM (core-loss EFTEM), zero-loss cryo-EFTEM, and cryo-TEM with summation of images. This set of data was successful in obtaining a detailed characterization of the full protein corona thickness and morphology while making possible an unequivocal visualization of unstained hard and soft coronas.

**Keywords**
SAXS, protein corona, silica, adsorption, aggregation

SESSION 9C: HYBRID MATERIALS AND BIOMATERIALS 2
Chair: Prof. Renata C. Kaminski

## P231 - SMALL ANGLE-X RAY AND NEUTRON SCATTERING TO DETERMINE THE MECHANISM OF INTERACTION OF SHORT ANTIMICROBIAL PEPTIDES

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INTRODUCTION: The increased prevalence of multi antibiotic-resistant pathogens has been listed by the World Health Organisation (WHO) as one of the biggest threats to modern day healthcare, food security and development.1 Short peptides can be effective antimicrobials, and peptides that self-assemble may have a prolonged half-life and potential to self-deliver.2,3 Here we examine the self-assembling properties of 7 cationic peptides, with antimicrobial activity. We investigate the interactions of different short antimicrobial peptides with model membranes based on human red blood cells (hRBC’s), and three types of bacteria (E.coli, P.aeruginosa, and S.aureus) using small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS), comparing this data to the in vitro biological data: haemolysis, bacteriostatic and bactericidal assays, and SEM imaging, to determine whether small-angle scattering techniques can be used as a tool to predict AMP activity, AMP Mechanism and AMP potency.

METHODS: Antimicrobial assays and SEM imaging for three strains of bacteria: E.coli(K12), P. Aeruginosa (PA01) and S. Aureus, in motile and biofilm form was determined. Model membranes based on lipid bilayers were made and studied using Small-angle X-ray scattering (SAXS) at Diamond Light Source, UK, beamline B21 and Small-angle Neutron scattering (SANS) ISIS Muon and Neutron source, Zoom.

RESULTS AND DISCUSSION: Incorporation of D-amino acids increased the bactericidal activity compared to cyclisation and lipidation against PA01 for peptides rich in arginine. However, cyclisation of the peptide had better activity against bacteria in the biofilm phase. For lysine-rich peptides, the substituting the hydrophobic block unit for a lipid chain caused increased bactericidal activity, but also human blood cell death. SEM imaging of the bacteria with and without peptide showed disruption of the bacterial cell membrane. SAXS and SANS were used to determine the effect of peptides with model cell membranes, to determine whether head groups and tail groups effect how the peptides interact with the lipids. Peptides were found to reorder membranes at sufficient concentrations into cubic and hexagonal phase symmetry. Peptides were found to reorganise bilayers and prevent liposome formation at sufficiently higher concentrations. The changes in ordering which was invoked by different peptides depended on the membrane composition, both head groups and tail groups, giving information on the mechanisms of interaction of the lipid membranes in the bacteria themselves, supported by in vitro data.

CONCLUSION: To conclude, we have examined the self-assembly and antimicrobial activity of short peptides rich in arginine and lysine. We have found that addition of D-amino acids increases the bactericidal effect whereas, cyclisation is more optimum for reducing biofilm formation. SAXS and SANS determine changes of structure based on different membrane models which gives insight into the initial mechanism of antimicrobial activity. This work has application and relevance to the design and development of new antimicrobial materials.

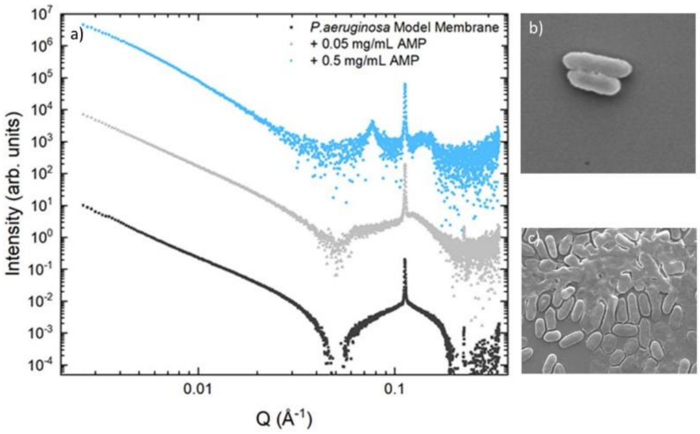

**Fig. 1) Peptide interaction with bacteria membranes** a) SAXS data collected on B21 of a membrane model based on *P.aeruginosa* (dark grey) with different concentrations of an AMP shown in grey and blue. Addition of the peptide causes a change in the membrane from a lamellar structure to a cubic phase structure. SEM images of control bacteria b) and AMP treated bacteria c) showing changes in the membrane surface roughness, shape and size. SAXS gives information on how lipids alone are interacting with the peptide, which gives information into the mechanism of these interactions.

**Keywords**
Antimicrobial Peptides, Self-Assembly, SAXS, SANS, Lipid phases

**References**

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# P258 - INFLUENCE OF ORGANIC MATTER INTO THE MICROSTRUCTURE IN CHERT: FIRST INSIGTHS FROM A (U)SAXS PERSPECTIVE

**MONTECINOS MUNOZ, Patricio (1); ILAVSKY, Jan (2); OLIVEIRA, Cristiano (3); WETTER, Niklaus (4); LOURENÇO, Rafael (5); ANDRADE, Marcelo (6); MARTINS, Tereza S. (7); DIPOLD, Jessica (4); FREITAS, Anderson Zanardi (4)**
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Chert, deposits of amorphous silica (SiO2) now quartz, have been interpreted as a record of life´s evolution on Earth as most of these silica-rich sedimentary rocks preserve microfossils and organic matter (OM). Silica diagenesis, driven by the conversion of amorphous silica to quartz, reduces the permeability of silica aggregates, isolating the OM during geological timescales [1, 2]. Therefore, characterization of the pore network is critical in understanding OM preservation in chert. We report (U)SAXS measurements in two cherts of different ages (134 Ma and 1.8 Ga) to gain first insights into the influence of OM on the silica-pore network in chert. Thus, we follow the procedure by [3] using combustion up to 1000°C to remove OM from pores, collecting (U)SAXS data before and after combustion (Figure 1). Our initial data show that samples are simple mineralogic systems predominantly composed of quartz particles supporting a pore network. Samples bear aliphatic and polycyclic aromatic hydrocarbons yielding an increasing aromatic/aliphatic ratio from the younger to the older sample. This trend points to a progressing graphitization of OM in older cherts. Pore size distributions (PSDs) estimated using the maximum entropy method in Irena [5] indicate volume fractions lesser than 0.04 for all scattering curves (Figure 1). Mesopores (2 to 50 nm) control a significant part of estimated total volume fractions. The younger sample yielded a greater porosity (combusted and intact fragments, Figure 1B). A long burial and geological history can explain the lesser porosity observed in the older sample. A greater porosity is observed in combusted fragments (insets 1a2 and 1b2) than those displayed by intact fragments indicating remotion of organics from the pore network. Finally, considerations about PSDs, sample ages, and aliphatic/aromatic ratios will be discussed.

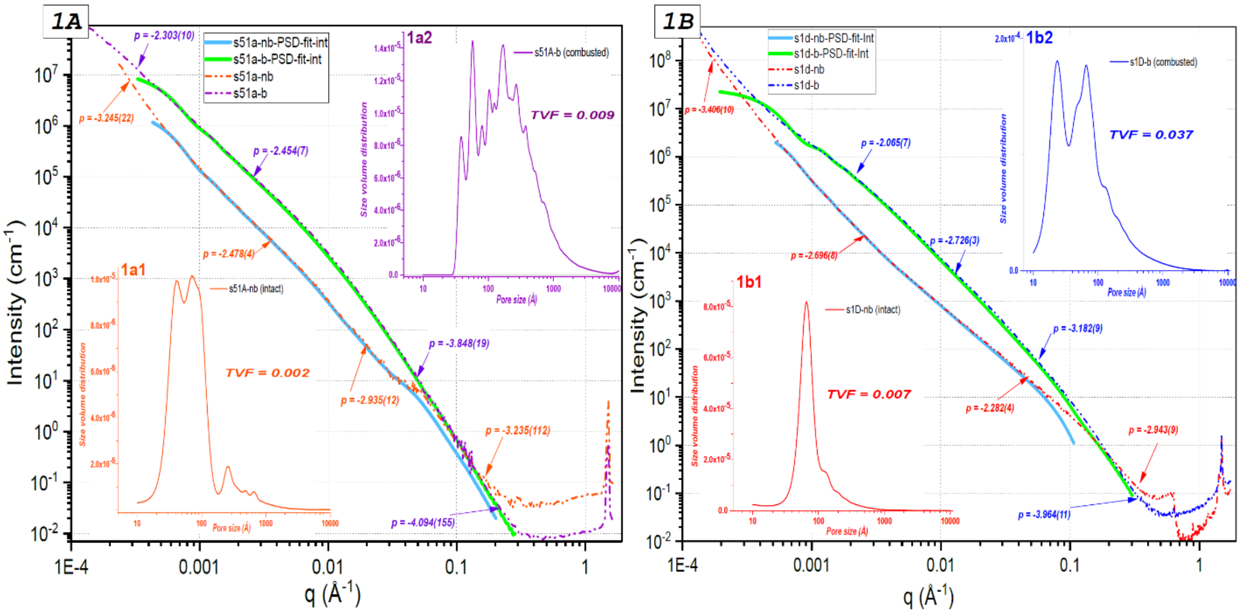

**Figure 1.** USAXS/SAXS/WAXS data were collected at APS 9ID-C beamline for samples s51A (1A) and s1D (1B). In 1A, the violet bracketed curve show data for the combusted fragment (b, mineral matrix) and the orange bracketed curve for the intact fragment (nb, no combusted, mineral matrix + OM). In 1B, the blue bracketed curve show data for the combusted fragment (b, mineral matrix), and the red bracketed curve show data for the intact fragment. In these bracketed curves, italic numbers indicate values for power-law slopes for different segments of scattering profiles and numbers in parenthesis highlight 1SD error in the last digits. On both diagrams, 1A and 1B, green and cyan continuum curves display the fitting output of the maximum entropy method applied via Irena [4]. In general, the quality of fits is acceptable for most scattering curves. Insets (1a1, 1a2, 1b1, and 1b2) show the size volume distributions estimated via the maximum entropy method. Estimated values for total volume fraction (TVF) are included on each inset. SAXS experimental details will be discussed. Gradual heating experiments were performed using a TGA instrument at the Hybrid Materials Laboratory, Federal University of the São Paulo State (UNIFESP). Sample 1D corresponds to chert (~134 Ma) collected for IODP at Ocean Pacific near Japan. Sample 51A corresponds to a 1.8Ga chert from Gunflint Formation provided for Prof. A. Knoll (Harvard University).

**Keywords**
Silica-rich sedimentary deposits, chert, organic matter, USAXS, SAXS

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## Acknowledgements

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## V166 - ASSESSING THE EFFECTS OF DEGRADATION IN WOOD USING X-RAY AND NEUTRON SCATTERING

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Exposing wood to detrimental environmental conditions such as fire exposure, and/or decay organisms can lead to physical and chemical changes in the wood structure that can adversely affect the wood properties and ultimately, its performance. Conservation and protection treatments typically aim to react with the wood hydroxyls to make wood less susceptible to these environmental conditions. A better understanding of how different degradation mechanisms alter the wood nanostructure and/or the polymers inside the wood cell walls would accelerate the development of new protection treatments that can hinder the degradation process. Here, we combined wide-angle x-ray scattering, small angle x-ray scattering and small angle neutron scattering to measure the wood nanostructure as well as the cellulose diffraction in wood samples degraded by different processes, namely, chemically, biologically, and thermally. Moreover, the effects of long-term degradation were assessed by studying two archaeological wood samples that were over 1200 years old. By combining these techniques, we were able to determine how different degradation processes altered the wood nanostructure in terms of the cellulose microfibril alignment, elementary fibril spacing and cellulose crystalline structure inside the wood cell walls.

**Keywords**
SANS, SAXS, WAXS

SESSION 9C: HYBRID MATERIALS AND BIOMATERIALS 2
Chair: Prof. Renata C. Kaminski

# V265 - SMALL- AND WIDE- ANGLE X-RAY SCATTERING FROM PHOTONIC STRUCTURES OF LUCANIDAE AND SCARABAEOIDEA BEETLES

**CHANG, Je-Wei (1)**; **LIAO, Kuei-Fen (1); YEH, Yi-Qi (1); SHIH, Orion (1); WANG, Chen-An (1); SU, An-Chung (2); TSAI, Jing-Fu (3); JENG, U−Ser (1,2)**
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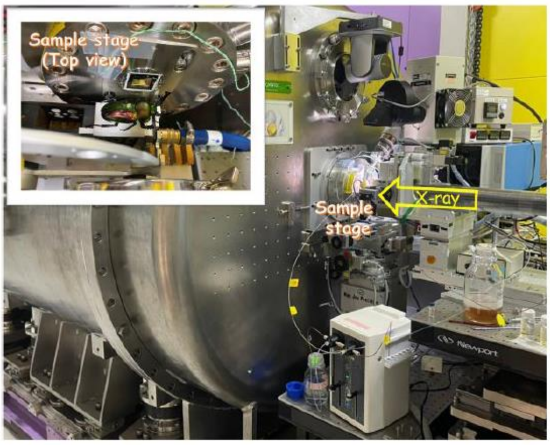
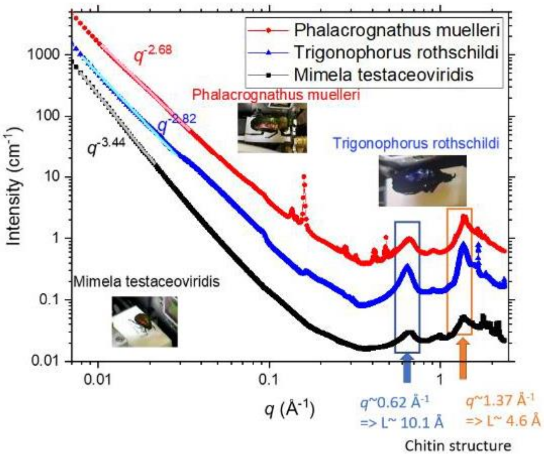
The hard exoskeletons of beetles often demonstrate outstanding structural properties, including crush resistance, sensory response, and color changeability. Consequently, the intrinsic complex hierarchical structures and the arrangement of crystalline to nano- and micrometer scaled structures near the surface of exoskeletons have received considerable attention recently. These beetles have somehow evolved to grow complex nanostructures of photonic structures that can give metallic shining colors under light illumination. Mechanism of forming such photonic structures, however, remains poorly understood. In the present study, the elyra (forewing) of one Lucanidae and two Scaraaeidae (Phalacrognathus muelleri, Trigonophorus rothschildi and Mimela testaceoviridis) are investigated using synchrotron small/wide angle X-ray scattering (SWAXS) and ultra-SAXS of the 13A biological SWAXS beamline at the Taiwan Photon Source [1][2]. The results indicated highly oriented layering structures of few hundred nm d-spacing existing near the surface of the exoskeleton of P. muelleri of a larger size; rich nanostrucutres of 5-6 nm characteristic size are also observed. Also observed are the perpendicularly oriented b-type chitin crystallites in the shell surface layer. Optical properties are correlated to the observed molecular arrangements in the surface layers of the hard exoskeletons of the beetles. The results shed lights on the formation origin of the photonic structure, which understanding would help in the design of displays and surface coating technologies in biomimetic applications.





**Keywords**
photonic structures, Small- and wide-angle X-ray scattering, TPS13A BioSWAN

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PLENARY 6
Chair: Dr. Aline Ribeiro Passos

# V440 - DYNAMICAL PROPERTIES OF OUT-OF-EQUILIBRIUM MATERIALS STUDIED WITH COHERENT X-RAYS

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X-ray Photon Correlation Spectroscopy (XPCS) is a spatio-temporal coherent X-ray scattering technique that probes slow collective dynamics at the nanometric and atomic scale based on the observation of fluctuating far-field speckle patterns [1].

This technique has been successfully applied to the investigation of the slow relaxation processes occurring in disordered materials undergoing dynamical arrest, aging and poliamorphic transitions such as glasses, concentrated colloidal suspensions and viscous liquids [2-4].

The advent of 4th generation synchrotrons has extended dramatically the dynamical range of XPCS, opening the field to new ground breaking experiments. For the first time, it will be possible to explore microsecond fluctuations in hard materials undergoing heterogeneous dynamics, and to unveil the particle motion of complex materials under extreme conditions.

In this talk, I will present some examples on the relaxation dynamics in metastable complex systems and I will also illustrate some of the future scientific possibilities offered by 4th generation synchrotrons as ESRF-EBS.

**Keywords**
XPCS

**References**

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# V448 - SMALL-ANGLE SCATTERING FOR DEVELOPMENT OF SELF-ASSEMBLING CHIMERIC PROTEIN COMPLEXES – POTENTIAL VACCINES AGAINST SARS-COV-2

**VLASOV, Alexey (1,2); SUDAREV, Vsevolod (1); VLASOVA, Anastasiia (1); BAZHENOV, Sergey (1,3); RYZHYKAU, Yury (1,2); GUSHCHIN, Ivan (1); BONDAREV, Nikolay (1); MANUKHOV, Ilya (1,3); KUKLIN, Alexander (1,2)**
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Self-assembling chimeric protein complexes of apoferritin fused with immunogen are prospective vaccines against a wide range of pathogenic diseases[1]–[3]. The bottleneck of engineering of large protein complexes is a self-assembly control. In literature, electron microscopy (EM) technique is commonly used to verify the assembly of apoferritin-immunogen complexes[1]–[3]. Such an approach seems challenging and time-consuming in terms of sample preparation and measurements.

Previously, we showed that small-angle scattering (SAS) can be applied as a highly-efficient technique for quality control of self-assembling protein complexes and, therefore, development of new vaccines and drug-design[4]–[6]. We designed two genetic constructs comprising apoferritin subunit fused with a receptor-binding domain (RBD) of the S-protein of SARS-CoV-2 and the part of the S1 domain of the S-protein – ApofRBD and ApofS1RBD, respectively. After overexpression in E. coli and purification using standard procedures, we investigated the samples by SAS techniques and showed the self-assembly of the 8-mers of ApofRBD and 24-mers of ApofS1RBD protein complexes. The results obtained by SAS are complementary to those obtained by EM technique, that we also applied for measuring 24-mers of ApofS1RBD. Thus, we demonstrated that the SAS approach can be efficiently used for structure-based immunogen design allowing rapid self-assembly quality control and determination of the oligomeric state of protein complexes.

In addition, our approach allowed us to develop recombinant protein complexes – potential vaccines against SARS-CoV-2, which can be produced in E. coli cells. In case of confirmed immunological function and successful preclinical trials such an approach would allow cheap mass-production in contrast with using human cells (e.g. HEK) or a hybrid method (e.g. ferritin from E. coli and RBD from HEK)[3].

**Keywords**
Ferritin, SARS-CoV-2, self-assembly, recombinant vaccines

**References**

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## Acknowledgements

AVV, ADV, SVB, YLR, IVM and IYG acknowledge the support from the Ministry of Science and Higher Education of the Russian Federation (agreement 075-03-2022-107, project FSMG-2021-0002).

SESSION 10A: PROTEIN STRUCTURE, ASSEMBLIES AND DYNAMICS 4
Chair: Dr. Guillaume Tresset

## P301 - HIERARCHICAL ASSEMBLY PATHWAYS OF SPERMINE-INDUCED TUBULIN CONICAL-SPIRAL ARCHITECTURES

**DHARAN, Raviv; SHEMESH, Asaf; MILLGRAM, Abigail; ZALK, Ran; FRANK, Gabriel A.; LEVI-KALISMAN, Yael; RINGEL, Israel; RAVIV, Uri**
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Tubulin, an essential cytoskeletal protein, assembles into various morphologies by interacting with an array of cellular factors. One of these factors is the endogenous polyamine spermine, which may promote and stabilize tubulin assemblies. Nevertheless, the assembled structures and their formation pathways are poorly known. Here we show that spermine induced the in vitro assembly of tubulin into several hierarchical architectures based on a tubulin conical-spiral subunit. Using solution X-ray scattering and cryo-TEM, we found that with progressive increase of spermine concentration tubulin dimers assembled into conical-frustum-spirals of increasing length, containing up to three helical turns. The subunits with three helical turns were then assembled into tubules through base-to-top packing and formed antiparallel bundles of tubulin conical-spiral tubules in a distorted hexagonal symmetry. Further increase of the spermine concentration led to inverted tubulin tubules assembled in hexagonal bundles. Time-resolved experiments revealed that tubulin assemblies formed at higher spermine concentrations assembled from intermediates, similar to those formed at low spermine concentrations. These results are distinct from the classical transition between twisted ribbons, helical, and tubular assemblies, and provide insight into the versatile morphologies that tubulin can form. Furthermore, they may contribute to our understanding of the interactions that control the composition and construction of protein-based biomaterials.
Hierarchical assembly pathways of Spermine-induced tubulin conical-spiral architectures

**Keywords**
Tubulin

**References**

R Dharan, A Shemesh, A Millgram, R Zalk, GA Frank, Y Levi-Kalisman, ... ACS nano 15 (5), 8836-8847
doi.org/10.1021/acsnano.1c01374

# P262 - RESOLVING SURFACTANT MONORMER- AND MICELLE-UNFOLDING STAGES OF BOVINE SERUM ALBUMIN USING SIMULTANEOUS SEC-SAXS, UV-VIS ABSORPTION AND REFRACTIVE INDEX.

**YEH, Yi-Qi (1); LIAO, Kuei-Fen (1); SHIH, Orion (1); WU, Wei-Ru (1); SU, Chun-Jen (1); JENG, U-Ser (1,2)**
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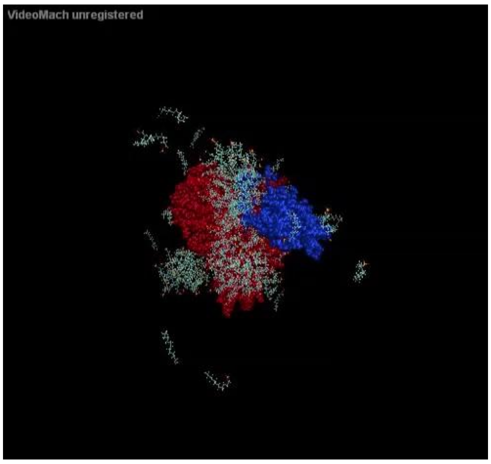
Detergents are commonly used to disrupt noncovalent interactions of proteins, leading to detergent-protein complex, stabilized recombinant proteins. Such protein unfolding process is often revealed with the local structural changes of the protein of the complex with optical spectroscopies. How the detergent molecules proceed these actions is, however, elusive up to date. Resolving the role of detergents in a protein unfolding process requires tools of sensitivity to the detergent and kinetic measurements that allow separating the effects contributed by the coexisted protein/detergent complex and detergent micelles in the complex solution of excess detergent in the equilibrium protein unfolding.

In this work, we show that sodium dodecyl sulfate (SDS), a frequently used surfactant in analytical technique to separate proteins based on their molecular weight, can bind to bovine serum albumin (BSA) for multi-stage unfolding. The newly installed small- and wide-angle X-ray scattering (SWAXS) beamline 13A at the 3.0 GeV Taiwan photon source (TPS) 13A of NSRRC, equipped with online protein purification system of high-performance liquid chromatography (HPLC) incorporated with UV-vis absorption and refractive index measurements, allows composition and conformation measurements in one sample elution. separating the scattering contributions from the BSA/SDS complexes and the coexisting SDS micelles, thereby, differencing the SDS monomer-unfolding from the micelle-unfolding stages of BSA. HPLC-SWAXS of SDS/BSA sample solutions were simultaneously and successively collected during the HPLC sample elution with 1 data frame per 2 s using in vacuum Eiger-9M and 1MX detectors. Together with simultaneous observed UV-vis absorption and refractive index (RI), we have resolved the stoichiometric unfolding conformations of BSA by SDS monomers followed by micelles. As a function of SDS concentration, the corresponding association numbers and Rg of protein-SDS along the unfolding process reveal a multi-stage unfolding route. The SWAXS data reveal the SDS-associated conformational changes of BSA from globule to extended structure with attached SDS micelles. Molecular dynamic simulation further supports the SDS micelles aggregation on the unfolded protein sites. The corresponding protein-SDS association numbers retrieved from the unfolding process characterize further the monomer-micelle cooperative unfolding process of BSA.



**Keywords**
SAXS, BSA, SDS, unfolding

SESSION 10A: PROTEIN STRUCTURE, ASSEMBLIES AND DYNAMICS 4
Chair: Dr. Guillaume Tresset

## V263 - THE BIOSAXS BEAM LINE BL4-2 AT SSRL: EXPERIMENTAL AUTOMATION AND REMOTE EXPERIMENTS

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The biological small-angle x-ray scattering station BL4-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) provides state-of-the-art experimental facilities for studies focused on structural biology and biophysics. The SAXS instrument can be rapidly configured and optimized for a variety different experiments ranging from static and time-resolved solution scattering to lipid and fiber diffraction. The instrument features a variable camera length (from 0.3m to 3.5m in seven discrete steps) and a tunable X-ray energy (from 7keV to 17keV). A high flux multilayer monochromator provides sufficient flux for millisecond scale time-resolved experiments and a microfocus beam option is available using a modular in-hutch Kirkpatrick-Baez mirror system enabling experiments using microfluidic sample handling and mixing devices as well as small, micron sized samples and scanning applications. The beamline is controlled using a customized version of the BluIce/DCS software, which provides an intuitive graphical user interface with dedicated tabs for the various supported experiments. The interface tabs contain all the handles required for the different aspects of the experiments. A data reduction analysis pipeline provides real-time data analysis during the ongoing experiment.

Here we present some recent advances using robotic sample handling to automate and optimize the experimental setup in order to enable high quality, truly remote controlled SAXS experiments at the beamline. For biomacromolecular solution samples our high throughput Autosampler allows now for pipetting and mixing of samples on the tray just before the SAXS measurement if required and can run through several 96-well plates of samples without further intervention. A size-exclusion chromatography (SEC) option can be remotely selected to switch between regular solution SAXS and SEC-SAXS experiments. Our regular SEC-SAXS data collection setup is highly optimized for minimizing sample dilution during the chromatography as well as for preserving the full chromatographic resolution before the SAXS data collection. For more viscous samples typically measured in single pre-filled capillaries a high-capacity cassette system was developed allowing for shipment and save handling of the capillaries at the beamline. The cassettes are robotically mounted at the beamline and the samples can be aligned for the X-ray measurement using a remotely accessible sample microscope integrated into the BluIce interface. The whole experiment can thus be run fully remotely.

**Keywords**
bioSAXS, solution scattering, instrumentation, automation, robotics, protein solution, lipid diffraction

SESSION 10B: DYNAMICS, KINETICS, IN SITU AND TIME-RESOLVED 2
Chair: Dr. Aline Ribeiro Passos

# P233 - COMBINED TIME-RESOLVED USAXS/WAXS/XPCS IN-SITU EXPERIMENTS FOR THE INVESTIGATION OF ZEOLITES FORMATION MECHANISM

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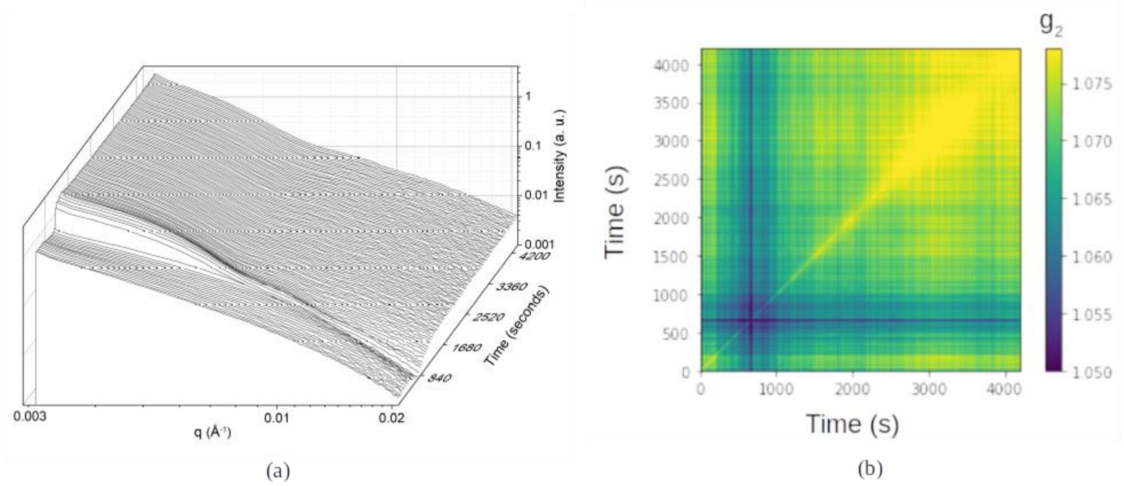
Zeolites are porous crystalline aluminosilicates formed by frameworks of AlO4- and SIO4 tetrahedrons. The 3D cage-like structure with pores and channels makes zeolites of high interest for industrial applications such as catalysis and molecule separation. In this context, knowledge about the formation of the zeolite structure is crucial since it is a prerequisite for the control of morphological properties desired for a specific application. In this work we investigated the formation of sodalite zeolite by performing time-resolved in situ USAXS/WAXS/XPCS experiments. The description of the scattering data acquired during the synthesis of the zeolites by a Monte Carlo theoretical SAXS model allowed to unveil the temporal evolution of structural features from different populations of nanoparticles during the formation process. WAXS allowed the identification of the different phases, the amorphous precursor and the crystalline LTA and SOD topologies. The correlation of the structural knowledge obtained by SAXS/WAXS with information about the dynamics provided by the XPCS characterizations allowed a deeper comprehension of the mechanisms behind the formation of the zeolites as we will show in this presentation.



(a) (b)

**Figure 1**: Time-resolved SAXS intensity curves (a) and two-time intensity autocorrelation graph (b) obtained *in situ* during the nucleation and growth of zeolite.

**Keywords**
SAXS, WAXS, XPCS, zeolite, in situ, formation, sodalite, lta, monte carlo

## V324 - PROBING PROTEIN DYNAMICS USING XPCS DESPITE RADIATION DAMAGE

**CHUSHKIN, Yuriy (1); GULOTTA, Alessandro (2); ROOSEN-RUNGE, Felix (2,3); PAL, Antara (2); STRADNER, Anna (2,4); SCHURTENBERGER, Peter (2,4)**
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X-ray Photon Correlation Spectroscopy (XPCS) is a well-established technique to study slow dynamics in disordered materials at nanometer down to angstrom length scales [1]. The method exploits the coherent fraction of the synchrotron radiation and benefits enormously from the recent upgrade of the ESRF source (EBS) [2]. The high degree of coherence opens new avenues for application of XPCS. One of the promising avenues is the study of dynamics in concentrated protein solutions at nearest neighbor distances. Diffusion of proteins on length scales of their own diameter in highly concentrated solutions is essential for understanding biological systems such as a living cell, but its experimental characterization remains a challenge. Our work addresses this problem and discusses the use of X-ray Photon Correlation Spectroscopy at a recently upgraded 4th generation synchrotron source for this purpose. While X-ray radiation damage was generally believed to seriously threaten the application of XPCS to biological systems, we now present a dedicated experimental and analysis strategy [3] to overcome this obstacle. We report a successful test of this approach to highly concentrated solutions of the eye lens protein alpha crystallin [4], which has previously been established as a model protein exhibiting the classic behavior of hard sphere colloids under these conditions [5]. The thus obtained intrinsic relaxation times for so-called long-time cage diffusion indeed agree with macroscopic measurements of the zero shear viscosity [6].

Our experiments also reveal a complex dependence of the key structural and dynamic properties of the protein solutions on both the total absorbed radiation dose as well as the dose rate. We discuss possible mechanisms responsible for the observed radiation effects and their consequences for future applications of XPCS.

### Keywords

XPCS, protein diffusion, glass transition, radiation damage

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SESSION 10B: DYNAMICS, KINETICS, IN SITU AND TIME-RESOLVED 2
Chair: Dr. Aline Ribeiro Passos

# V214 - INTERPLAY BETWEEN THE SELF-ASSEMBLY AND DYNAMICS OF COLLOIDAL RODS STUDIED BY SAXS AND XPCS

**PAL, Antara (1,2); KAMAL, Md. Arif (1); ZINN, Thomas (3); NARAYANAN, Theyencheri (3); SCHURTENBERGER, Peter (1,4)**
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Anisotropic colloids are known to exhibit a rich phase behavior. In addition to the usual gas, liquid, crystal and glassy states found for spherical particles, anisotropic particles such as rods are known to exhibit additional liquid crystalline phases. Here we present the self-assembly and dynamics of colloidal rods for aspect ratio, ρ~8.0. The self-assembly and (an)isotropic dynamics of these particles at the nearest neighbor length scale were investigated over a wide concentration range using SAXS and multispeckle ultrasmall-angle X-ray photon correlation spectroscopy (USA-XPCS). At low concentrations, the self-assembled phase as well as dynamics are isotropic. However, beyond a certain critical concentration a nematic and a smectic phase are formed, which makes the dynamics anisotropic. We have also explored the relation between the resulting diffusion coefficients and the structure factor of the self-assembled structures. The results indicate that the particle dynamics strongly depends on the structure factor. Further, the diffusion coefficients at the nearest neighbor length scale slow down considerably at high concentrations and the system approaches a kinetic arrest.

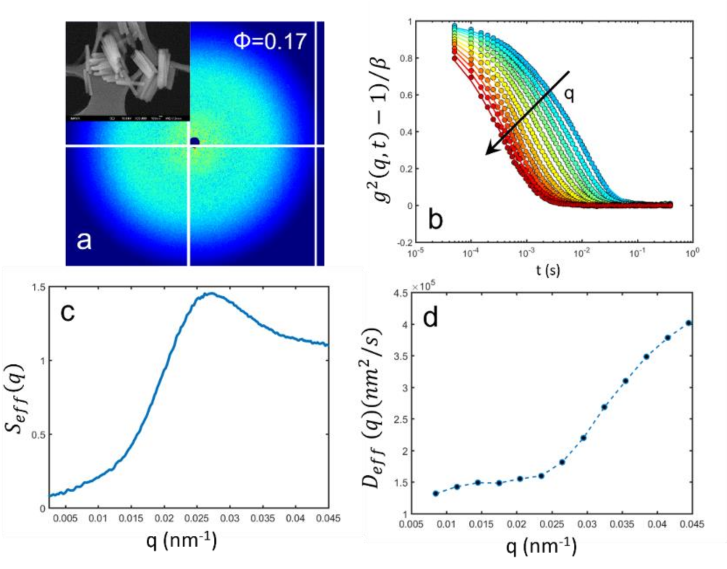

*Figure 1. (a) 2D diffraction pattern of colloidal rods (inset) at volume fraction φ=0.17. (b) correlation functions for different scattering vectors q. (c) Effective structure factor and (d) corresponding effective diffusion coefficient.*

**Keywords**
Dynamics, Self-assembly, Colloids, SAXS, XPCS

## SESSION 10B: DYNAMICS, KINETICS, IN SITU AND TIME-RESOLVED 2

Chair: Dr. Aline Ribeiro Passos

# V187 - STRUCTURE AND DYNAMICS OF EXTREMELY SWOLLEN LYOTROPIC PHASES

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Microemulsions (ME) are a class of thermodynamically stable oil/water/surfactant mixtures with droplet sizes of ~ 1 – 100 nm [1] that are important for a variety of industrial applications, from drug formulations [2] to personal care products [3]. Microemulsions have also found use in structural colour applications as all-liquid-type artificial colouration materials [4]. While self-assembly in simple, bicomponent systems is reasonably understood, self-assembly in more complex systems is less studied. Therefore, to fully exploit such systems, a combined structural and dynamical approach must be employed.

This work studies the self-assembly of structures formed in pseudo-quaternary systems containing two amphiphilic species using high resolution small-angle X-ray scattering (HR-SAXS). In such systems, Peter et al. [5, 6] reported extremely dilute lyotropic phases with long periodicities (ξ up to 2200 Å) with cubic, hexagonal, or tetragonal symmetries as a function of oil and 1-octanol content, beyond the conventional definition of ME. These phases were reinvestigated using HR-SAXS [7], where, for the ordered symmetries, Bragg reflections of 2D-hexagonal ordering were observed, $q_{1,0}:\sqrt{3}q_{1,0}:\sqrt{4}q_{1,0}:\sqrt{7}q_{1,0}:\sqrt{12}q_{1,0}$, with $\xi > 2000$ nm. As there was no clear compressibility region, the phase was described as a hierarchical structure of hexagonally ordered microemulsion droplets held within large emulsion droplets. Other morphologies observed were a disordered emulsified-microemulsion and a bicontinuous microemulsion. The dynamics of the microemulsion droplets were probed using X-ray photon correlation spectroscopy (XPCS), which revealed two relaxation modes typically found in dense colloidal systems below their glass transition. The combined structural and dynamical approach provides a consistent picture of the underlying morphology and enables the discussion of self-assembly and multiscale dynamics of coexisting phases.

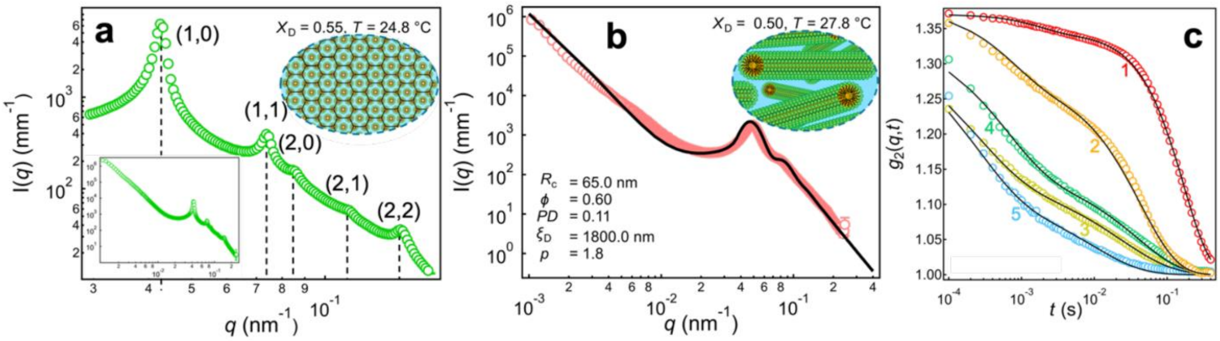

Figure 1 (a) An example 1D SAXS profile of the emulsified hexagonal phase with schematic (top, inset) and full q-range (bottom, inset). (b) An example 1D SAXS profile of the disordered emulsified-microemulsion with schematic (top, inset). The black line represents modelling to a dense colloidal cluster, with parameters: cylinder radius Rc, volume fraction f, polydispersity PD, correlation length xD, and power p. (c) The g2(q,t) functions for the q values: 1 0.0085, 2 0.0165, 3 0.0245, 4 0.0265, and 5 0.0345 nm-1. The black lines represent modelling to a sum of two stretched exponential decays.

## Keywords

Microemulsions, self-assembly, small-angle X-ray scattering (SAXS), swollen lyotropic phases, X-ray photon correlation spectroscopy (XPCS)

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SESSION 10C: INSTRUMENTATION, DATA FORMAT AND BEAMLINES 3
Chair: Dr. Clement E. Blanchet

## P228 - EBS – THE RISE OF BIOSAXS AT THE ESRF: BEAMLINE BM29

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A world class SAXS beamline, dedicated exclusively to bio-solutions, the ESRF leads the way. BM29, BioSAXS station opened to users in 2008 [1]. With the number of BioSAXS publications based on ESRF-collected data growing near-exponentially, BM29 is significantly oversubscribed. This has been a worldwide trend and in recent years a combination of advances in sample handling, computer modelling and synchrotron sources have made BioSAXS more and more attractive. Moreover, whereas in the past even experienced crystallographers may have complained that SAXS experiments required too much time and effort, now they consider them indispensable.

The ESRF-Extremely Brilliant Source (EBS) project started in 2020 and was completed on time in September 2021. During this long shutdown BM29 moved to a new source, a 2-pole wiggler, to replace the bending magnet. This has provided a smaller, more intense X-ray beam at the sample position. A new detector has been installed as well as replacing our ground-breaking sample-changer unit, developed at the BM29 12 years ago, with the newest version. These upgrades will generate high quality, low noise data with lower concentrations of sample (0.1mg/ml) necessary.

The software on BM29 was also extensively upgraded over the shutdown. Our beamline control software SPEC was replaced by BLISS. We also would like to introduce our new data collection software, BSXCuBE3 (BioSAXS Customized Beamline Environment) the layout and functionality were designed with a "User first" principal, clean, unobtrusive and intuitive to new users but powerful for more expert users and the Local contacts. Simple colours and an ergonomic stepwise progression with an emphasis on limiting the button clicks required to start a data collection, to add to the simplicity of use. Our data analysis suite has also migrated from ATSAS to the newly developed opensource, FreeSAS [2], developed in part at the ESRF. All data collection parameters and results are logged and stored in a modified ISPyB database [3].

BM29 experiments are highly automated, we have offered two main modes of operation: BioSAXS with a robotic liquid handling sample changer (SC) and BioSAXS with online size-exclusion chromatography (SEC). We are now starting to offer a third sample environment, in conjunction with EMBL Grenoble and EMBL Hamburg a new sample exposure unit (SEU2B) was developed that allows the introduction of in-vacuum microfluidics. An off-the-shelf suite of devices is being developed for users, to give a greater, more diverse experimental set-up. A project that would not be possible without the smaller beam, thanks to the ESRF EBS upgrade.

**Keywords**
BM29, BioSAXS, EBS, microfluidics

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## P315 - SAPUCAIA: THE SMALL-ANGLE X-RAY SCATTERING BEAMLINE AT SIRIUS

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Small-Angle X-ray Scattering (SAXS) is a structural characterization technique used to study morphological (shape, size, and spatial organization) and dynamical properties of nano- and micro-structured objects. It is a well-established technique, having applications in a wide variety of research fields such as physics, chemistry, biology, engineering, and industry. Sapucaia beamline will be able to answer several significant scientific questions, concerning life science (biological and medical applications), structural biology (proteins, nucleic acids, lipids, and general macromolecules), and a vast field of material science, including nanotechnology, polymers, and environmental sciences. The beamline will be dedicated to the study of both in-solution as well as solid samples. It is being designed to cover a large q-range and a large X-ray energy window (from 6 to 17 keV). This design was chosen in order to make the beamline as stable as possible, allowing highly reproducible and low-noise data. Outside the shielding wall, the beamline is organized in two main hutches (the optical and the experimental ones) with a 2 m diameter tunnel which contains the detector under low pressure (~10-3 mbar). The first hutch house is the optical devices, where among other things, it has the vertical-bounced double-crystal monochromator and the horizontal-bounced toroidal mirror – for horizontal and vertical focalization and harmonic rejection (which in turn arises from the undulator source). The second hutch house contains the main experimental station, with absorbers, a fast shutter, and sample-holders/environments. The tunnel is attached at the end of this station, housing the detector (PiMega 540D) and a 10 m long rail, inside the 15 m-long steal tunnel. The definition of the beamline design was based on three main characteristics that will make Sapucaia one of the most important SAXS beamlines worldwide, which are: (i) low parasitic X-ray scattering, (ii) low beam divergence, and (iii) high stability of the optical components. Thus, at Sapucaia, scientists will be able to measure the so-called: Conventional SAXS, as well as, SEC-SAXS, and anomalous SAXS, and perform time-resolved experiments, among other possibilities.

**Keywords**
SAXS, SEC-SAXS, TR-SAXS

# P216 - TIME-OF-FLIGHT SMALL ANGLE NEUTRON SCATTERING FROM THE HYDROGEN-CONTAINED SOFT MATTER: BREAKING STIGMA OF ITS UNBEARABLE COMPLEXITY

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Bilby [1] is a Time-of-Flight (ToF) small angle neutron scattering instrument at the Australian Center for Neutron Scattering, Australian Nuclear Science and Technology Organization (ANSTO).
Bilby is also equipped with a monochromatic option, though a majority of the experiments for the six years of its operation have been performed in the ToF mode. The design of Bilby opens the possibility to vary wavelength resolution in a wide range (from 4% to 30%). Two arrays of position-sensitive detectors in combination with utilizing of wide wavelength range (from ~2Å to ~20Å) provide the capability to collect scattering data of wide angular range without changing the experimental set-up. The instrument can cover Q (momentum of transfer) range from 1 x 10-3 to 1.8 Å-1, with the most common settings allowing simultaneous data collection in the range between 1·10-3Å-1 and 0.6Å-1. Offered instrument design opens the possibility to collect scattering from a wide range of samples, with a unique capability to record fast kinetics data.
The time-of-Flight mode has enormous advantages at a price of several complexities which require a good understanding to be able to overcome them [2]. A quite common opinion is the SANS society that the ToF mode is too complex for studies of materials with high content of hydrogen which causes massive incoherent elastic and inelastic background. Having an instrument that is ideal for the analysis of the issues, we have accumulated some experience in the reduction of heavily contaminated data and a good understanding of the elastic/inelastic incoherent background. We are not proposing a universal solution of course, but we think our results might be useful for scientists operating ToF SANS machines.
We also plan to present several examples of the scattering data from the soft matter systems, including surfactants and liquid crystals, all reduced using customized algorithms implemented in Mantid software [3].

**Keywords**
SANS, incoherent scattering, ToF, hydrogen background

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[3] O. Arnold, et al., Nuclear Instruments and Methods in Physics Research Section A. 764 (2014), DOI: https://doi.org/10.1016/j.nima.2014.07.029

# V268 - CENTAUR, THE SMALL- AND WIDE-ANGLE NEUTRON SCATTERING DIFFRACTOMETER AT THE FUTURE SECOND TARGET STATION OF SNS

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The Centaur instrument has been selected as one of the first eight instruments to be built in the Second Targe Station of SNS at Oak Ridge National Laboratory. As a work-horse SANS instrument, it provides capabilities well beyond a traditional single purpose instrument. The high flux, broad wavelength band and large angular detector coverage provide simultaneous small/wide-angle neutron scattering and diffraction capability with a large dynamic range, enabling measurement of length scales across interatomic distances (diffraction) to hundreds of nanometers (small-angle scattering). Further, with a high-speed Fermi chopper it can be used as a direct geometry spectrometer for probing the dynamics of relatively large length-scale structures.

We are designing Centaur to fill a capability gap in the current instruments at ORNL. Notably, the WANS and diffraction capability will be unique among SANS instruments in the United States. Centaur will enable in situ/ operando experiments on materials with hierarchical architecture, for kinetic and/or out-of-equilibrium studies of phenomena with time-resolution down to seconds in many areas of materials research including soft matter, polymer science, geology, biology and quantum condensed matter. The spectrometer mode extends the momentum transfer and energy transfer to a lower Q than those typically covered by other spectrometers and provides a unique capability for inelastic SANS experiment. Additionally, beam polarization will enable detailed structural and dynamical investigations of magnetic materials and quantum materials.

**Keywords**
SANS, WANS, neutron scattering

SESSION 11A: PROTEIN STRUCTURES, ASSEMBLIES AND DYNAMICS 5
Chair: Barbara Bianca Gerbelli

# P313 - ARTIFICIAL NEURAL NETWORKS FOR SOLUTION SCATTERING DATA ANALYSIS

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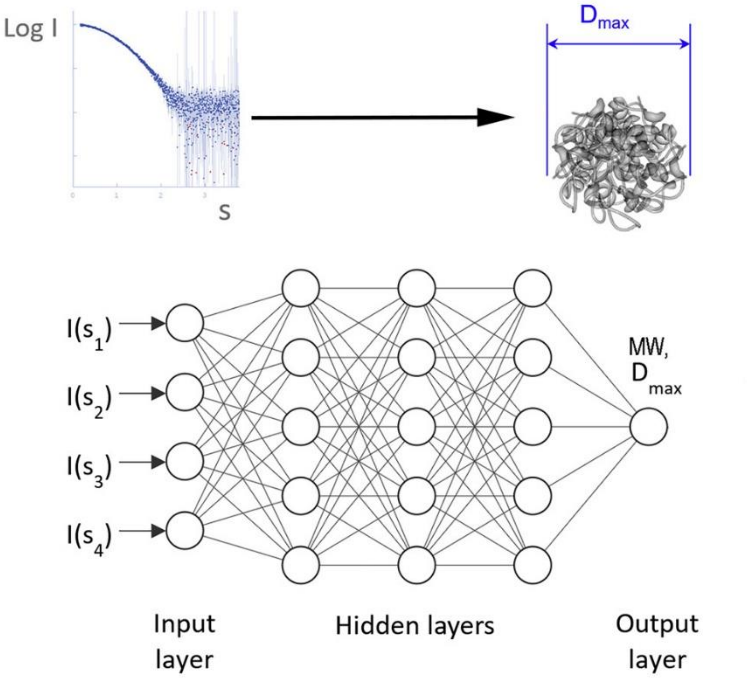
Small angle X-ray scattering (SAXS) is widely used for the characterization of biological macromolecules in solution. SAXS patterns contain information on the size and shape of dissolved particles at nanometer resolution. We propose a method to compute overall parameters from SAXS data based on the application of artificial neural networks (NNs) [1]. Trained on synthetic SAXS data, shallow feedforward NNs are able to reliably predict molecular weight and maximum intraparticle distance (Dmax) directly from the experimental data. The method is applicable to monodisperse solutions of folded proteins, intrinsically disordered proteins and nucleic acids. Extensive tests on synthetic SAXS data generated in various angular ranges with varying levels of noise demonstrated a higher accuracy and better robustness of the NN approach compared to the existing methods.



**Keywords**
Neural networks, machine learning, proteins, RNA, DNA

**References**

A web implementation of the method is available at https://dara.embl-hamburg.de/mwdmax.php
The original code has been deposited on GitHub.

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**Acknowledgements**
This work was supported by the BMBF grant 16QK10A (SAS-BSOFT).

## P180 - STRUCTURES OF THERMOMYCES LANUGINOSUS LIPASE-SDS COMPLEXES AT PH 4.0, 6.0 AND 8.0 FROM SAXS INVESTIGATIONS

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Lipases break down lipids and are used in various industries such as the detergent industry, where they are added to laundry products to enhance the efficacy. In these formulations the lipases must withstand rather harsh conditions involving alkaline pH and various surfactants. The thermomyces lanuginosus lipase (TlL) from Novozymes has been shown to be more stable towards surfactants at alkaline pH compared to acidic pH [1]. In our study, we explore the remarkable robustness of TlL from a structural point of view by titrating in the anionic surfactant sodium dodecyl sulphate (SDS) and determine the formed structures by small-angle X-ray scattering (SAXS) at pH 4.0, 6.0 and 8.0 [2]. At pH 4.0, the samples become milky white at low [SDS] owing to formation of large dense structures. SAXS modelling of these structures involves two different structure factors (random flight and complex cluster) built up in a hierarchical manner to describe the structures at various length scales. These complexes become less dense as more SDS is added. At SDS saturation, TlL wraps around one SDS micelle forming a core-shell structure. At pH 6.0, SDS initially induces a TlL dimer where a SDS cluster attaches near the interface. To model this structure, we have developed a program that can optimize the size, shape, and position of a SDS cluster around the TlL dimer structure using Monte Carlo generated points for representing SDS and random searches for optimizing the structure. Upon addition of more SDS, TlL is unfolded and adopts the core-shell structure. In contrast, SDS does not unfold TlL at pH 8.0, instead the dimer structure, also induced at low [SDS], stays intact with the SDS cluster growing gradually. To further interrogate the structure at pH 8.0, hydrogen/deuterium exchange measured by mass spectrometry (HDX-MS) is used and corroborates that TlL remains folded at pH 8.0 at high [SDS]. Furthermore, HDX-MS reveals some initial anchor points for SDS. We find that the structure is strongly pH dependent in accordance with TlL being much more robust at alkaline pH. The SAXS modelling elucidates a broad range of different protein-surfactant complexes (Fig. 1), and thus provides detailed insight into protein-detergent interactions, which are important for understanding the intricate interplay in various solutions such as detergent formulations.

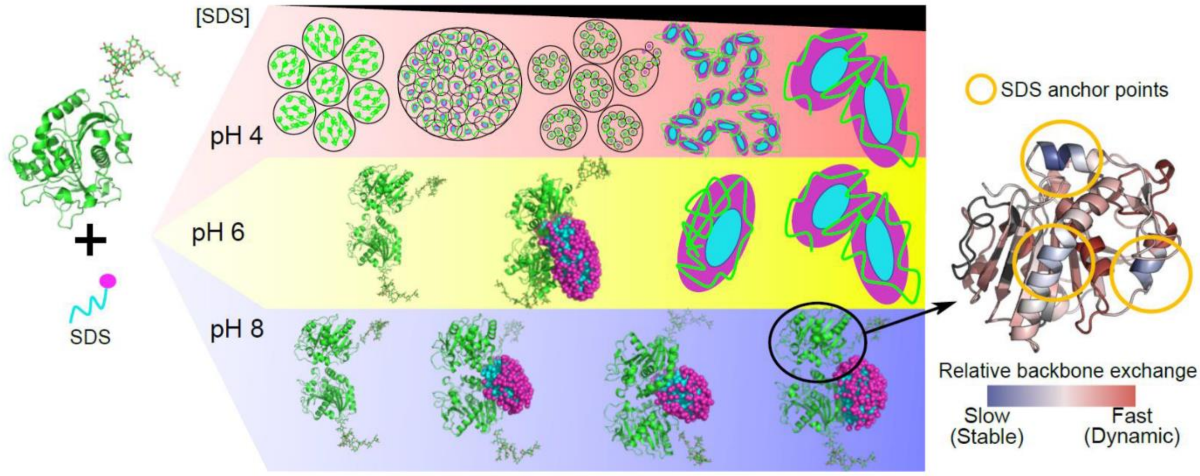

Fig. 1: Graphical abstract depicting the complexes formed by SDS (tail group in cyan, head group in magenta) and TlL (green) as a function of [SDS] at pH 4.0, 6.0 and 8.0. To the right is shown a relative backbone exchange map measured by HDX-MS where the three SDS anchor points can be identified.

**Keywords**
SAXS, Modelling, Lipase, Surfactant, HDX-MS

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SESSION 11A: PROTEIN STRUCTURES, ASSEMBLIES AND DYNAMICS 5
Chair: Barbara Bianca Gerbelli

## V172 - HYDRATION BEHAVIOR AROUND PROTEINS PROBED BY SMALL- AND WIDE-ANGLE X-RAY SCATTERING

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Small- and wide-angle X-ray scattering (SWAXS) data provides information about the shape and size of bio-macromolecules in solution. The newly developed BioSAXS endstation at the beamline 13A of the Taiwan Photon Source features an in-vacuum SWAXS detecting system comprising two mobile area detectors (Eiger X 9M/1M) and an online size-exclusion chromatography system incorporated with several optical probes including UV-vis absorption spectrometer and refractometer. The instrumentation allows simultaneous SAXS and WAXS data collection with a high signal-to-noise ratio, enhancing structural studies of biomolecules by accessing finer details of solution structures. Here we examine some model protein SWAXS data and use SAXS-guided all-atom molecular dynamics (MD) simulations to study the local hydration structure and its influence on the SWAXS pattern. The analysis of the effect resulting from protein dynamics is also provided.

**Keywords**
BioSAXS, MD simulation, SAXS-guided MD, SWAXS

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SESSION 11A: PROTEIN STRUCTURES, ASSEMBLIES AND DYNAMICS 5
Chair: Barbara Bianca Gerbelli

## V377 - ASAXS-BASED ABSOLUTE INTRA-MOLECULAR DISTANCE MEASUREMENTS FOR PROTEINS

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Measurements of molecular distances are key to dissect the structure, dynamics, and ultimately function of biological macromolecules. X-ray scattering interferometry (XSI) 1-3 is based on labeling macromolecules of interest with small (down to ~ 1 nm) gold-labels and uses X-ray scattering as a read out to determine the label-label distance distributions. XSI measurements have the advantage over FRET or NMR-based approaches that they can determine intra-molecular distances i) over a large range (> 10 nm), ii) provide exact absolute distances, and iii) determine the entire distance distribution of the molecular ensemble.

Traditional XSI measurements rely on measuring multiple samples, including the double-labeled, single-labeled, and unlabeled constructs, to separate the gold-gold scattering term and to obtain the molecular distance distribution. ASAXS provides a promising alternative route that only requires the double-labeled sample: by tuning through an absorption edge of gold, the label-label contribution can be separate without the need for multiple samples 4. We have previously demonstrated ASAXS-based molecular distance measurements for nucleic acids 5. Here, we expand the method to proteins and present accurate intra-molecular distance measurements for several variants of the maltose binding protein, a key molecular transporter.

**Keywords**
ASAXS, proteins, molecular distances

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SESSION 11A: PROTEIN STRUCTURES, ASSEMBLIES AND DYNAMICS 5
Chair: Barbara Bianca Gerbelli

## V271 - A COMPLETE PICTURE OF PROTEIN UNFOLDING AND REFOLDING IN SURFACTANTS: A SYNCHROTRON SAXS STUDY EMPLOYING STOPPED-FLOW TECHNIQUES

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The anionic surfactant (AS) sodium dodecyl sulfate (SDS) can denature and unfold globular proteins under many conditions. This is exploited in mass determinations by electrophoresis (SDS-PAGE), however, it limits the efficiency of enzyme in detergent formulations. Therefore, studies of the interactions between proteins and AS as well as non-ionic surfactants (NIS) are of high basic and applied relevance. In contrast to the denaturing effect of SDS, the NIS octaethylene glycol monododecyl ether (C12E8) may protect proteins from unfolding in SDS1. In fact, C12E8 can be used to refold proteins from their SDS-denatured state. While the structural development under unfolding and refolding, when the surfactants are gradually added to the solutions, has been studied in detail at equilibrium condition by scattering techniques, the kinetics of the processes has until recently been much less investigated. Therefore, we performed the present study using synchrotron SAXS in combination with stopped-flow techniques for rapid mixing2. We used the β-sheet-rich globular protein β-lactoglobulin (bLG). We combined stopped-flow time-resolved SAXS, fluorescence and circular dichroism, respectively, to provide an in-depth picture of the different steps involved in both protein unfolding and refolding in the presence of SDS and C12E8. During unfolding, core-shell bLG-SDS complexes are formed within ~10 ms. There is an initial fast process where protein and SDS formed aggregates, followed by two slower processes where the complexes dissociate into single protein-SDS structures, where the protein is situated asymmetrically on the SDS micelles; this is followed by redistribution of the protein and formation of a symmetric core-shell structure. Refolding took more than 100 s and was slower than unfolding that took less than 30 s. The refolding involved rearrangements within the mixing deadtime (~5 ms) and transient accumulation of unfolded random coil monomeric protein structures. Subsequently, the refolding of bLG involved two steps: Extraction of most of the SDS from the complexes followed by protein refolding. The results reveal that surfactant-mediated unfolding and refolding of proteins are complicated processes with rearrangements ranging from sub-milliseconds to minutes.

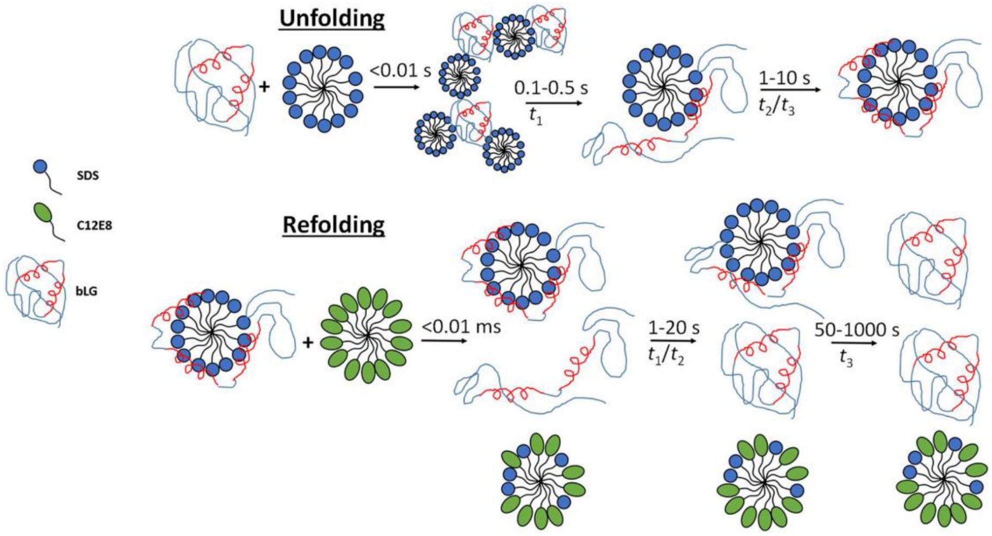

Fig. 1: Sketch showing the suggested unfolding and refolding scheme when bLG is unfolded with SDS and subsequently refolded with $C_{12}E_8$. Unfolding occurs in three steps with an initial clustering of SDS and protein and formation of core-shell structures at the late stages. In the refolding, three species are present after the deadtime, random coil protein, complexes and mixed micelles. First the random coil protein is folded to a native state and finally the protein still in complex refolds.

## Keywords

Kinetics, protein-surfactant interactions, synchrotron SAXS, unforlding and refolding

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SESSION 11B: DYNAMICS, KINETICS, IN SITU AND TIME RESOLVED 3
Chair: Prof. Aldo Craievich

# P439 - DYNAMICS OF HYDROGELS AND HYDROGEL-NANOPARTICLE COMPOSITES STUDIED BY X-RAY PHOTON CORRELATION SPECTROSCOPY. FIRST EXPERIMENTS

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Soft materials exhibit complex dynamic behaviors on a wide time and length scale. It is not unusual for them to behave like solids at nanometer scales while being fluid at macroscopic scales or behaving like fluids over long periods of time and like elastic solids at millisecond scales.

Thus, the dynamic behavior of soft materials is the consequence of a structural organization with several hierarchical levels and with a subtle balance between the entropic and enthalpic contributions to the free energy of the system.

In the particular case of polymeric gels and gel-nanoparticle composites, it is possible to identify several characteristic length scales (monomer size, crosslink distance, size of pendant chains, etc.) Furthermore, the incorporation of nanoparticles also introduces particle size as a new characteristic scales of the system.

In addition to theoretical approaches for the prediction of the structure and dynamics of a polymeric gel, there are various experimental methods that allow obtaining this information. Thus, X-ray and neutron scattering are the techniques-of-choice to obtain structural information, while rheological methods provide information on the dynamics of the system at frequencies up to 1 KHz.

There are, however, a set of methods based on the study of the temporal evolution of the interference pattern of a coherent radiation beam when it passes through a material. These methods, known as photon correlation spectroscopy, have their best-known example in dynamic light scattering, which allows obtaining information on relaxation processes on time scales between 1us and 10 ms by exploring the spatial scale of several microns (depending on the wavelength used and the angle of observation). A method that has become more popular in recent years is X-ray photon correlation spectroscopy (XPCS) technique that takes advantage of the great coherence length and high brightness of 4th generation synchrotron light sources to obtain the temporal autocorrelation function of the scattering intensity, G2(t). This function allows to determine the characteristic relaxation times of the dispersion fluctuations and, from them, to determine the dynamics of the system. Furthermore, the possibility of detecting scattering by means of area detectors allows correcting non-ergodic effects of the sample, as well as obtaining G2(t) for different values of q=2Pi/L, where L is a characteristic length of the system.

In this work we will present the results obtained from XPCS experiments carried out in the CATERETE line of the SIRIUSin hydrogels of 2-hydroxyethyl methacrylate cross-linked with Di(ethylene glycol) dimethacrylate (in concentrations between 0.1 and 1% and the composites of these gels with SiO2 nanoparticles (of different sizes) and ZIF-8 (Zn(2-methylimidazole)2) nanoparticles, an archetypal system among “metal-organic-frameworks” (MOF). The results obtained for the distributions of correlation times will be correlated in the context of the structure of the gels and their rheology will be studied from these distributions.

**Keywords**
XPCS, gel, colloid

**Acknowledgements:**
As far as the authors are aware, this is the first report of XPCS experiments performed using CATERETE facilities (proposal 20220451). We appreciate the collaboration and hospitality of Dr. Aline Ribeiro Passos and Dr. Florian Meneau during the development of the project.

SESSION 11B: DYNAMICS, KINETICS, IN SITU AND TIME RESOLVED 3
Chair: Prof. Aldo Craievich

# V140 - HIGH TIME-RESOLUTION SAXS/WAXS STUDY OF MORPHOLOGY RELAXATION IN ELASTOMERS AFTER SUDDEN CHANGES IN ELONGATION

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With every step we take in running shoes, the incorporated polyurethane layers are abruptly loaded and unloaded. How does the morphology from hard domains in a soft phase respond to such load changes? Our pneumatic relaxometer shoots elastomers back and forth between two strain states within 13 ms. In the time between the excitations, we monitor the structural change using SAXS and WAXS. A feasibility study [1] shows that a time resolution of 100 ms is insufficient because a fast relaxation decays within 250 ms. In a follow-up study (WAXS part submitted [2] – SAXS-manuscript in preparation) we increase the sampling frequency from 10 Hz to 50 Hz with a significantly improved quality of the 2D scattering data. 50000 patterns are evaluated. Thus, we can also follow the course of the fast relaxation in detail. The analysis shows that not only the temporal resolution increases. The smooth data of fast scanning also opens the door to a new dimension of morphology analysis.

For example, our WAXS analysis illustrates a complex but also detailed mesh of relationships between scattering, strain, relaxation, chain clustering, chain orientation and relaxation time. The associated analytics can be mastered by algorithmic formalization, but their results themselves remain complex. While we can present how cluster density and orientation change as a function of time, understanding the structural changes still requires intensive study of the resulting curves, maps, and environmental data, such as changes in force not yet even considered but also measured.

We study 7 elastomers of different hardness and chemical composition both as-molded and annealed. We also analyze the first and the fifth load cycle. In [2] we study morphology changes in the soft matrix phase. The shape and intensity of the amorphous halo are analyzed. Changes of the halo can be explained by attributing it to bundles of parallel chain pieces. Harder materials tend to form two ensembles of bundles with different airiness. This tendency is suppressed by annealing, but reappears after five load cycles. Unpublished results of the SAXS analysis are communicated in the conference.

**Keywords**
elastomers, strain, morphology, orientation, relaxation

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# P297 - MICROSTRUCTURE EVOLUTION IN SINGLE CRYSTAL TI-15MO METASTABLE Β-TI ALLOY AT ELEVATED TEMPERATURES

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Titanium alloys have plenty of applications in industry and medicine due to the unique combination of high strength, low density, and excellent biocompatibility. Ti-15Mo alloy is a metastable β-Ti alloy, which could contain ω (hexagonal) and α (hcp) precipitates in the β-phase matrix. Particular microstructure resulting from the heat treatment has a large impact on the mechanical properties and thermal stability of the alloy. One of the techniques able to deliver bulk information on the precipitate evolution directly at elevated temperatures is Small-Angle Neutron Scattering (SANS). V4 SANS facility of HZB Berlin was used for the investigation of Ti-15Mo (wt.%) alloy. SANS data were acquired in-situ up to 600 °C at three orientations of the single crystal sample – with <111>, <110>, and <100> directions of β-phase parallel to the neutron beam. Heating rates of 1 K/min and 5 K/min were used during the in-situ heating. Observed 2D intensity distribution at temperatures lower than 560 °C was due to isothermal prolate-spheroidal ω precipitates arranged on a simple cubic-like grid. Morphology (size and distance) of the ω particles and their evolution were deduced from the SANS data using 3D modeling and fitting of the 2D SANS data by NOC software. Initially, an increase of temperature above 400°C leads to the volume fraction growth and to the increase of the interparticle distance. ω phase became invisible when the temperature is approaching 580 °C. Simultaneously, strong scattering appears from α-phase particles having specific morphology and orientation. Precipitation sequence and possible co-existence of ω and α phases are assessed. The microstructure of α precipitates was not changed during cooling down from 600 °C to room temperature.

**Keywords**
Small-Angle Neutron Scattering, metastable β-Ti alloy, ω phase

## SESSION 11B: DYNAMICS, KINETICS, IN SITU AND TIME RESOLVED 3
Chair: Prof. Aldo Craievich

# P154 - MELTING AND FREEZING TEMPERATURES AND RELATED PROPERTIES OF PB NANOPARTICLES EMBEDDED IN A LEAD-BORATE GLASS DETERMINED BY SAXS

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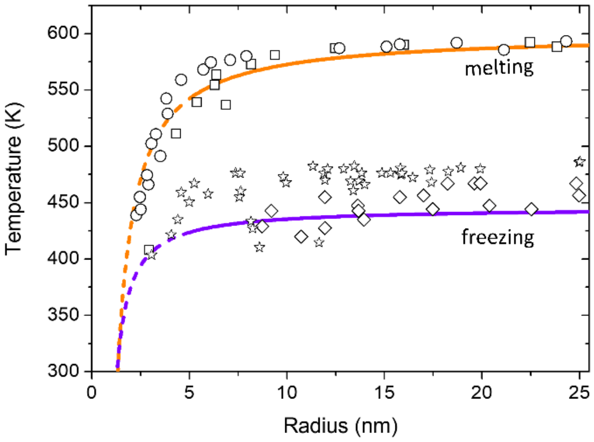
We present here a novel method exclusively based on the results of SAXS measurements for the determination of the radius dependences of the melting and freezing temperatures and other related properties of nanoparticles embedded in solid matrices. The method was applied to the determination of the radius dependences of the melting temperature of Pb nanocrystals and the freezing temperature of Pb nanodroplets embedded in a lead-borate glass (Fig. 1). A good agreement was achieved between the radius dependence of the melting and freezing temperatures of Pb nanoparticles embedded in the lead-borate glass, determined by using the SAXS technique, and those previously reported in the literature [1-3]. In addition, this procedure was applied to determine the ratio of solid/liquid specific mass and coefficients of thermal expansion of Pb nanocrystals and liquid Pb nanodroplets. Modeled SAXS intensity functions for several scattering wavevectors were fitted to the experimental SAXS intensities recorded during the heating and cooling processes of the samples over the 298-638 K range. The best-fitted modeled scattering curves for both heating and cooling processes agreed well with the temperature dependence of the experimental SAXS intensity. This procedure provided several unknown parameters associated with the theoretical models intending to predict the dependence on the radius of the melting and freezing temperatures. Our results indicate that the coefficient of thermal expansion of solid Pb nanocrystals is much higher than that of bulk Pb crystals while the coefficient of thermal expansion of liquid Pb nanodroplets is significantly lower than that of bulk liquid Pb.



Solid lines: Radius dependences of the melting temperature (orange line) and freezing temperature (violet line) of spherical Pb nanoparticles determined from the temperature dependent SAXS intensity, respectively. The dashed lines are the same functions extrapolated to lower radii. Symbols: Previously reported data for the radius dependence of the melting (O [1] and _ [2]) and freezing (☆ [1] and ◊ [3]) temperatures.

**Keywords**
Melting, freezing, nanocrystals, glass, nanocomposite

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## SESSION 11B: DYNAMICS, KINETICS, IN SITU AND TIME RESOLVED 3
Chair: Prof. Aldo Craievich

# V145 - ANALYSING PRECIPITATION KINETICS IN THERMALLY PROCESSED AL-ALLOY 7050 USING IN-SITU SAXS & WAXS

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Aluminium alloys are favoured as light weight material in industry due to their high strength-to-weight ratio. Especially alloys of the 7xxx series, which are age-hardenable, are often used in structural components in aerospace and automotive industries. Through complex thermal aging processes, they form strengthening precipitates, which lead to their outstanding mechanical properties. Main strengthening phases in these alloys are η' and η-phase. η' is a metastable phase, which is semi-coherent with the matrix. The η-phase, with the compositon MgZn2, is the stable phase, which is incoherent with the matrix [1, 2]. However, microstructural evolution of these phases is complex and competitive growth of these phases must be considered [3].

Numerical modeling is a powerful tool for the description of precipitation kinetics and a Kampmann-Wagner numerical model (KWN) has been developed in previous work [3]. To enhance the understanding of precipitation phenomena in these complex systems, it is necessary to study the kinetics of these Al alloys in-situ at high temperatures in more detail. With that data our model can be improved and precipitation behavior under non-equilibrium conditions could be understood.

Therefore, in this work simultaneous in-situ SAXS/WAXS measurements using high-energy X-rays were conducted using the alloy AA7050 in T7451. Reversion experiments at four different temperatures (200, 230, 260, 290 °C) with a high temporal resolution were carried out as well as an isothermal experiment (180 °C for 12 h) and heating ramps. Volume fractions, mean radius and number of precipitates during these time-temperature cycles were successfully studied via SAXS and modeled with the KWN model.

In the figure below volume fractions of the reversion experiments, using SAXS, can be seen. Differences between reversion temperatures are clearly visible. However, three stages, which also have been described in literature before [4], can be identified: rapid dissolution of precipitates shortly after heating, increase of volume fraction and a stage of constant volume fraction. With the help of the KWN model these stages have been reproduced and precipitation reactions such as dissolution, nucleation and growth of precipitates have been characterized.

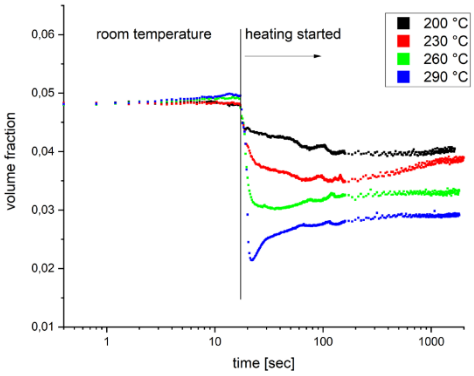

Figure 1: Evolution of volume fraction of AA7050 during reversion experiments at 200, 230, 260 and 290 C measured by SAXS

## Keywords

Aluminum alloys, precipitation kinetics, Kampmann-Wagner numerical model

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SESSION 11C: INSTRUMENTATION, DATA FORMAT AND BEAMLINES 4
Chair: Dr. Mark Tully

## P331 - CONTROL AND DATA ACQUISITION FOR MILLISECOND TIME-RESOLVED EXPERIMENT USING TANGO, SARDANA AND PANDABOX AT COSAXS BEAMLINE

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CoSAXS is the Coherent Small-Angle X-ray Scattering beamline placed at the diffraction-limited 3 GeV storage ring at MAX IV Laboratory. The beamline can deliver a very high photon flux, which enables experiments with a high time-resolution to be performed. In this work we present the control and data-acquisition strategy for a millisecond time-resolved X-ray solution scattering (TR-XSS) experiment using infrared (IR) laser light to induce temperature jumps and structural changes. The beamline control system is based on TANGO and, built on top of it, there is Sardana which provides an advanced scan framework. In order to synchronize the IR laser pulse on the sample and the detector readout during TR-XSS, hardware triggers are used. This implementation is done using PandABox to generate both the pulse train for the IR laser, composed by a primary pulse used to heat the sample until a pre-defined target temperature, and by secondary shorter pulses to keep the temperature constant during the data-acquisition; as well as the triggers for all active experimental channels, such as counters and detectors. Moreover, all data is recorded and linked in a HDF5 file that is automatically created and written by Sardana according to NeXUS data format. After successful initial operation, the same setup is being commissioned to run experiments with different light sources in replacement of IR laser.

**Keywords**
Time-resolved SAXS, TANGO, Sardana, PandABox

## SESSION 11C: INSTRUMENTATION, DATA FORMAT AND BEAMLINES 4

Chair: Dr. Mark Tully

# P207 - EIGER2 FOR ADVANCED SYNCHROTRON SWAXS EXPERIMENTS

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Hybrid photon counting (HPC) X-ray detectors are crucial components for cutting-edge synchrotron research [1] by providing noise-free detection with advanced acquisition modes. In this regard, the latest HPC detector generation EIGER2 is setting new performance standards that push current horizons in X-ray science. These detectors combine all advantages of previous HPC detector generations while offering (i) 75 µm × 75 µm pixel size, (ii) kilohertz frame rates, (iii) negligible dead time, and (iv) count rates of more than 107 photons per pixel – the ideal combination for advanced SAXS experiments at current- and next-generation synchrotron sources.

In detail, we optimized the electronics within each EIGER2 pixel for best-possible signal-to-noise measurements at increased speed. In the EIGER2, each pixel acts as an independent photon-counting detector with (i) two separate energy thresholds for simultaneous, energy selective detection, (ii) separate retrigger units that ensure ideal counting linearity over the full dynamic range, and (iii) two digital counters for fast and noise-free readout. Particularly for time-resolved and fast scanning-SAXS experiments, this architecture of two digital counters per threshold results in a negligible readout dead-time with duty cycles of >99.99 %, making sure that no photons arriving on the detector are lost. More recently, we upgraded the capabilities of the EIGER2 by releasing the 8-Bit mode for double the image frame- and hence scanning rate [2] as well as a Lines-ROI mode, enabling WAXS studies at up to 98 kHz.

In this talk, we present how the EIGER2 can advance SAXS experiments at modern synchrotron sources. We first introduce the general advantages of hybrid photon-counting detectors for X-ray scattering measurements. We then focus specifically on the EIGER2 series, showing how state-of-the-art experiments, such as fast-scanning SAXS tensor tomography or in-situ time-resolved SAXS experiments, benefit from the detectors' capabilities. Supported by experimental data from beamlines around the world, these results evidence how the EIGER2 will advance experiments for both static and dynamic SAXS.

## Keywords

hybrid photon-counting, X-ray detector, time-resolved, fast-scanning

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## SESSION 11C: INSTRUMENTATION, DATA FORMAT AND BEAMLINES 4

Chair: Dr. Mark Tully

# V386 - DEVELOPMENT OF REFERENCE STANDARD FOR SMALL ANGLE SCATTERING MEASUREMENT Q-CALIBRATION

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We report on the development of a q-calibration reference standard optimized for small angle scattering. The standard is designed to work over a large range of energies from soft X-rays to hard X-rays. The standard consists of a 100 nm pitch tungsten line grating on a free-standing silicon nitride membrane. The membrane allows transmission measurements to be made across all energies. The 100 nm tall tungsten line grating gives very strong scattering and allows measurements to be made on lab sources in less than a minute. The structure includes a 1 um pitch square grating superimposed over the 100 nm pitch line grating. The combined structure gives rise to a 2 dimensional, hiercharchical scattering pattern that produces scattering peaks over a large range of q-space from 6e-4 Å-1 to greater than 0.1 Å-1. The 100 nm pitch structure is resolvable on most systems while the 1 um pitch structure is only resolvable on high resolution systems. We have tested prototypes of the reference sample at several beamlines and a variety of lab instruments covering energy ranges from 250 eV to 24.5 keV. Measurements on a lab system resulted in 13 orders of diffraction from the 100 nm pitch spacing in 60 s. We are now in the process of fabricating and certifying a large batch of the reference samples and the standard should be available to the small angle scattering community in the near future.

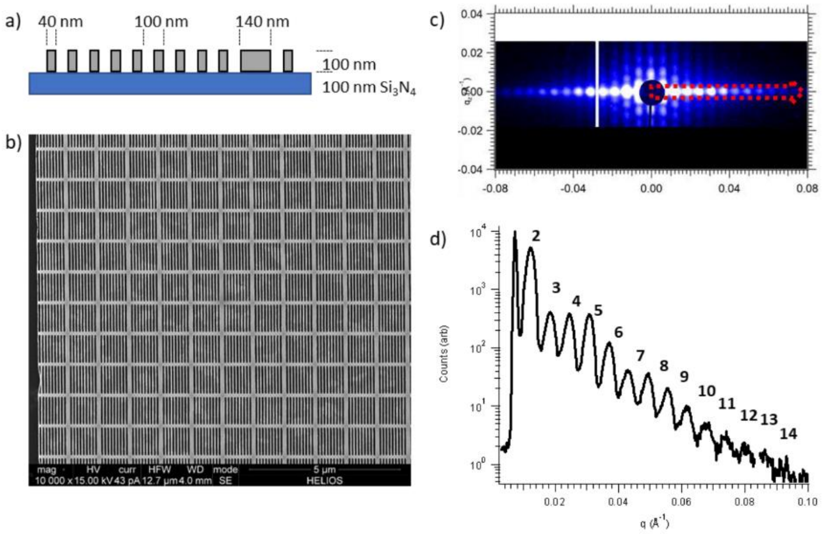

**Figure 1**. a) Schematic of 100 nm pitch tungsten test structure, b) SEM image of reference structure prototype, c) lab SAXS pattern in 60 s of prototype, d) 1D integration of SAXS pattern.

**Keywords**
Calibration standard, reference material, small angle scattering

SESSION 11C: INSTRUMENTATION, DATA FORMAT AND BEAMLINES 4
Chair: Dr. Mark Tully

# V372 - REAL-TIME OBSERVATION OF NUCLEATION AND GROWTH OF PVP STABILIZED AG NANOPARTICLES: INSIGHT EFFECT OF POLYMER CHAIN

**BHARTI, Amardeep (1); AMENITSCH, Heinz (2); MARMIROLI, Benedetta (2); BERNSTORFF, Sigrid (1)**
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Metal nanoparticles remain the interest of research due to their widespread applications in photonics, microelectronics, and biotechnology, because of their size-dependent localized properties [1,2]. The efforts have been constructed to precisely control the size and shape of the nanoparticles [3-6]. In the last decade, numerous research activities have been made to understand the nucleation and growth of the nanoparticles[7-9], however, a comprehensive understanding of the effect of surfactant on the nanoparticle’s core growth and its relative interaction is still a challenge. Therefore, we investigate the reaction dynamics and growth kinetics of the Ag nanoparticles under the effect of variable chain-length surfactant polymer using time-resolved small-angle X-ray scattering at the Austrian-SAXS beamline of Elettra Sincrotrone Trieste, Italy. In order to study the pure interaction between the metal-core and the polymer, we adopt the radiation-induced synthesis using water radiolysis to avoid the external chemical reducing agent[4-6]. In this presentation, we will describe the step-by-step reaction dynamics and kinetics of the metal nanoparticles. The insight into the mechanism of the reaction of polymer stabilized Ag nanoparticles will be demonstrated.

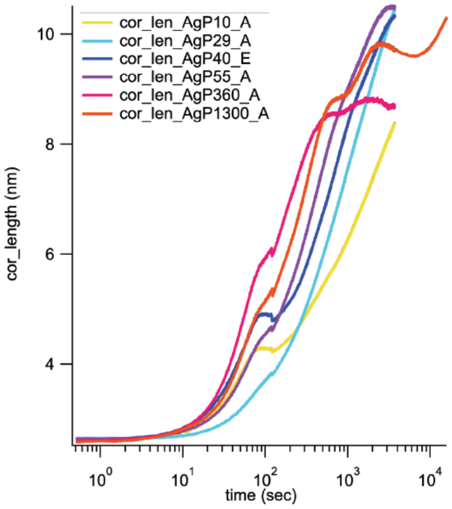

Figure1: Correlation length of the variable chain-length capped Ag-nanoparticles as a function of time.

**Keywords**
Polymer capped Nanoparticles, Nucleation and growth mechanism, time-resolved SAXS

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SESSION 11C: INSTRUMENTATION, DATA FORMAT AND BEAMLINES 4
Chair: Dr. Mark Tully

## V166 - ASSESSING THE EFFECTS OF DEGRADATION IN WOOD USING X-RAY AND NEUTRON SCATTERING

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Exposing wood to detrimental environmental conditions such as fire exposure, and/or decay organisms can lead to physical and chemical changes in the wood structure that can adversely affect the wood properties and ultimately, its performance. Conservation and protection treatments typically aim to react with the wood hydroxyls to make wood less susceptible to these environmental conditions. A better understanding of how different degradation mechanisms alter the wood nanostructure and/or the polymers inside the wood cell walls would accelerate the development of new protection treatments that can hinder the degradation process. Here, we combined wide-angle x-ray scattering, small angle x-ray scattering and small angle neutron scattering to measure the wood nanostructure as well as the cellulose diffraction in wood samples degraded by different processes, namely, chemically, biologically, and thermally. Moreover, the effects of long-term degradation were assessed by studying two archaeological wood samples that were over 1200 years old. By combining these techniques, we were able to determine how different degradation processes altered the wood nanostructure in terms of the cellulose microfibril alignment, elementary fibril spacing and cellulose crystalline structure inside the wood cell walls.

**Keywords**
SANS, SAXS, WAXS

PLENARY 7

Chair: Dr. Mateus Cardoso

## P186 - SOFT MATTER SYSTEMS INVESTIGATED BY SMALL-ANGLE X-RAY SCATTERING

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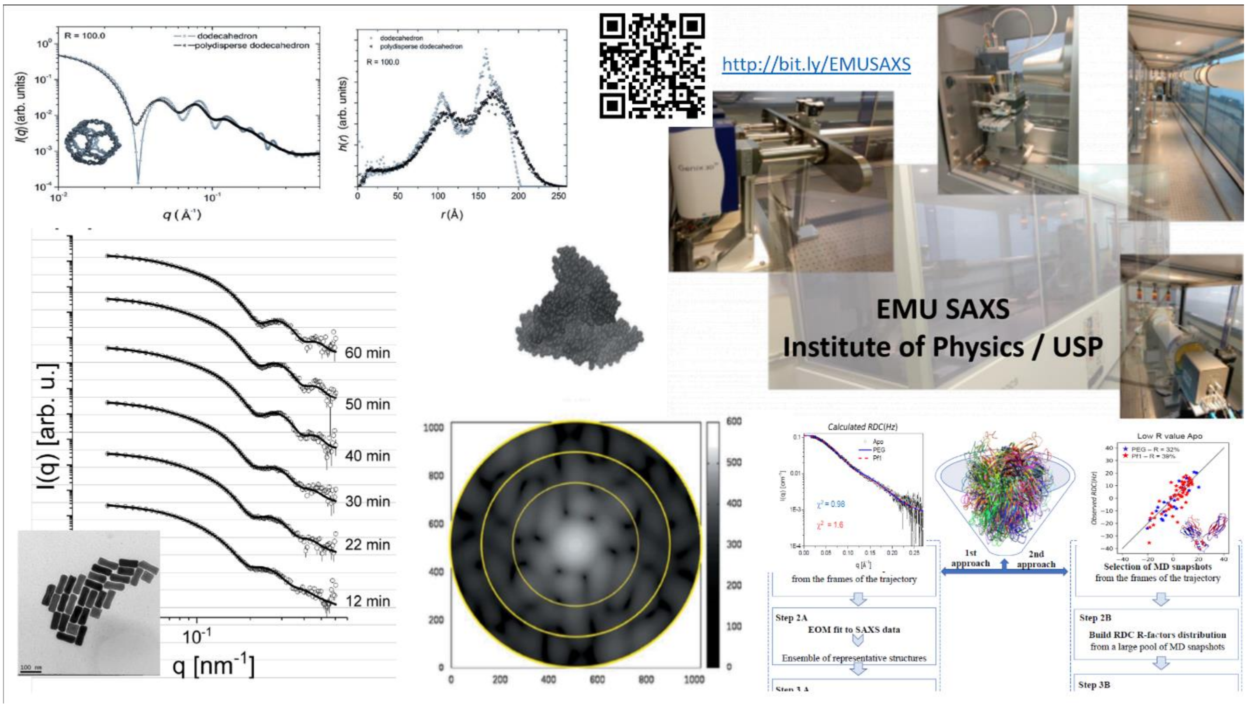
Soft matter is a fascinating research field. In this topic one finds an enormous number of systems and products we consume and use in our everyday life. Food, washing products, plastics, liquid crystals are just few examples of such systems. One striking property of soft-matter is its ability of self-assembly in highly hierarchic structure. Surfactant systems, for example, in aqueous media can form different types of micelles or supramolecular arrangements, depending on the system characteristics (concentration, temperature, etc). The structural investigation of this type of system has to be performed in such a way that does not disturb its thermodynamic equilibrium. Scattering methods, in particular small-angle X-ray scattering (SAXS), are very suitable for these studies since it has a minimum interaction with the system, preserving the equilibrium. Even though the experimental data provides information in the so-called reciprocal space, requiring the use of specialized modeling and analysis methods, the information reflects a reasonable ensemble average, since the data results from the contribution of a very large number of scatterers.

At the Institute of Physics of University of São Paulo we recently opened a Multi-user Scattering Center composed of three laboratory based SAXS instruments, allowing the development of a large number or projects of our research group and also, giving support for users from Brazil and other countries. This center is allowing researchers to obtain high quality SAXS data, particularly during the period where the new Brazilian synchrotron, Sirius, has been finalized and will continue to be a useful place for the use of the SAXS/WAXS/USAXS techniques. In this talk several examples of the use of the SAXS methods for investigating soft matter systems, with the development of advanced modeling methods, will be shown. Advanced studies of lipid membranes, protein systems, nanoparticles, liquid crystals, human hair and several other examples are presented and discussed [1-11].



**Keywords**
Soft Matter, SAXS, modeling, proteins

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## SESSION 12A: SOFT MATTER AND SELF ASSEMBLY 2

Chair: Dr. François Boué

# P241 - TIME-RESOLVED LIGHT-TUNABLE NANOPARTICLES BY ELECTROSTATIC SELF-ASSEMBLY

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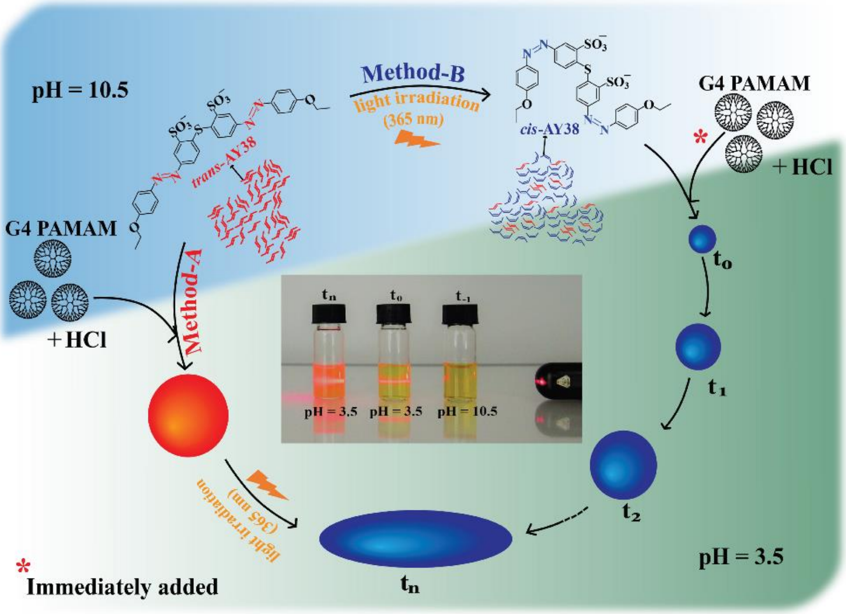
Electrostatic self-assembly is a well-known technique to form nearly monodisperse nanoparticles using coulombic interactions between oppositely charged species in the aqueous phase. In this study, the opposite charges originate from cationically charged polyelectrolytes and multivalent organic counterions. Self-assembly of these charged, multi-responsive building blocks leads to the formation of a wide range of shapes, for example, spheres, rods, ellipsoids, cylinders, etc. Various external triggers such as pH, light irradiation, and charge ratio could be used to tune these electrostatic self-assembled structures.
In the present work, small-angle neutron scattering (SANS) plays a crucial role in determining the formation mechanisms and structure-directing effects. As a model system, a divalent azo dye (AY38, Acid Yellow 38) and cationic polyamidoamine (PAMAM) dendrimers were used as the key components to construct self-assembled structures in aqueous solution. The isomerization capability of AY38 and pH-responsiveness of the dendrimers make them suitable candidates to alter the size and the shape of self-assembled particles through light irradiation and degree of protonation. In particular, the preparation method has been modified to gain insight into the formation mechanism (see in Scheme). Slow assemblies' growth was observed time-dependently whilst the dye-molecules reconverted to the trans-isomer. A home-built device is designed to analyze the structural changes using in-situ UV irradiation on the SANS instrument. Various complementary methods are used towards understanding the formation and restructuring mechanism, especially dynamic and static light scattering (DLS/SLS), zeta potential, isothermal titration calorimetry (ITC), and UV/Vis spectroscopy.



Scheme: Different methods influencing Electrostatic self-assemblies

**Keywords**
Electrostatic self-assembly, Polyelectrolytes, Azo dyes, Small-angle neutron scattering

# P346 - CO2 INTERCALATION INTO NICKEL HYDROXIDE EXCHANGED MONTMORILLONITES

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Anthropogenic CO2 emissions to the atmosphere is a global challenge, threatening all life on earth. There is an ongoing race to find good solutions for carbon capture and storage to reduce the damage of the CO2 emission. One of the efforts in this direction is the capture of CO2 in clay minerals. Clay minerals are abundant, environmentally friendly and have a good capacity for storing CO2 (1). Previously, our group has studied synthetic Nickel Fluorohectorite using X-ray diffraction and found that the exceptional CO2 storage capacity comes from nickel hydroxide residing in between the clay sheets of every other layer (2). To utilize this further we have performed various cation exchange processes on natural montmorillonite clays to get nickel hydroxide in every clay layer. The results of the cation exchange process have been studied by X-ray diffraction and show that half of the layers get a cation exchange with nickel hydroxide, and that the montmorillonites do intercalate CO2 after such a cation exchange.

**Keywords**
Clay, CO2 capture, X-ray diffraction

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## V286 - SAXS-REVEALED NANOSTRUCTURES OF LIGHT-RESPONSIVE POLY(ETHYLENE GLYCOL)-GRAFTED LIPOSOMES

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Nanomedinince and nano-drug delivery systems are a relatively new and rapidly developing field. Liposomes are the most common and well-studied nanocarriers for targeted drug delivery. In this study, we use FDA-approved (Food and Drug Administration) liposome formula with higher biocompatbility to design PEGylated liposome (L), PEGylated liposome with surface-modified light-responsive membrane-cleaving peptide (PL) and PEGylated liposomal peptidyl doxorubicin (PLD). We integrated SAXS/SEC MALS/CyroEM structural analysis tools to successfully resolve the nanostructures of the complexed vesicles of PEGylated phospholipids, including the particle size and distribution of liposomes, the thickness of lipid bilayers, the crystal structure and size of the drug doxorubicin crystal, and configuration of the surface PEG layer. The structural changes of the liposome are further observed under in-situ UV-irradiation for drug releasing using time-resolved SAXS with 2s resolution. The results are further correlated to the drug releasing efficiency observed, providing a structural basis for the design of controlled drug delivery.

**Keywords**
SAXS, PEGylated liposomes, membrane structure, drug delivery

## V146 - STRUCTURAL CHARACTERIZATION OF MRNA - LIPID NANOPARTICLE UPON PH CHANGES: A SANS STUDY

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Therapeutic treatments based on the production of proteins by delivering messenger RNA (mRNA) represent a versatile approach. Lipid nanoparticles (LNPs) are promising vehicles for mRNA delivery and are formed by a cationic ionizable lipid (CIL), DSPC, cholesterol (Chol) and a pegylated (PEG) lipid. Even though some LNPs for small interference RNA (siRNA) delivery were recently FDA approved, and vaccines against SARS-CoV-2 based on mRNA-LNPs have been developed and given emergency approval in the last months, there are still concerns about the safety profile of LNPs. In addition, it is not clear how to improve their efficacy following endocytosis. It is suggested that there is a pH change from 7.4 in the extracellular region, to 6.5 in early endosomes, 5.5 in late endosomes and 4.5 in lysozomes. Moreover, the release of siRNA from LNPs occurs within 5-15 min of endocytosis, which implies that LNPs must be designed to escape early endosome compartments at pH 6.5. A good understanding of the physical and chemical characteristics of the LNPs under study is necessary to progress from pre-clinical testing.

We employed small angle neutron scattering (SANS) to investigate the LNP structure and the distribution of components in the LNPs at pH values mimicking the endosomal compartment for 3 different LNP compositions.for the 3 formulations, the LNP core-shell structure was disrupted suggesting that a redistribution of the components occurs upon lowering the pH.

**Keywords**
lipid nanoparticle, gene delivery, neutron scattering

SESSION 12B: MODELLING AND DATA ANALYSIS 3
Chair: Dr. Leandro Barbosa

# V165 - THE HUMAN FACTOR: RESULTS OF A DATA ANALYSIS ROUND ROBIN

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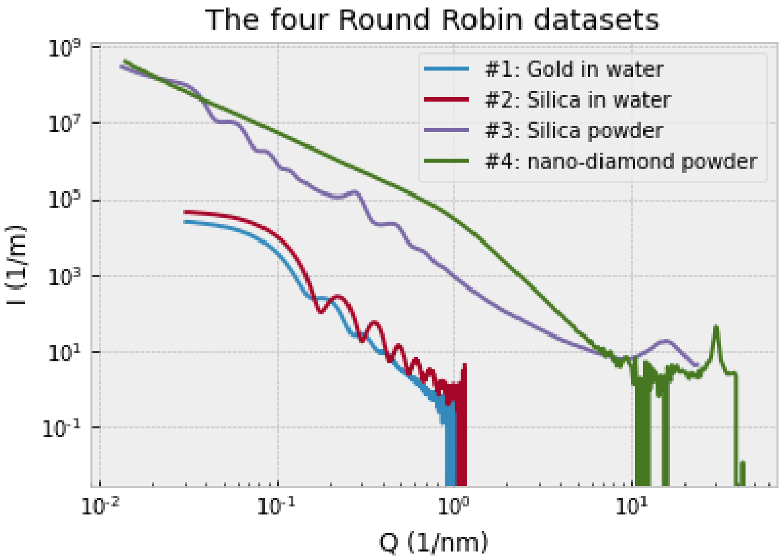
How much do we, the small-angle scatterers, influence the results of an investigation? What uncertainty do we add by our human diversity in thoughts and approaches, and is this significant compared to the uncertainty from the instrumental measurement factors?

After our previous Round Robin on data collection, we know that many laboratories can collect reasonably consistent small-angle scattering data on easy samples1. To investigate the next, human component, we compiled four existing datasets from globular (roughly spherical) scatterers, each exhibiting a common complication, and asked the participants to apply their usual methods and toolset to the quantification of the results (https://lookingatnothing.com/index.php/archives/3274).

Accompanying the datasets was a modicum of accompanying information to help with the interpretation of the data, similar to what we normally receive from our collaborators. More than 30 participants reported back with volume fractions, mean sizes and size distribution widths of the particle populations in the samples, as well as information on their self-assessed level of experience and years in the field.

While the Round Robin is still underway (until the 25th of April, 2022), the initial results already show significant spread in the results. Some of these are due to the variety in interpretation of the meaning of the requested parameters, as well as simple human errors, both of which are easy to correct for. Nevertheless, even after correcting for these differences in understanding, a significant spread remains. This highlights an urgent challenge to our community: how can we better help ourselves and our colleagues obtain more reliable results, how could we take the human factor out of the equation, so to speak?

In this talk, we will introduce the four datasets, their origins and challenges. Hot off the press, we will summarize the anonymized, quantified results of the Data Analysis Round Robin. (Incidentally, we will also see if a correlation exists between experience and proximity of the result to the median). Lastly, potential avenues for improving our field will be offered based on the findings, ranging from low-effort yet somehow controversial improvements, to high-effort foundational considerations.



**Keywords**

data analysis, variation, Round Robin, particle quantification

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SESSION 12B: MODELLING AND DATA ANALYSIS 3
Chair: Dr. Leandro Barbosa

# V157 - CHARACTERIZATION OF SMALL ANGLE X-RAY SCATTERING DATA BY AN AI BASED APPROACH

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Small Angle Scattering of X-rays and neutrons (SAXS and SANS) is a fundamental tool to study the structural properties of materials at the nanoscale. It has changed from a special method into a general technique for lipid research and structural biology.

The evaluation of X-ray related data and its storage in publicly accessible databases has a very long tradition in structural biology. Access to freely accessible databases is a decisive factor in enabling researchers and developers of key technologies to compare data even without explicit expert knowledge. Now that experimental data acquisition is largely standardised and the first data analysis steps are also automated in many cases, many data are already available in digital form. In the field of structural biology, these data are currently entered by researchers mostly on a voluntary basis into repositories such as the pdb or SASBDB database.

Since data acquisition from diffraction and scattering experiments nowadays has reached a high level of automation and allows recording of a very large amount of data. This holds especially for large-scale research facilities such as storage rings (e.g. DESY, Hamburg, Germany) or neutron reactors (e.g. Institute Laue-Langevin ILL, Grenoble, France). This means that there are several terabytes of SAS data from biological soft matter, e.g. lipids, that could be made available to the public. However, expertise in the respective research area is necessary to evaluate these data. The aim of the project SAS-BSOFT is to provide curated and validated small-angle scattering data. This enables users from different research and technology fields to make use of these data.

Such a large amount of data cannot be managed manually. Instead, we use TensorFlow (TF), an AI-based Convolutional Neural Network (CNN) system designed by Google. TF is a proper tool for image processing and recognition. In the first step, experimental data are converted into images. By doing so, the data can be more easily and quickly sorted into predefined categories, such as ‘to be investigated further’ and ‘no information content’. Using these categories, data with information content can be filtered out for further analysis. It is also possible to load and use self-trained models via the user interface.

Our developed procedure can be use in the next step to identify and export important information such as the position, width and height of scattering peaks. The possibility to use not only predefined but also self-trained models for the categorization and further analysis of the data allows a flexible integration of other data (and sources). This way, information can be extracted with a good degree of certainty – of data that might otherwise not have been further investigated. With this approach, public databases such as the SASBDB can be filled with automatically pre-analyzed data.

So far, missing metadata often hinder the exploit of data from other researchers, even if it was publicly available, and additionally limit model accuracy. Therefore, a future version of our tool will have an automated integration of metadata.

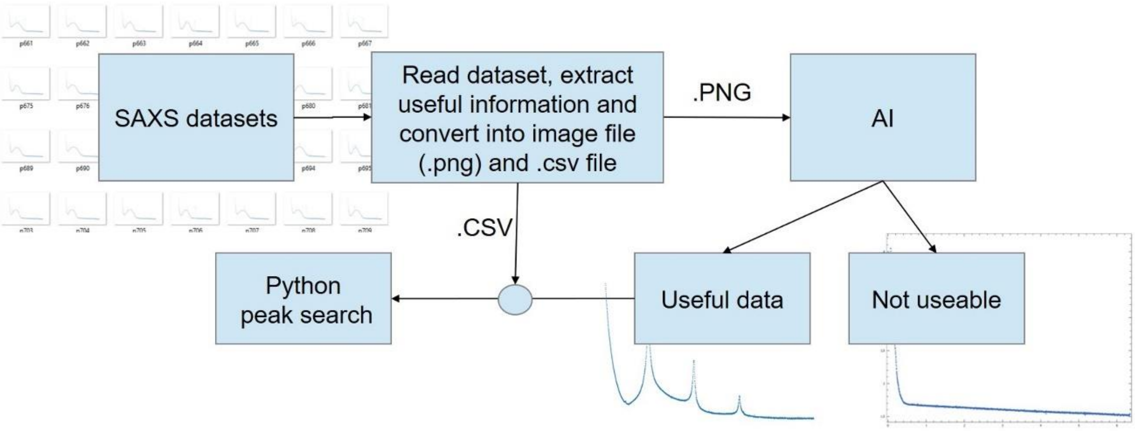

Fig. 1: AI based SAS data categorization process.

## Keywords

Data Analysis, Artificial Intelligence, CNN, Data Bank

SESSION 12B: MODELLING AND DATA ANALYSIS 3
Chair: Dr. Leandro Barbosa

# V158 - EXPERIMENTAL NOISE IN SMALL-ANGLE SCATTERING CAN BE ASSESSED USING BAYESIAN INDIRECT FOURIER TRANSFORMATION

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Experimental errors are essential when assessing whether a hypothesized model fits a given SAS data set. Likewise, the errors are important when weights are assigned to multiple data sets used to refine the same model. Therefore, it is problematic when experimental errors are over- or underestimated, which is indeed the case for many data sets in the SAS Biological Data Bank (SASBDB) [1].

We have developed a method to assess whether or not a given SAS data set has over- or underestimated errors. The method is simple to use and implemented as a web application (https://somo.chem.utk.edu/bayesapp/). After running the application, the user gets the noise level of the input data, i.e. what reduced chi-square to aim for when fitting the data; in the case of over/underestimated data, this value can be significantly different from the textbook-mandated target value of unity. Moreover, the application provides a rescaled dataset, with corrected errors.

I will present the principles of the method, which is based on a Bayesian indirect Fourier transformation of the data, and I will show how the method was tested against simulated and experimental data (Figure 1).

The method is also useful, when the errors are appropriately determined; it is inherently ambiguous whether a model fits sufficiently well to a given dataset, as the ‘true’ reduced chi-square of the data is not necessarily unity, but follow a distribution with mean of unity. This is relevant for approaches where overfitting is a challenge, such as reweighting of a simulated molecular dynamics trajectory against SAS data [2], or ab initio modelling [3]. In these approaches, an arbitrarily small value of the chi-square can often be obtained. So when should the algorithms stop improving the fit? Using the outlined method, it is shown that one can determine what chi-square to aim for in such cases.

Finally, I will outline what type of data the method can be used for, and importantly, discuss where the assumptions break down.

The method is also described in our recent publication [4].

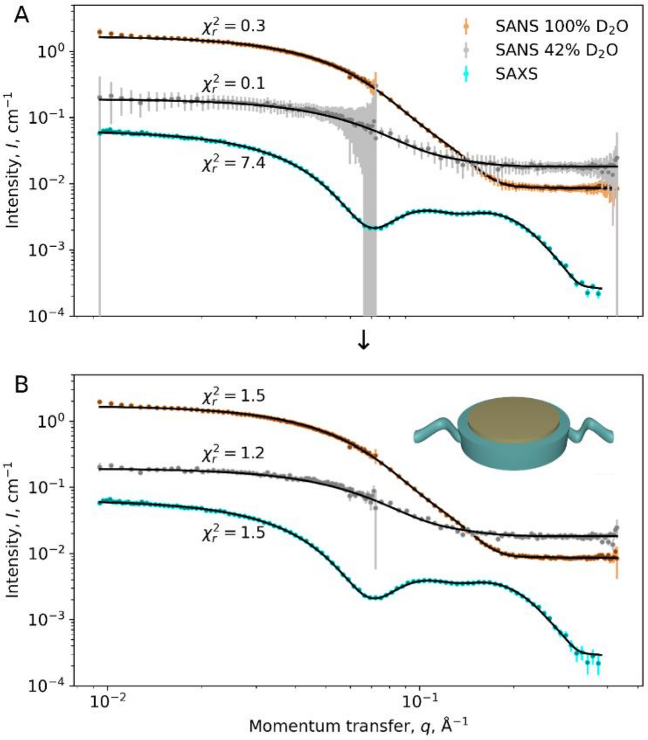

Figure 1. SAXS and SANS data for a sample of phospholipid bilayer nanodiscs [5]. A geometrical nanodisc model refined from the data is shown in the inset, and the model fit is shown in black, with corresponding reduced chi-square values displayed. (A) Data and fits before rescaling the errors. (B) Data and fits after rescaling.

**Keywords**
error assessment, error bars, goodness of fit, molecular dynamics, combining data

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SESSION 12B: MODELLING AND DATA ANALYSIS 3
Chair: Dr. Leandro Barbosa

# V270 - A MORE COMPLETE MODEL ON ABSOLUTE SCALE FOR THE SCATTERING FROM BOVINE CASEIN MICELLES

**PEDERSEN, Jan Skov (1); MØLLER, Thea Lykkegaard (2); RAAK, Norbert (2); CORREDIG, Milena (2)**
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One of the main components of bovine milk is casein micelles, which are particles consisting mainly of protein and calcium phosphate. They are 100 - 400 nm in diameter with a network of protein, where the CaPO4 forms colloidal calcium phosphate nanoclusters (CCPs) in the size range 2 - 4 nm that contributes to binding the proteins together. In skimmed milk, the concentration of casein micelles is about 35 mg/mL, where protein makes has a concentration of 93 w/w% and calcium phosphate 7 w/w%. The casein micelles are hierarchical structures with a very characteristic scattering curve1: There is a Guinier behavior related to the overall structure at low values of the scattering vector modulus, . At higher , there is a characteristic bump with a weak indication of a maximum, which originates from substructures within the casein micelles. At intermediate q, in the Porod region from the particle surface, there is sometimes a weak bump referred to as 'incompressible regions' in the literature. Scattering data from casein micelles were obtained with our in-house SAXS and light scattering instruments. Two settings were used for SAXS instrument to cover the region q = 0.0045 to 1.0 Å-1, and light scattering was used to cover scattering vectors below 0.0028 Å-1. To analyze the data, a rather complete and self-consistent model for the scattering of casein micelles was developed. It is derived from the 'dirty snowball' model2. The scattering is expressed on absolute scale and the concentrations of, respectively, protein and calcium phosphate are used as constraints. Correlations between protein heterogeneities/particles (PPs) and CCPs within the micelles are taken into account in terms of partial structure factors. Polydispersities of the particle size are described by a Schulz distribution yielding analytical expressions. During the derivations of the equations for the scattering of models including subparticle interactions have been checked. This was done by simulating the scattering of such structures by Monte Carlo methods and analyzing them by the analytical expressions. When applying the model to the experimental data, the CCPs are modelled as oblate ellipsoids and the PPs as star structures, and correlations are included in terms of partial effective hard-sphere structure factors. The model also includes the scattering from the incompressible regions. The model gives very good fits to the experimental data and allows the structure of the various components of the micelles to be determined.

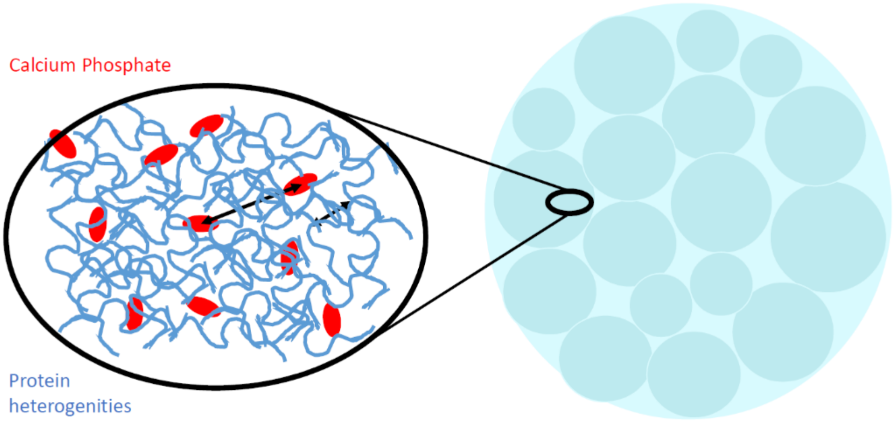

Fig. 1: Schematics of the casein micelle model (right side) with the 'incompressible regions' indicated. Substructure with protein heterogeneities in blue and colloidal calcium phosphate in red (left side).

**Keywords**

magnetic fluids, aggregation, self-assembly, SANS, NR

**Preferences**

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# P249 - 3D SHAPE RETRIEVAL ON FEO NANOCRYSTALS FROM SAXS: FROM STARS TO CUBES

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The chemical synthesis of colloidal nanocrystals (NCs) is a well-established method providing highly monodisperse quantum dots [1] for applications such as e.g., fluorophores or magnetic nanoparticles [1,2]. The morphology of NCs has a substantial influence on their highly diverse physical properties.

Controlling the morphology of nanocrystals during the synthesis and the ability to analyse this morphology of a significant number of particles is one key research interest in this field. Besides the more common transmission electron microscope (TEM), small angle X-ray scattering (SAXS) is a leading technique to analyse the morphology of colloidal nanocrystals with sub-nanometre resolution. Unlike TEM the probed sample in SAXS experiments is usually orders of magnitude larger, giving the data more statistic relevance. From the scattering data the average size is easily deducible, however using modern ab initio bead modelling techniques, also the 3D mean shape of an expressive sample of nanocrystals, seen in all directions, can be retrieved from the SAXS data [3, 4].

In this study the size and shape of varyingly complex superparamagnetic iron oxide nanocrystals (FeO NCs), as well as the crystallographic growth direction are analysed. The FeO NCs range in size from 20 to 40 nm and transform in shape during growth from stars with eight arms to nearly perfect cubes (see [2] and Fig. 1). Complementary X-ray diffraction experiment support the findings from the SAXS data. The excellent congruence of the results are demonstrated by comparison to TEM micrographs (see Fig.1). The 3D SAXS mean shapes allows, however, to gain additional information on the internal dimensions of the FeO NCs that are not visible in the TEM images alone [5].

Furthermore, we plan to apply the 3D shape analysis to anomalous SAXS (ASAXS) data [4, 6] of this FeO NCs samples series. During a synchrotron beamtime (May 2022) at the new SAXSMAT beamline P62 at DESY/PETRA III we will record ASAXS spectra around the Fe-k-edge (7.11 keV), from which we will separate the non-resonant from the resonant SAXS curve that contains the information on the Fe-ions alone [6]. This will allow deriving the 3D Fe-distribution within the FeO NCs.

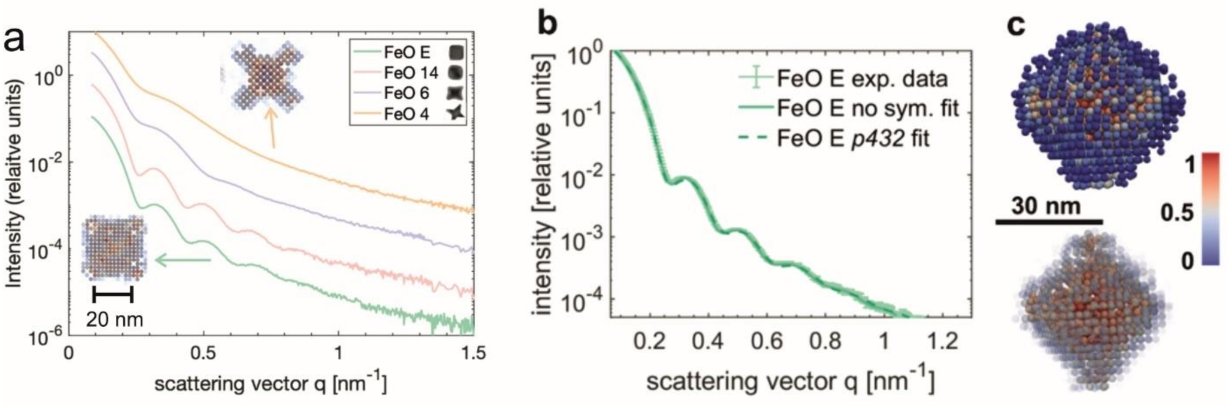

**Fig 1: a)** Lab based SAXS-data of FeO-NCs with shapes from cubes to stars as can be seen from the TEM images in the legend. **inset:** *Mean 3D shapes* of a large ensembles of NCs (~ $10^8$ individual NCs) as derived from the shown SAXS data by a 3D shape retrieval method. **b)** SAXS data of the best FeO E cubes together with the fits. **c)** The best defined 3D shapes we derived by assuming a cubic (p432) shape symmetry during the fitting procedure. The 3D shape models are built by dummy atoms (DA), where the colour code gives the occupancy probability. From the DAs with an occupancy larger than 0.5 we can deduce the real nanoparticle dimensions.

**Keywords**
SAXS, XRD, 3D shape retrieval, colloidal nanocrystals

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SESSION 12C: COLLOIDS AND POLYMERS 7
Chair: Dr. Andy James Smith

## P261 - INTERACTION BETWEEN INORGANIC NANOPARTICLES AND THEIR AGGREGATES

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Here, we synthesized magnetite ($Fe3O4$) NPs as a model system to carry out an experimental and theoretical study on the interactions between NP aggregates and their implications for colloidal stability. First, from small-angle X-ray scattering (SAXS) and dynamic light scattering (DLS) measurements, we determined the fractal dimensions (df) and the hydrodynamic size (Dh) of the aggregates formed in the 3-10 pH range. Then, using a cluster-cluster algorithm, we simulated the fractal structures formed at each pH. Finally, from finite element numerical calculations, we simulated the EDL formed around the aggregates and quantified the influence of the structure and size on the interparticle interaction energy. Its implications for the interpretation of the colloidal stability and clustering mechanisms for this system are discussed. $Fe3O4$ NP aggregates have a surface charge dependent on the pH of the solution. Close to pH 7.2 the surface charge is zero, while at higher pH values the charge is negative and at lower pH values the charge is positive. This behavior is reflected in the observed SAXS profiles, as well as in the values of the Dh, determined by DLS. As the pH approaches the zero-charged pH, the df values decrease, while the Dh values increase. This suggests that the densification of the aggregates is decreasing, which is characteristic of a transition between the RLCA to DLCA regimes. The simulated fractal structures confirm this behavior. As the charge of $Fe3O4$ NP decreases, aggregates grow, and the barrier against the aggregation decreases. Numerical simulations show that the structure of the formed aggregates strongly influences the magnitude of the interparticle interaction. non-uniform charge distribution and strong overlaps between the EDLs around the primary particles within the aggregates. Considering the effect of the aggregate structure in the interaction energy calculation is fundamental to obtaining correct predictions for the colloidal stability and identifying the transition range between the clustering mechanism for charged NPs.

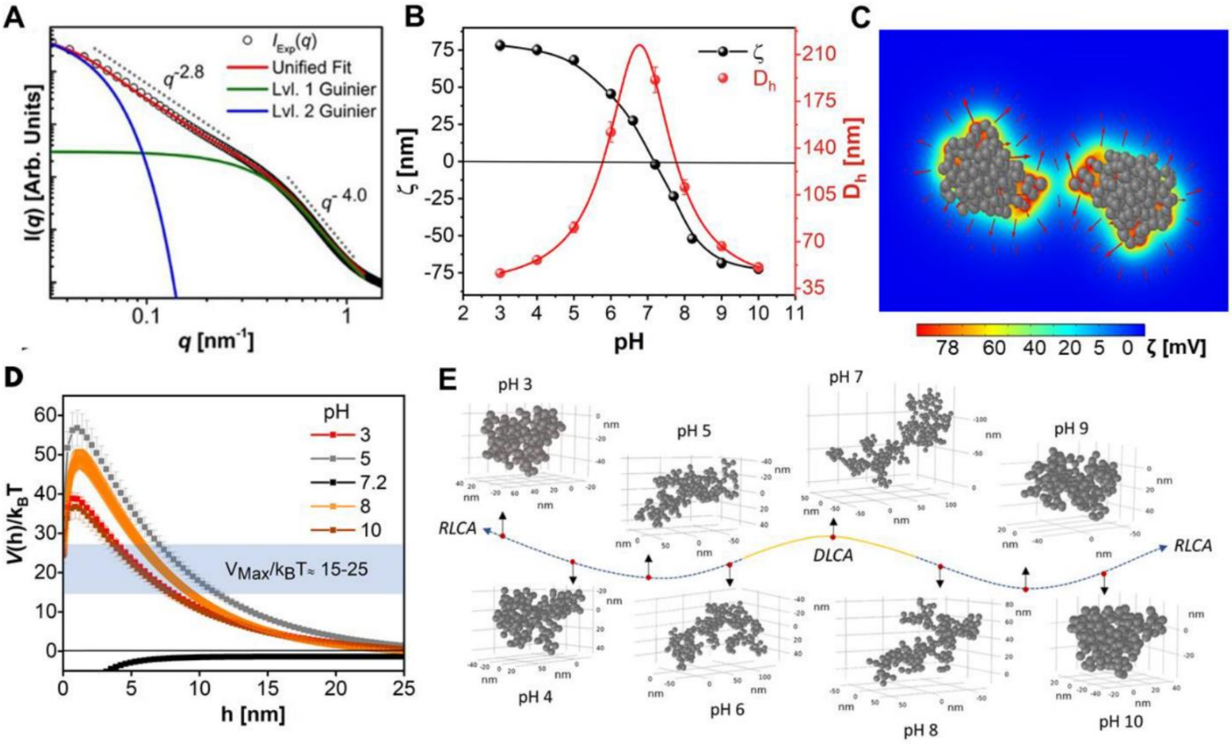

**Figure 1.** Experimental data and numerical simulations for the $Fe_3O_4$ NP aggregates. (**A**) SAXS curves for the NP dispersions. The value of the exponent $\alpha$ (indicated in $q_\alpha$) is the slope of the curve. (**B**) Zeta potential ($\zeta$) and hydrodynamic diameters ($D_h$) as a function of pH. (**C**) Finite element simulation results of the surface charge (or $\zeta$) distribution around two aggregates as a function of the separation distance of the nearest particle pair. (**D**) Calculated total interaction energy of the NP aggregates for different pH values. The $V_{max}/k_BT \approx 15–25\ k_BT$ values indicate the value necessary to overcome the average thermal energy of the NP aggregates and provide kinetic colloidal stability. (**E**) Transition between the RLCA and DLCA aggregation regimes and their impact on the structures of NP aggregates as a function of pH.

**Keywords**

Nanoparticles interactions, clustering, numerical simulations

SESSION 12C: COLLOIDS AND POLYMERS 7
Chair: Dr. Andy James Smith

# V125 - DECIPHERING THE STRUCTURE-PROPERTY CORRELATION OF PEDOT-BASED ELECTRONIC INK WITH SMALL-ANGLE SCATTERING

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Recently, electronic inks have attracted widespread attention in the field of printed flexible electronics. Among them, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is recognized as the most promising candidate owing to its mechanical flexibility, biocompatibility, solution processability and good environmental stability. However, untreated PEDOT:PSS film displays poor electrical conductivity as low as about 1 S cm-1. To solve this issue, secondary doping agents like ionic liquid (IL) are generally introduced into PEDOT:PSS, i.e., secondary doping, to achieve 3 orders of magnitude improvement on the conductivity. However, the influence of secondary doping on the structure and conductivity of PEDOT:PSS is largely unknown yet.

In this report, we study the electrical conductivity of PEDOT:PSS films with salts that have various cations but the same bis(trifluoromethanesulfonyl)amide anion. Doping salts of small-sized cations led to higher conductivity because of the improved crystalline order and p-doped level of PEDOT, as revealed by the grazing-incidence wide-angle X-ray scattering and UV−vis spectrum, respectively. We understand this phenomenon with the fact that small-sized cations with stronger Coulombic interactions can lead to rearrangement of PEDOT:PSS and thus high doping. Moreover, we decipher the solution assembly of PEDOT:PSS/IL hybrid with small-angle X-ray and neutron scattering to get in-depth information of the structure formation process. These findings help us to develop recipes based on the PEDOT:PSS/salt hybrid for the applications of thermoelectric.

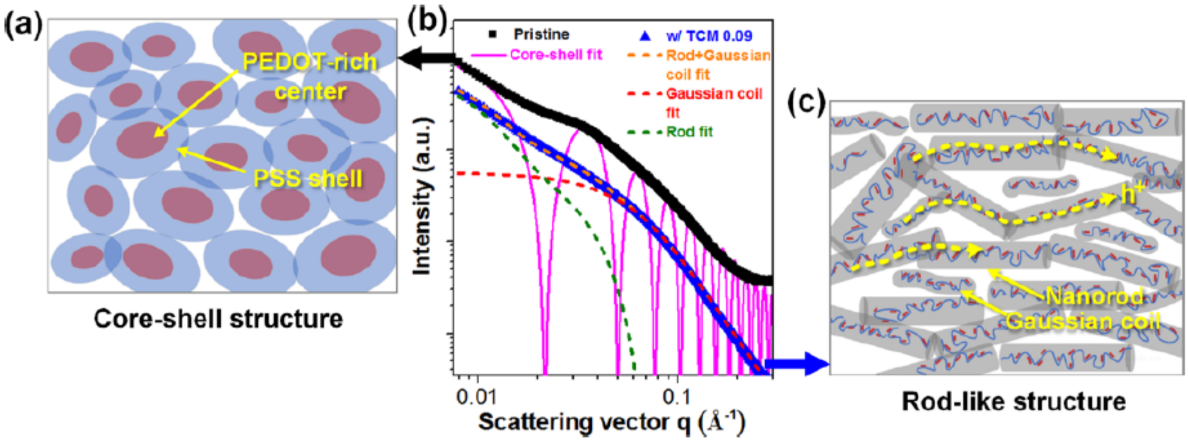

Fig.1 An exemplary study of the IL-doping induced structure change of PEDOT:PSS with SAXS. (a) Typical “core-shell” structure of PEDOT:PSS in aqueous dispersion. (b) SAXS data and the fitting based on “core-shell” and “rod and coil” models. (c) Extracted “rod-coil” structure of IL doped PEDOT:PSS in aqueous dispersion.

## Keywords

PEDOT, electronic ink, structure-property correlation, small-angle X-ray scattering, small-angle neutron scattering

## Acknowledgements

We acknowledge the financial support of National Natural Science Foundation of China (No. 11905306 and U2032101).

SESSION 12C: COLLOIDS AND POLYMERS 7

Chair: Dr. Andy James Smith

## V294 - IN-SITU STUDY OF THE CORE/SHELL STRUCTURE OF IRON OXIDE NANOPARTICLES USING ANOMALOUS SAXS

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Due to their biocompatibility and magnetic properties, iron oxide nanoparticles (NPs) are especially interesting for applications such as targeted drug delivery and hyperthermia therapy. According to its oxidation states, iron may form various crystal structures and thus show different magnetic properties. FeO is a bulk antiferromagnet with a rock salt crystal structure at room temperature. Bulk magnetite and maghemite are ferrimagnet with TC = 858K and 948K, respectively. However, they show different magnetic properties in nanoscale due to the finite size effect.

We observe a shift in the hysteresis loops of various sizes of iron oxide NPs (5-20nm). This is due to an exchange interaction between the magnetite core and an oxidized shell. In order to understand the relationship between the exchange bias effect and the size of the core and the thickness of the oxidized shell, we performed in-situ anomalous SAXS experiments on iron oxide NPs.

Anomalous SAXS is an element sensitive technique. When the energy of the incoming beam is tuned close to the absorption edge of the element, the resonance effect starts to play a role. Therefore, the scattering amplitude becomes a complex number. Comparing the SAXS patterns at more than 3 different energies below the absorption edge, the pure resonant contribution of that element can be separated. Thus, the number density of the resonant element can be calculated. It has been reported that the absorption edge of the iron ion shifts towards higher energies as the oxidation state of iron increases. Therefore, anomalous SAXS is a perfect technique to estimate the fraction of Fe2+ and Fe3+ inside the NPs. In this work, we focus on the change in the core/shell structure of iron oxide during different annealing procedures. The SAXS pattern of the as-prepared sample can be fitted well with a spherical model. After the reduction procedure, a shell with a slightly higher scattering length density is observed. This indicates that maghemite at the surface of the NPs is reduced to magnetite. Moreover, the ratio of different phases of iron oxide obtained from anomalous SAXS is compared with that obtained from the X-ray absorptions spectroscopy.

**Keywords**
Magnetic, anomalous SAXS, nanoparticle

## P316 - CUBOSOMES FOR DRUG DELIVERY SYSTEMS: THE INFLUENCE OF (NOT SO) SMALL MOLECULES ON ITS INNER CUBIC STRUCTURE.

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Cubosomes are nanoparticles composed of a specific combination of some types of amphiphilic molecules, such as phytantriol (PHY), and a nonionic polymer, like poloxamer (F127). Cubosomes have a high hydrophobic volume (> 50%) and are good candidates for drug delivery systems. In our research group, we have been studying these nanoparticles for the last years, mainly observing the influence of different molecules on the nanoparticle size, shape, and inner structure. To do so, we mainly used Small-Angle X-ray Scattering, and Cryogenic Transmission electron microscopy. For instance, we studied the influence of Miltefosine, (hexadecylphosphocholine, HePC) in phytantriol-based cubosomes. HePC is a broad-spectrum antimicrobial, anti-leishmanial drug, originally developed as an anti-cancer agent. Because of its toxic side effects, several nanotechnology-based formulations have been considered carriers for HePC. As we observed, HePC is able to induce a cubic-to-cubic phase transition on the cubosomes. Ionic liquids (IL), on the other hand, are cationic amphiphilic molecules that are being used lately as green solvents. In this study, we observed the possibility of using IL as cationic agents to create an adjuvant nanoparticle for gene therapy or even a base for RNA-base vaccine. It is clear that the loading efficiency and bioavailability are strongly correlated to the structural properties of the considered nanocarries. Therefore, the interplay between the structure stability and the entrapped compounds is worthy of investigation. Thus, in the present study, we will show how we can use SAXS technique to evaluate the inner cubic structure of phytantriol-based cubosomes both in the absence and in the presence of external molecules. As we have shown, in some specific cases, it is quite evident inner phase transitions, indicate a significant change in the average inner packing parameter.

**Keywords**
Cubosomes, Nanoparticles, Drug delivery

# V188 - STRUCTURE AND STABILITY OF ARTIFICIAL OXYGEN CARRIERS INVESTIGATED BY (U)SAXS – A NANOMEDICINE SMALL ANGLE SCATTERING STUDY

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Red blood cell concentrates (RBC) are an indispensable tool in various clinical scenarios; however, the available quantity is already highly limited, which will become an even more severe problem in the future. To overcome these peculiarities and limitations of RBCs, we developed albumin-derived perfluorocarbon-based artificial oxygen carriers (A-AOCs), that are comprised of a perfluorodecalin (PFD) microemulsion core and an albumin shell, and have already successfully supplied oxygen in extra-corporally perfused hearts and various animal models [1].

The structure and stability of A-AOCs is sensitive to changes of the carrier solution, so we needed to learn more about the structure and structural changes on the nanoscale. Conventional characterization techniques lack the spatial resolution (e.g. light scattering) or need dried and thus non-physiological samples (e.g. SEM, TEM), and thus yield limited information on A-AOC structure in solution. We therefore used (ultra-)small angle X-ray scattering, which does not have such limitations and allows studying also especially dense, opaque suspensions.

In our contribution, we present recent results of (U)SAXS measurements on A-AOCs covering a wide, clinical-relevant concentration and temperature range. We investigate A-AOCs from different synthesis approaches, using ultra-sound [2] and microfluidizing techniques, which reveal different sizes and stabilities. Based on these findings, it is now possible to optimize the synthesis parameters, in order to yield stabile A-AOCs of the wanted size and dispersity.

This study therefore shows the huge potential of small angle scattering for the study of pharmaceutical and medical-relevant samples [3], with direct implications for the development of new formulations.

**Keywords**
Nanomedicine, Artificial Oxygen Carriers, USAXS

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## V168 - HEXAGONAL AND CUBIC MESOPOROUS SILICA WITH EXPANDED PORES TAILORED TO ENCAPSULATE BIOLOGICAL MOLECULES

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Ordered mesoporous silica (OMS) with hexagonal or cubic symmetry is synthesized with a variety of triblock copolymer templates presenting a narrow distribution of pore diameters, providing strict control of synthesis conditions. By changing the preparation parameters such as salts, swelling agents and temperature it is possible to adapt the sizes of the pore´s entrance and their mean internal diameter. These conditions can lead to changes in the structural organization of the pores. For parenteral and oral transport of biological substances, the silica matrix proved to be useful to decrease toxicity [1] and to increase humoral immunity [2]. In particular the delivery of substances across the harsh gastric medium, preserving their properties, is a difficult task, but it can be optimized by controlled release from the OMS. Combination of morphological and structural analysis, as SAXS, was used to investigate many different materials that were planned to deliver specific molecules. The use of papain, a proteolytic enzyme, as a model substance to analyze its delivery from different OMS will be reported.

**Keywords**
Porous silica, Papain

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## V419 - TAILORING BLOCK CO-POLYMER DESIGN - DRUG-LOADED NANOPARTICLES VIEWED WITH SMALL ANGLE NEUTRON SCATTERING

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Nanoparticles, through their ability to partition and provide targeted delivery of hydrophobic drug molecules, are able to provide enhancements to pharmacokinetics for many drugs. When used in conjunction with cell studies, which provide very direct information on the uptake of particles in different kinds of cells, small angle neutron scattering (SANS) provides a perspective on nanoparticle structure and their the interaction with drugs. We discuss nanoparticles synthesized from very carefully controlled polymerisation reactions where the block co-polymers have precisely defined stoichiometry. The nanoparticles resulting from the self-assembly of these block-copolymers offer and exquisite control over particle shape and surface characteristics. SANS offers a direct evaluation of these structural parameters in an environment very close to that of the physiological milieu. The twin experimental perspectives provide an associative relationship between simple structural parameters of nanoparticles and cell uptake1-3.

**Keywords**
block co-polymer, self-assembly, drug delivery

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SESSION 13A: HYBRID MATERIALS AND BIOMATERIALS 3
Chair: Dr. Charlotte Jennifer Chante Edwards-Gayle

# V360 - SMALL-ANGLE X-RAY SCATTERING INVESTIGATION OF NANOSTRUCTURAL CHANGES DURING LONG-TERM RELEASE OF PENICILIN G IN SILOXANE-PPO HYBRID MATERIALS

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Polyether-Siloxane hybrids prepared by Sol-Gel process, in which siloxane nanoparticles are interconnected by polyoxyethylene (PEO) or polyoxypropylene (PPO) chains, present technological interest due do their flexibility, transparency, biocompatibility and chemical stability [1] and have been used as controlled drug-delivery devices [2]. However, for several drugs it is necessary to develop systems able to promote release during very long periods. This is the case for penicillin G (PenG), a water soluble and antibacterial drug used for treatment of kidney fever, the most common form of paediatric cardiac disease [3]. For this purpose, our group recently showed [4] that the high hydrophobic Siloxane-PPO hybrid can be used as carrier matrix for prolonged PenG release in aqueous medium. In this work, Small-Angle X-ray Scattering has been employed to follow the structural changes occurring at nanometer scale during the different steps of PenG release process. SAXS results showed that drug incorporation in Siloxane-PPO matrix leads to the formation of a hierarchical structure consisting of large nanosized and quite cubic-shaped hybrid aggregates (secondary aggregates) dispersed in the matrix, in which siloxane nanoparticles (primary particles) are spatially correlated. After immersion of the samples in aqueous medium, the drug molecules located inside the secondary aggregates are released, leading to the disappearance of the hierarchical structure and the homogeneous dispersion of the siloxane particles in the PPO matrix. This first period, allowing release of 35% wt of the PenG during the first 12h, is promoted by the more hydrophilic character of the siloxane-rich secondary hybrid aggregates comparing with the PPO matrix, attracting water. In the second and much slower regime, around 25% wt of the drug is released during two weeks. SAXS results have evidenced that during this period the hybrid nanostructure does not suffer significant changes, since this regime corresponds to dissolution and release of PenG aggregates dispersed between the PPO hydrophobic chains which inhibits water penetration in the hybrid matrix. Interestingly, SAXS measurements also evidenced that after the second release regime, entanglement of PPO chains promoted by water penetration leads to approximation and spatial correlation between siloxane nanoparticles and the consequent formation of a new hierarchical structure (non-cubic shaped). Further investigation are needed to investigate if the formation of such new nanostructure should explain why no more drug release is observed after the second regime.

## Keywords

Drug delivery, Sol-Gel, hybrid Materials, Penicilin

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SESSION 13B: MODELLING AND DATA ANALYSIS 4
Chair: Dr. Melissa Ann Graewert

# P250 - ADDRESSING THE RESOURCE PROBLEM THROUGH COMMUNITY. SASVIEW: AN “OPEN, COLLABORATIVE, COMMUNITY DEVELOPMENT” PLATFORM FOR SMALL ANGLE SCATTERING ANALYSIS SOFTWARE.

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As the needs for computational tools become increasingly critical for the extraction of new scientific knowledge from scattering data, the need for increasingly sophisticated tools has become a bottleneck despite relatively large investments in software and the “cyberinfrastructure revolution.” We posit that this problem is not going away, fundamentally because analysis needs are, and will remain, effectively infinite, while resources will always be finite. Here we will look at the SasView experiment in this area which we suggest provides some ideas for potential paths forward.

SasView is a SAS data analysis package that originated out of the NSF funded DANSE project and has evolved into an international collaborative effort that is experimenting with ways of providing robust and sustainable analysis software in this new cyberaware age. This presentation will not focus on the software and its features per se, but rather on how it is trying to deliver those features sustainably in a funding environment that tends to value “new shiny things” over long term sustainability, maintenance and support. We will take a particular look at how each word in “open, collaborative, community development” is currently addressed, and discuss how we got to where we are, the lessons learned along the way, and the challenges faced, then and now. As a “work in progress” feedback on new ideas and solutions to challenges are very welcome.

Besides helping to optimize the use of limited resources by not ending up with excessive duplication, this type of grass roots community approach has the potential of being a way to self-select the areas of most important need on which to focus the finite resources. While this “experiment” remains a work in progress, we propose that this basic model, should, at the very least, be considered as an important part of any holistic plan for providing scientific software tools in the future, particularly for data emanating out of large scale facilities.

**Keywords**
Data Analysis, Software, Community

SESSION 13B: MODELLING AND DATA ANALYSIS 4
Chair: Dr. Melissa Ann Graewert

# P250 - ADDRESSING THE RESOURCE PROBLEM THROUGH COMMUNITY. SASVIEW: AN "OPEN, COLLABORATIVE, COMMUNITY DEVELOPMENT" PLATFORM FOR SMALL ANGLE SCATTERING ANALYSIS SOFTWARE.

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**Keywords**
Data Analysis, Software, Community

SESSION 13B: MODELLING AND DATA ANALYSIS 4
Chair: Dr. Melissa Ann Graewert

# P131 - SIMPLIFIED POLYDISPERSION ANALYSIS OF SMALL-ANGLE SCATTERING DATA

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In case of polydisperse inhomogeneities, the analysis of Small-Angle Scattering (SAS) data is possible by fitting the experimental data with theoretical models. Despite scientific softwares are available for this task, many scientists of many different scientific fields do indeed prefer other techniques for their investigations. With the Simplified Polydispersion Analysis presented here, it is possible to analyse the SAS data in a much simplier way. A straightforward interpolation of the SAS data by using any commercial software, requiring no advanced advanced computational skills, allows the determination of the Size Distribution Function of the polydisperse inhomogeneities. Here the innovative approach has been tested against simulated SAS data of spherical inhomogeneities as well as experimental data with excellent results. The results reported here open new opportunities for many scientists that never used the SAS technique for the investigations of their polydisperse systems.

**Keywords**
Polydispersion Small-Angle Scattering

## V340 - NEW TOOLS TO QUANTITATIVELY ANALYZE ANOMALOUS SMALL-ANGLE X-RAY SCATTERING DATA FROM NANOMATERIAL SYSTEMS

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Anomalous Small Angle X-ray Scattering provides element-sensitive structural information from systems of interest in the length scales of a few nanometers to hundreds of nanometers. Since its first use in the early 1980s, although the experimental methodology for ASAXS data collection has not changed considerably, some efforts have been made in the quantitative analysis of the data. One of the most known methods of analyzing ASAXS data is to split the energy-dependent SAXS data into three scattering components, namely, the SAXS-term, the Cross-term, and the Resonant-term. Both the SAXS- and Cross-terms comprise scattering contributions from all the elements present in the system of interest whereas the Resonant-term only comes from the distribution of the resonant element in the system. Although the splitting method sounds very promising and works for certain systems, in this talk I will present both simulation and experimental data from some model nanomaterial systems where the component splitting method does not work. I will also present some of our recent efforts at NSF’s ChemMatCARS, Sector 15 at Advanced Photon Source, in the quantitative ASAXS data analysis from nanomaterial systems of different morphologies. The development is done in the form of ASAXS functions written in a python-based modeling and data fitting software called XModFit (https://github.com/chemmatcars/XModFit).

**Keywords**
Anomalous Scattering, Nanomaterials, Modeling, Data Analysis

SESSION 13B: MODELLING AND DATA ANALYSIS 4
Chair: Dr. Melissa Ann Graewert

## V417 - ATSAS-3.1: AN OVERVIEW OF NEW DEVELOPMENTS

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The ATSAS software package (Manalastas-Cantos et al., 2021) provides a number of widely used applications for data analysis and modelling in the field of biological small angle scattering of biological macromolecules. During the two years since its previous major release, significant efforts were made to improve not only the accuracy and performance of these applications, but also their usability and accountability.

In particular, the application to calculate scattering patterns from atomic coordinates, CRYSOL (Svergun et al., 1995) was re-implemented with modern software design principles. In addition to all its previous functionality, CRYSOL now includes an alternative water-shell implementation and individual form factors for dummy residues. CRYSOL can be used directly on dummy atom models, handle both PDB and mmCIF formatted files, and has been seamlessly integrated into various other applications. All data sources used by CRYSOL, e.g. Cromer-Mann form-factor coefficients, dummy residue form-factors or anomalous SAXS energy correction terms, are available as open mmCIF data and are user-verifiable, configurable and extensible. As Python became a popular platform for scientific application development, native Python bindings for CRYSOL are provided as a proof-of-principle and test for the community.

The ab initio modelling post-processing suite DAMAVER (Volkov & Svergun, 2003) was consolidated into a single program, that also allows to utilize multiple similarity measures. Further, DAMAVER, as well as most other analysis and modelling applications of the ATSAS package, received performance improvements. The speed up factors range from small, but noticeable gains for some applications to orders of magnitude for others. This was achieved by replacing key algorithms in addition to careful application of CPU-based multithreading via OpenMP (www.openmp.org). Additional gain was provided by platform specific performance libraries for common linear algebra operations (LAPACK).

The graphical user interface PRIMUS was modernized and extended. A ribbon-style toolbar was implemented with a new icon theme that supports light and dark modes to provide convenient access. The data comparison now provides alternative views of expected and observed distributions of residuals or chi-square values to aid the assessment of the accuracy of error estimates. Additional wizards, e.g. for hybrid modelling applications (predict and fit modes) have been included.

The ATSAS-3.1 installer package is available for download on all major software platforms (Linux, MacOS and Windows) and is free of charge for academic users (https://www.embl-hamburg.de/biosaxs/software.html).

**Keywords**
small-angle scattering; data analysis; biological macromolecules; structural modelling; ATSAS

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SESSION 13C: INTERFACES, SURFACES AND GRAZING INCIDENCE 2
Chair: Dr. Antonio Augusto Malfatti-Gasperini

# P364 - FORMATION, STABILIZATION AND CRYSTALLIZATION OF MESOPOROUS TIO2 THIN FILMS STUDIED BY SAXS

**ZALDUENDO, M. Mercedes (1); STEINBERG, Paula Y. (1); BOROVIK, Paula F. (1); FUERTES, M. Cecilia (1); AMENITSCH, Heinz (2); ANGELOMÉ, Paula C. (1)**
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Mesoporous TiO2 thin films (MTTFs) have attracted a great deal of attention in the last years, due to the combination of interesting properties from the material and from its structure. TiO2 is a wide band gap semiconductor and as such presents optical and electronic properties that allow its use as a photocatalyst and as a part of photovoltaic devices. Adding porosity to TiO2 increases its surface area, allowing the use of smaller amounts of material, and enhances its reactivity by boosting surface interactions. Interestingly, the high monodispersity and order of the mesopores (in the 2−10 nm range) allows controlling the species that can diffuse through its structure. Also, obtaining the material as a thin film permits easy integration with well stablished techniques to prepare more complex multiscale devices. Hence, the potential applications of such engineered MTTFs include optical, electronic, and electrochemical devices, batteries, sensors, and catalyst supports.

MTTFs are obtained by the combination of sol-gel reactions, which give rise to the oxide, and self-assembly of amphiphilic molecules that act as templates of the pores, in a process known as Evaporation Induced Self Assembly. The pore array structure depends on the template identity and concentration, and the processing conditions. Due to the high dree of order in the tens of nanometer range, the mesostructure can be determined and studied by SAXS, either in transmission or Grazing Incidence modes. In particular, SAXS experiments performed in synchrotron facilities allow studying all the steps involved in the MTTF preparation: synthesis, thermal stabilization and crystallization.

In this presentation, we will show different approaches to study by SAXS the evolution of the MTTFs mesostructure (i.e pore array and interplanar distances) as a function of synthetic and post- processing conditions. Firstly, we will show how the first stages of the MTTFs formation can be in situ followed by GISAXS or SAXS to understand the way the solvent influences the final pore array, in the case of TiO2 templated with the diblock copolymer Brij 58 and triblock copolymer F127. Afterwards, we will present results of SAXS measurements performed along these MTTFs aging, that allowed determining which aging conditions (humidity, temperature, time) has stronger influence over the final pore ordering. Finally, we will present combined in situ GISAXS-WAXS studies performed during MTTFs thermal treatment (from room temperature until 500 ºC) that give interesting information about the crystallization temperature in different substrates.

As a whole, this work demonstrates the potentiality of in situ SAXS measurements to design synthesis and post synthesis procedures for the reproducible obtention of MTTFs.

**Keywords**
mesoporous oxides, TiO2, thin films

SESSION 13C: INTERFACES, SURFACES AND GRAZING INCIDENCE 2
Chair: Dr. Antonio Augusto Malfatti-Gasperini

# P314 - UNRAVELING THE TIMESCALE OF THE STRUCTURAL PHOTO-RESPONSE WITHIN ORIENTED METAL-ORGANIC FRAMEWORK FILMS

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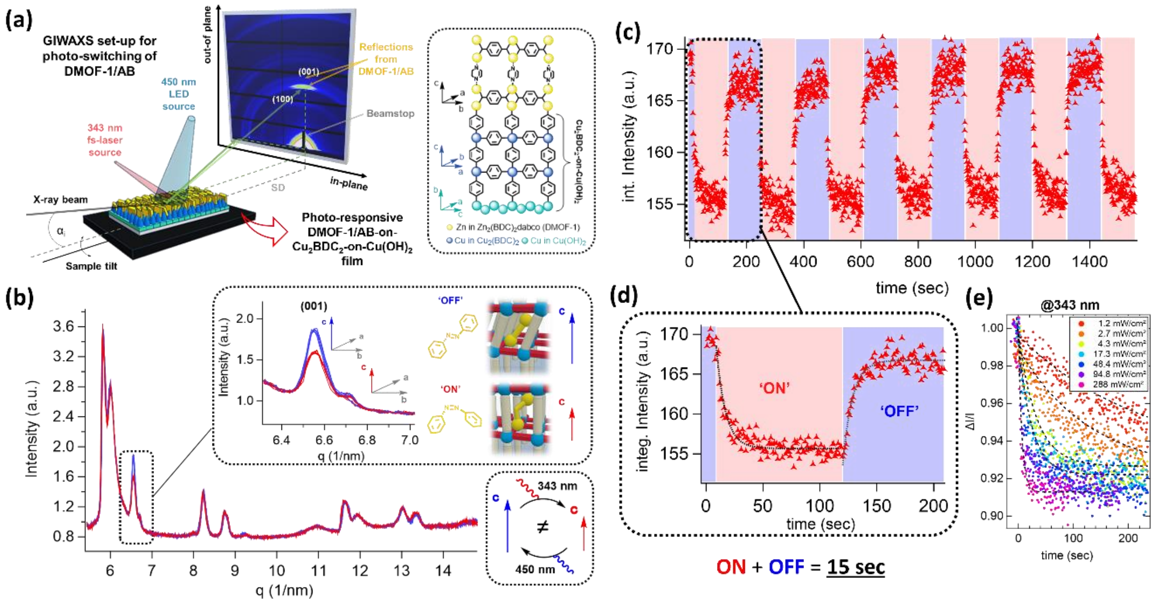
Grazing incidence (wide-angle) X-ray scattering (GI(WA)XS) techniques that operate with short acquisition times, as provided by synchrotron sources, are a powerful tool to probe the structural evolution within soft-matter films when, e.g., applying a stimulus such as light irradiation [1]. Yet, photo-triggered structural changes in solid films are scarcely observed and if, the temporal response characteristics of the structure towards the incoming stimulus remain largely unknown [2]. In this work, for the first time, on the example of a preferentially oriented photo-responsive Metal-Organic Framework film system (DMOF-1/azobenzene) [3,4], the intrinsic timescales of the photo-triggered structural transformations within the crystalline film are studied and quantified [5,6]. When altering the length of the azobenzene molecule by photo-isomerization (trans-to-cis, 343 nm; cis-to-trans, 450 nm), we find that GIWAXS can decouple a flexible and non-flexible structural response within the oriented DMOF-1/azobenzene film system [4]. Hence, within 15 seconds, a reversible DMOF-1/azobenzene response along the (001) crystallographic axis occurs due to a cooperative movement of the DMOF-1 crystallites. The photo-response of our oriented DMOF-1/azobenzene film is one of the fastest observed structural transition for azobenzene-containing solid crystalline films, and one of the first for photo-responsive MOF films. Moreover, we demonstrate that the duration of the structural response can be deliberately tuned by altering the aspect ratio of the DMOF-1 crystallites [4]. Our work thereby suggests a new avenue to elucidate the timescales and the photo-responsive behaviour in similar or even more advanced soft-matter film systems.



**Keywords**
GIWAXS, Photo-response, Structural Dynamics, Films, Metal-Organic Framework, Azobenzene

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SESSION 13C: INTERFACES, SURFACES AND GRAZING INCIDENCE 2
Chair: Dr. Antonio Augusto Malfatti-Gasperini

## V130 - REAL-TIME INSIGHT INTO NANOSTRUCTURE EVOLUTION DURING THE RAPID FORMATION OF ULTRA-THIN GOLD LAYERS ON POLYMERS

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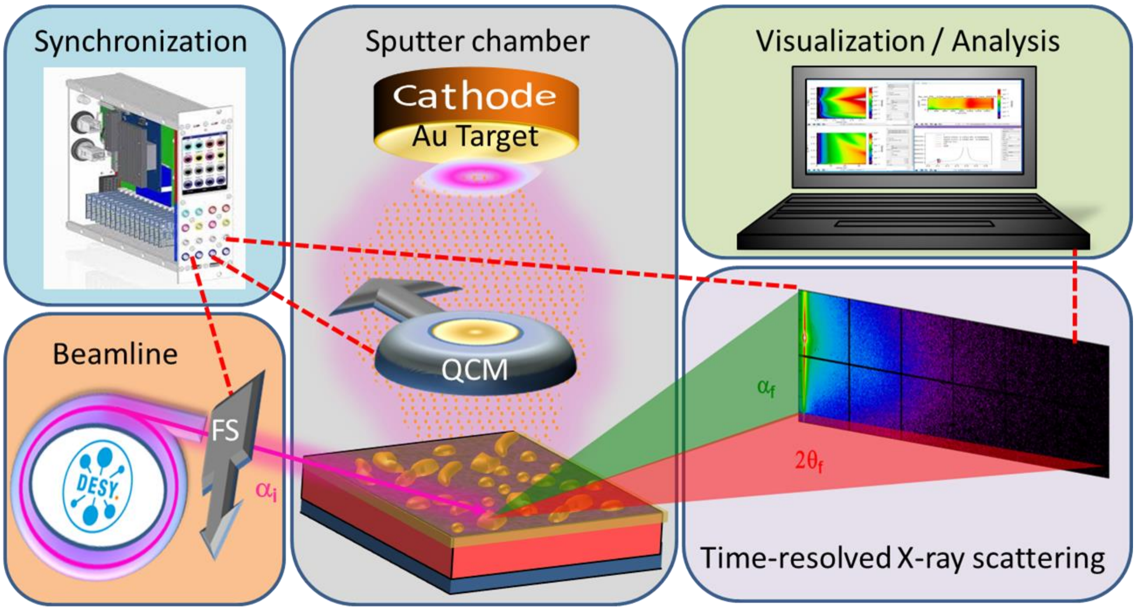
Hybrid nanomaterials composed of polymers covered with ultra-thin metal layers are widely used in advanced technologies – such as OLEDs, OPVs, sensors, or fuel cells. Ultra-thin metal layers are created by sputter deposition in few seconds in industrial applications. Using for the first-time sub-millisecond GISAXS at the P03 beamline of PETRA III allowed us to examine the growth of an ultra-thin gold layer on polymeric substrate with a sub-nanometer spatial resolution. In the first few milliseconds, a fraction of the incoming gold atoms manages to penetrate the polymer matrix, while others begin to form vertical diatomic clusters. Subsurface enrichment and doping of polymer layers with gold atoms changes the material's thermodynamic behavior, which could be exploited in some applications. This real-time observation of nanolayer formation could be used to study the effect of different deposition conditions, e.g., substrate temperatures, and allow us to control and optimize the manufacturing of metal-polymer hybrid materials.



### Keywords

sub-millisecond GISAXS, time-resolved X-ray thin film interference, metal-polymer hybrid formation

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https://doi.org/10.1039/D0NH00538J

SESSION 13C: INTERFACES, SURFACES AND GRAZING INCIDENCE 2
Chair: Dr. Antonio Augusto Malfatti-Gasperini

## V246 - TOWARDS SCALABILITY: EFFECT OF FABRICATION TECHNIQUE ON THEIR STRUCTURE AND THERMOELECTRIC PROPERTIES P3HT-BASED THIN FILMS

**SOCHOR, Benedikt (1); BETKER, Marie (1,2); OECHSLE, Anna-Lena (3); HARDER, Constantin (1,3); SCHWARTZKOPF, Matthias (1); CHUMAKOV, Andrei (1); VOROBIEV, Alexei (4,5); MÜLLER-BUSCHBAUM, Peter (3); ROTH, Stephan Volkher (1,2)**
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This study aims to investigate the influence of different scalable fabrication techniques on the thermoelectric properties of organic thin films. Here, Poly(3-hexylthiophen-2,5-diyl) (P3HT) is chosen as a model system, since it is one of the most prominent semiconducting, conjugated polymers in the fields of organic electronics and photovoltaics [1]. Besides its high electric conductivity, it shows thermoelectric properties when doped with metal chlorides or nanoparticles [1]. For comparing fabrication techniques, we choose both spinscasted and sprayed polymer substrates as well as spray and sputter deposition for the doping process of the thin films, since they offer excellent scalability in future industrial applications. From our previous studies, we know that the fabrication routes will influence the surface morphology, whether spray [2, 3, 4] or sputter despotion [5, 6] is used. While the sprayed bulk solutions were characterized via small- and wide-angle X-ray scattering (SAXS/WAXS), the structure and morphology of the resulting doped thermoelectric thin films were investigated using grazing incidence small- and wide-angle X-ray scattering (GISAXS/GIWAXS), atomic force microscopy (AFM), ellipsometry as well as neutron reflectivity (NR). This combinatory approach of different techniques allowed us to correlate the structural properties of these functional thin films with their thermoelectric properties, which gives important information for any future scalable industrial application.

**Keywords**
sputter deposition, spray deposition, x-ray scattering, neutron scattering, thermoelectrics

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## V251 - GUIDED SELF-ASSEMBLY OF HARD MAGNETIC NANOPLATELETS

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The high concentrated water-based surfactant-free magnetic colloids of ferromagnetic disc-like SrFe12O19 nanoparticles (MNPs) with a mean lateral size of 50 × 5 nm were investigated in ultra small-angle X-ray scattering (USAXS). Individual magnetic particles stabilized by an electric charge have a large permanent magnetic moment and exhibit high values of intrinsic coercivity field Hc (of about 0.4 T). A high concentration of MNPs in a solution leads to their self-ordering into stacks under the action of their magnetic moments.

The distance between the platelets inside the stack and the distance between the stacks may vary in the range from 5 to 50 nm and from 200 nm to 500 nm and above, respectively, depending on the pH of the solution in the stability range. The stacks of MNPs in the absence of an external magnetic field are oriented disordered inside the colloid, which is manifested in the form of rings in the patterns of USAXS. The presence of a small external magnetic field of the order of several mT leads to the reorientation of the stack of MNPs according to the magnetic lines of the field. This ordering is manifested in the form of clear diffraction peaks of USAXS.

As a result of the experiments conducted by the USAXS, with different orientations of the external magnetic field, the dependence of the inter-particle distance of the MNPs of the stack to the distance between the stacks was established. In addition, the area was revealed when this dependence was not respected.

This study can be useful as a base for the development of novel smart materials and devices like magnetic switches, amplifiers, actuators, tunable optical filters, magnetically switchable dilatants, pseudoplastic fluids, etc.

**Keywords**
USAXS, magnetic nanoparticles, magnetic colloid, hexaferrite

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XVIII INTERNATIONAL SMALL
ANGLE SCATTERING CONFERENCE

# POSTER
ABSTRACTS

POSTER

# 385 - EPOXY-SILICA NANOCOMPOSITES APPLIED AS CORROSION PROTECTION COATINGS ON ALUMINUM ALLOY

**ALMEIDA, Adriana; UVIDA, Mayara; HAMMER, Peter; SANTILLI, Celso**
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The corrosion process triggered by exposure to aggressive conditions, such as the marine environment, is the main challenge involving the use of metallic materials. To overcome these problems, different protection methods have been adopted, including the chromate conversion layer. Although efficient, the use of hexavalent chromium makes this methodology highly toxic to humans and with potential risks to the environment. Organic-inorganic hybrid coatings prepared by combining polymeric and inorganic phases dispersed at the nanometer scale are a promising and viable alternative to replace conventional corrosion protection routes, since they act as a passive barrier limiting the contact of the metallic surface with the corrosive environment [1]. Epoxy resins are widely used as a coating on different surfaces; however, they have some disadvantages such as low resistance to crack propagation and residual porosity that act as a percolation paths for electrolyte. These limitations can be overcome with the incorporation of silica phase on the nanoscale. Therefore, to evaluate the influence of the siloxane nanoparticles on the anticorrosive performance of epoxy coatings, samples of the hybrids with different proportions of the inorganic phase were prepared. Coatings based on poly(bisphenol-A-co-epichlorohydrin), (DGBEA), diethyltriamine (DETA) and tetraethoxysilane (TEOS) precursors were applied with a thickness of approximately 10 µm by dip-coating on AA7075 aluminum alloy substrate [2]. The nanostructure of unsupported hybrids was studied using the SAXS technique, which allowed to obtain important information such as size and shape of silica nanoparticles and their average spacing in the epoxy matrix. The scattering profiles were fitted according to the Guinier-Porod model, relating the radius of gyration (Rg) to the average size, the dimension variable (s) to the shape and the Porod coefficient ($\alpha$) to the geometry of the silica particles. The results indicate that independent of the formulation the silica domains have a fractal interfacial structure with an average size around 8 nm. For different hybrid compositions the formation of the epoxy network, promoted by the opening of the epoxy rings by the DETA curing agent, was evaluated using infrared spectroscopy. Wetting experiments showed that coatings with different proportions of organic and inorganic phases had a contact angle greater than 80° and are therefore lightly hydrophilic. Electrochemical impedance measurements in a 0.6 mol L−1 NaCl solution showed a high corrosion resistance of coatings with a low frequency impedance (~4 mHz) of about 100 MΩ cm2, that is, 5 orders of magnitude higher than that for the uncoated substrate.

**Keywords**
Epoxy-silica hybrids, coatings, self-healing agents, corrosion protection.

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POSTER

# 312 - PICOSECOND PUMP-PROBE X-RAY SCATTERING AT THE AUSTRIAN SAXS BEAMLINE AT THE ELETTRA.

**NAUMENKO, Denys (1); BURIAN, Max (2); MARMIROLI, Benedetta (1); KLOKIC, Sumea (1); RADETICCHIO, Andrea (1); MORELLO, Christian (3); DAL ZILIO, Simone (4); BIASIOL, Giorgio (4); AMENITSCH, Heinz (1)**
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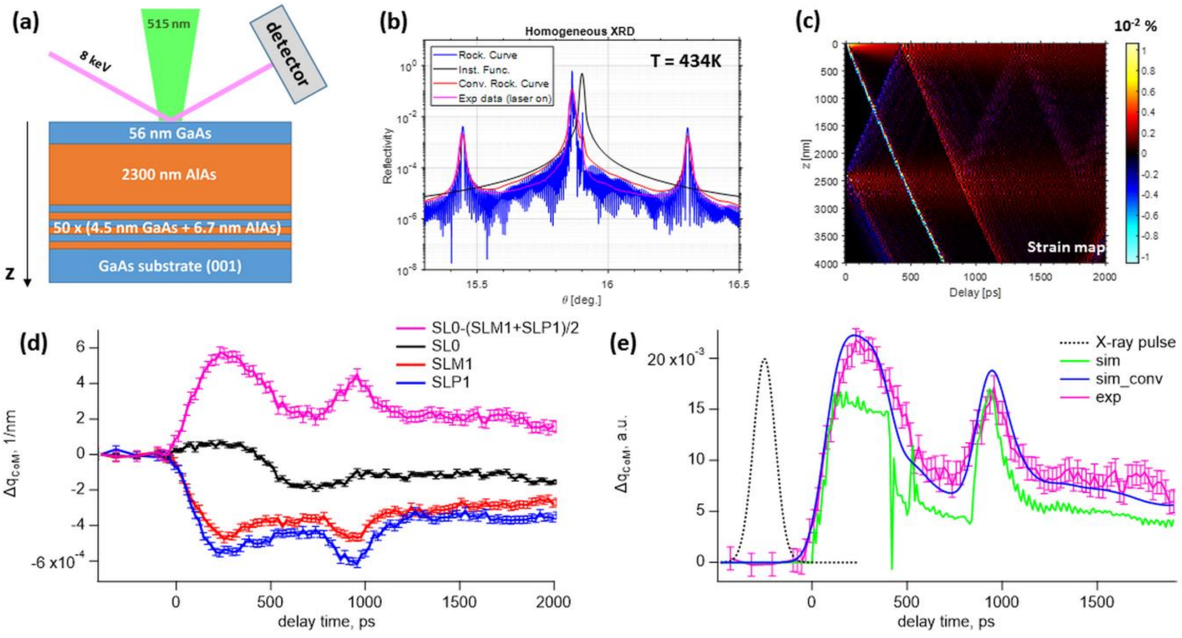
The use of single bunched X-ray pulses at synchrotron facilities is bridging the gap between all-optical (using table-top femtosecond lasers) and optical/X-ray pump-probe schemes (implemented at free-electron laser facilities). Hard X-ray diffraction/scattering setups with picosecond time-resolution track light induced structural changes of condensed matter on an atomic scale whereas currently only a few instruments in the world can access this temporal range with high repetition rate [1-4]. Over the last years, the Austrian SAXS beamline at the Elettra synchrotron has implemented such a picosecond X-ray diffraction/scattering setup [4]. Using InAs/GaAs superlattices (SL), we have recently demonstrated that rapid spatial and temporal cross correlation of optical pump and X-ray probe pulses can be achieved and transient heat transfer in SL structures can be studied. This has finally paved the way for a wider scientific usage of this new beamline feature. In this work we study transient heat transport in GaAs/AlAs SL structures. We demonstrate (Fig.1) that the experimental data with approx. 100 ps time resolution are in outstanding agreement with theoretical calculations which have been performed using dynamical scattering theory [5]. We also discuss the future beamline upgrades which will allow to perform pump-probe experiments on bio-structures in liquid, photo-switchable systems, T-jump experiments in water etc. Figure 1. (a) Sketch of the setup. (b) Omega scan (rocking curve) of the sample shown in (a) at T = 434 K testifying a high quality of the SL structure. (c) Simulated temporal evolution of strain in the structure after absorption of fs laser pulse. (d) Relative shifts of zero-order and ±1 SL satellite peaks as function of delay time between the laser pump and X-ray probe pulses. The pump fluence is 1.65 mJ/cm2. (e) Experimental data and the convolution of the simulated SL response with X-ray probe pulse (133 ps pulse width).



**Keywords**
pump-probe, superlattice, semiconductors

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POSTER

# 162 - BIOSAXS OF A LIPIDATED PEPTIDE DRUG AND ITS SELF-ASSEMBLED NANO DELIVERY CARRIERS

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The self-assembly propensities and the stability of lipid-peptide drug conjugates depend both on the properties of the anchored lipid moiety and the hydrophobic-hydrophilic balance of the aminoacid sequence. In the present work, a lipid-peptide conjugate of the docosahexaenoic acid (DHA) and the pituitary adenylate cyclase-activating polypeptide (PACAP) is created. PACAP is a neuropeptide, which can attenuate the amyloid Abeta (1–42)-induced toxicity under neurodegenerative disease conditions. DHA exerts anti-apoptotic activities, but the bioavailability of the individual molecules is insufficient and should be increased. We performed a structural BioSAXS analysis of the self-assembly behaviour of the lipidated peptide PACAP-DHA in aqueous micellar medium created by the PEGylated amphiphile vitamin E a-tocopheryl polyethylene glycol 1000 succinate (VPGS-PEG1000) with enrichment by vitamin E and DHA [1]. Fitting of the small-angle X-ray scattering patterns, after background subtraction and extraction of the distance distribution functions, yielded the compacted conformation and the shape of the lipid-peptide conjugate in a dispersed solution state suitable for the design of pharmaceutical formulations. Liquid crystalline nanoparticles with inner cubic lattice organization (cubosomes) with incorporated PACAP-DHA were created as carriers of the lipidated peptide drug by self-assembly with the lyotropic nonlamellar lipid monoolein [2]. The obtained structural information is significant for the development of future nanomedicine-based strategies against neurodegenerative disorders [1,2].

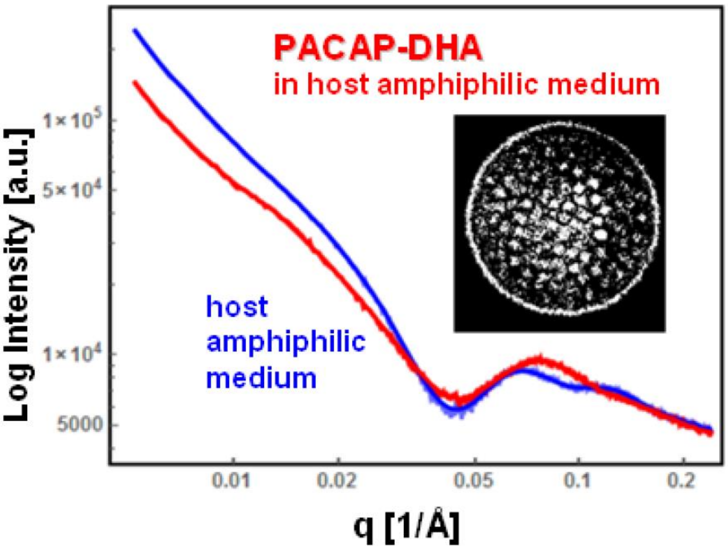

Figure: Synchrotron SAXS patterns of the lipidated peptide PACAP-DHA co-assembled in PACAP-DHA/vitamin E/VPGS-PEG1000 amphiphilic mixtures. Inset: Topology of the self-assembled core-shell structures deduced from a processed cryo-TEM image.

**Keywords**
high pressure, barotropic phase transition, low-density lipoprotein

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## Acknowledgments

The performed research was funded by the projects “Advanced research using high-intensity laser produced photons and particles” (CZ.02.1.01/0.0/0.0/16_019/0000789) and “Structural Dynamics of Biomolecular Systems” (ELIBIO) (CZ.02.1.01/0.0/0.0/15_003/0000447) from the European Regional Development Fund. B.A. obtained a financial support from the collaborative project with JINR, Dubna (3+3 program, No. 204, item 27 from 25.03.2020). AA acknowledges a membership in CNRS GDR2088 BIOMIM network.

POSTER

# 405 - GYPSUM AND SELENITE DEHYDRATION PROCESS INVESTIGATED BY THE SAXS TECHNIQUE

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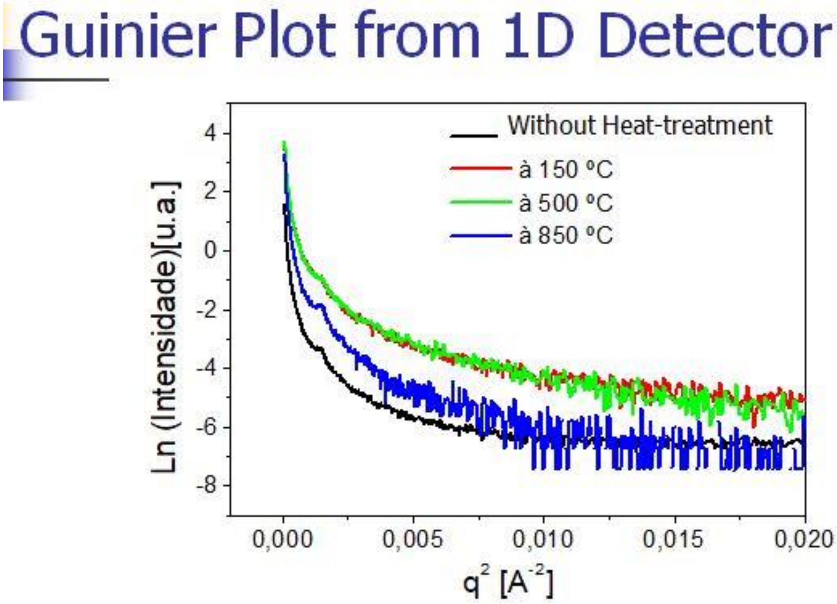
Gypsum ($CaSO_4.2H_2O$) is the main mineral in the rock found in nature, after mining, it is ground, heated up to 180oC to dehydrate into bassanite ($CaSO_4.0.5H_2O$) to be used as building material, in dentistry, orthopedics, and so on. Brazil has large reserves of natural gypsum and more than 90% of domestic production of bassanite for commercial use is made in the Northeast region, more specifically in Pernambuco State. The understanding of dehydration process of gypsum into bassanite it is a high industrial interest. So far, gypsum dehydration process has been largely investigated by the thermodynamic point of view at atmospheric and high pressures, crystal growth.

So, aiming to understand the dehydration process of gypsum into bassanite under heating at atmospheric pressure, gypsum and single crystal gypsum known as selenite were investigated by the SAXS techniques at synchrotron laboratories of Brazil and in Germany using heating furnace up to 1000o C. SAXS measurements in transmission mode were conducted at SAXS beam lines at LNLS – Laboratorio Nacional de Luz Sincrotron, Campinas, Brazil and also DESY - Deutches Elektronen-Synchrotron, Hamburg, Germany. Furthermore, the characterization of gypsum and selenite were also investigated by the thermal analysis TG/DTA, infrared spectroscopy, chemical analysis by the X-ray fluorescence, crystalline phase by the X-ray diffraction to support the SAXS data.

As a result, a strong X-ray scattering at small angle could be observed up to 180o C at LNLS using linear detector and 2D detector at DESY. The SAXS data analysis was conducted by the Guinier plot and 10 Å channel-like formation was attributed in the gypsum and selenite dehydration into bassanite.



**Keywords**
Gypsum, selenite, Dehydration, SAXS

POSTER

# 195 - STRUCTURAL INVESTIGATIONS OF HAIR FIBERS USING SMALL ANGLE X- RAY SCATTERING.

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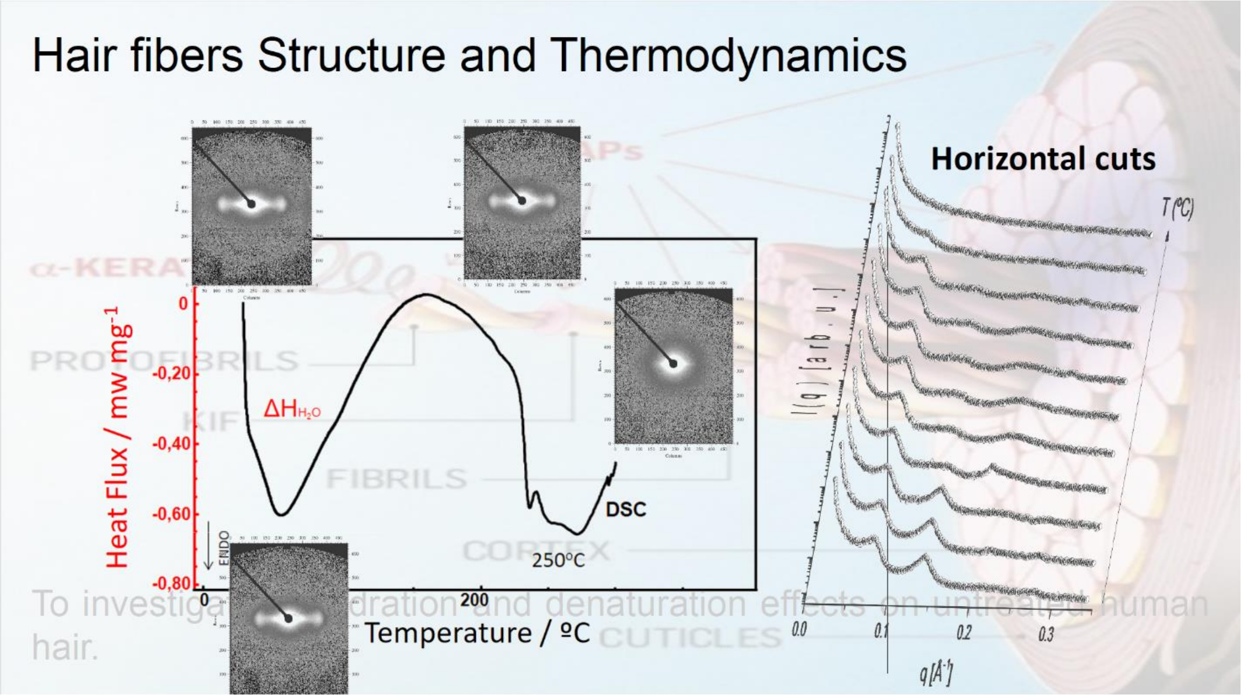
Human hair has two major morphological regions well distinct: the cuticle and cortex. Between the cells of the cuticle and cortex, cell membrane complexes (CMCs) are present, consisting of lipid layers and bilayers. The main function of the cuticle, the outer structure, is to provide mechanical protection for the cortex, which contains a helical fraction comprising a crystalline phase (intermediate filaments - IFs) embedded in amorphous matrix filaments that is sensible to water, largely influenced by the relative humidity. High temperatures can induce changes in the hair structure and it is possible to relate [the use of small angle x-ray scattering (SAXS) measurements to evaluate the changes in the IFs in the cortex, lipid molecules in the CMC and damages caused to the hair. In this context, we initiate a study in order to investigate dehydration and denaturation effects on untreated human hair by heating. In situ SAXS measurements (from 30 Celsius to 300 Celsius) were performed and compared to differential scanning calorimetry (DSC) data. As will be shown, important features seen in the DSC scans could be related to changes in the SAXS patterns, allowing the correlation between the enthalpy variation and structural temperature induced changes.



**Keywords**
human hair, SAXS, structure

POSTER

# 341 - APPLICATION OF ANGULAR CROSS CORRELATION TO EVALUATE AND COMPARE LOCAL STRUCTURE SYMMETRY IN GLOBALLY DISORDERED SYSTEM

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Self-assembly of strongly interacting nanoparticles is a very complex phenomenon to artificially fabricate and control. For instance, porous-yet-interconnected structure, like a checkerboard pattern of self-assembled nanoparticles is yet to be achieved. In an attempt to create such structures guided by computational prediction, we observed that the sample doesn't show a uniform checkerboard pattern all over the real space, but usually it is the prevalent one among many local structure formations hosting different local symmetries. To characterize the strength of checkerboard pattern emergence - we turned to analyzing the scanning electron microscopy(SEM) images using angular cross correlation of the two dimensional fourier transform taken on the SEM images.

This method had been first utilized on coherent small angle x-ray scattering outcomes by Wochner et al [1] and discussed in great detail by Altareli et al [2] where they study spatial distribution of identical structures. Here we will show that the power of angular cross correlation analysis can be extended towards analyzing spatial distribution of non-identical local structures up to a bound of finitely many scatterers. Thus, this method becomes a useful tool to compare the strength of a certain local symmetry in different SEM images.

Understanding the dynamics of a self-assembling process is an important step towards control and understanding of the process. We will end our discussion with an outlook where the angular cross correlation analysis can be applied to monitoring the kinetics of the nanocubes while the dynamics is studied via X-ray Photon Correlation Spectroscopy.

**Keywords**
Self-assembling nanocubes, Coherent Small Angle Scattering, Local order in disorder

**References**

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POSTER

# 199 - HIGH-THROUGHPUT SYNTHESIS AND CHARACTERIZATION OF LEAD-FREE CESIUM BISMUTH BROMIDE PEROVSKITE NANOPARTICLES

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Halide perovskite emerged in the last decade as important material for solar energy harvesting and light-emitting devices. However, most of them are based on lead, a toxic element. A scientific effort is ongoing toward lead-free perovskites, with reduced toxicity keeping the same or similar optical properties. The Materials Acceleration Platforms (MAPs) are an initiative to accelerate the discovery and optimization of new materials. It consists of robotic systems that can perform high-throughput experimentation, allowing a large number of syntheses and characterization to be made in a short amount of time. However, currently, MAPs present significant challenges, such as designs suitable only for specific reactions and a high initial cost of implementation. Our approach to addressing this challenge involves the combination of the robotic systems with sonochemical synthesis can achieve high-throughput experimentation with a fraction of the typical cost. We use a liquid handling robot, OT-2 from Opentrons, and a custom-built motion platform with an ultrasonication tool, called "sonication station". We used the sonication platform to perform the sonochemical synthesis of our lead-free cesium bismuth bromide (Cs3Bi2Br9) perovskites. The syntheses were carried out under different chemical reaction media to evaluate which routes could lead to the formation of the desired perovskite without impurities. The modifications to the chemical reaction media included the use of different ligands (oleylamine, oleic acid, mercaptopropionic acid, and citric acid), solvents (hexanol, dimethyl-sulfoxide (DMSO), m-xylene, and n-decane), precursor ratios (3:2 and 2.7:3.3), and dopants (Cu+ and Fe3+). All the procedures were performed in an environment atmosphere at room temperature. The samples were characterized by UV-Vis and PL spectroscopy to determine their optical properties, SAXS for size measurements, and WAXS and XRD for crystalline phase determination. WAXS of the sample solutions and XRD of the powder after precipitation were compared to identify the differences in the crystalline structure after precipitation of the material. Additionally, WAXS is found to be a promising technique for crystalline structure determination in a high-throughput fashion, due to reduced sample preparation in comparison with traditional powder XRD.

**Keywords**
Nanomaterials, perovskites, synthesis, SAXS, WAXS

POSTER

# 433 - SAXS EXPERIMENTS ON BRADYKININ/DNA COMPLEXES

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Bradykinin (BK) is a peptide-hormone involved in the kinin-kallikrein system, and widely used in the pharmaceutical industry as an active ingredient for antihypertensive drugs. However, no studies are reported on nanostructured BK materials. An important BK analog is des-Arg(9)-BK (DBK), in that the arginin at position 9 is deleted. This analog has a different mechanism of action, being an agonist of the B1 receptor. The objective of this work was to investigate the supramolecular organization of nanostructures based on BK and DBK, and study the interaction of these physiologically-relevant peptides with DNA. To determine the nanoscopic structure, we used small-angle X-ray scattering combined with transmission electron and atomic force microscopy. To assess the critical aggregation concentrations, we used steady-state fluorimetry and the secondary structure was analyzed through circular dichroism experiments. Confocal microscopy was used to analyze if BK and/or DBK could be characterized as cell-penetrating peptide. We have found that BK forms globular aggregates. In the case of BK/DNA complexes, the nucleic acid strand behaves as a template for BK strands wherein BK preferentially binds to the major grooves and forms nanoscopic fibrils. Interestingly, the deletion of one arginine residue on the DBK sequence inhibits supramolecular assembly, and spectroscopy data indicate that DBK intercalates between nucleotide bases. Moreover, BK could be characterized as a cell-penetrating peptide, as it was able to take the DNA to the cytosol region of HEK293T cells. Importantly, BK/DNA fibrils were found to modulate calcium influx in HuVEC cells, thus preserving the bioactivity of the native peptide. In conclusion, small-angle scattering allowed to fully characterize nanostructured matrices based on BK and to establish structure-activity relationships on these superstructures endowed with biomedical potential.

**Keywords**

nanostructure, DNA-peptide complexes, peptide-hormone

**Acknowledgements:**

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POSTER

# 384 - SOL-GEL PU-SILICA HYBRID COATING: A SAXS ANALYSIS OF EACH SYNTHESIS STEP

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To understand how the nanostructure of the organic-inorganic hybrid based on PU-silica coating, affects the physical barrier efficiency against oxidative agents, each step of synthesis , from the PU pre-polymer formation to its final stage at the thermal curing process, were analyzed by SAXS. The PU pre-polymer is formed from 4,4'-MDI, a diisocyanate with two aromatic rings, and glycerol, a triol that promoted a cross-linked structure for the PU. For the PU functionalization, APTES ((3-aminopropyl)triethoxysilane) was used providing a connection between the organic polymer and the inorganic nanoparticles formed from the hydrolysis and condensation of TEOS (tetraethyl orthosilicate). The SAXS curves for the PU pre-polymer without thermal curing present a maximum around q = 0.6 nm-1, that disappear after the curing. These maximum are attributed to a micro phase separation process caused by aggregation of the polymer's hard segment (HS).1; 2; 3 With the thermal cure, the polymeric chains show a more homogenous distribution, indicated by the maximum disappearance.1 The HS correlation length goes from 2.5 nm to 1.2 nm after the curing process. After APTES functionalization the SAXS log-log graphic presents a second maximum at 3.3 nm-1 (sample without thermal curing) that corresponds to the correlation distance (d=1.9 nm) of the scatter particles from APTES. The functionalization caused the growth of the correlation length from 2.5 to 3.2 nm. After the hybrid thermal curing, the scattering of PU characteristic elements are not present, and for all the samples the contribution of the inorganic particles (q>1 nm-1) are noticed by the power law decay for q<0.4 nm-1, with a slope between -2.3 and -2.6. The curve fitting was made considering an hierarchical model of two levels: i) inorganic particles, describe by Guinier;4 ii) fractal aggregates of theses inorganic particles. As the cure temperature increases from 150 to 200 °C, the gyration radio (Rg) of the inorganic particles grows from 0.54 to 0.64 nm, while the dimensionality D of the mass fractal stayed invariant (D=2.5). These results allowed us to observe how each step of the synthesis of the PU-silica hybrid affects the nanostructure of the coating.

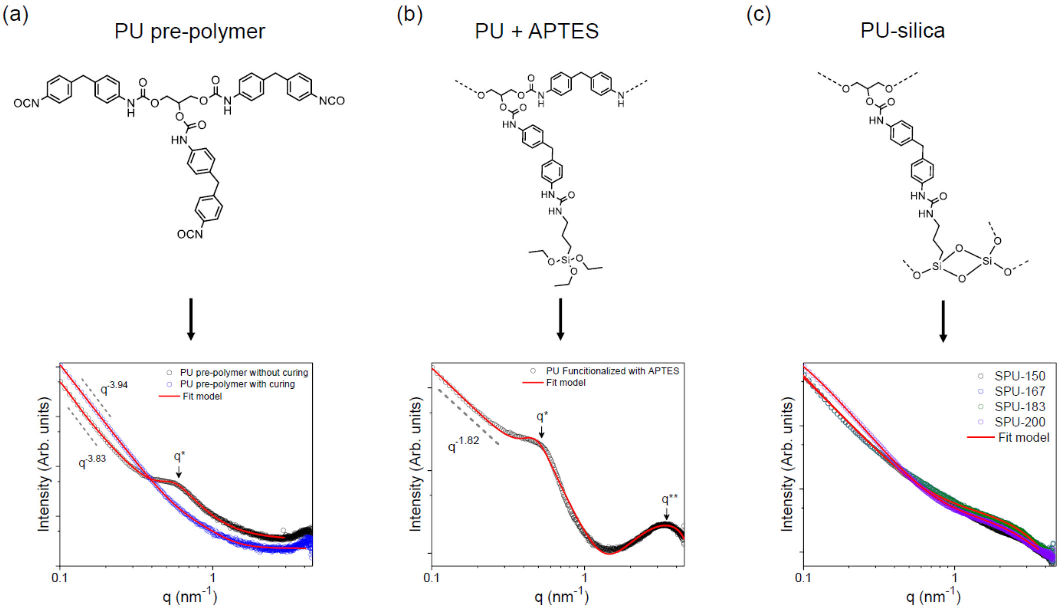

**Figure 1.** Chemical structure and respective SAXS curves for (a) PU pre-polymer, (b) functionalized PU and (c) PU-silica hybrid.

**Keywords**
PU-silica, step analysis, thermal curing, nano characterization

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POSTER

# 379 - COLLOIDAL PROPERTIES OF DISSOLVED ORGANIC MATTER EXTRACTED FROM SOILS FROM DIFFERENT VEGETATION COVER

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Dissolved organic matter (DOM) in soils, also referred to as soil DOM, is ubiquitous in the terrestrial environment. Through leaching, runoff, or flooding, the soil DOM is displaced along the soil profiles, thereby having an important influence on the biogeochemical cycle and mobility of soil organic matter (SOM). Furthermore, due to its active biogeochemical properties, soil DOM also plays a substantial role in the carbon cycle (i.e., CO2 and CH4). Nonetheless, we have knowledge of components of DOM since from sub-nm molecules to colloidal aggregates of several hundred nm. So, the study of the colloidal fraction of DOM is important in this context inasmuch as it contributes to the stability of its constituents and of the fractions of greater diameters of the SOM (Figure 1) with respect to microbial degradability. Therefore, this study focuses on the colloidal properties of DOM extracted from soils from different areas of different vegetation cover. The DOM samples were collected at two depths (0-5 cm and 50-60 cm) and obtained by common water extraction procedures, however, their chemical characterization is in progress, so our investigation will have as an experimental approach to the association of chemical analysis with light scattering and X-ray techniques. Our focus on the colloidal structure and DOM size of the soil aims to link its properties to SOM stabilization. This small-angle X-ray scattering approach holds promise for generating new insight into DOM structure, and the interaction between OC and minerals in natural environments.

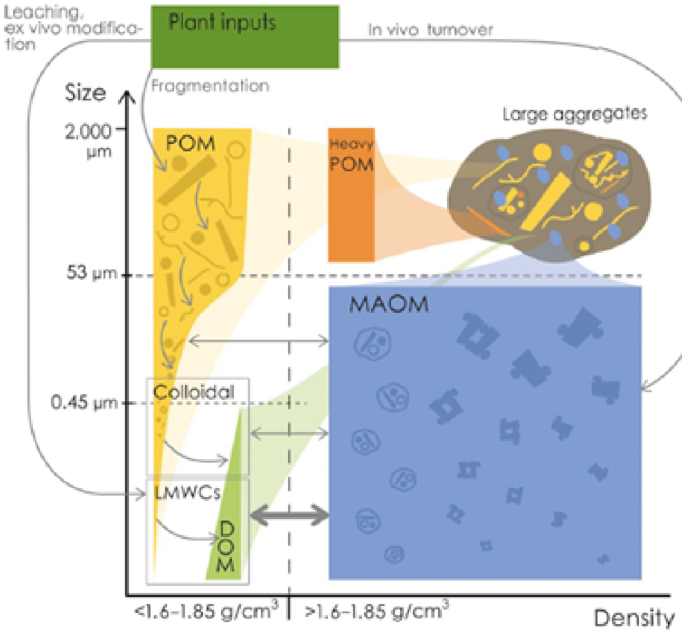

**Figure 1** - Conceptual representation of major soil organic matter (SOM). These SOM componentes are physically defined based on size and density, shown on the y and x axes, respectively. The upper size limit specification for MAOM varies by region, from 20 to 63 µm; we show 53 µm here for simplicity. Dissolved organic matter (DOM) is generally defined as <0.45 µm and water-extractable. Mineral-associated organic matter (MAOM) has multiple forms, including small particulate organic matter (POM)-like structures encapsulated by minerals, organo-mineral clusters, and primary organo-mineral complexes. Arrows leading from plant inputs to different componentes represent hypothesized SOM formation pathways (Lavallee et al. 2019).

**Keywords**
Chemical characterization; Carbon cycling;organic matter fractions

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Meklesh V., Gentile L., Andersson E., Bhattacharya A., de Farias MA., Cardoso MB., Stålbrand H., Loh W., Škerlep M., Kritzberg E., Tunlid A., Olsson U and Persson P (Characterization of the colloidal properties of dissolved organic matter from forest soils. Front. Soil Sci. 2:832706. 2022). https://doi.org/10.3389/fsoil.2022.832706

POSTER

# 333 - STRUCTURAL CHARACTERIZATION OF ORGANIC BIOGENIC AEROSOLS: A SMALL-ANGLE X-RAY SCATTERING APPROACH

**BRUNELLI, Thais Costa (1); MARQUES, João Basso (1); VICENTIN, Flavio Cesar (2); RAMOS, Lucas Cardoso (1); DA SILVA, Amanda Crystina Araujo (1); DE OLIVEIRA, Nicolas Neves (1)**
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The study of particles suspended in the air was established with the experimental work of John Aitken, who collected samples of dust in the atmosphere along with meteorological phenomena, dating them and evaluating the impact not only on climate but on human health in the years 1891, 1892 and 1893. Currently, suspended particles are called atmospheric aerosols which, depending on their diameter, are characterized by four modes: nucleation mode ($d<10$ nm), aitken mode (10 nm $< d<100$ nm), accumulation mode (100 nm $< d <1$ µm) and coarse mode (1 µm $<d<10$ µm) [1] . The dynamics of the terrestrial radiative energy balance is directly affected by atmospheric aerosols by the processes of scattering and absorption of solar and terrestrial radiation, as well as indirectly by being effective agents in the formation of clouds and acting in the hydrological cycle as precipitation. The abundance of gases in Earth's atmosphere can be modified by aerosols through heterogeneous chemical reactions and other multiphase processes [1]. Forest ecosystems emit volatile organic compounds (VOC) that react with atmospheric gases, to quickly form secondary organic aerosols (SOA) such as monoterpenes (C10Hx) reacting with nitrogen oxides (NOx) and ozone (O3) [2]. Several researches developed in Amazon advances in the clarification of the dynamics of formation of secondary organic aerosols and cloud condensation cores in untouched forest, such as the Large-Scale Experiment on the Biosphere and Atmosphere of the Amazon – LBA. Great advances have been done to deeply understand the role of these particles in the atmosphere and climate. New questions are being established to be clarified, being increasingly necessary techniques of great precision and resolution, due to the low concentration of aerosols (~300 particles cm-3). Therefore, characterization of representative aerosols for particle collections in short times (1 h or less), where we have ultra-low concentrations, remains a challenging analytical objective, just as the use of small angle X-ray scattering (SAXS) at ambient temperature and pressure in low volume aerosol samples with short collection time. The low volume fraction of the nanoparticles matches with the lower detection limit of the synchrotron-based SAXS (107 centimeter-3). This provides to obtain the average sizes of the newly formed SOA with the SAXS analysis using the two-level unified Beaucage adjustment, the right-of-power regime and the Guinier region [3]. Structural parameters of fractal-mass aggregates, as well as primary particles, are obtained from SAXS data, revealing the mechanisms of SOA formation.

**Keywords**
SAXS, Atmospheric Sciences, Secondary Organic Aerosols

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## Acknowledgements

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POSTER

## 387 - LIQUID SAMPLE CHANGER FOR SAPUCAIA BEAMLINE

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The SAPUCAIA beamline will be dedicated to SAXS technique in SIRIUS. Besides completely new experiments, it will also inherit the SAXS community from UVX, the old Brazilian synchrotron source, where two thirds carried their studies in liquid samples. To attend these users, a versatile sample holder for liquids (SHL) is been developed. This holder will allow to program the measurements of dozens of samples with fast temperature control – from -20 °C up to 120 °C. Also, it will allow the control of the sample injection through meniscus visualization, automatic cleaning and UV-Vis spectroscopy measurements. SHL would not only keep the good features from the SAXS-UVX old sample holders but also will improve substantially the possibilities opened by the new beamline. It will consist in a capillary enclosed by a heater/cooler device placed in vacuum. It will have a reasonable wide exit angle ($2\theta$ close to 30°), allowing simultaneous SAXS/WAXS techniques, what was not possible in the previous sample holders from UVX, and will be monitored by an optical camera which will give information such as the position of the meniscus and the capillary cleanse. This information is essential since the experiments will be held with the liquid moving along the capillary during data acquisition to avoid beam damage. The capillary temperature is going to be measured using an IR thermal 2D camera, giving precise information of the temperature in the location of the beam. The designed sample-holder hosts the capillary-holder, which is based on the versions made for UVX-SAXS beamlines. The idea is to easily change the capillary holder if the capillary breaks or became dirty but keeping all other facilities untouched. Upstream and downstream of the holder vacuum pipes will be attached. The UV-Vis spectrophotometer will face the capillary just a few millimeters above the place where the X-ray beam touches it, permitting the measurement of the liquid just before being irradiated with X-rays. The temperature is controlled by two cartridge resistances and is refrigerated with cold silicon oil, which makes the temperature to change faster when compared to other thermal-bath based sample holders.

**Keywords**
SAPUCAIA SIRIUS Holder Sample Liquid

POSTER

## 290 - SIMULATION OF LIQUID JET EXPLOSIONS AND SHOCK WAVES INDUCED BY X-RAY FREE-ELECTRON LASERS

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X-ray free-electron lasers (XFELs) produce X-ray pulses with very high brilliance and short pulse duration. These properties enable structural investigations biomolecular nanocrystals, and they allow resolving the dynamics of biomolecules down to the femtosecond timescale. To deliver the samples rapidly into the XFEL beam, liquid jets are used. The impact of the X-ray pulse leads to vaporization and explosion of the liquid jet, while the expanding gas triggers the formation of shock wave trains traveling along the jet, which may affect biomolecular samples before they have been probed. Here, we used atomistic molecular dynamics simulations to reveal the structural dynamics of shock waves after an X-ray impact. Analysis of the density in the jet revealed shock waves that form close to the explosion center and travel along the jet. A trailing shock wave formed after the first shock wave, similar to the shock wave trains in experiments. Although using purely classical models in the simulations, the resulting explosion geometry and shock wave dynamics closely resemble experimental findings, and they highlight the importance of atomistic details for modeling shock wave attenuation.

**Keywords**
X-ray free-electron lasers, shock waves, MD simulations

POSTER

# 435 - AI-ASSISTED IMAGE RECOGNITION FOR SYNCHROTRON M-BEAM SAXS ON SINGLE POLYMER FIBER

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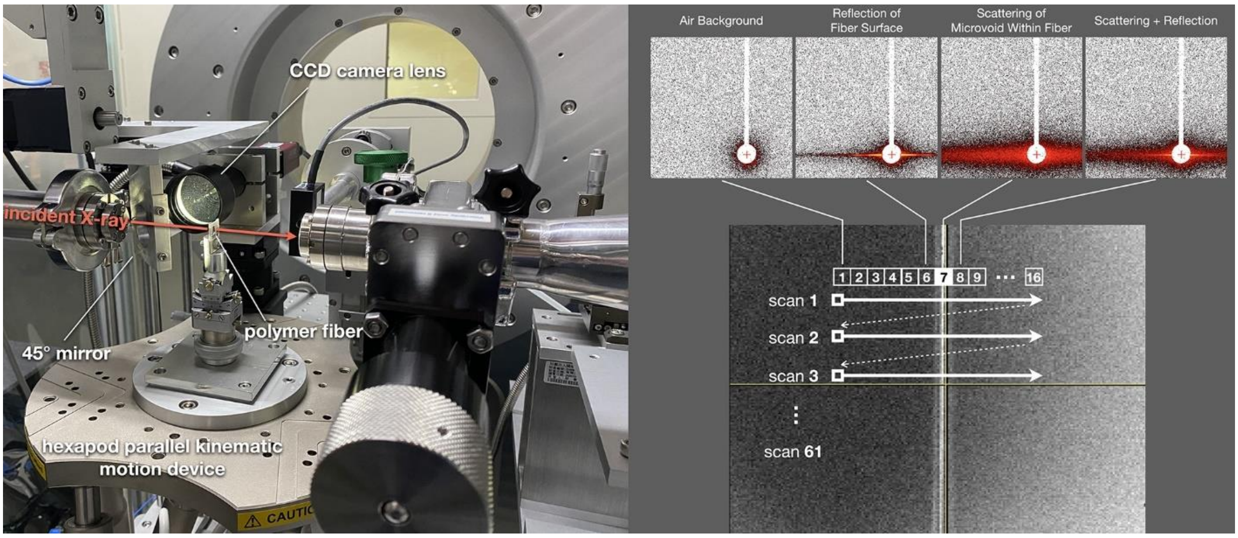
The formation of microvoids in the spinning process of fibril manufacture dramatically affects the mechanical properties of high-performance industrial fibers. While the synchrotron μ-beam SAXS is arguably the best method for evaluating the dimension and orientation of the microvoids in a single fiber, the radiation damage from the intensive focusing X-ray beam destroys the intrinsic microstructure of the fiber, which is almost unavoidable. Therefore, the best way to prevent the radiation damage and enhance the signal-to-noise ratio is to reduce the exposure time as short as possible and use a 2D grid scan to collect the scattering patterns at different positions of the fiber. Then the AI-assisted image recognition with the convolutional neural network (CNN) is applied to the SAXS datasets. With this procedure, the air background, the scattering of the microvoid within the fiber, the reflection of the fiber surface, or the mix-up results can be distinguished correctly and efficiently. Thus, the high-quality SAXS patterns of the microvoid within the fiber are obtained by combining the scattering patterns from different sub-dataset. The concepts are developed with the present case and would also be carried over to varied materials studies based on μ-beam SAXS/WAXS. More importantly, in addition to taking advantage of the small beam size for the structure mapping, the AI-assisted μ-beam SAXS/WAXS techniques are helpful to decouple or couple the global and local structure features in materials according to the demands of different research.



**Keywords**
μ-Beam, SAXS, AI techniques

POSTER

# 329 - STRUCTURE-PERFORMANCE RELATIONSHIP OF ECO-FRIENDLY ORGANIC/INORGANIC HYBRID ELECTRODES IN ALL-SOLID-STATE FLEXIBLE SUPERCAPACITORS

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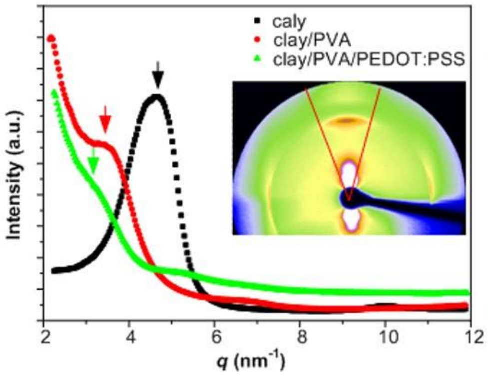
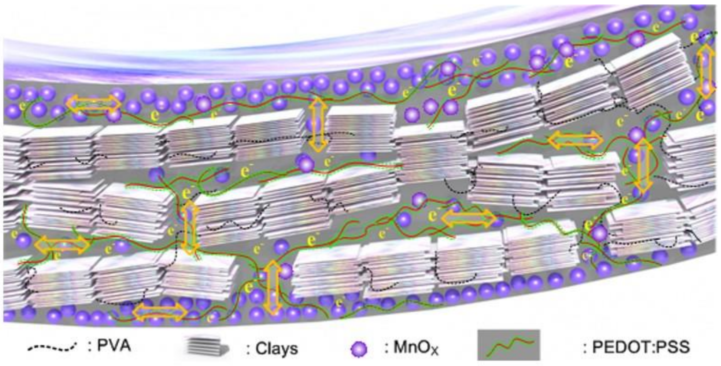
Life cycle thinking has been proposed that is to reduce the impact of excessive industrial development on the environment and society through reducing the resource of product materials and carbon emissions of manufacturing process. In this work, an organic/inorganic hybrid is developed and fabricated as a safe and ECO-friendly electrode for the all-solid-state flexible supercapacitor. We propose a nanoclay-inclusion approach to synthesize nanoparticles (NPs) as active materials in the polymer/clay nanocomposite electrode. In addition to avoid the NPs agglomeration, the inclusion of the NPs into the nanoclay nanocomposite not only avoids the NPs agglomeration, but also results in two nanosheet-stacked morphologies of nacre-like and house-of-cards nanostructures. Influence of the inclusion on the morphologies, mechanical properties and electrochemical performance has been reveled using synchrotron based X-ray characterization (scattering, diffraction and absorption), testing machine and cyclic voltammetry measurement. The evaluation of the possibility of the nanocomposite electrodes recycling and reuse is also one of the focuses of this work which will be of great help to sustainable development.





**Keywords**
Flexible supercapacitors; Biomimetics; Self-organization; Hierarchical structure; Shapeable electrode; High energy density

POSTER

## 280 - SANS INSTRUMENTATION ON ITS WAY TO CROSS THE ATLANTIC OCEAN

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After the shut-down of the Berlin Experimental Reactor (BER II) the neutron beam laboratory at the Atomic Energy Commission of the Argentine Republic (CNEA), and the Penn State-Radiation Science and Engineering Center expressed their interest in the small-angle scattering instruments V4 and V16, as well as in other equipment and instrumentation. Within HZB's program for transferring neutron scattering equipment to science centers all over the world we concluded contracts. We describe the processes and the status of the transfer project for the two versatile small-angle scattering instruments which is an enormously important activity for keeping the valuable BER II experimental facilities available to the international user community at emerging neutron scattering centers in the Americas. Especially, the construction of a new experimental hall, a newly installed cold source and guide system for the V16 instrument to build up a new PSU-SANS instrument serving the university communities as well as external users as a first neutron scattering instrument at this constantly modernized source displays the efforts even at a smaller source to benefit from the unique possibilities of neutron research. On the other hand, the renowned V4 with its numerous capabilities in standard and polarized SANS will guarantee for a working horse instrumental basis at the large scale Argentine neutron beam laboratory RA-10 reactor at Buenos Aires which is urgently needed for the wide area of research using SANS in South America.

**Keywords**

SANS instrument, time-of-flight

POSTER

## 212 - SAXS/WAXS TOMOGRAPHY AT SAXSMAT BEAMLINE P62 AT PETRA III

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For many scientific questions gaining three-dimensional insight, coupled with the ability to probe structures across multiple length scales of a specimen can provide precious information. This is the case, for example, of the multifunctionality of materials, dictated by their (sub-) microstructural architecture1. The SAXSMAT beamline provides dedicated instrumentation for the spatially-resolved mapping of the orientation and degree of organization of hierarchical nanostructures and, then deciphering the intricate interplay of mechanisms acting at different scales — from the atomic to the macroscopic, which is crucial for the development of new functionalities and new materials, since multifunctionality is a matter of design strategy.

The dedicated SAXS/WAXS-CT approach at the SAXSMAT beamline is composed basically of a sample environment, two detectors and a pipeline for data acquisition, treatment, and online reconstruction based on either SAXS/WAXS Tensor Tomography2 or SAXS/WAXS Invariant Tomography3 techniques. The sample environment (in air, helium, or vacuum) consists of a stack of high-resolution nano-positioners allowing translation horizontally and vertically as well as a rotary stage on top where the sample is positioned and aligned using a laser that mimics the X-ray beam and a microscopy. An additional high-load rotary stage is used to tilt the rotation axis, as required for the tensor tomography technique. Moreover, a pico-scale feedback system for online correction of potential misalignment of the sample during the measurement is also utilized. The two large-area single-photon counting detectors (“Eiger2 X 9M” and “Eiger2 X 4M-DESY”) record the scattered photons at small and wide-angle, respectively. The acquired SAXS/WAXS images are submitted to an in-house workflow accelerated by a cluster of graphics processing units (GPUs) for the data processing and tomographic reconstruction.

Finally, we here present the initial results obtained with the dedicated instrument for high-resolution 6D scanning X-ray elastic scattering at wide (WAXS) and small-angle (SAXS) microscopy available at the SAXSMAT beamline at the PETRA III storage ring.

**Keywords**
SAXS, WAXS, Tensor Tomography, beamline

POSTER

# 235 - IN SITU STUDY BY GISAXS OF THE GROWTH OF NISI2 NANOPLATES IN SI(001) WAFER

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Composite thin films formed by NiSi2 silicide nanocrystals embedded in single-crystalline Si have attracted a renewed interest due to their potential applications in electronic devices and thermoelectricity [1,2]. The formation of highly oriented NiSi2 nanoplates embedded in a Si(001) wafer – on which a Ni-doped thin film was previously deposited – was studied in situ by GISAXS during isothermal annealing at 405 °C. This thermal treatment leads Ni atoms initially dispersed in the thin film to diffuse into the Si wafer, thus reacting with Si atoms and forming well-separated NiSi2 nanoplates with a shape of nearly regular hexagons. During their growth, the hexagonal nanoplates remain with their larger surfaces parallel to the lattice planes of the Si{111} crystallographic form. From the analysis of the GISAXS intensity patterns, we determined the average value of the largest diameter of the hexagonal surface, thickness, number and total volume of the nanoplates as a function of the treatment time [3]. The results showed the nanoplates reach their final size after 10 minutes of annealing while the number of nanoplates increases until 50 minutes. This behavior indicates the final size of the nanoplates is not limited by the concentration of Ni atoms in the thin film. The dependence of the total volume of the NiSi2 nanoplates as a function of time, V(t), was compared to the function predicted by the Jhonson-Mehl-Avrami theory. The parameters determined from the best fit of this function to the experimental V(t) function are consistent with the growth of planar nanoparticles formed by a heterogeneous nucleation process.

**Keywords**
GISAXS, NiSi2 nanoplates, In situ measurements

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POSTER

# 132 - INVESTIGATION OF HYDRIDE PHASE OF TI-V-CR ALLOY BY USING IN-SITU NEUTRON DIFFRACTION

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Hydrogen has attracted a permanent interest as a future energy carrier because of its high ignition power and pollution free nature. Among various materials body centered cubic (BCC) solid solutions and alloys are found very promising hydrogen storage materials. In general, first hydrogenation of body centered cubic (bcc) alloys is difficult, needed a lengthy heat treatment to make the activation easier and quicker. It has been reported that addition of 7Zr+10Ni to Ti-V-Cr bcc alloys enable first hydrogenation at room temperature and low hydrogen pressure without prior heat treatment. In the present case, hydrogenation and crystal structure characteristics of Ti50V20Cr30 added with 7Zr+10Ni have been studied. It was found that first hydrogenation of as-cast alloy at room temperature and under 20 bars of hydrogen was quick and reached a capacity of 3.6 wt.% of hydrogen in 15 minutes. Before hydrogenation, alloy had shown pure body centered cubic (bcc) phase and after hydrogenation bcc phase transformed into single face centered cubic (fcc) phase. Pressure composition isotherm (PCI) showed that this alloy desorbed 1.5 wt% of hydrogen at 150 °C. In order to locate the hydrogen in the crystal structure neutron measurements had also been done. As this alloy is effectively a null matrix for neutron diffraction the hydride phase was easy to detect. For these measurements, temperature was raised from 120 C to 266 C. Neutron patterns revealed that hydride phase started to desorb very quickly at 200 C. It was found that the fcc dihydride phase directly desorbs to a bcc alloy without going through a bct monohydride phase. This was confirmed by X-ray diffraction pattern of the partially hydride sample.

**Keywords**
XRD, Neutron diffraction, Hydrogen Storage, BCC alloy

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POSTER

# 337 - ANISOTROPIC ULTRASMALL-ANGLE X-RAY SCATTERING (USAXS) TO QUANTIFY HIERARCHICAL POROSITY IN LI4TI5O12 FREEZE CAST MICROSTRUCTURES

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Effectively pin-hole collimated USAXS was used to study lithium titanate (Li4Ti5O12) freeze-cast microstructures. Freeze-casting delivers anisotropic and hierarchical porosity with pore sizes ranging from 5nm to 20µm. There are few techniques which permits quantitative microstructural analysis from thousands of pores. USAXS curves covering the scattering vector q from 0.0001A-1 to 0.02A-1 were collected at several sample orientations (ranging from -10o to 190o). The use of 2D collimated Bonse-Hart geometry permits measurement at lower q values (larger feature sizes) than is achievable by pinhole SAXS cameras, however only in one direction of q at one time. The instrument used is located at the Advanced Photon Source, Sector 9-ID.1 In order to gauge relative anisotropy, samples were rotated within the beam to provide I vs. azimuthal angle polar graphs at q values of 0.0003A-1, 0.0006A-1, 0.001A-1, and 0.005A-1. Six Li4Ti5O12 samples were measured. The samples salt additives, gel additive (to change viscosity during freeze casting), and lithium titanate particle size were varied. It was found that samples are strongly anisotropic at low q (aspect ratio of 0.3 to 0.4) which maps intercolumnar porosity and mildly anisotropic at high q (aspect ratio of 0.8) which tracks interparticle pores. Samples cast with gels contained smaller domains (300µm) which were anisotropic. This had the effect of averaging the anisotropy so that the aspect ratio ranged from 0.6 (for large pores) to 0.8 (for small ones). Early modeling of data suggests the overall pore microstructure is comprised of one large anisotropic pore population 0.9µm (volume fraction 0.8; surface area of 2.9815m2/cm3) and two small, relatively isotropic pore populations which are 48nm (volume fraction 0.02; surface area 1.1040m2/cm3) and 15nm (volume fraction 0.16; surface area 38.3117m2/cm3).

**Keywords**
USAXS, Lithium Ion Batteries, Porosimetry

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POSTER

# 257 - SHAPESPYER - A NOVEL WORKFLOW FOR SOFT MATTER MOLECULAR DYNAMICS AND SMALL-ANGLE SCATTERING

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The uptake of molecular dynamics (MD) as an analytical tool for the analysis and interpretation of small-angle scattering (SAS) data has been limited in the field of soft matter, especially when compared with current analysis methods in biological scattering. A key limiting factor is that the generation of the simulation start point - often referred to as the initial trajectory - is highly complex, often presenting a high activation barrier to most small-angle scattering groups.

Here we will describe Shapespyer, a state-of-the-art Python toolkit supported by a set of batch (Bash) scripts implementing semi-automated, high-throughput parallel workflows for preparation and subsequent equilibration of complex multicomponent molecular structures to seed computational studies of condensed soft matter systems. The workflow is capable of generating start structures with a wide variety of geometries, including worm like micelles and complexes with crystallographic lattices, which can then be used in appropriate molecular dynamics packages such as Gromacs. We will illustrate this with particular examples from the project partners, including our study of surfactant morphology as a function of concentration and ionic strength. We will further compare the output from Shapespyer with alternative approaches such as coarse graining, and give our perspective on the best approaches users can adopt in the technical configuration of their simulations, such as the effect of box size, and how the workflow can be used in both planning and analysis of experimental data.

**Keywords**
coarse-grain, MD, surfactants, workflows

POSTER

## 201 - LABORATORY RHEOSAXS STUDIES OF NON-IONIC SURFACTANTS

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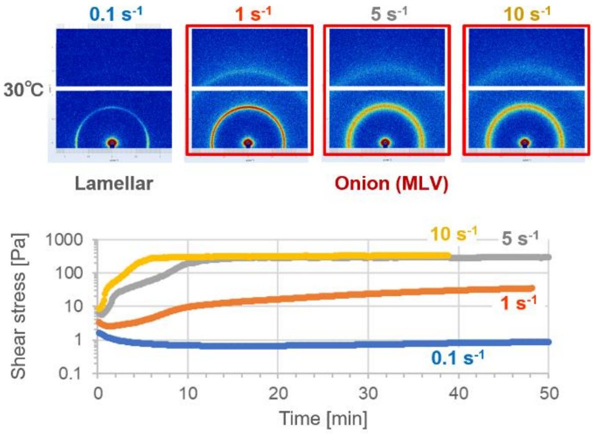
Non-ionic surfactants are widely used in the form of cleaning agents, detergents, wetting agents, emulsifiers and solubilizers in cosmetics, to name just a few. Here, we demonstrate the results of a combined rheological and X-ray scattering (RheoSAXS) study of a non-ionic ethoxylate surfactant in water system. The experiments where done using the unique RheoSAXS module for SAXSpoint 5.0 by Anton Paar. The RheoSAXS module is based on the DSR 502 rheometer head, which is fully integrated into the SAXSpoint sample chamber. This setup allows for full rheological measurements during a small-angle experiment. Combined RheoSAXS studies of surfactant systems such as non-ionic surfactants reveal material properties that are not accessible with other techniques or simple shear-cell add-ons.

Using this setup, we were able to characterize not only the macroscopic properties such as the sample's flow behavior but also simultaneously changes to the nanostructure of the non-ionic surfactant polyoxyethylene alkyl ether (CmEn)-water two-component system upon shearing force. These systems are known to form planar lamellae at no shear or low shear rates, however, at higher shear rates and in dependence of the temperature onion-like structures can evolve.1 For analyzing the present surfactant system the sample was measured at varying shear rates and temperatures. An in-depth evaluation of the nanostructure was done using the generalized indirect Fourier transformation (GIFT) approach.2

Summa summarum, in this study the formation of an onion-like structure of the non-ionic polyoxyethylene alkyl ether surfactant at higher shear rates was studied. Furthermore, a detailed data evaluation revealed valuable information on the structure of bilayers as well as their flexibility in dependence of the shear rate.3



**Keywords**
RheoSAXS, surfactants

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POSTER

## 247 - RNA STRUCTURAL CHARACTERIZATION BY SMALL ANGLE X-RAY SCATTERING

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Small-angle X-ray scattering (SAXS) is particularly well suited for the characterization of RNA because the contrast between RNA and buffer is high due to the electron-rich phosphate backbone in RNA. The large RNA can be difficult to crystallize, and NMR characterization is challenging due to chemical shift overlap and fast relaxation. SAXS is appropriate for RNAs from 25 to hundreds of nucleotides in size. SAXS allows studying the structure and dynamics of RNA under varying buffer conditions such as salt concentration, pH, with or without ligand as well as under changing sample environments such as temperature and pressure. SAXS data provide not only global information about the size and shape of the RNA, but also the extent of its structural variation manifested as an ensemble of conformers. SAXS data can also be used together with other biophysical methods (including crystallography, NMR, AFM and cryo-EM) by providing additional restraints that further improve and validate structural models. The SAXS Core Facility of the National Cancer Institute (NCI) opens to all intramural and extramural research communities. The mission of the SAXS Core Facility is to provide support to the user communities with expertise in experimental design, data collection, processing, analysis, and interpretation. This presentation gives a brief introduction to the NCI SAXS Core Facility and highlights recent scientific achievements in RNA structure characterization produced by the NCI SAXS Core users.

**Keywords**
RNA, SAXS

**References**

The NCI SAXS Core website: https://ccr.cancer.gov/center-for-structural-biology/saxs-core-facility

**Acknowledgments**
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POSTER

# 160 - TIME-RESOLVED SANS PROVIDES UNIQUE INSIGHT INTO SUBSTRATE PROCESSING BY THE PAN-PROTEASOME COMPLEX

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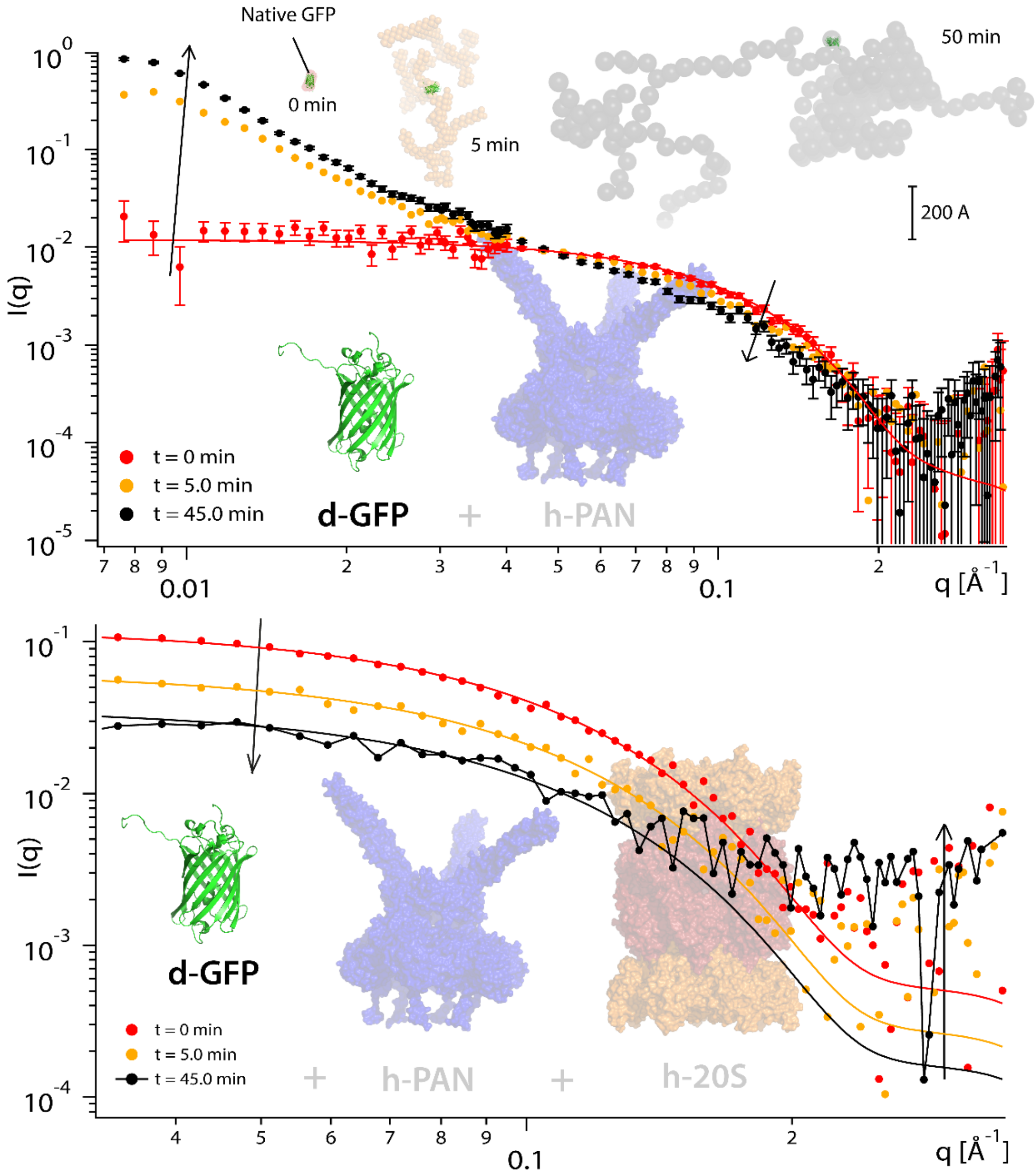
A multitude of structural biology techniques, including crystallography, NMR and cryo-EM, as well as single molecule experiments, have recently provided new and exciting mechanistic insight into protein substrate degradation by AAA+ ATPases and the proteasome. However, direct structural information on the conformational changes of the working complex and on the respective substrate state(s) and populations, during the active unfolding and degradation process in solution, remains scarce.

We use time-resolved small angle neutron scattering (TR-SANS), in combination with selective macromolecular deuteration and solvent contrast variation (H2O:D2O exchange), to obtain structural information on the respective components during the active degradation process in solution. SANS, in contrast to its sister technique SAXS (small-angle X-ray scattering), allows to distinguish between individual proteins in solution if they are differentially labeled (deuterated vs hydrogenated).

By using the PAN-proteasome complex from the hyperthermophilic archaeon Methanocaldoccus jannaschii, it is possible to temperature-active and fine-tune the unfolding and hydrolysis process at 55 °C. Combined with online fluorescence and specific deuteration, we were able to obtain separate structural information on the conformational state of PAN and on the GFPssrA substrate during the active reaction in solution [1]. We find that PAN undergoes a reversible conformational contraction during the substrate unfolding process. GFP aggregates rapidly in the presence of PAN alone but is being hydrolyzed very efficiently once the proteasome is present during the reaction [2].

Our SANS data allow to quantify the time evolution of natively folded GFP substrates and oligopeptide products at a sub-minute time resolution and to propose a working mechanism for substrate processing in solution. In particular, they suggest a tethering of the PAN-proteasome complex by the substrate in a conveyor belt-like, coupled unfolding and hydrolysis process, and the necessity of a tight regulation of the degradation process in vivo. Furthermore, we find a strong direct correlation between the time-rates of the disappearance of native GFP structures with those of ATP-hydrolysis and fluorescence decay [2].

In conclusion, TR-SANS is a very promising technique that can provide structural kinetics data on solution ensembles, complementary to results obtained by crystallography, cryo-EM, NMR and single molecule experiments [3]. AAA+ ATPases and the proteasome, as well as related biological systems, are ideally suited for these kind of studies.



**Keywords**

SANS, time-resolved, in situ spectroscopy, protein degradation

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POSTER

# 446 - DEVELOPMENT AND CHARACTERIZATION OF A THERMOSENSITIVE HYDROGEL FOR ATOPIC DERMATITIS TREATMENT: PRELIMINARY RESULTS AND FUTURE PERSPECTIVES

**GARCIA, Pamela SOTO (1,2); ASAMI, Jessica (1,3); SABINO LEOCÁDIO ANTUNES, Bianca (1,4); KOMATSU, Daniel (1); HAUSEN, Moema (1); DICKO, Cedric (2); DE REZENDE DUEK, Eliana (1,3)**

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Background: Atopic dermatitis (AD) is a skin disease which implies on recurrent eczematous lesions, intense itch, pain, discomfort, bacterial infection of the wound site, and loss of life quality. It has no cure, and the treatments are focused on symptom relief and control of infections/inflammation. However, the long-term treatments may lead to damaging side-effects. In this context, this project focus on the development and characterization of a thermosensitive hydrogel formulated with Pluronic F127 (PF127), chitosan modified with hyaluronic acid (Ch+HA) and Propolis, which would be able to deliver the medications on the affected skin to promote relief, avoid bacterial infection, and enhance the wound healing. The main benefits of the hydrogel under development are the lower cost of the product, and the patient would not experience the aggressive effects of traditional long-term treatments.

Objective: To develop and characterize a thermosensitive hydrogel formulated with PF127, Ch+HA and bee Propolis.

Material and methods: Firstly, the chitosan was modified with hyaluronic acid and characterized (FTIR, solubility test). Secondly, the bactericidal effect of propolis was evaluated. In sequence, different concentrations of PF127 were prepared and characterized with FTIR and Rheology to choose the most suitable one. With the elected PF127 concentration, it was added CH+HA and Propolis, and characterized with FTIR and Rheology (currently under data analysis). Further steps will include the characterization of the most suitable solutions applying SUrF and NUrF platforms, which consists of advanced characterization methods using synchrotron sources X-ray/Neutron small-angle scattering simultaneously with optical spectroscopies (UV-visible, fluorescence and optionally Raman), at Lund University. The last steps will be in vitro and in vivo assays.

Preliminary results: (i) chitosan modification with hyaluronic acid has increased the solubility of the Ch+HA when compared to the raw chitosan; (ii) the Propolis demonstrated effective bactericidal properties; (iii) related to the different concentrations of Pluronic analyzed, the 20 wt% presents the most suitable gelation characteristics. Rheological assay with incorporating of Ch+HA and Propolis are currently under analysis. The chosen formulations after the previous analysis will be separated to be analyzed in Lund, which will be fundamental to the progress of the material's development, impacting directly on the accurateness of the analysis, therefore granting the achievement of a high-quality final product.

Conclusion: So far, the development of the hydrogel is a promising material; further analysis with SUrF and NUrF will enable that the final product will achieve a reliable and safe-to-use formulation, without the aggressive side-effects of the long-term medications currently used and being a low-cost treatment to the patient.

**Keywords**

Biomaterials, Pluronic, Atopic Dermatitis, FTIR, Rheology, SUrF, NUrF

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POSTER

# 206 - EIGER2 CUSTOM GEOMETRIES FOR SIMULTANEOUS SAXS/WAXS MEASUREMENTS

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Simultaneous SAXS/WAXS experiments at synchrotron sources have made a significant scientific impact by enabling both static [1] and time-resolved [2] measurements with atomic to mesoscale structural resolution. However, particularly if the experimental focus is set on minimizing unwanted background scattering, such simultaneous SAXS/WAXS experiments require in-vacuum compatibility of the used X-ray detectors, increasing the demands on modern detector development.

The EIGER2, being the latest generation hybrid photon counting (HPC) X-ray detector, brings noticeable advantages for both SAXS and WAXS experiments at synchrotron sources. At its core, the EIGER2 detectors combine all advantages of previous HPC detector generations while offering (i) 75 µm × 75 µm pixel size, (ii) kilohertz frame rates, (iii) negligible dead time, and (iv) count rates of more than 107 photons per pixel. In addition, thanks to its modular design the EIGER2 enables custom geometries and solutions for simultaneous SAXS/WAXS setups, both in-air and in a vacuum.

On this poster, we provide numerous visual examples of current and future custom-made detector solutions realized for both in-air and in-vacuum SAXS beamlines around the world. We further provide experimental data from beamlines around the world, highlighting the extended capabilities of simultaneous SAXS/WAXS detector arrangements.

**Keywords**
hybrid photon-counting; X-ray detector; SAXS/WAXS; custom geometry

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POSTER

## 311 - FORMAX – A NEW BEAMLINE FOR MULTI-SCALE STRUCTURAL CHARACTERIZATION OF HIERARCHICAL MATERIALS

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ForMAX – a new beamline for multi-scale structural characterization of hierarchical materials
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ForMAX is a new beamline at the MAX IV Laboratory, combining small- and wide-angle x-ray scattering (SWAXS), scanning SWAXS imaging, and full-field microtomography for multi-scale structural characterization of hierarchical materials from nm to mm length scales, with temporal resolution to study materials processes in situ under specific environments. ForMAX is founded by industrial partners and private foundations to advance research and development of sustainable materials and specialty chemicals from forest raw materials, but the beamline will also be open for general users. Here we will describe the beamline concept, focusing on the novel combination of SWAXS and full-field tomography. ForMAX is presently in commissioning phase, with regular user operation expected to commence in early 2023.

**Keywords**
SAXS, WAXS, tomography

POSTER

## 208 - INDUSTRIAL ENZYMES AND THEIR INTERACTIONS WITH BIOSURFACTANTS STUDIED BY SAXS

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Sustainability is one of the major concerns in the modern world. For products used in everyday life, origin, degradability, and energy consumption of production are essential aspects to be consider for moving towards greener society. Laundry formulations have improved a lot due to additives like alkaline enzymes and zeolites, largely decreasing the energy consumption during the cleaning procedure. However, there is great potential for further improvement since the traditional surfactants are derived mostly from petroleum, requiring chemical modifications like sulfonation, ethoxylation, or esterification. When used, they are polluting the environment, as they are toxic and difficult to degrade. An alternative to these surfactants are biosurfactants, which are produced by microorganisms; they display promising properties, like low toxicity, excellent biodegradability, and good washing performance. Therefore, it is of great interest to study this type of surfactants and their potential in laundry formulations, with special focus on their interactions with some of the enzymes usually used. Conventional enzymes are lipases1, cellulases2, α-amylases, and proteases, and it is these that are investigated in the present project. Novozymes® has provided enzymes of each type, respectively, LIPEX®, CAREZYME®, STAINZYME®, and ALCALASE®, which are studied in the presence the most common biosurfactants, namely, rhamnolipids, sophorolipids3, and surfactin. For comparison, different fossil-based surfactants commonly used in the field, like anionic sulfonated surfactants (sodium alkyl sulfates and sodium ethoxylated alkyl sulfates) or non-ionic surfactants (ethoxylated alcohols) are also included in the study. An initial characterization of each elements (enzymes and surfactants) by Small-angle X-ray scattering (SAXS) provides valuable information on the oligomeric states of the different enzymes and morphology of the micelle formation for the biosurfactants and surfactants. Afterward the stability, activity, and complex formation in different mixtures are studied using isothermal titration calorimetry, circular dichroism, tryptophan fluorescence, and activity assays. Subsequently, the mixtures for which interactions are present are studied by SAXS to determine the structure of the formed complexes.

### Keywords

Biosurfactants, Enzymes, SAXS, Complexes, Biophysics

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3 Mortensen, H. G., Madsen, J. K., Andersen, K. K., Vosegaard, T., Deen, G. R., Otzen, D. E., & Pedersen, J. S. (2017). Myoglobin and α-lactalbumin form smaller complexes with the biosurfactant rhamnolipid than with SDS. Biophysical journal, 113(12), 2621-2633.

POSTER

# 243 - DIFFRACTED X-RAY TRACKING (DXT) AT DIAMOND LIGHT SOURCE

**<u>INOUE, Katsuaki (1)</u>; SEKIGUCHI, Hiroshi (2); FOX, Oliver (1); CREVATIN, Giulio (1); OMAR, David (1); TARTONI, Nicola (1); COWIESON, Nathan (1); SASAKI, Yuji C. (3); RAMBO, Robert (1)**
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Diffracted X-ray Tracking (DXT) is a powerful technique which can track the single molecular dynamics with using X-ray. DXT exploits X-ray diffraction which is highly sensitive to rotation and pitch motions in the 3-dimensional space. The concept of the method is relatively simple. The gold nanocrystal (the source of diffraction, diameter ~ 20 nm) is covalently attached to the target protein. Using micro to millisecond diffraction imaging, the trajectory of diffraction spots is recorded. Any structural change of protein molecule synchronizes the motion of nanocrystal on the protein, thus it is reflected in the motion of diffraction spots. It is practically possible to observe the pitch motion and rotation of individual nanocrystal, which is linked to a specific site in an individual molecule and then it is possible to understand the motion of a “specific part” of the molecule through the motion of tracked spots. DXT has so far been used in observing the structural dynamics of proteins, protein-protein complexes and protein-nucleotide complexes, for example, observing picometer scale Brownian motions of individual membrane protein (bR, KcsA, KvAP, nAChR, AChBP, a7AChR etc), antigen-antibody interactions, peptide/ MHC complex for T cell activation, ATP ligand protein (Myosin, Chaperonin) and in monitoring super-weak force (pN) field. It was recently improved to make this technique working on living cells as well. It has also been proved that DXT works in a very wide range of experimental conditions, which means the application possibility of DXT technique is widely open to all the scientific fields. Despite the usefulness of DXT, it is not so popular in the world now. The first DXT measurements at Diamond Light Source have been performed in 2019 on B16. We have successfully assembled the measurement system, including a newly developed detector TRISTAN and measurements on 3 different protein systems (CTIP/Zn, AIP/Hsp90 and FluB/nucleotides) have been done successfully. DXT data showed meaningful changes of the structural dynamics on each protein system and indicated that the internal motions related to the ligand binding or the formation of complex can initiate a significant change of molecular fluctuations on each protein molecule. As it has given full recognition to the significance of DXT measurements for the comprehensive understanding of protein dynamics, we are currently planning to build a new DXT platform on a sub end station on B21 (high-throughput BioSAXS beamline). Our goal is developing a highly automated throughput DXT station, which also can be combined other techniques (such as a rapid flow system, UV/fluorescence measurement, etc), and making such DXT system standard at the synchrotron facility.

**Keywords**
Diffracted X-ray Tracking, single molecular dynamics

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Y. Matsushita, H. Sekiguchi, JW. Chang, M. Nishijima, K. Ikezaki, D.Hamada, Y. Goto, Y.C. Sasaki, Nanoscale Dynamics of Protein Assembly Networks in Supersaturated Solutions, Scientific Reports, 7, 13883 1-8, (2017)

POSTER

# 322 - DYNAMICS AND STRUCTURE OF INTRINSICALLY DISORDERED REGION OF HEF AS STUDIED BY SOLUTION SCATTERING

**INOUE, Rintaro (1); ODA, Takashi (2); NAKAGAWA, Hiroshi (3); TOMINAGA, Taiki (4); KAWAKITA, Yukinobu (3); SATO, Mamoru (5); SUGIYAMA, Masaaki (1)**
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For long time, it is believed that a three-dimensional ordered structure is indispensable for proper development of protein’s intrinsic function. Contrary to such common perception, the existence of intrinsically denatured protein (IDP), which lacks three-dimensional ordered structure even in its functionally active state, was reported by Wright and Dyson. Since IDP plays biologically significant roles especially for Eukaryotes, they are still attracting attention. Because of the limitation of applicability of existing conventional method such as X-ray crystallography to IDP, the relationship between function and structure has remined to be unknown. To overcome such a situation, it is essential to apply the solution scattering method than can directly solve the flexible structures of the IDPs and extract the dynamical information. For this purpose, we investigated the structure and dynamics of IDP in solution by combining small-angle X-ray/neutron scatterings and quasielastic neutron scattering, which can directly study protein’s internal dynamics by utilizing slow neutron with incident energy comparable to that of thermal fluctuations of protein in solution.

In this presentation, we will discuss the origin of the specificity of internal dynamics of Hef-IDR in solution, the response of structure and dynamics by changing the solution environment, and the correlation between structure and internal dynamics, especially focusing on Hef-IDR, an intrinsically disordered region of the archaeal protein Hef, as a sample.

**Keywords**
IDP, neutron scattering

POSTER

# 436 - AMYLOID-BETA PEPTIDE (25-35) TRIGGERS A REORGANISATION OF LIPID MEMBRANES DRIVEN BY TEMPERATURE CHANGES

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The amyloid-beta peptide (Aβ) is considered a key factor in Alzheimer's disease (AD) ever since the discovery of the disease. The understanding of its damaging influence has however shifted recently from large fibrils observed in the inter-cellular environment to the small oligomers interacting with a cell membrane. We studied the effect of temperature on the latter interactions by evaluating the structural characteristics of zwitterionic phosphatidylcholine (PC) membranes with incorporated Aβ25-35 peptide. By means of small angle neutron scattering (SANS), we have observed for the first time a spontaneous reformation of extruded unilamellar vesicles (EULVs) to discoidal bicelle-like structures (BLSs) and small unilamellar vesicles (SULVs). These changes in the membrane self-organization happen during the thermodynamic phase transitions of lipids and only in the presence of the peptide. We interpret the dramatic changes in the membrane's overall shape with parallel changes in its thickness as the Aβ25-35 triggered membrane damage and a consequent reorganization of its structure. The suggested process is consistent with an action of separate peptides or a small-size oligomers of peptides
rather than the result of a large Aβ fibril.

**Keywords**
Amyloid-β peptide, Phosphatidylcholine membrane, Lipid phase transition, Peptide-lipid interactions, Small angle neutron scattering, Molecular dynamics

**Acknowledgements**
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POSTER

# 422 - THE GROWTH OF ULTRA-SMALL SILVER NANOPARTICLES IN SILICA MATRIX USING TEM AND IN SITU ANNEALING GISAXS/GIWAXS EXPERIMENTS

**JATAV, Hemant (1); CHAKRAVORTY, Anusmita (1); MISHRA, Ambuj (1); SCHWARTZKOPF, Matthias (2); ROTH, Stephan V. (2); MICETIC, Maja (3); KABIRAJ, Debdulal (1)**

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The nanocomposites (NCs) comprising ultra-small metallic Nanoparticles (NPs) embedded in silica matrix have piqued attention because of their unique optical property called Localized Surface Plasmon Resonance (LSPR) [1-2] and their wide range of applications in plasmonics [3], nano-photonics [4], bio-medical [5], catalysis [6] etc. These NCs are more stable over time as compared to chemically grown NPs and have shown improved practical efficiency over classical NPs (D > 10nm) and their bulk counterparts. The LSPR frequencies associated with NPs are strongly dependent on their size and shape, thus an understanding of the growth mechanisms of NPs at different annealing temperatures (ATs) is essential to control the morphology of NPs for application purposes.

In this study, we have prepared Ag-SiO2 NC thin films using atom beam co-sputtering technique. The post-deposition growth of silver NPs inside the silica matrix is systematically investigated using UV-Visible spectroscopy, in situ annealing Grazing-incidence small-angle/wide-angle X-ray scattering (GISAXS/GIWAXS) and ex situ Transmission Electron Microscopy (TEM). In UV-Visible absorption spectra, a red shifting in the LSPR peak position is observed, indicating the increase in the size of NPs with ATs. The morphological changes in NPs with ATs are monitored by ex situ TEM. The majority of the NPs are spherical in shape, with a diameter of less than 10 nm, as observed by the findings. The diameter of the NPs varies from ~5 nm to 6.5 nm when the temperature rises from RT to 800 °C. To support the above results, in situ annealing GISAXS/GIWAXS measurements are performed. A three-dimensional (3D) paracrystal model [7], which integrates the 3D distribution of NPs inside silica, is used to quantify NP size from the observed two-dimensional GISAXS spectra. The change in the size of NPs as measured by these techniques are in good agreement. Further, based on the results, a three-stage mechanism is proposed to understand the process of nucleation and growth of the silica-embedded Ag NPs.

## *In situ* annealing GISAXS

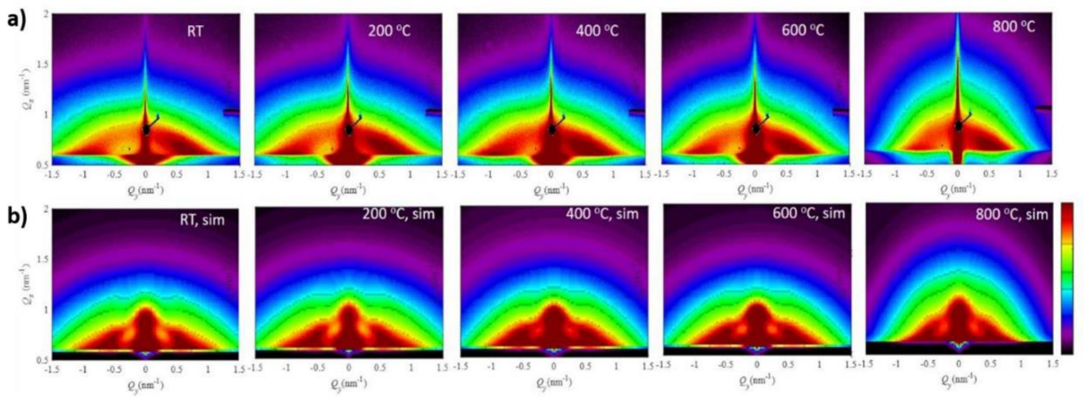

**Figure 1.** (a) 2D GISAXS patterns for Ag-Silica NCs and (b) their corresponding simulated maps at different annealing temperatures (ATs). The ATs are indicated in the respective figures. 2D GISAXS images in FIG 1 (a) show the intensity distribution of scattered signals in the forward direction and a black dot on the plot shows the specular beams, which are blocked by beam stops to protect the detector from intensity oversaturation.

**Keywords**

in situ annealing GISAXS and GIWAXS, Metal-dielectric nanocomposites, LSPR, HRTEM, growth of nanoparticles

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POSTER

# 284 - REVEALING COMPOSITION AND CONFORMATION OF LIPOSOMES USING INTEGRATED METHODS OF HPLC/AF4, UV-VIS ABSORPTION, REFRACTIVE INDEX, MALLS, DLS, AND SAXS-WAXS

**HSU, Ting-Wei (1); LIAO, Kuei-Fen (1); YEH, Yi-Qi (1); SHIH, Orion (1); MANSEL, Bradley W. (1); CHANG, Je-Wei (1); JENG, U-Ser (1,2)**
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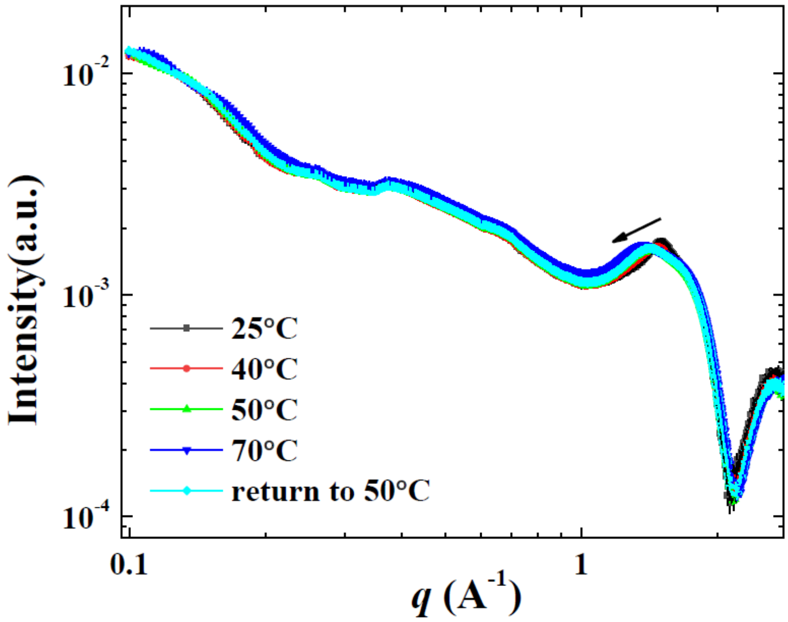
Liposomes are increasingly better developed as efficient drug carriers. Structural characterization of the functional loposomes with and without drug-uptake and the consequent drug-transport and conditional drug-delivery, is of interest in biomedical applications. Here, we report an established combined methods using high-performance liquid chromatography(HPLC), asymmetric flow field-flow fractionation (AF4), UV-Vis absorption, refractive index (RI), multi-angle laser light scattering (MALLS), dynamic light scattering (DLS), and small- and wide-angle X-ray scattering for structural characterization of liposome solutions. We demonstrate an example of using the integrated system to successfully determine hydrodynamic radius and its distribution, molecular mass, lipid aggregation number, of a model liposome system of unilamellar vesicles (ULV). The radius of gyration Rg of 50 nm, hydrodynamic radius Rh of 50 nm, bilayer thickness, and lipid aggregation number of the ULV, with and without drug molecule loading, are determined using simultaneous small- and wide-angle X-ray scattering, incorporated with HPLC/UV-vis/RI, at the high-flux 13A BioSAXS undulator beamline of the 3.0 GeV Taiwan Photon Source. Moreover, a chain-chain packing peak of the ULV bilayers could be observed at q = 1.488Å-1 (d = 4.28 Å); reversible changes of the peak position and peak broadening with temperatures between 20 – 50 °C, providing a direct evidence of the correlation of the lipid chain-chain packing with the commonly observed gel-ripple-fluid phase transitions of multilamellar vesicles.



[1] Nanocharacterization of liposomes for the encapsulation of water soluble compounds from Cordyceps sinensis CS1197 by a supercritical gas anti-solvent technique

**Keywords**
liposome, structure, SAXS

POSTER

# 406 - PREDICTION OF WAX DEPOSITION IN CRUDE OIL BY SMALL- AND WIDE-ANGLE X-RAY SCATTERING

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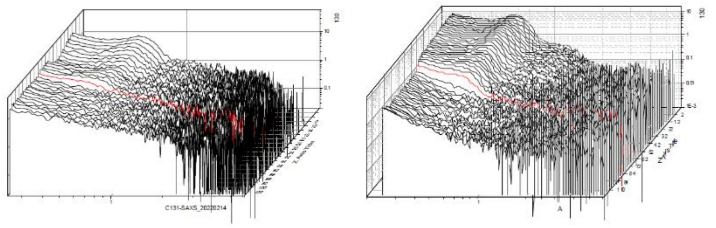
Waxes are complex mixtures of high molecular weight or high carbon number alkanes that consist of straight, branched, and cyclic chains. Petroleum waxes are generally categorized into two groups, paraffin wax (straight chain saturated hydrocarbons with carbon atoms ranging from C18 to C36) and microcrystalline wax (branched and cyclic hydrocarbons with carbon atoms ranging from C30 to C60), present in petroleum distillates and residues. [1] Many crude oils in the world contain significant quantities of wax (3–44%) that crystallizes during the oil production, transportation, and storage. [2] This is known as wax deposition and it is one of the chronic problems during oil production, transportation, and storage. [3] The temperature that at which n-paraffins start to solidify and may deposit on the pipe walls is defined as wax appearance temperature (WAT) and its appropriate determination is fundamental for the wax deposition problems that leads to significant additional production costs. Additionally, the development of operational remediation techniques such as pigging or chemical inhibition requires a deep understanding of the complex behavior of waxy crude oils. [4]

In order to a better understanding of the problem, we studied structural behavior of petroleum paraffin directly in crude oils by small- and wide-angle X-ray scattering (SAXS/WAXS). We explore de SAXS and WAXS images from one crude oil, the paraffins extracted from it and the dewaxed crude oil, cooling the sample between 130 to 0 °C on the Linkam temperature-controlled sample holder. Paraffin extraction was carried out by cold fractional precipitation of the crude oil sample. This procedure is a modification of the UOP Method 46-85 standard.[5] Then, all samples were filled into glass capillaries and placed on the Linkam and heated for a few minutes to 130 °C. Finally, the scattered intensities were measure whereas the temperature was cooled down from 130 to 0 °C.

The recomposed 1D curves obtained at only a few temperatures for the crude oil and extracted samples are shown in Figure 1. There it is possible to observe the simple WAT determination as the temperature at which the most intense narrow Bragg peaks appear[H1] . These peaks were attributed to an orthorhombic crystal system. Furthermore, it was possible to adjust the form of the crystals such as discs or lamellae and determine the maximum crystallite size, in direction c, is found to be of the order of 100 Å in the crude oil. These sizes are typical of anisotropic objects, which is in good agreement with lamellar crystals. So, these techniques provide information on crystals interarrangement, their size, and shape. The knowing of these properties enable a better characterization of wax deposit structure and a deeper understanding of the different mechanisms that lead to wax deposit formation. Up to now, this is the promising technique for wax deposition problems. Actually we are working in the calibration curve, to determine de paraffins concentration and realize a complete comparison with the differential scanning calorimetry (DSC) ASTM-D-4419 test method currently employed in petroleum industry.



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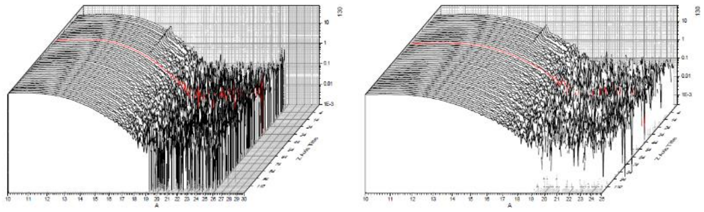

**Figure 1.** SAXS/WAXS diffractograms for a sample of crude oil and extracted paraffins from it, measure at different temperatures.

## Keywords

WAXS, WAT, SAXS, PETROLEUM WAXES

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## POSTER

# 425 - STRUCTURAL STUDY OF CATECHOL 1,2 –DIOXYGENASE FROM PSEUDOMONAS STUTZERI

**JUAREZ, Arisbeth Guadalupe Almeida; PARDO LOPEZ, Liliana; RUDIÑO PIÑERA, Enrique**
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One of the enzymes involved in the degradation of aromatic compounds is catechol 1,2-dioxygenase. This intradiol-type dioxygenase is Fe (III) dependent and participates in the oxidation of catechol or other catechol substituents. In this project, we study catechol 1,2- dioxygenase (C12D) from a marine Pseudomonas stutzeri strain isolated from the Gulf of Mexico. This species of Pseudomonas was one of the first microorganisms isolated as alkane degraders and has biotechnological relevance in bioremediation processes.

To date, we have purified the enzyme and demonstrated that its quaternary structure varies depending on ionic force (as a trimer in low ionic force and as a dimer when it is higher) also the protein is active even in higher salt concentrations (700 mM NaCl). We have performed some techniques like DLS, Native electrophoresis, and SEC to characterize these oligomeric states of C12D (all these results have been published on (10.3389/fmicb.2020.01100)). In the case of tridimensional structure, all homologous and non-homologous catechol 1,2 dioxygenases deposited in PDB are only in dimeric form, in this work we aim to determine the tridimensional structure of C12D in both oligomeric states by X-ray crystallography and SAXS. In our preliminary results in crystallization trials, the crystals didn’t have good quality ( higher mosaicity ) but we are working on optimizations, and our interest to analyze the samples in solution by SAXS is to elucidate the trimer envelope and determine the difference between dimer-trimer states

**Keywords**
dioxygenase, SAXS, protein oligomerization

## POSTER

# 376 - ELECTRICAL CONDUCTIVITY AND IN SITU SAXS PROBING OF BLOCK COPOLYMER NANOCOMPOSITES UNDER MECHANICAL STRETCHING

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Block copolymers are materials that form different ordered structures at the nanoscale. The addition of nanomaterials to these copolymers makes it possible to form nanocomposites with unique properties, depending on the interaction between the nanomaterial and the domains of the blocks.

In this context, an important field of application involves conductive polymeric systems. Electrically conductive nanomaterials such as carbon nanotubes (CNT) have been added to block copolymers to obtain soft nanocomposites for applications such as sensors and actuators1. Due to the high aspect ratio of these nanomaterials, the percolation threshold can be reached at lower volume concentrations than other nanomaterials2. Thus, the degree of orientation of these nanomaterials is an essential factor in the conductive network. A series of works have been carried out on the morphological orientation of the block copolymer using different processing techniques, such as melt injection3 and melt extrusion4, obtaining distinct properties in the direction of alignment and the transverse direction to the preferred orientation. So, it is essential to understand the effect of morphological orientation and electrical response in different directions on large deformations of block copolymer nanocomposites.

The technique of small-angle x-ray scattering (SAXS) is an excellent tool that allows the evaluation of the morphological orientation of the order structure of the block copolymer5.

In this work, we used the block copolymer polystyrene-b-poly(ethylene-co-butylene)-b-polystyrene (SEBS) with the addition of CNT. The samples were melt-injected, providing highly oriented nanocomposites in the injection flow direction. Tensile tests of these materials were carried out in the injection flow direction and transverse to the flow. Simultaneously, we carried out electrical resistivity measurements and monitored the morphological orientation by SAXS, using the synchrotron source of National Synchrotron Light Laboratory (LNLS), Campinas, Brazil. This way, we were able to follow the evolution of the morphological orientation as a function of mechanical deformation and the simultaneous effects on electrical properties.

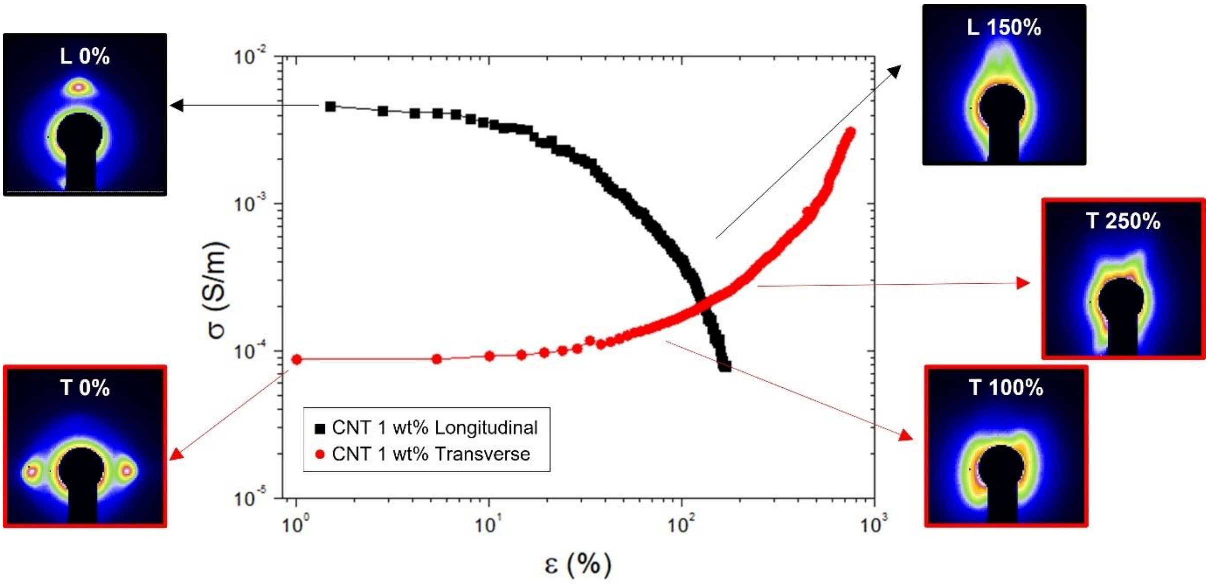

Figure 1. Electrical conductivity as a function of strain in the longitudinal and transverse directions. The SAXS images indicate the morphological orientation in specific deformations.

**Keywords**
Block copolymer, nanocomposite, electrical properties, mechanical stretching

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## POSTER

# 409 - CATERETÊ: THE COHERENT X-RAY SCATTERING BEAMLINE AT SIRIUS

**KALILE, Tiago; POLO, Carla; PASSOS, Aline; ZERBA, João Paulo Castro; MANOEL, Laís; GARCIA, Paulo Ricardo; FERNANDES, Francine Faia; MARASCALCHI, Rachel Andrade; MENEAU, Florian**
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Cateretê, the coherent X-ray scattering beamline at the new Brazilian synchrotron 5bent-achromat source, Sirius is dedicated to coherent diffraction imaging (CDI) as well as X-ray photon correlation spectroscopy (XPCS) studies. Making the most of the coherence properties of the ultra-low emittance of the Sirius accelerator, will enable to perform 3D imaging of micrometer sized specimen down to few nanometers spatial resolution.

The Cateretê beamline is equipped with an undulator source, in a low-beta straight section, and two cryo-cooled focussing mirrors creating a 41 x 36 mm2 (FWHM at 9 keV) coherent beam at 88 m from the source. The beamline operates in the 4 to 24 keV energy range using a horizontally deflecting 4-bounce crystal monochromator (4CM). Moving the 4CM laterally by a few mm, enables to operate the beamline in pink beam mode, maintaining the beam position unchanged. The experimental station is located 88 m from the source, followed by a 28 meters vacuum chamber hosting the Medipix (3k x 3k pixels2) in-vacuum detector.

The beamline, now accepts users and will enable to perform imaging in reciprocal space, with a particular focus on in situ imaging as well as cryo-imaging experiments.

**Keywords**
Coherent small angle scattering

## POSTER

# 156 - XRDYNAMIC 500: HIGH QUALITY SAXS DATA ON A LAB-BASED POWDER X-RAY DIFFRACTOMETER

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With the launch of the XRDynamic 500 automated multipurpose powder X-ray diffractometer, Anton Paar is breaking new ground in XRD and taking materials research to the next level. However, XRDynamic 500 is not only suitable for XRD measurements, but also allows high quality SAXS data to be measured routinely in the lab. In this presentation the key features and benefits of XRDynamic 500 for SAXS measurements will be presented.

The core of XRDynamic 500 is the TruBeam™ concept. TruBeam™ comprises a large goniometer radius and evacuated optics units, automatic change of the beam geometry and all optics components, and automated instrument and sample alignment routines. All of these features combine to deliver outstanding data quality (in terms of both resolution and signal-to-noise ratio) that can be measured with high efficiency in a straight-forward manner.

These features, especially the large goniometer radius and evacuated beam path, also ensure that excellent quality SAXS data can be measured. This is particularly the case when XRDynamic 500 is equipped with the EVAC module. This evacuated sample stage has over 90% of the beam path under vacuum and features sample holder mounts with dedicated SAXS optics to further optimize the data quality, achieving a qmin = 0.05 nm-1.

In addition to the key instrument features and benefits, application examples will also be presented. XRDynamic 500 is suitable for all types of line-collimation SAXS measurements. A wide variety of sample stages and sample holders ensures that there is an optimized instrument configuration available no matter the type of sample.

## Keywords

SAXS, XRD, non-ambient

# POSTER

## 326 - IN-SITU OBSERVATION OF PHOTOCATALYTIC HYDROGEN PRODUCTION OF LINEAR CONJUGATE POLYMERS IN SOLUTION USING SMALL- AND WIDE-ANGLE X-RAY SCATTERING

**LAI, Ze-Yu (2); CHANG, Je-Wei (1); LIU, Jia-Jen (2); MANSEL, B. W. (1); WANG, Chen-An (1); CHOU, Ho-Hsiu (2); JENG, U-Ser (1,2)**
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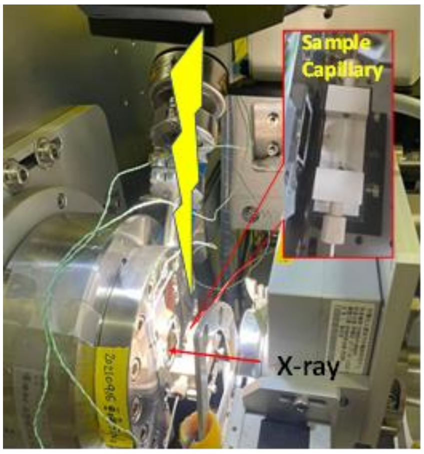
In recent years, the use of photocatalytic water splitting to generate hydrogen has received extensive attention in the research of solar-to-chemical energy conversion. In this study, side-chain modification linear conjugated polymers were synthesized as photocatalysts for photocatalytic hydrogen production. Adopting molecular heterojunctions in linear conjugate polymers could develop donor-acceptor (D-A) junctions of the polymer to facilitate charge carrier separation and suppress charge carrier recombination. Side-chain modifications of such linear conjugated polymers are shown to influence the photocatalytic performance of hydrogen production in water. The solution structures of the linear conjugate polymers are observed under sample flow with a syringe pump, using small- and wide-angle X-ray scattering (SAXS-WAXS). Moreover, sample solutions containing the organic conjugated polymers, TEA, and Pt precursors in methanol-water were also measured under light illumination during in situ hydrogen production, under UV-Visible irradiation. The observed excess SAXS intensity corresponds to growth of 1-2 nm nanostructure, which further cluster along one dimension after eliminating the illumination. Corresponding X-ray sample transmission suggests that these nanostructures may be hydrogen nano-bubbles generated by the system. The structural observations are correlated to the different hydrogen production capabilities observed for the linear conjugate polymers.



**Keywords**
linear conjugated polymers, side-chain modification, photocatalytic hydrogen production, in situ SAXS-WAXS

POSTER

# 289 - SELF-ASSEMBLY DYNAMICS OF POLYMER-GRAFTED INORGANIC NANOCRYSTALS EMBEDDED WITHIN A POLYMER THIN FILM

**LE, Dong V. (1); BASAK, Rourav (2); FRANO, Alex (1,2); ILAVSKY, Jan (3); KUZMENKO, Ivan (3); WIEGART, Lutz (4); FLUERASU, Andrei (4)**
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Inorganic nanoparticles (NPs) embedded in soft polymer materials can be chemically programmed to self-assemble to a variety of non-close-packed mesoscopic structures. This phenomenon is extremely valuable to investigate both for fundamental and technological reasons, such as the design of porous, responsive, plasmonic, and catalytic materials. A current limitation in this self-assembly process is understanding assembly dynamics, which have profound effects on the types of mesostructures formed and the formation of defects. Characterizing and understanding both the local (particle-particle) and ensemble structural dynamics during the self-assembly process will be necessary to tackle this problem. Here, we propose to investigate the fluctuation of the evolution to reach an equilibrium self-assembled structure of polymer-grafted silver nanocubes in polymer thin film using coherent X-ray Photon Correlation Spectroscopy (XPCS). We hope to develop XPCS as a new in-situ tool for characterizing how nanocomponents with different shapes lock into various configurations during the self-assembly process.

**Keywords**
Self-assembly, Anisotropic nanocrystals, polymer, Coherent X-ray Photon Correlation Spectroscopy

POSTER

## 242 - SAXS AT THE CANADIAN LIGHT SOURCE

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We will present an overview of SAXS activities at the Canadian Light Source (CLS), a 3rd generation synchrotron in Saskatoon, Canada. In 2020, CLS SAXS capabilities moved from the Hard X-ray Micro-Analysis (HXMA) beamline to the recently completed Brockhouse X-ray Diffraction and Scattering (BXDS) Sector [1]. BXDS is a suite of three hard X-ray beamlines in full user operation, which are dedicated to diffraction and scattering techniques for materials science. The in-house developed SAXS instrument has been revised as part of the move. The major components now include scatterless slits, a modular light weight plastic flight tube up to 4 meters long with silicon nitride entrance window, improved beamstops, and out of vacuum Rayonix MX300 detectors. The revised instrument has been in user operation since the first quarter of 2021. It can operate on all three beamlines, which offer a variety of X-ray source parameters: Energy scanning in the 5 to 20 keV range for anomalous SAXS, focusing on the sample or detector plane, a high flux multi-layer only mode, and high energy (>40 keV) SAXS. Our diverse user community has been applying SAXS to research areas including photovoltaics, polymers, food science, and pharmaceuticals.

**Keywords**
Synchrotron, instrumentation, beamline

**References**

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https://doi.org/10.1107/S1600577521002496

POSTER

# 438 - ENHANCED PIEZOELECTRIC RESPONSES OF POLYMER FERROELECTRIC CRYSTALS UPON MUTUAL INTERACTIONS OF ANTIPARALLEL CRYSTAL DIPOLES

**LIN, Kun Ta; HUANG, Sheng Hao; LI, Wet ting; LIN, Hsin Hui; RUAN, Jrjeng**
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The secondary molecular interactions are well known able to influence the organization behaviors and electrooptical responses of dispersed molecules. [1, 2] Whereas, for the dispersed phase domains of organic and inorganic components, including amorphous and crystalline phases, mutual polarization/interactions are much less recognized. In general, the interactions among phases, especially crystalline phases, have not been envisaged yet as a factor of crystal engineering and electrooptical features of phase domains.

With the blending of ferroelectric semi-crystalline PVDF-TrFE and amorphous PMMA polymers in selected ratios, the evolved phase distribution patterns have been known able to serve as a template for the dispersion and assembly of inorganic crystallites during thermal treatment. Based on favorable interactions between zinc acetates, the precursor of zinc oxide, and PMMA, the dispersion and assembly of zinc oxide precursors around the PMMA-rich domains have been revealed by the in-situ grazing incidence small-angle X-ray scattering (GISAXS) and in-situ grazing incidence wide-angle X-ray scattering (GIWAXS). After hydrothermal process, standing ferroelectric ZnO nanorods evolve from precursors with polarization orientations antiparallel to surrounding PVDF-TrFE lamellar crystals, which is viewed as a new type of epitaxial relationship. With guided clustering of zinc acetates, the controlled dispersion of ZnO nanorods are found able to significant increase the piezoelectric constant of PVDF-TrFE lamellae to a record value of more than 120 pm/V, and also there is a four-times increase of piezoelectric responses of ZnO nanorods. Furthermore, the increased dielectric constant of the whole films to more than 100 is observed. These results have unveiled mutual interactions between antiparallel crystal dipoles as a new mechanism able to enhance phase polarity. These phase interactions are conceived related to the accumulation of electric fields yielded by interacting crystal dipoles, and therefore decay with the increase of mutual separation, and the decrease of sizes and numbers of interacting crystals.

**Keywords**
mutual phase interactions, Ferroelectric polymers, in-situ, grazing incidence

POSTER

# 424 - VISUAL OPERATIONS OF THE SMALL- AND WIDE-ANGLE X-RAY SCATTERING BEAMLINE BASED ON THE CONTROL-SYSTEM STUDIO

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Equipped with a 4-m in-vacuum undulator (IU24) (consisting of 168 magnets arranged in a period length of 24 mm), the 13A biological small- and wide-angle X-ray scattering beamline (SWAXS) at the Taiwan Photon Source (TPS) of NSRRC, provides high brilliance X-rays in the energy range from 4.0 to 23 keV (Liu et al., 2021; Shih et al. 2022). The beamline features with an in-vacuum SWAXS detecting system comprising two mobile area detectors of Eiger X 9M and 1M in a large vacuum vessel of 12 m long and 1.5 m diameter. The TPS 13A endstation adopts the Experimental Physics and Industrial Control System (EPICS) for integrated controls of the beamline hardware and software, including all motors and components. In this presentation, the graphic calculation and control of the two-detector system (of a position-encoder system) for a combined scattering vector q-range on the basis of a graphical user interface of Control System Studio (CSS), will be detailed; which includes the visual displays of the positions of the two detectors in the vacuum vessel and the three beamstops on the simulated Eiger 9M SAXS detector area. The visualized detector control system allows convenient and quick decision on allocating the two detector positions. Also demonstrated are the programmable sample temperature controls (via heating rods or a chiller) on the basis of CSS's dynamic tracing of the components status registered in the process variables of the Experimental Physics and Industrial Control System (EPICS) for integrated and in situ controls of sample environment and SWAXS data collection.

**Keywords**
EPICS, CSS

POSTER

# 429 - PROBING INTERACTIONS BETWEEN METAL‒ORGANIC FRAMEWORKS AND FREESTANDING ENZYMES IN A HOLLOW STRUCTURE

**CHEN, Sheng-Yu (1); LO, Wei-Shang (2); HUANG, Yi-Da (3); SI, Xiaomeng (1); LIAO, Fu-Siang (3); LIN, Shang-Wei (4); WILLIAMS, Benjamin P. (2); SUN, Ting-Qian (3); LIN, Hao-Wei (3); AN, Yuanyuan (1); SUN, Tu (1); MA, Yanhang (1); YANG, Hsiao-Ching (4); CHOU, Lien-Yang (1); SHIEH, Fa-Kuen (3); TSUNG, Chia-Kuang (2)**
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My talk is about the research work recently published in Nano Letters. It has been reported that the biological functions of enzymes could be altered when they are encapsulated in metal-organic frameworks (MOFs) due to the interfacial interactions between them. Herein, we compared the interfacial interactions of catalase in solid and hollow ZIF-8 microcrystals. The solid sample with confined catalase is prepared through a reported method and the hollow sample is generated by hollowing the MOFs crystal, sealing freestanding enzymes in the central cavities of hollow ZIF-8. The samples were characterized by electron microscopy, powder X-ray diffraction (PXRD), and nitrogen sorption. The hollowing process was monitored by small angle X-ray scattering (SAXS) spectroscopy which are sensitive to structural changes in the mesostructured range. (Figure 1). The interfacial interactions of the two samples were studied by infrared (IR) and fluorescence spectroscopy. IR study shows that freestanding catalase has less chemical interaction with ZIF-8 than confined catalase, and fluorescence study indicates that the freestanding catalase has lower structural confinement. We have then compared the hydrogen peroxide degradation activities of confined and freestanding catalase and revealed that the freestanding catalase in hollow ZIF-8 has higher activity. This discovery implies that reducing interfacial interactions could lead to a higher biological activity.

**Keywords**
metal‒organic Frameworks, freestanding protein, hollowing process, small angle X-ray scattering

POSTER

# 438 - ENHANCED PIEZOELECTRIC RESPONSES OF POLYMER FERROELECTRIC CRYSTALS UPON MUTUAL INTERACTIONS OF ANTIPARALLEL CRYSTAL DIPOLES

**LIN, Kun Ta; HUANG, Sheng Hao; LI, Wet ting; LIN, Hsin Hui; RUAN, Jrjeng**
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The secondary molecular interactions are well known able to influence the organization behaviors and electrooptical responses of dispersed molecules. [1, 2] Whereas, for the dispersed phase domains of organic and inorganic components, including amorphous and crystalline phases, mutual polarization/interactions are much less recognized. In general, the interactions among phases, especially crystalline phases, have not been envisaged yet as a factor of crystal engineering and electrooptical features of phase domains.

With the blending of ferroelectric semi-crystalline PVDF-TrFE and amorphous PMMA polymers in selected ratios, the evolved phase distribution patterns have been known able to serve as a template for the dispersion and assembly of inorganic crystallites during thermal treatment. Based on favorable interactions between zinc acetates, the precursor of zinc oxide, and PMMA, the dispersion and assembly of zinc oxide precursors around the PMMA-rich domains have been revealed by the in-situ grazing incidence small-angle X-ray scattering (GISAXS) and in-situ grazing incidence wide-angle X-ray scattering (GIWAXS). After hydrothermal process, standing ferroelectric ZnO nanorods evolve from precursors with polarization orientations antiparallel to surrounding PVDF-TrFE lamellar crystals, which is viewed as a new type of epitaxial relationship. With guided clustering of zinc acetates, the controlled dispersion of ZnO nanorods are found able to significant increase the piezoelectric constant of PVDF-TrFE lamellae to a record value of more than 120 pm/V, and also there is a four-times increase of piezoelectric responses of ZnO nanorods. Furthermore, the increased dielectric constant of the whole films to more than 100 is observed. These results have unveiled mutual interactions between antiparallel crystal dipoles as a new mechanism able to enhance phase polarity. These phase interactions are conceived related to the accumulation of electric fields yielded by interacting crystal dipoles, and therefore decay with the increase of mutual separation, and the decrease of sizes and numbers of interacting crystals.

**Keywords**
mutual phase interactions, Ferroelectric polymers, in-situ, grazing incidence

POSTER

## 163 - STRUCTURE AND DYNAMICS OF HUNTINGTIN. A SEGMENTAL LABELLING APPROACH

**LUND, Xamuel Loft (1,2); GABEL, Frank (3); MARTEL, Anne (1); BERNADÓ, Pau (2)**
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Huntington's Disease (HD) is a genetically inheritable neurodegenerative disorder caused by a mutation in the gene encoding the protein Huntingtin (Htt)1. The mutation causes an increase in CAG trinucleotides in the first exon, which increases the number of glutamines in the poly-glutamine (Poly-Q) tract of the intrinsically disordered N-terminal region of the protein2. HD symptoms only manifest in individuals with a poly-Q tract of more than 35 consecutive glutamines. The length of the Poly-Q tract beyond the threshold is correlated with the age of onset and the severity of the pathology. The exon-1 of Htt is a low complexity region that contains the N-terminal 17 residues, the poly-Q tract and a proline rich region. My project aims at elucidating the structural differences between non-pathogenic and pathogenic Htt exon-1 constructs using Small-Angle Neutron Scattering (SANS) measurements in amino-acid specific deuterated samples. Profiting of the distinct scattering properties of deuterium and hydrogen, we aim at extracting valuable structural information of the Poly-Q region. Constructs with specific deuteration patterns (Gln/Pro) are produced using the Cell-Free protein expression system.

SANS data, collected at the D22 Beamline at ILL, and Small-Angle X-ray Scattering (SAXS) data measured at Soleil and ESRF Synchrotrons are combined with atomistic models to derive unique structural information of different Htt constructs3. Synergistic analyses of the data are performed using the ensemble optimization method (EOM)4. Currently, eleven SANS samples have been measured for pathogenic (HttQ36) and non-pathogenic (HttQ16) constructs of the protein and ensemble analyses are in progress.

**Keywords**
Hungtington's Disease, Poly-Q, Cell-free, SANS, SAXS

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POSTER

# 184 - USING ELECTRON MICROSCOPY DENSITY MAPS IN THE ANALYSIS OF SMALL-ANGLE X-RAY SCATTERING OF LARGE BIOMOLECULAR COMPLEXES

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SAXS has proven to be a powerful complementary low-resolution tool for determination of structure of large biomolecular complexes. The analysis is greatly facilitated by availability of high-resolution structures from protein crystallography and solution NMR. When structures are available of the whole complex of the various components constituting it, rigid-body refinement with suitable physical restraints can be performed by fitting to the experimental SAXS data. A variety of analysis software for this has been developed by several groups. They all apply random searches and therefore involve repeated calculations of many scattering curves. We have also developed our own software with focus on self-consistent and fast performance. For self-consistency, we re-generate at each step of the optimization the hydration shell of the complex, which contributes significantly to the scattering signal. Therefore, fast methods for the hydration shell generation and calculation of the SAXS scattering curve have been developed. Additional efforts have been invested in using electron density maps from transmission electron microscopy (TEM) in the analysis of SAXS data. Since TEM provide single particle maps, they are not influenced by crystal packing effects and the maps are closer to describing those present in solution, which are measured by SAXS. We have developed software that calculates the SAXS curve from electron density maps from negative stained or cryogenic TEM. The software scans the threshold electron density level and fits the corresponding calculated scattering curve to the measured SAXS data taking the resolution of the maps into account. In this way, the correct threshold level is determined and the maps for this level can be used for docking high-resolution structures and in this way provide good starting models for rigid body refinement. The methods have been tested both on simulated and experimental electron density maps and SAXS data.

**Keywords**
Data analysis, SAXS, TEM

POSTER

# 420 - SPYGUIFIT: THE SAPUCAIA PYTHONIC GRAPHICAL USER INTERFACE FOR SIMULATION AND DATA FIT

**MALFATTI-GASPERINI, Antonio Augusto**
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In the last decades, the continuous advancement in synchrotron sources and detection technologies opened new possibilities in different research areas due to the high quality of the acquired data and the increase in the acquisition rate. For small-angle scattering technique, however, the information that can be obtained is deeply hidden in the experimental data and must be properly extracted, usually by using simulation or fit procedures. To this end, a great effort is being made to facilitate access to these types of tools, as only a very small fraction of scientific groups has specialists with the necessary knowledge to develop their own tools or the time to dedicate themselves to this goal. In this sense, easy-to-master data analysis tools have been widely developed, but most of them for more traditional research areas, such as proteins in solution. General modeling tools are very attractive for other areas, but most of the time the built-in models implemented are very simple or would need some specific changes to describe the systems correctly; furthermore, even with the correct model, most programs do not allow to accurately visualize the effect of each parameter on the simulated curve, which makes the initial estimate of the parameters poor and makes the fitting procedure difficult.

Python has grown in recent years and has become one of the most used programming languages. The practicality, ease of learning, zero cost and the huge amount of open-source libraries produced, allied to the possibility of integration with other faster and lower-level programming languages, made Python become the preferred language for a large part of the scientific community.

Here we present SPyGUIFit: a Python library that aims to facilitate the visualization of the simulation and fit procedures. It is a wrapper for lmfit [1] – a library for fitting purposes that handles many useful functionalities, which were kept into the library – and uses the concept of sliders – which became popular in Mathematica software [2] and was imported into Python by Matplotlib library [3] – to allow changing parameters in a smooth and practical way, allowing the visualization of the effect of each parameter on the simulated curve on the fly. The SPyGUIFit library helps to create a PyQt based graphical user interface where the users can include general functional buttons and sliders that will help to visualize, simulate and fit their experimental data.

**Keywords**
Data Fitting, Python, Graphical User Interface, Simulation

## References

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[2] https://www.wolfram.com/mathematica/
[3] https://matplotlib.org/

POSTER

# 443 - MAGNETIC GUINIER LAW

**MALYEYEV, Artem (1); MICHELS, Andreas (1); TITOV, Ivan (1); HONECKER, Dirk (1); CUBITT, Robert (2); BLACKBURN, Elizabeth (3); SUZUKI, Kiyonori (4)**
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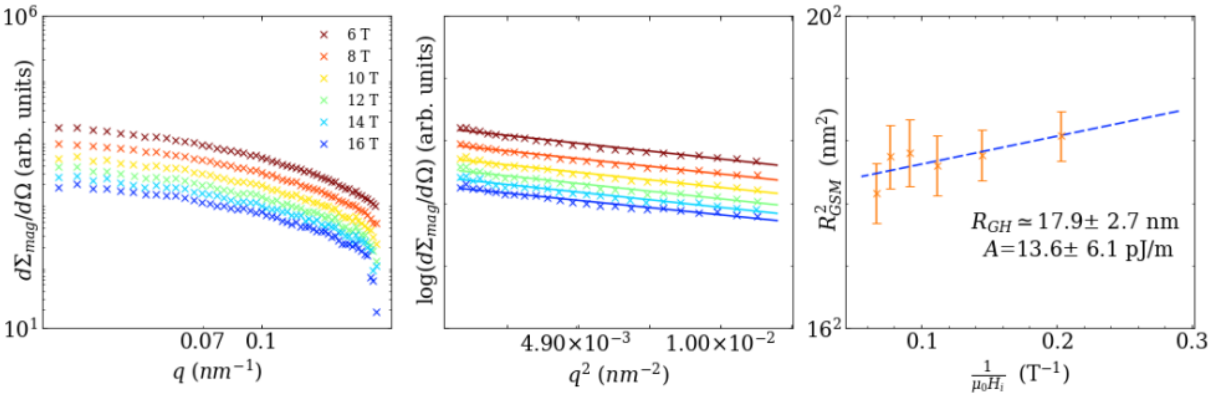
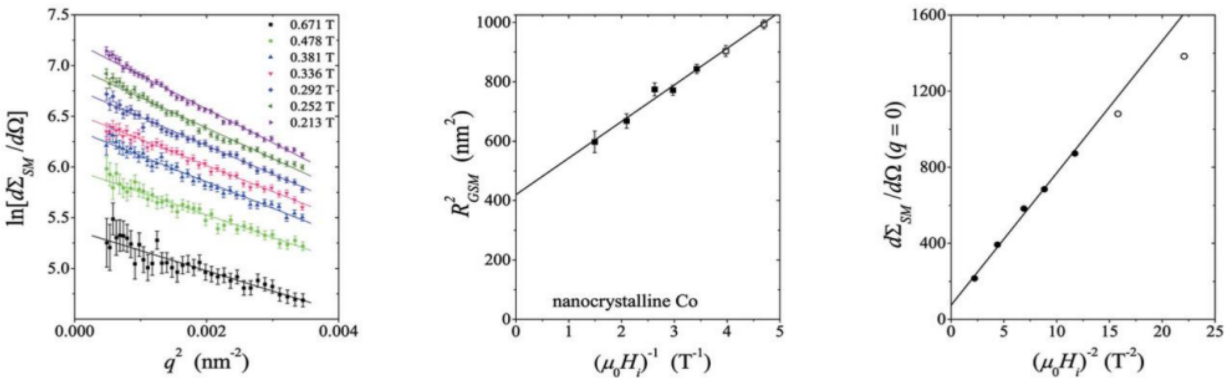
We are interested in the studies of the microscopic mechanism and theory in the synthesis-structure-property relation of polymer nanocomposites via the using of X-ray and neutron scattering techniques. As the general issue of material science research, the unclear inherent structure-property relation of the polymer nanocomposites resulting from their multi-component, hierarchical structures is aimed to be resolved. We applied polymer-molecular cluster composites with well-defined structures as model systems and studied the materials comprehensively with the extraction of experimental data in both temporal and spatial dimensions. X-ray and neutron scattering techniques with complementary contrast for material characterization are developed for the research on fine structures of amorphous material systems. This helped break the limit for the research on solutions and non-crystalline sample systems and brought in the capability in quantifying the hierarchical structures and dynamics from chain segments to single chain/molecular cluster to co-assemblies of multiple units. The reaction kinetics, solution dynamics and structure-property relation can be obtained and the previous theories on ‘reducing agents-controlled synthesis of clusters’ and ‘static property of metal-organic polyhedron’ were revised. The research can finally lead to the concept of material-by-design with required hierarchical structures and dynamics. The decoupling of multi-functionalities can be achieved, facilitating the precise design of materials with the effective integration of ion conduction, gas transportation and promising mechanical properties as well as transformative topological explosion-proof materials.



Summary of the magnetic Guinier law analysis on a Nd-Fe-B-based nanocomposite. The value obtained for the exchange-stiffness constant $A \simeq 13.6 \pm 6.2$ pJ/m coincides with the value obtained *via* the micromagnetic route ($A \simeq 13.1 \pm 3.2$ pJ/m) and the radius of gyration is comparable with the particle size $d \simeq 22$ nm [5].



Summary of the magnetic Guinier law analysis on nanocrystalline Co [8]. The value obtained for the exchange-stiffness constant $A \simeq 15{\pm}2$ pJ/m coincides with the values reported in the literature [9,10]. The $R_{GH}$ value corresponds to a spherical particle of radius $R \simeq 26.5$ nm (assuming $R^2_{GH} = (3/5)R^2$, which is valid for monodisperse particles). This value is larger than the average crystallite size of 10 nm determined by X-ray diffraction, which can be naturally explained by the presence of a particle-size distribution in the Co sample.

**Keywords**
small-angle neutron scattering, Guinier law, magnetic materials, micromagnetics, nanoscience

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## Acknowledgements

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POSTER

## 275 - NANO-ARCHITECTURE OF GRASSES CELL WALLS REVEALED BY CRYO-PTYCHOGRAPHY

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Lignocellulosic feedstocks are widely used to product biofuels and bioproducts and play an important economical role. Nonetheless, the biochemicals properties of lignin reduces the cellulose extraction yield of degradation being one of the strategies to improve this process the genetic manipulations to down regulated the lignin synthesis pathway. In this sense, our study aims to understand how genetic manipulation of lignin metabolism affects the cell wall nanostructure in Sorgum bicolor plants using Coherent X-ray Diffractive Imaging (CDI). The CDI experiment was performed in 3D ptychography configuration, under cryogenic conditions, at cSAXS beamline of the Swiss Light Source (SLS) at the Paul Scherrer Institute (Villigen PSI, Switzerland). This setup allowed us to study extended samples (up to hundreds of microns) and still obtain to 100 nm resolution. Such high resolution allowed us to understand the organization of the plant cell wall and to evaluate the histological integrity. Besides, we could extract accurate morphological and quantitative information that enable us to understand the relationship between the cell wall thickness and the lignin deficiency and how this can impact biotechnologic biomass processing.

**Keywords**
lignin, sorghum bmr6 mutant, plant cell wall

**Acknowledgements**
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POSTER

# 437 - REVEALING THE GLOBAL AND LOCAL STRUCTURES OF AMYLOSE OLIGOMERS IN SOLUTION WITH SMALL- AND WIDE ANGLE X-RAY SCATTERING

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Amylose, a polysaccharide, and amylopectin constitute semi crystalline starch granules, which are efficient energy storage vaults of most green plants. Amylose is used extensively as a thickener, water binder and emulsifier in the food industry. With repeating bulky glucose moieties connected through 1,4 glycosidic linkages, amylose possess considerable rigidity for extended conformations. The partially rigid structure of amylose in solution, however, is elusive to date. Previous molecular dynamics simulation suggested that for lengths of twelve glucose units, amylose oligomers form double helices [1]; nevertheless, random coil, worm-like helical conformation and extended helical segments [2] were also proposed on the basis of experimental observations [3]. These unconverged forms originated from the difficulty in observing the partially ordered conformation of amylose in solution. Using the Taiwan Photon Source bioSAXS beamline [4,5], capable of simultaneous small- and wide angle X-ray scattering (SWAXS) measurements for solution structures of biomolecules, we examine the solution structures of several oligomeric amyloses of 3 to 10 glucose moieties (3-mer to 10-mer), in different salt concentrations. Combined SWAXS data analysis with molecular dynamics simulations (MD), we show that the solution structures of 3- to 10-mer all display loose single helix with no sign of the previously proposed structure of double helix, in aqueous solution without or with 0.5 M KCl; a few minor changes in the local structures, however, are observed with the salt condition.

**Keywords**
Polysaccharide, SAXS, amylose

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POSTER

# 171 - MAXS FOR MOLECULAR PROJECTION OF ANTIBODY CONFORMATIONAL CHANGES

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The use of biopharmaceuticals, especially antibody drugs, has expanding dramatically over the last few years. While antibody drugs have the advantage of high specificity and low side effects, they have the disadvantage of both high development and production costs, and difficulties in maintaining quality of the deliverable. In general, it is considered that structural information is essential in drug development to enhance drug efficacy, and that it is necessary to confirm heterogeneity, such as the presence or absence of sugar chains in the manufacturing process, to ensure quality and reliability. However, it is difficult to obtain the structural information by single crystal X-ray structure analysis because of variability of the sugar chains attached to the antibody and the highly flexible nature of the antibody itself. Even if a crystal structure is obtained, it may differ from the structure in solution due to the crystal packing forces.

If the structures of flexible molecules such as antibodies and their conformational changes in solution can directly be visualized, the time and economic costs associated with these drugs could be dramatically be reduced, while improving the functionality, quality and stability of molecules. X-ray solution scattering experiments are a powerful technique for analyzing structures and conformational changes without the artifacts due to crystal packing forces.

In addition, the scattering from the middle range of the resolution region [q values between 0.30 to 0.65 Å-1] contains important information such as the inter-domain distances and inter-secondary structure distances in the molecule. This data allows us to visualize more detailed molecular behaviors and conformational changes. The solution scattering that contains this important middle-angle region information is called mid-angle X-ray scattering (MAXS).

Therefore, we decided to test the method by determined if the flexible structure and conformational changes of human IgG in solution can be captured by MAXS analysis. We found that the solution structure of human IgG revealed significant differences between the solution and crystalline states. We also observed interesting modes of flexibility in the human IgG. Additionally, we now have a clear understanding of the conformational changes in human IgG with and without sugar chains.

In this presentation will discuss solution structure analysis by MAXS and show that is essential to correctly evaluate the native structural information and conformational changes of human IgG.

**Keywords**
Solution scattering, IgG, conformational change, mid-angle X-ray scattering (MAXS)

POSTER

# 399 - GIXOS STUDIES OF CLAY NANOSHEETS AT THE AIR-WATER INTERFACE.

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Clay nanolayers are 2D soft materials, like graphene oxide layers. Clay nanolayers are of significant general and practical interest. Previous reports suggest that clay sheets could only adhere at oil-water or air-saline-water interfaces in the aggregated state. However, in the present work we demonstrate that unmodified clay nanolayers actually can adhere to air-deionized-water interfaces. We report this using a combination of different experimental methods: Grazing-Incidence X-ray Off-Specular Scattering (GIXOS) at XRD2 LNLS, Campinas - Brazil, Brewster angle microscopy (BAM) and, scanning electron microscopy (SEM) studies of films made using the Langmuir–Schaefer method. The GIXOS results confirm presence of clay nanosheets at the air–water interface, whereas the BAM results indicate a dynamic equilibrium between clay sheets on the interface and in the sub bulk phase. In addition, we find that by functionalizing the clay nanosheet surfaces with a branched polymer, we increase significantly the probability of confinement to the interface1.

**Keywords**

Clay, 2D material, Air-water interface, Langmuir Trough, GIXOS

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POSTER

# 349 - SAXS STUDIES OF AQUEOUS SUSPENSIONS OF MAGNETIC JANUS CLAY NANOSHEETS

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2D nanosheets are of high interest for various applications, such as for those relying on encapsulation of droplets or particles, capture of molecules or liquid crystalline organization. Of particular importance are nanosheets that respond to, and can be manipulated by applied magnetic fields, thus enabling extractions or aiding nematic algnement. Here we report the successful and efficient approach of decorating inert nanosheets in liquid phase with magnetic nanoparticles (NPs) on one side. We use functionalized iron oxide nanoparticles and high-aspect ratio sheets of insulating synthetic sodium fluorohectorite clay. The efficiency of the process is confirmed by several complementary characterization methods, Small Angle X-ray Scattering (SAXS), spectroscopy (FTIR, UV-VIS), microscopy techniques (SEM and AFM) and magnetic properties were characterized. Options for tuning magnetic NP coverage density on the nanosheets are demonstrated. Magnetic manipulation of the Janus nanosheets are demonstrated, and possible applications od this will be discussed.

**Keywords**
Clay, Self Assembly, magnetic nano particles

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POSTER

# 338 - INTEGRATED METHOD WITH ANALYTICAL ULTRACENTRIFUGATION AND SMALL-ANGLE SCATTERING (AUC-SAS) FOR THE STRUCTURAL ANALYSIS OF A BIOMACROMOLECULE IN A POLYDISPERSE SOLUTION.

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Small-angle X-ray and neutron scatterings (SAXS and SANS; collectively called SAS) are promising techniques for elucidating the structure of a biomacromolecule in a solution. Especially, state-of-the-art computational analyzing methods for SAS offer a high resolution three-dimensional structural model and/or its dynamics in the solution. To make a reliable structural model through the advanced analyses, it is essential to obtain the precise SAS profile from only a target biomacromolecule. Hence, a sample should be purified to be a monodisperse solution prior to a SAS measurement. Nevertheless, non-specific oligomers, namely aggregates, often remain in the solution even after purification. Even if the weight fraction of aggregates is a few %, the experimental SAS profile is deteriorated by them. As the result, an incorrect structural model is built as the target biomacromolecule: This is the fatal problem on the structural analysis with SAS.

To overcome this problem, a new data-reduction method, "AUC-SAS"[1], was developed with integration of analytical ultracentrifugation (AUC) and SAS. AUC provides the weight fractions and molecular weights of all components in solution without destruction of aggregates and complexes. AUC-SAS derives the scattering profile of a target biomacromolecule from the deteriorated experimental profile using the information provided by AUC. This method successfully derived the precise SAS profile for the solution including aggregates up to 20 % of weight fraction. Aiming for broad SAS users, Igor Pro-based software of the AUC-SAS is released at [http://www.rri.kyoto-u.ac.jp/NSBNG/activity.html]. Since AUC-SAS does not require a large amount of sample nor very high flux beam compared with size-exclusion chromatography (SEC)-SAXS, it has a potential to be applicable not only to a synchrotron-based SAXS but also to laboratory-based SAXS and SANS. In fact, this method already applied to various biomacromolecules and made the detailed structural modeling possible.[2]-[4]

Furthermore, AUC-SAS is also applicable to another polydisperse system, a multi-components system such as an association-dissociation equilibrium. SEC-SAXS is unavailable to obtain the scattering profile of a complex under fast association-dissociation equilibrium due to destruction of the complex during the SEC process. Hence, AUC-SAS is one of the most useful approach for such systems.

In the presentation, we will show our established methodology and several applications of AUC-SAS.

**Keywords**
SAXS, SANS, AUC, protein solution, polydisperse

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POSTER

# 319 - DEVELOPMENT OF A SOLID SAMPLE HOLDER FOR EXPERIMENTS WITH TEMPERATURE AT SAPUCAIA BEAM LINE.

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A substantial portion of the small-angle X-ray scattering (SAXS) users leads their studies using solid samples. Although the setup for batch measurements for these systems is very simple, a common limitation is to allow the change of the temperature, which limits SAXS applications. A very common solution is the use of hot-blowers; however, they dissipate the heat for many samples at the same time and generally are not fast. In order to optimize the time per experiment and automatize the sample change in the experiment, this work presents a simple system, which is able to change the temperature of a unique sample in a considerable reduced time, without heating or freezing the others. The system is able to set temperature in a range between -173 K and 873 K with a temperature rate close to 100°C K/min and it is based on a Linkam heating device. The implementation of the system on the SAPUCAIA beam line, localized at the Sirius synchrotron, will expand the range of possible experiments on solid samples involving temperatures changes using the SAXS techniques.

**Keywords**
Sample holder for solids, linkam, high throughput

POSTER

# 237 - IN-SITU LOADING AND MULTI-SCALE DEFORMATION MEASUREMENTS OF NANOSTRUCTURED MATERIALS AT THE COSAXS BEAMLINE AT MAX IV

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In this work the current development of the capabilities for in-situ mechanical testing and multi-scale analysis of deformation and microstructure at the CoSAXS beamline at Max IV are presented. A uniaxial setup, coupled to a 3D-surface digital image correlation and a quantitative beamstop detector, has been adapted for simultaneous SAXS and WAXS measurements during continuous load. The design allows a fast scan and high resolution (beam size H: 100 µm × V: 100 µm) of the sample for structural analysis. Image acquisition is synchronized with the detector triggering for optimal correlation between the strain field and the corresponding scattering patterns. Measurements of the local evolution of nano-/micro-structural order and strain in the block co-polymer material SEBS (poly(styrene-b-ethylbutylene-b-styrene)) shows the presence of out-of-plane deformations near the center of the sample, which are typically missed by other methods, the structural evolution from a lamellar to a chevron morphology, as well as sample shearing.

**Keywords**
In-situ loading, block co-polymer, SEBS

POSTER

# 308 - STRUCTURAL DESIGN OF POLYELECTROLYTE-PROTEIN NANOCARRIERS FOR TARGETED DRUG DELIVERY

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Co-assembly of oppositely charged polyelectrolytes with proteins is a well-studied approach for designing stimuli-responsive nanocarriers for targeted drug delivery. However, the complexity of protein structure limits the ability to predict and tune the properties of formed nanoparticles. The ultimate goal of our research is to reveal the main triggers for the morphological transition of protein/polyelectrolyte complexes, their encapsulation efficacy and particles stability by systematic study of complexes formed by block copolymers with proteins and encapsulated ionic drug. Using scattering and microscopy techniques, we showed that block copolymers consisting of a weak polyelectrolyte block and a neutral hydrophilic block co-assemble with proteins at pH close to protein isoelectric point and the morphology of the formed particles can be tuned by varying pH and nature of proteins. Moreover, we observed that formed protein/polyelectrolyte complexes with an excess of a charge can be used for encapsulation of an oppositely charged drug thus allowing us to use one carrier for both protein and drug delivery, and to design nanocapsules with such tunable properties as charge, stability, and size.

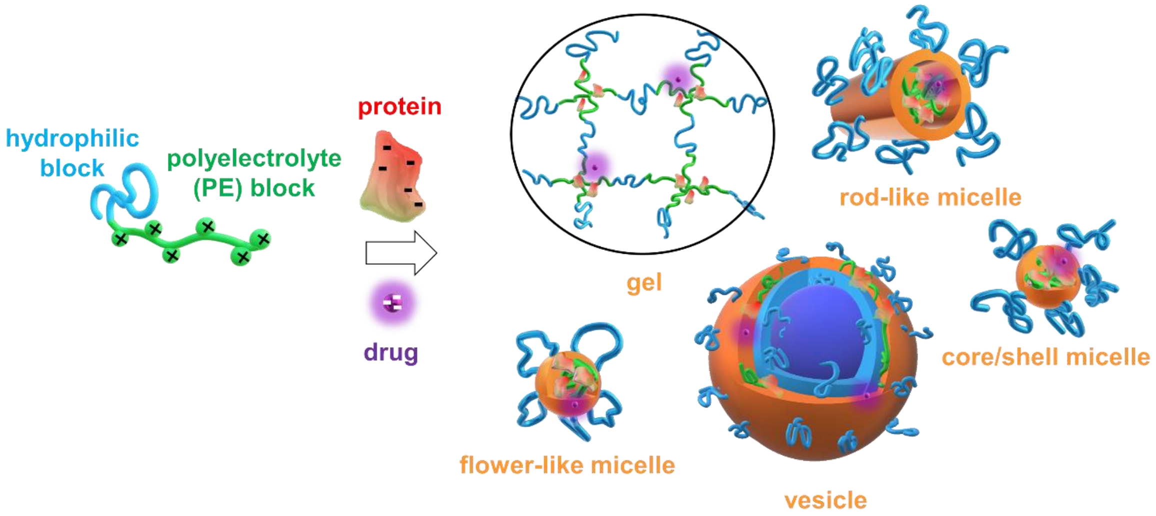

Fig. 1. Co-assembly of a block copolymer with a protein and a drug

**Keywords**
polyelectrolyte, protein, soft matter

POSTER

# 351 - USAXS STUDIES OF HIGH ASPECT-RATIO CLAY NANOSHEET AQUEOUS SUSPENSIONS WITH LARGE NEMATIC SPACINGS IN THE VISIBLE PHOTONIC RANGE

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Structural colors are vivid colors that originate by constructive interference following reflection and scattering from periodic structures with length scales in the range of visible light. Recently we demonstrated that bright non-iridescence structural coloration easily and rapidly can be achieved from 2D clay nanosheets suspended in water[1]. The non-iridescent structural colors can be precisely and reproducibly controlled from varying interlayer distances by clay concentration and ionic strength independently. In follow-up studies, the aqueous salinity (NaCl) on the clay suspension were studied using Ultra Small Angle X-ray Scattering (USAXS) at the CoSAXS beamline, Max IV, Lund, Sweden. In the future, embedding such clay nanosheets in solid transparent matrices instead of simply in water could open up for a new generation of sustainable structurally colored pigments.

**Keywords**
Structural Color, Clay, Nanosheets, 2D Material, Photonics

## References

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POSTER

# 352 - SOLUTION STRUCTURE ANALYSIS OF THE MULTI-DOMAIN PROTEIN, ER-60 BY SMALL ANGLE SCATTERING

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ER-60, an oxidative folding enzyme, is a multi-domain protein with the a-b-b'-a' domain structure. Depending on the redox state of the active centers in a and a' domains, ER-60 folds unfolded proteins through oxidation and reduction. In this process, ER-60 might have the appropriate domain conformations to function. Therefore, it is assumed that the conformation fluctuates according to the redox state of the active centers in the solution.

To observe the structure of ER-60 in solution, the highly purified recombinant oxidized and reduced ER-60 were prepared. Then, to remove the effects of contaminants and aggregates on the SAXS profile, SEC-SAXS [1] which combined size exclusion chromatography (SEC) and small angle X-ray scattering (SAXS), followed by AUC-SAXS [2], sophisticated data processing using the weight fractions of components obtained from analytical ultracentrifugation (AUC). Comparing the high-precision SAXS profiles of ER-60 from these experiments with the one calculated from the crystal structure, it was found that the solution structures are different from the crystal structure. Furthermore, with Guinier analysis of these profiles, it was revealed that a significant difference in the radius of gyration (Rg) between oxidized and reduced ER-60, indicating that oxidized ER-60 has a more extended structure than reduced ER-60 in solution [3].

In addition, we will also present an advanced structural analysis by small angle neutron scattering (SANS) with protein deuteration [4] and protein ligation techniques, planned in the future.

**Keywords**
Multi-domain proteine, Small angle X-ray scattering, Small angle neutron scattering, Deuterated protein

**References**

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POSTER

# 343 - INTERCALATION DYNAMICS OF VARIOUS DRUG MOLECULES INTO LITHIUM - FLUOROHECTORITE CLAY MINERALS

**PACAKOVA, Barbara (1); SANTOS, Everton (3); CAVALCANTI, Leide (2); BORDALLO, Heloisa (4); FOSSUM, Jon Otto (5)**
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Smectite clays belong to the family of layered silicates, and exhibit the net negative charge of the layers, which is compensated by the positively charged interlayer cation. Swelling of smectites is strongly dependent on the type of the interlayer cation 1–3 and allows trapping of small molecules into the interlayer space of smectite. It has been shown that smecites can host not only small gas molecules 4 but also intercalate drug molecules, such as ciprofloxacin.

We have studied intercalation dynamics and mechanism of four different drugs: metronidazole, diclofenac, tramadol and trimethoprim. As the drug molecules can possess different charge (negative, neutral or positive) depending on the pH of solution, we assumed that intercalation of drug into the clay would be pH dependent, and the easiest intercalation should occur for positively charged drug molecules, whereas negatively charged drug molecules should not intercalate into the smectite at all.

Dynamics of drug intercalation was studied by synchrotron SAXS, for aqueous suspensions of clay and drugs by the in-situ diffraction in the q-range of 0.9-5.8 nm-1, acquiring the scans continuously. We followed the shift and change of intensity/FWHM for d001 peak, which corresponds to inter-lamellar spacing of smectite clays. The drug intercalation experiment was performed by mixing of aqueous solutions of LiFh and drug solution (both kept at similar pH and temperature), when the drug solution was injected into the solution of the LiFh.

We have made several important and promising observations during the experiment. Drug intercalation dynamics is observable, and varies with the drug type, pH and temperature of solution. The slowest dynamics has been observed for intercalation of trimethoprim at pH 2 and 5, for which the d001 peak stops to evolve with time after app. 15 min from drug injection (Figure 1). The fastest dynamics has been detected for metronidazole at pH 2, when d001 spacing of LiFh changes within the time frame of drug injection and does not evolve with time.

Results of dynamic in-situ studies are currently being compared with the S-XRD measured on dried powders, UV-VIS spectroscopy and TGA measurements, that all together finally shows whether the drug was intercalated into the LiFh interlayer at given pH and temperature or not. Observed dynamic effects from our in-situ study of drug intercalation would be then explained in the context of the intercalation efficiency, dependent on the pH and temperature of the solution. Collected data would bring new insight into the explanation of mechanism of drug intercalation into the smectite clay and its dynamics.

## Keywords

smectite clay, fluorohectorite, intercalation, antibiotics, drug

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4.Michels, L. et al. Sci. Rep. 5, 8775 (2015).

POSTER

# 374 - SAXS ANALYSIS FOR CUBOSOMES: FROM THEORY TO PRACTICE

**SANTOS PALMA, Amanda (1); DIAS CASTRO, Raphael (1,2); MALHEIROS, Barbara (2); LOTIERZO, Mayra Cristina (2); CASADEI, Bruna Renata (1); RAMOS SOUZA BARBOSA, Leandro (1,2,3)**
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## Introduction

Cubosomes are nanoparticles with cubic inner structure composed by water channels and are used as a drug delivery system. It can be used to encapsulate drugs, improving the desired effects and minimizing the side effects. In order to determine the cubosomes' structure, one can perform SAXS (small-angle x-ray scattering) experiments [1]. The data show Bragg peaks that correspond to Miller indices and thus one can determine the cubosome structure as well as the lattice parameter [2]. In this study, the cubosomes will interact with ionic liquid ([C14mim][Cl]) and a cationic surfactant (TTAB) and observe via SAXS the interference in the structure.

## Methodology

To analyze the data collected, we will use a program made by Me. Raphael Dias de Castro called Scrypta [1]. The program is able to identify the Bragg peaks and assign Miller indices (h, k, l) to them and the interplanar distance (d). Finally, the program will identify the structure associated with those Miller indices. Besides, the program can also calculate the lattice parameter (a), which is the water channel size [2].

q = (2*π/a)*sqrt(h2+k2+l2) d = a/sqrt(h2+k2+l2)

## Results

This study is still under development, therefore the results are yet to be done. Here, we aim to observe the changes in the cubosome structure due to its interaction with the ionic liquid and the cationic surfactant. The cubosome structure can change as the interaction between the molecule and the lipid influences the water channel arrangement. It is valid to remember that this study is a revision of Mr. Raphael Dias de Castro dissertation.

## Conclusion

One can conclude that the diffraction theory can describe quite well the SAXS results for cubosomes.

**Keywords**
cubosomes, SAXS, TTAB, ionic liquid

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POSTER

# 285 - MONOCHROMATIC SANS INSTRUMENT AT THE TU DELFT REACTOR

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The TU Delft in the Netherlands operates a small 2.3MW research reactor, we are in the process of upgrading and adding a hydrogen cold source which will increase significantly our cold neutron flux. With this flux gain we are in the process of updating and upgrading a monochromatic SANS instrument. The detector will have a new 60x60cm 3He detector, velocity selector and a range of sample environment options.

The instrument is currently in commisioning and is expected to be operational at the end of the year.

I will present the status of the instrument, expected performance and also an overview of the expected science that we hope to use the instrument for. Furthermore I will detail how this will be available to the community. I will also briefly discuss the overlap with our spin echo SANS (SESANS) instrument which allows for the probing of larger structures up to the 10's microns.

**Keywords**
monochromatic, SANS, neutron

POSTER

# 281 - EVOLUTION OF DYNAMICS DURING SOFT-CHEMISTRY SYNTHESIS OF SILICA-SUPPORTED METAL CATALYSTS

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Supported catalysts where noble metals precursors are added during the soft-chemistry synthesis of the support have several advantages such as high dispersion and stability [1]. However, the introduction of metal ions into the sol-gel matrix is not straightforward, the metal precursors can aggregate and/or induce the gel to collapse [2]. To ensure the best interaction between the reacting species and high dispersion of metal precursors, the nanoscopic organization and mobility mechanisms of colloidal particles in presence of an additive should be revealed. We applied in situ X-ray photon correlation spectroscopy (XPCS) in the small angle scattering (SAXS) geometry to investigate the structural evolution and nanoscopic dynamics in silica metal gel at 11-ID beamline (NSLS-II) and Cateretê beamline (Sirius). For the pure silica samples as gelation occurs, the dynamics slow down, and the relaxation functions transform into compressed exponentials indicating a jamming transition occurring during the initial gel stages. At the late stage where the gel network formation matures, the dynamics are characterized by the slow ballistic regime due to the relaxation of internal stresses built into the sample at the gelation transition (Figure 1). The SAXS results obtained from the same measurements reveal that the silica gel is made up of highly branched clusters from approximately 33 nm in size. The Au induces an increase in the clusters size, the size of the scattering units is 50 nm. The presence of Au also modifies the dynamics of the silicate gels. Contrary to the pure silica, the Au containing samples exhibit compressed exponential decays after the gel point, no ballistic motion is observed. At a nanoscopic level, the presence of Au affects the strength of the internal stress centers, and consequently the aggregation process, but without leading to the gel collapse. XPCS is uniquely suited to capture the evolution of the structure and dynamics of such complex systems with length and time scales of particle motion extending from microns down to nanometers and from minutes to microseconds.

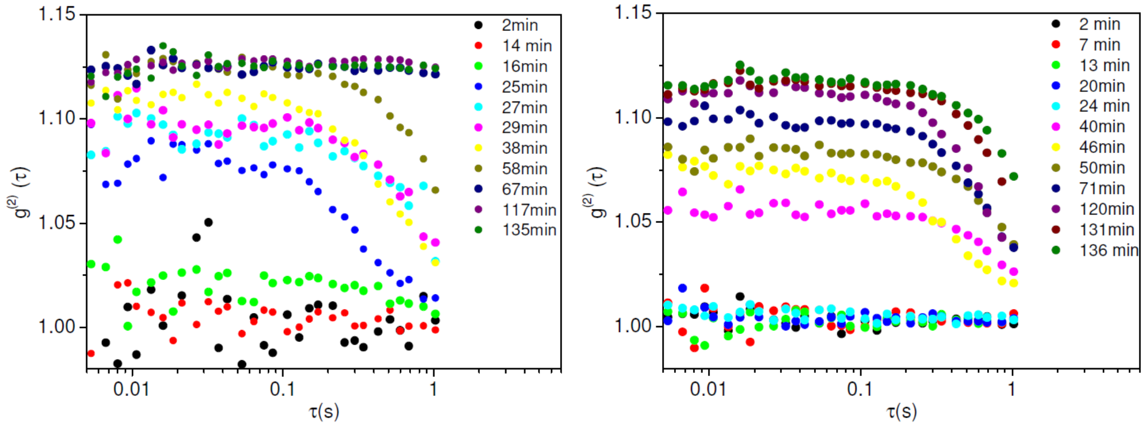

Figure 1. Correlation functions g(2)(t) at q=0.0089Å-1 during the gelation of (a) pure silica and (b) gold silica samples.

**Keywords**
XPCS, sol-gel, silica

**References**

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**Acknowledgements**
FAPESP, Sirius and NSLS-II

POSTER

# 197 - MULTIPHASE FORMATION BETWEEN SURFACTANT AND POLYELECTROLYTE COACERVATES IN BULK MIXTURES AND IN COMPLEX COACERVATE CORE MICELLE

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A wide range of complex coacervates are immiscible leading to the formation of multiple phases [1]. These systems, called multiphase complex coacervates, have caught the attention in the recent years mainly because of their potential for use as model systems for membraneless organelles and protocells [1]. To the best of our knowledge, these studies have only comprised systems formed by polyelectrolytes. Here we investigate the issue of miscibility in a system containing the cationic surfactant cetyltrimethylammonium (C16TA+) and two homopolymers with opposite charge, namely, poly(diallyldimethylammonium) (PDADMA+) and poly(acrylate)(PA-). This system leads to the formation of a multiphase complex coacervate with one of the phases rich in PA- + PDAMA+ and the other (less dense) phase rich in CTA+ + PA-, assembled as a Pm3n micellar cubic phase.

In addition, the substitution of the PA- homopolymer by a neutral-charged copolymer (e.g. poli(ethylene oxide)-b-poly(acrylate) (PEO-b-PA-)) in the mixture with C16TA+ confines the macroscopic phase separation to nanometric domains and leads to the formation of complex coacervate core micelle (C3M)[2]. Since the behavior of the coacervate in the C3M core reproduces the behavior of the coacervate in the bulk [3], we investigated how C3Ms are affected by a multiphase complex coacervation. The C3Ms formed by C16TA+ +PDADMA++PEO-b-PA- for systems with different proportions between CTA+ and PDADMA+, were investigated, keeping their charge equivalence. Two populations of C3Ms were formed: a population rich in PEO-PAA + PDADMAC with a hydrodynamic radius (RH) of 30 nm and another one rich in PEO-PAA + CTAB with a RH of 150 nm and a Pm3n micellar cubic phase core.

These findings reveal, for the first time, that there is multiphase formation between surfactant and polyelectrolyte coacervates, both in bulk mixtures and in confinement, in the form of C3Ms.

**Keywords**
Complex coacervate core micelles, multiphase complex coacervates, block copolymers, ionic surfactants, polyelectrolyte complexes.

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## Acknowledgements

LNNano/Brazil for cryoTEM analyses, C.L.P Oliveira, IF-USP for SAXS analyses and FAPESP for PhD scholarship (grant numbert 2020/16062) and financial support (grant number 2015/25406-5).

POSTER

# 401 - ADDRESSING THE ISSUE OF WATER CONTENT IN B- TYPE STARCH CRYSTALS: MIGHT SAX BE USED TO EXPLAIN THE STRUCTURAL CHANGES OF NANO STARCH CRYSTALS SUBJECTED TO ULTRASOUND AND HYDROLYSIS PROCESSES?

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A commercial potato starch sample was submitted to structural modifications using high energy ultrasound followed by acid hydrolysis and was characterized by powder X-Ray diffraction measurements. X-Ray diffraction patterns were described as B-type amylopectin and simulated using the Rietveld refinement Method. Based on this method, it was proposed an easy approach for estimating crystallite sizes and the amylose content. Apparent crystallite sizes was found to be stable after ultrasound processing, while crystallinity increased 10% after hydrolysis.

The crystallites of the commercial raw potato starch (Control), US, Hydrolyzed and US-Hydrolyzed samples were determined in order to illustrate the application of the method. It was verified that in both Control and Ultrasound-assisted processed potato starch the acid hydrolysis procedure promotes similar reduction in the crystallinity degree. Additionally, the Rietveld Method provided fine details of the hydrolysis effects in the B-type crystals, including the crystalline positions in which the water molecules are distributed in the unit cell: those intracrystalline water molecules are located in discrete pockets that defines the B-type starch lamellae. After hydrolysis, the relative intensity of this lamellar peak decreases, suggesting broken fibers toward the C-axis. This observation features a substantial advance, which opens the way for many more B-type starch investigations that take in account the crystallographic studies of this structure.

A particularly interesting advance for this study would be understanding, via Small Angle Scattering, how the observed changes in the water content inside this macromolecule unit cell (seen as the increased intensity in the 1 0 0 XRD peak) might be further explored in future works through SAX technique.

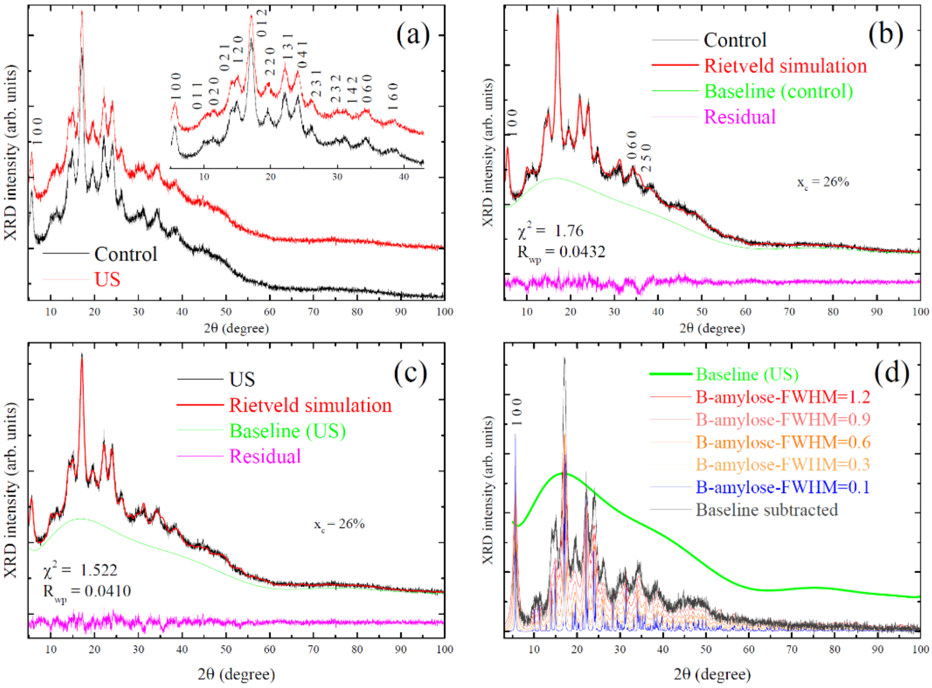

Fig.1

## Keywords

starch nanocrystals, XRD, Rietveld Method

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POSTER

# 203 - KWS-3 VERY SMALL-ANGLE NEUTRON SCATTERING FOCUSING DIFFACTOMETER AT MLZ

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KWS-3 is a very small angle neutron scattering diffractometer operated by JCNS at Heinz Maier-Leibnitz Zentrum (MLZ) in Garching, Germany. The principle of this instrument is one-to-one imaging of an entrance aperture onto a 2D position sensitive detector by neutron reflection from a double-focusing toroidal mirror. In current state, KWS-3 is covering Q-range between 3·10-5 and 3.5·10-1 Å-1 and used for the analysis of structures between 2 nm and 20 µm for numerous materials from physics, chemistry, materials science and life science, such as alloys, diluted chemical solutions, hydrogels and membrane systems. Within the last few years we have finalized several big "evolutionary" projects; we have completely re-designed and commissioned the main components of the instrument: selector area, mirror positioning system, main sample station at 9.3m and 1.7m, beam-stop system; implemented new sample stations at 10m, 4m, 3m and 2m, automobile position from 0.05 m to 0.40 m, second (very-high resolution) detector, polarization and polarization analysis systems; adapted the instrument to almost any existing/requested sample environment like 6-position Peltier furnace (-25°C to 140°C), high-temperature furnace (< 1600°C), cryostats/inserts (>20 mK), liquid pressure cell (<5 kBar/10-80°C), CO-2-/CD4 gas pressure cell (<0.5 kBar/10-80°C), humidity cell/generator (5-95%/10-90°C), magnets (horizontal < 3T, vertical < 2.2T), Bio-logic® multimixer stopped flow (5-80°C), rheometer Anton paar MCR 501 (tangential/radial) etc.

**Keywords**
KWS-3, VSANS

POSTER

## 427 - SANS DATA REDUCTION SOFTWARE QTISAS FRAMEWORK: CURRENT STATUS

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QtiSAS1 (previously QtiKWS) is the cross-compiled program designed for the graphical visualisation, reduction, analysis, and fit of data produced by a small-angle neutron scattering (SANS) instrument. Initially QtiSAS was developed to analyse data “produced” by SANS instruments of the Jülich Centre for Neutron Science JCNS at the high flux reactor FRMII at Heinz Maier-Leibnitz Zentrum MLZ in Garching (Germany), but most of tools could be used for data analysis generated by any SANS instrument or data having nothing to do with SANS.
Current status of the QtiSAS framework will be presented here.

### Keywords

SA(N)S Data Reduction, Fitting, Visualisation

### References

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POSTER

# 303 - SAXS DETERMINATION OF PORE SURFACE AREA IN METAL ORGANIC FRAMEWORKS

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Specific surface area on porous solids is key parameter for various application fields. Its reliable and fast determination is therefore crucial for materials development and product quality management. Well established methods like BET adsorption are the first choice for surface area determination. However, those experiments are time consuming and require lot of sample. Moreover, BET experiments are only sensitive to accessible surface area mostly in the mesoporous regime. Alternative methods like Small Angle X-ray Scattering (SAXS) arise as powerful tools for reliable and fast surface area determination.

This presentation evaluates in a rigorous way SAXS as an alternative approach for reliable and fast surface area assessment.

Based on our previous experience, we chose Metal Organic Framework (MOF) materials and specially Zeolitic Imidazole Frameworks (ZIF) as target for our experiments. We prepared ZIF8 (Zinc(methylimidazole)2) starting from 2 different ratios (Zn(NO3)2:2-metilimidazol) = (1:2) and (1:4) as a well-defined system with micropores and mesopores, for systematic SAXS and BET studies (nitrogen at 77 K). Also, ZIF-L (a MOF with no mesoporous structure) was used for comparison.

In fact, we demonstrate that the determination of specific surface area can be brought with SAXS to a new level, where parameters such as size of the probing adsorptive, its orientation and thus its effective cross-sectional area (when adsorbed on the surface) are no longer affecting the value of the specific surface area determined.

Furthermore, SAXS was shown to be significantly faster than gas adsorption. For the MOFs used, the study shows that SAXS does not require degassing and – along with analysis times of only few minutes per sample – provides an accurate and extremely fast, high-throughput approach.

This fundamental study can be considered a major step in enabling SAXS for reliable surface area assessment for applications both in nanoporous materials development and quality control, thus boosting SAXS for surface area determination in general, but in particular also for materials, where the usage of gas adsorption is restricted or not possible at all.

**Keywords**
surface area, porosity

POSTER

## 363 - COSAXS BEAMLINE AT MAX IV LABORATORY, FIRST COHERENCE AND SAXS RESULTS

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Complex and multifunctional materials are at the heart of many current scientific and technological advances, from new composites for energy storage to complexes formed in proteins. Structural and dynamical studies of relevant soft and hard matter are driving most of the recent efforts to understand these materials, of which Small Angle X-ray Scattering (SAXS) based techniques form a key method to characterise the nanostructures formed.

CoSAXS is a multipurpose beamline at the 3 GeV diffraction limited ring of MAX IV Laboratory-Sweden. The optical design delivers X-ray beams on the energy range 4 to 20 keV and 0.01% bandwidth with a photon flux estimated to be 1012 – 1013 ph/s. The coherent photon flux portion could be up to 10 % at 7.1 keV. The coherent nature of CoSAXS instrument has been demonstrated using ptychography and XPCS measurements.

At CoSAXS, the in vacuum SAXS Eiger2 4M detector can be translated along and perpendicular to the beam within a 15m vacuum vessel, whilst the in vacuum L-shaped WAXS Pilatus3 is fixed in one plane at the entrance to the vacuum vessel. The resulting q-range is approximately 6 x 10-4 < q < 6 Å-1 (from 1 μm to 1 Å d-spacings) in simultaneous USAXS or SAXS/WAXS detection. First results showing combined SAXS/WAXS data are also presented. Data handling and reduction is supported by multiple pipelines implemented at the beamline, capable of process data up to 500 Hz, to facilitate optimization and decision-making during experiments. It is also possible to develop tailored python-based routines for friendly data visualization and analysis.

CoSAXS started general user operation at the end of 2020. A number of experimental setups supporting solid state and solution scattering experiments have been implemented. Among them, a high throughput automated BioSAXS setup with Size Exclusion Chromatography (SEC) has recently fully commissioned. Time resolved scattering experiments have been successfully tested down to 2 milliseconds resolution, in laser-induced temperature jump studies in proteins in solution. A platform for the solution sample delivery within microfluidic chips has been developed (Adaptocell project). Future developments at CoSAXS will include the delivery of several complex sample environments, e.g. SUrF (combined UV-VIS,fluorescence spectroscopy with SAXS), a dedicated setup to applied medium magnetic fields (up to 3.5 Teslas) and combined in situ uni and bi-axial loading stages for characterization of nanostructured polymers and fibrils.

In conclusion, the CoSAXS beamline, now open for general users applications, offers numerous features that minimizes instrument background and provides stable optics and state of the art 2D detectors, for high quality measurements in a broad range of research and development fields.

**Keywords**

SAXS beamline, SAXS/WAXS, XPCS, Time-resolved solution scattering, complex sample environments

POSTER

# 256 - CHARACTERIZATION OF FLEXIBILITY OF THE GLYCOSIDE HYDROLASES USING SAXS

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The Glycoside Hydrolases (GHs) are responsible for the enzymatic deconstruction of complex carbohydrates. Most of the families of GHs are characterized by the conservation of the catalytic machinery and molecular mechanisms. Most of these enzymes comprise multidomain proteins linked together through peptides called linkers. In general, multidomain proteins show high flexibility. Research on mobility, structural determination, changes in biochemical conditions and mutual orientations of individual domains are extremely important as they become indicators for understanding them. The study of factors such as temperature and pH are of great interest as they are capable of altering enzyme activities. The analysis of solutions provides a broad understanding of the behavior of biomolecules, such as structural and functional information. Small-angle X-ray scattering (SAXS) is widely applied to obtain information from biological macromolecules, however, there are technical limitations that make it difficult to fully understand the sample characteristics during the analysis. A particular case is the inherent flexibility that samples may present. Conformational variety impairs the contribution of scattering by X-ray due to domain movements or flexible regions on the macromolecule. The use of Kratky (I(q).q2 vs q) and Porod-Debye (I(q).q4 vs q4) were done for the characterization of flexibility in GHs. The Glycoside Hydrolases were produced in the lab under the direction of Prof. Dr. Igor Polikarpov (Molecular Biotechnology group, IFSC/USP) and the SAXS data were collected on B21 SAXS Beamline on Diamond Source (UK).

**Keywords**
SAXS, glycoside hydrolases, flexibility

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POSTER

# 353 - COMBINING SANS, CRYO-EM AND COMPUTATIONAL MODELING TO REVEAL STRUCTURE OF HEPATITIS B VIRUS.

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The genetic material of viruses is typically protected in an icosahedral capsid, which is primarily assembled from over a hundred subunits of the same protein in a spontaneous self-assembly process. Due to the dynamic nature of self-assembly it is difficult to determine the interaction of capsid protein and nucleic acid even at the fully assembled state. Our research aims to provide a detailed understanding of how the RNA is incorporated into the capsid of Hepatitis B virus (HBV) and how the overall structure of capsid is affected by the presence of RNA. In order to address these questions, we developed a method combining contrast variation SANS, Cryo-EM and computational modelling. We used Bayesian statistical modeling to decompose profiles of protein and RNA from the contrast variation data. One of the advantages of Bayesian framework is the possibility of incorporating prior information (data from another SANS experiment) to guide inference process. However, from Cryo-EM we generated radial profiles, which were used as constraints in modeling of SANS data. The decomposed SANS profiles together with Cryo-EM radial profiles were subsequently used in SasView [1] to fit coarse-grained models. Based on the inferred structural parameters we were able to draw conclusions regarding protein and RNA interactions in virus capsid.

**Keywords**
Contrast variation SANS, Cryo-EM, Bayesian statistics

## References

[1] SasView version 5.0.4, https://doi.org/10.5281/zenodo.4467703

POSTER

# 430 - SASVIEW – A COLLABORATIVELY DEVELOPED DATA ANALYSIS TOOL FOR SMALL ANGLE SCATTERING

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SasView is a data analysis package for Small Angle Scattering, which primarily provides model fitting to 1D and 2D scattering patterns including fitting of polarized/magnetic neutron scattering data. There are also modules for performing P(r) inversion, calculating the scattering invariant, correlation functions and numerous auxiliary tools (e.g. scattering length density calculator). However, in the recently released version 5.0.5 [1] the generic scattering calculator tool has been overhauled and its capabilities significantly expanded to perform magnetic/polarized SANS computations.

SasView is an open source project hosted at GitHub, written in Python and C and allows for computations on CPU and GPU. The collaborative development model is designed to encourage and enable contribution from a wide range of contributors not necessarily with software development background. In addition, users of the software are encouraged to participate through bug reports, submitting code and by providing new models. SasView provides easy installation for major operating systems, user friendly GUI, command line interface, extensive model library and ability to accept user plug-in models.

The developer team currently hails from 7 large scale facilities (neutron and photon) and few universities. However, few have SasView as a major component of their job. Given the nature of software development this currently means most development occurs during code camps and hackathons.

In this poster we will discuss the current status and developments in SasView as well as future aspirations. We look forward to community input and discussion.

**Keywords**
Software, Data Analysis

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POSTER

# 307 - DENSS-MULTIPLE: AN AB INITIO RECONSTRUCTION METHOD USING CONTRAST VARIATION DATA

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Based on DENsity from Solution Scattering (DENSS, denss.ccr.buffalo.edu) algorithm, we developed DENSS-Multiple, a method to work simultaneously on multiple datasets from small angle neutron scattering (SANS) contrast variation data, it provides a single structural result that include all the information represented by different contrast. The resolution of results is usually improved compared to that of a single dataset. And more subtle features can be enhanced in the density map. We will discuss the test results on various examples including simulated and experimental data, its applications, and limitations.

**Keywords**
Lysozyme, Cubosomes, Nanostructured System

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POSTER

# 432 - INSERTABLE SAMPLE FOCUSED X-RAY BEAM SET-UP FOR LABORATORY (GI)-SAXS/WAXS BEAMLINES AND APPLICATIONS

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State of the art laboratory SAXS/WAXS beamlines are typically composed of X-ray beam delivery systems producing a low divergence beam using collimating or long focusing distance optics to achieve measurements of small scattering vectors using long sample to detector distances (about a meter or more). Such optical set-up can easily be adjusted to provide high useful flux for diluted solutions or low scattering contrast systems characterizations with a compromise in resolution. Change of measurement configuration is achieved by changing beam size at sample position from few hundred microns to about a mm2 together with a change of sample to detector distance.

While X-ray beam footprint for transmission scattering measurements can be controlled down to dimensions as small as 150 microns typically, useful flux is then significantly reduced in such conditions. A search for gain in photon density could then be required for time resolved applications such as when coupling X-ray scattering measurements with micro-fluidics sample environments for structural analysis of dynamic processes1.

We will be presenting an additional x-ray beam set-up producing a focused X-ray beam on sample, that could be automatically inserted in the incident beam path of the low divergence source-optic set-up of a laboratory SAXS/WAXS beamline. Short focusing distance X-ray beam set-up is made of a microfocus sealed tube point focus source coupled to advanced 3D multilayer optics mounted on automatized, motorized platform for unattended, quick change of measuring configurations.

Measurement examples including GIWAXS experiments, nanoparticle size measurement of dispersions, semi-crystalline polymer SAXS/WAXS mapping2, mesoporous zeolite and liquid crystal characterization will be presented illustrating the impact of gaining up to two orders of magnitude in photon density. Subsequent experimental times can be therefore shorten accordingly. Typical screening time in the second range can be now envisaged. Typical resolutions such as maximum particle sizes that could be achieved with such set-up will also be discussed.

## Keywords

Mapping, SAXS/WAXS, Microfluidics, GIWAXS

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POSTER

# 147 - SMALL-ANGLE SCATTERING CAPABILITIES AT LAHN

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The Argentine Neutron Beam Laboratory (LAHN) will be a national facility for the study and characterization of matter through state-of-the-art neutron techniques. It will make use of the cold and thermal neutron beams provided by the RA-10 reactor, currently being built in Buenos Aires, Argentina. LAHN will be a regional hub for neutron studies, the techniques and instruments being available to the international scientific community and industry.

Out of the five neutron instruments that will be commissioned at the initial stage, two are dedicated specifically to small-angle scattering. One of them is the former V4 instrument that functioned at the Helmholtz-Zentrum Berlin (Germany) until Dec 2019, a 40-meter-long instrument which is being transferred to LAHN after the shutdown of the BER-II reactor. It provides the option of using a polarized neutron beam and a chopper for time-resolved experiments. It will be available as a general-purpose SANS in the context of the LAHN instrument suite. A second SANS instrument will be devoted to the study of soft matter systems, and it will be based on the former SANS-II instrument that was operated at Paul Scherrer Institut (Switzerland). The neutron flux available for the instruments in their new location is expected to be higher than at their original placements.

The relevance of these instruments for the Argentine academic community is backed up by more than 20 scientific cases presented by researchers working in such diverse fields as porous and nanostructured materials, polymers and polyelectrolytes, biological membranes, vortices in superconductors, intelligent materials and biophysical systems, among others. A deuteration facility and a variety of sample environments are projected in order to respond to the broad scope of expected scientific needs.

A laboratory-scale SAXS instrument will complement the neutron small-angle scattering instruments, providing a wide variety of sample environments and capabilities for GISAXS measurements. LAHN expects to establish itself as a complement to other Latin-American large research facilities, such as SIRIUS synchrotron source, to promote the development of small-angle scattering techniques in the region. We review the small-angle scattering capabilities that will be available at LAHN and the characteristics of each instrument.

**Keywords**
SANS, SAXS

POSTER

# 136 - MICROSTRUCTURAL CHANGES IN BUILDING MATERIAL AFTER VARIOUS CONSOLIDATING TREATMENTS STUDIED BY SANS

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Stone or rendered facades of historical buildings often encounter loss of cohesion as a symptom of material deterioration after long-term weathering. This damage of material can be hindered using a conservation technology based on the application of a new transparent liquid binder to the weak surface. Special consolidating agents designed for this purpose contain nanoparticles that penetrate the degraded layer to an appropriate depth. Correctly performed impregnation treatment should strengthen the historic material without bringing adverse consequences in the material life cycle. Detailed knowledge of the microstructure of the material to be preserved is essential for the treatment design. One of the techniques able to deliver bulk information on the consolidation output is Small-Angle Neutron Scattering (SANS). Double-bent-crystal SANS facility MAUD of NPL CANAM (NPI Řež, CZ) was used for the investigation within Strategie AV21 program. The measured samples were lime mortars impregnated with three types of consolidants: nano-lime suspension (NL), silicic acid ester (SAE), and ammonium phosphate (AP) solution. The scattering can be ascribed to three populations of pores: the large pores, medium-size pores (thousands Å), and small pores (hundreds Å). Multiple scattering influence hinders detailed quantitative conclusions for large pores. Nevertheless, the scattering is different for various samples, mainly in the medium range of Q-magnitudes. Therefore, a different response exists for different treatments. While the non-treated sample and the sample treated with SAE-based product do not exhibit a difference, the NL treated sample shows a decrease in the medium-size pores volume fraction by 16%. A difference was observed also by the sample treated with AP solution. Medium pore size increased while their volume fraction decreased. Nevertheless, a change in the large pores was also observed. Finally, the modeled small pores remain unaffected by consolidating treatment.

**Keywords**
Small-Angle Neutron Scattering, consolidation, consolidating agents, cultural heritage

POSTER

# 264 - RELATIONSHIP BETWEEN MICROSTRUCTURE AND MACROSCOPIC PROPERTIES OF HYBRID MATERIALS FORMED BY NANOCELLULOSES AND SURFACTANT LAMELLAR PHASES

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Cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF) have been extensively investigated as potential rheological modifiers in different products1. However, its interaction and rheological effects have been barely studied in other organized systems such as those formed by the surfactant self-assembled structures2. In this regard, we studied the structural and rheological properties of systems composed by CNC and CNF suspensions into lamellar phases of dioctadecyldimethylammonium bromide (DODAB), a double-chain cationic surfactant. The CNC have sulfate groups on the surface, while CNF are carboxylated, so electrostatic interactions would be expected between the liquid crystalline structures and the cellulose nanoparticles. The hybrid materials were prepared with surfactant concentrations in the range of 30 and 80 % w/w and CNC/CNF concentrations between 1 and 5 % w/w or 0.1 and 1 % w/w, respectively.
Oscillatory-shear stress sweeps had showed a gel like structure and a viscoelastic behavior for all systems (lamellar phases and hybrid materials). The results of frequency sweeps in the linear viscoelastic region suggested that the addition of CNC and CNF had increased the materials stiffness, while flow curves indicated minor changes in the samples viscosities. For the hybrid materials, DSC analyses revealed minor changes at the transition temperature (Tm) associated with the Lβ to Lα lamellar phase transition. SAXS measurements showed a shift of the scattered peaks towards higher q values with the addition of nanocelluloses in all the systems, which suggests smaller repeat distance of the bilayers.

**Keywords**
Liquid crystals, nanocellulose, rheology

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## Acknowledgments

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POSTER

# 194 - SAXS STUDY OF SOL-GEL TRANSITION COUPLED TO SPINODAL DECOMPOSITION TO CONTROL THE HIERARCHICAL POROSITY OF MONOLITHIC ALUMINA

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The controlled formation of hierarchical porous structure on alumina monoliths through coupling of concurrent processes, sol-gel transition and spinodal phase separation, has been investigated by in situ small-angle X-ray scattering (SAXS) measurements. The addition of low molecular weight poly(ethylene oxide) (PEO) in the aluminum chloride aqueous solution induces the phase separation between aluminate gel and PEO-solvent. Time-resolved SAXS measurements revealed that in absence of PEO the nanostructural evolution during gelation is dominated by the Ostwald ripening process. As PEO is added, this coarsening mechanism that occurs during the first 6 min, is followed by the coalescence of phase separating domains during the late stage of spinodal decomposition. The effect of PEO in the gelation mechanism also directly influences the porous structure formed during calcination of alumina xerogel monoliths. The in situ SAXS monitoring during calcination evidenced that the mesopores formation follows the spinodal decomposition mechanism proposed by the Cahn's theory. Alumina with well-defined meso and macropores families, high specific pore volume (2.0 cm3 g-1) and surface area (252 m2 g-1) were obtained as result of the spinodal decomposition during the sol-gel transition followed by heating treatment.

**Keywords**
Alumina, Sol-gel, Spinodal Decomposition, in situ SAXS

POSTER

# 339 - STRUCTURE AND BIOPHYSICAL CHARACTERIZATION OF THE EXFOLIATIVE E TOXIN WILD TYPE AND MUTANT OF STAPHYLOCOCCUS AUREUS

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Staphylococcus aureus is a commensal and opportunistic bacterium that can infect a variety of hosts, including humans and different species of cattle, represents a global public health problem, and causes enormous damage to the livestock industry. Exfoliative toxin E (ETE) is a virulence factor that facilitates the spread of the pathogen by inducing the generalized detachment of the granular layer of the epidermis in sheep. This serine protease is inactive in its native state. Occasional secondary interactions, which are still unknown in this system, and uncommon between serine proteinases induce specific hydrolysis of the peptide bond between Glu381-Gly382 of Desmoglein 1 (Dsg1). A better understanding of the mechanism of action of ETs is necessary to develop strategies to inhibit the pathogen. This work seeks to elucidate the mechanisms and modes of action at the atomic level, in interactions with the substrate Dsg1. For this, the native (ETEwt) and mutant (ETEmut) protein (Ser219Ala) were expressed in E. coli BL21 (DE3) -T1R. Subsequently, they were purified by gel filtration, on a Superdex® 75 10/300 GL column in 20 mM MES buffer pH 7.03, and pH 5.51. We analyzed the proteins with by circular dichroism, dynamic light scattering, and differential scanning calorimetry. its secondary structure, showing that both proteins have a predominance of random coil, in the particle size for the two proteins was 2.093 ± 0.3 (r.nm). Thermal unfolding experiments using circular dichroism and differential scanning calorimetry allowed us to establish the values of the melting temperature (49.0 ± 1.4), the calorimetric enthalpy (220 ± 50), and the Van't Hoff enthalpy (270 ± 70). Crystals obtained from the proteins were diffracted in the MANACÁ line of Sirius, from Campinas-SP. The refinement analysis was performed with the REFMAC5 and PYMOL programs, resulting in the final resolution of 1.6 Å for ETEwt and 2.4 Å for ETEmut, both forming dimers. Investigations by low angle X-ray scattering (SAXS) were carried out to determine the oligomeric state of the ETEwt and ETEmut proteins in solution and whether it corresponds to that obtained in crystallographic assays. Data integrations were processed and normalized in absolute scale with the SUPERSAXS program. The treated curves were analyzed with the ATSAS software package. The SAXS analyzes showed that the proteins have, mostly, a monomer-dimer balance, which varied depending on the concentration of the protein (5 mg / mL and 24 mg / mL) as well as the conditions of the buffer used where the pH and ionic strength were varied. The main result of the SAXS data is the indication of the presence of oligomers in the system, depending on the concentration of the sample. For more precise studies, we are studying the possibility of stabilizing the protein in a specific configuration, either monomers or dimers, to repeat the experiments and confirm the results.

**Keywords**
Staphylococcus aureus, exfoliative toxin E (ETE), X-ray crystallography, SAXS.

POSTER

# 381 - INFLUENCES OF SYNTHESIS PARAMETERS ON THE COLLOIDAL STABILITY OF COBALT FERRITE NANOPARTICLES IN MAGNETIC FLUIDS

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The addition of solids to coolant fluids increases these composites' heat exchange capacity; however, the colloidal stability becomes a significant challenge in obtaining an efficient heat exchange nanofluid. This work presents a study of the influences of synthesis parameters on the colloidal stability of magnetic nanoparticles (MNP) of cobalt ferrite (CoFe2O4) dispersed in water. We reported that different crystallite sizes (Dxrd 1.5 - 15 nm) were found depending on the synthesis conditions, but the structural differences did not influence the properties that control the colloidal stability. The hydrodynamic diameter (Dh) of MNP obtained by dynamic light scattering (DLS) shows no significant differences between Dh values found for the synthesized MNP prepared from different precursors (Dh = 65.7-67.8 nm, with PDI $\leq$ 0.17). Irrespective of the sample, results suggest that the primary particles of MNP form an aggregate in 1 mmol L-1 of NaCl solution (pH 10, at 25 °C). This behavior was confirmed by a small-angle X-ray scattering (SAXS) profile which showed two distinct power-law regimes. The scattering of primary MNP, which appeared in the highest q region (1.5 > q > 0.2 nm-1), had well-defined and smooth surfaces, following the classical Porod power-law, I(q) $\propto$ q-4.0. In the mean interval of q (0.07-0.1 nm-1), the scattering presented a power-law q-1.92, suggesting the existence of mass fractal aggregates formed by the clustering of primary MNP. The fractal dimensionality, df, indicated the MNP clusters formed a relatively dense structure, characteristic of reaction-limited cluster aggregation (RLCA). The mass fractal model fitting of the SAXS data indicated an average radius (rp) of 6.4 nm, in good agreement with transmission electron microscopy (TEM). This study evaluated the influence of different precursors and temperatures on the synthesis of MNP used to formulate magnetical fluids dispersed in water.

**Keywords**
magnetic fluids, two-step nanofluids, complex fluids.

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POSTER

# 345 - STRUCTURAL INVESTIGATION OF THE GELATION DYNAMICS OF COLLOIDAL SILICA

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Silica gels have a multitude of different applications in different areas such as drug encapsulation, matrix for production of metallic nanoparticles, fillers in cosmetic products and in oil recovery for plugging of high permeability zones. Colloidal sodium-silicates consist of anionic SiO2 particles and Na2O dissolved in water. As the electrolyte content of the solution is increased, for instance by adding salts (e.g. NaCl), the particle repulsion is screened and binding among the particles occur, causing gelation. The gelation is also influenced by other factors, such as temperature, solid content, divalent ion concentration and shear. We have investigated the structuring of colloidal silica using combined Small Angle X-ray Scattering (SAXS) and rheometry during gelation. Preliminary analysis of the results indicate that the gelation is most sensitive to changes in the salt concentration, compared to temperature, shear rate and solid content. Similarly, the rheological properties are also sensitive to the salt concentration, however they are also sensitive to temperature in an extent not observed for the structure of the gel.

**Keywords**
Colloidal Silica, Gelation, RheoSAXS

POSTER

# 198 - TEMPORAL EVOLUTION OF THE ASSEMBLY OF CELLULOSE NANOCRYSTALS AT MEDIUM MAGNETIC FIELDS

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Cellulose Nanocrystals (CNCs), given their favorable macro and nanoscopic physical and chemical properties, have been vastly investigated for a broad range of innovative and sustainable applications [1]. Some of these properties are directly dependent on their ordered assembly, as a consequence, the control of its alignment and 3D structure is of much interest both from the academic and the industrial side. A promising idea is to utilize external magnetic fields to align the CNC material in a controlled way. The initial work of Sugiyama et al. [2] concluded that cellulose fiber crystals oriented themselves such that their long axis is perpendicular to the direction of the field. Since then, the response of CNCs solutions exposed to magnetic fields have been extensively studied [3][4]. De France et al. [4] demonstrated that CNCs are capable of anti-aligning with respect to the magnetic field with weak strengths (0-1.2 T) over short time scales (<200 min) depending on the water to cellulose concentration. They also discovered that the ordering occurs in two stages: (1) partial alignment within minutes, (2) slower subsequent movement until a stable state.

In this work, we present a study of the magnetic alignment of CNCs employing simultaneously small and wide angle X-ray scattering measurements. The experiments were carried out at the CoSAXS beamline in the MAXIV Laboratory. A newly developed magnet sample environment capable of working with that reaches fields >3 T [5] was implemented. The SAXS measurements reveled clear signs of perpendicular cellulose alignment with respect to the magnetic field, consistent with the literature. The dynamic of this alignment could be categorized into three stages. More interesting, the calculations of the order parameter ”S” revealed that the orientation does not follow a symmetrical magnetic field-time correlation, that is to say, the orientation is faster while increasing the magnetic field than decreasing it, thereby showing a memory behaviour. The SAXS measurements exhibit the expected chiral cellulose plane rotations and suggest a 2D alignment of the CNCs at the atomic level. Overall, the displayed behaviors shows that utilizing medium-to-high magnetic fields is a favorable concept to tune CNCs aligned in a controlled way.

**Keywords**

Cellulose Nanocrystals, Magnetic Alignment, Orientation Dynamics, X-ray scattering

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POSTER

## 332 - EFFECTS OF TEMPERATURE ON THE STRUCTURE OF PLA-PEO-PLA TRIBLOCK COPOLYMER HYDROGELS

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ABA block copolymer gels have gained much attention due to their tunability to form associative networks of micelles over the critical micelle concentration by varying the block chain lengths and ratios, which could in turn determine the intrinsic properties of hydrogels. Poly(lactide)-poly(ethylene oxide)-poly(lactide) (PLA-PEO-PLA) has been extensively investigated for biomedical applications, due to the good biocompatible nature and biodegradability of PLA blocks. PLA-PEO-PLA triblock copolymers have been thoroughly studied about the effects of block length, polymer concentration, and stereochemistry on their self-assembly behavior in aqueous solutions. However, few studies focused on the effects of varying the gelation temperature on the structural properties. The nano- and microscale structural features could be diversified that are dependent on the gelation temperature. In this work, PLLA-PEO-PLLA triblock copolymer hydrogels were examined by Small-Angle X-ray scattering (SAXS) and confocal microscopy to study the influence of varying gelation temperature on the nano- and microscale structure of hydrogels. The scattering profiles suggest the existence of nanoscale micellar structures and the corresponding model fitting results characterize the length scale and geometrical shape of micelles. The predominant thickness of the shell compared to the core is due to the initial difference in stoichiometry during the preparation and the intrinsic properties of the two block chains shown in the solvent. Copolymer gels were found to preserve larger nanoscale structures at 80 oC than those at lower temperatures. Confocal images verify a large number of water-filled pores and internal channels running through the gel matrix, which could be important for biomedical applications for the transport of drugs. Although the wide size range of polydisperse aggregates from about one to hundreds of micrometers shown in confocal microscopy, it suggests the size difference of microscale structures of gels at varied temperatures, indicating that the formation of aggregates is a thermally favored process. This work could provide the potential approach to design biocompatible copolymer gels with tunable nano- and microscale structures for drug delivery and tissue engineering by controlling the gelation temperature.

**Keywords**
Hydrogel, Block copolymer, Gelation temperature, Microstructure

POSTER

# 328 - DOMAIN CONFORMATION OF MULTI-DOMAIN PROTEIN ER-60 STUDIED WITH HYBRID APPROACH OF COARSE-GRAINED SIMULATIONS AND SMALL-ANGLE X-RAY SCATTERING

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Small-angle scattering (SAS) profiles reflect structure of biomolecules in aqueous solution. For flexible biomolecules, crystal structures do not necessarily match their structures in solution. Thus, it is interesting to model molecular structures that match a SAS profile and compare them to their known tertiary structures.

However, there is not always a single molecular structure that matches a SAS data. Therefore, a possible strategy is to collect as many molecular structures as possible that match the SAS data and investigate their common features. Coarse-grained molecular dynamics simulation is a powerful technique to search for physically reasonable molecular structures with high efficiency. Compared to atomistic molecular dynamics simulation, coarse-grained simulation is more prone to transitions between several stable structures because coarse-grained simulation ignores tiny local minima of a free-energy landscape.

In this study, we studied structure of a multi-domain protein ER-60 using coarse-grained molecular dynamics simulation and small-angle X-ray scattering (SAXS) profile. ER-60 is composed of four structural domains: a, b, b', and a'. This protein has reactive cysteine motifs, and there can be two types of ER-60, oxidized or reduced, depending on whether the motifs form disulfide bonds. We performed structural modeling for each type of ER-60 and compered with a known crystal structure, where ER-60 forms "U-shape" [2].

From the snapshots of the molecular dynamics simulations, we collected total of 230 and 1,572 structural models matching a SAXS profile of the oxidized ER-60 and the reduced one, respectively [3].

Compared to the crystal structure, position of the a domain was different between our structural models and the crystal structure for both oxidized- and reduced ER-60. This suggests that the structure of ER-60 in aqueous solution is different from the known crystal structure.

**Keywords**
molecular dynamics simulation, protein disulfide isomerase, small-angle X-ray scattering

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POSTER

# 142 - SOLUTION FORMS OF TYPE I COLLAGEN STUDIED BY SAMLL ANGLE X-RAY SCATTEREING

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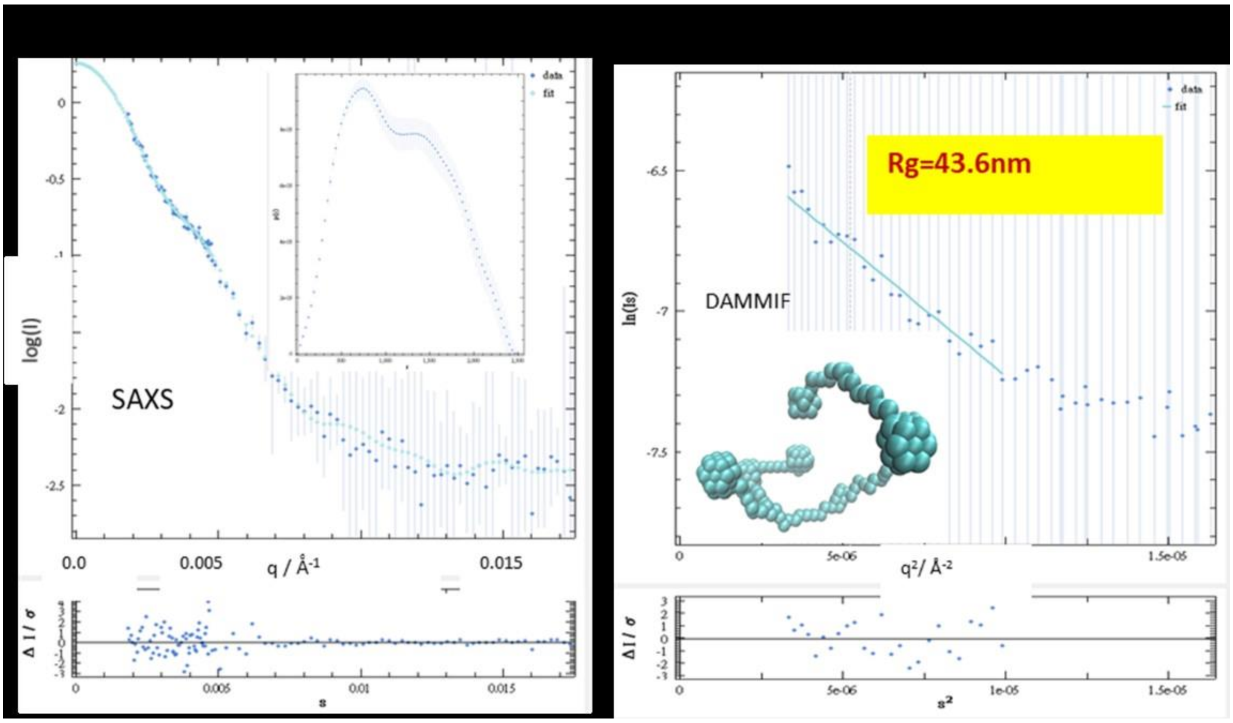
Collagen molecules, tropocollagens, comprise three left-handed helices of polypeptide strands (2α11α2) and twisted together into a right-handed coil for a triple helix. Up to date, there is no solution conformation of a single tropocollagen available. In this work, structural information of type I tropocollagen (bovine skin based) in acid solution with pH dependence is studied using the biological small- and wide-angle X-ray scattering beamline at the 3.0 GeV Taiwan Photon Source of the National Synchrotron Radiation Research Center. Concomitant SAXS-WAXS data are collected from the sample elution with an online size exclusion chromatography (SEC) and simultaneously monitored by the time resolved UV/vis absorption spectra, which promise the cosistent molecular weight and high concentration at the probed moments. In the SEC-SAXS-UV/vis measureemnt, the results show two monomer forms of the tropocollagen with the gyration radius Rg 75.6Å and 46.3 Å by polymer based and silica based types of SEC. The incorporated meaurements of diferential refractive of index (dRI), dynamic light scattering (DLS) and multi-angle light scattering (MALS), together indicated the molecular mass Mw 252 kDa and 320kDa, and the hydrodynamic radius Rh 21 Å and 24 Å of the collagen. The rod shape model suggests the dimension of collagen in length and diameter (L, D) are (169nm, 8.6nm) and (210nm, 9.3nm). Furthermore, the SAXS profile is simulated with the collagen structure from the Protein Data Bank (3HQV) by the Crysol method. The deduced gyration radius is 86.6 Å.



## Keywords

SAXS, collagen

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POSTER

# 185 - SOLUTION-STATE ANALYSIS OF HUMAN TRNA GUANINE TRANSGLYCOSYLASE USING SMALL ANGLE X-RAY SCATTERING

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In addition to the four canonical nucleosides adenosin, cytosin, uridin and guanosin, RNA molecules contain a wide variety of post-transcriptionally modified nucleosides. Among them, transfer RNAs (tRNAs) are the most heavily modified. The enzyme tRNA guanine transglycosylase (TGT) is a tRNA-modifying enzyme introducing queuosine, an extensively modified guanosine derivative to the anticodon of G34U35N36-tRNAsAsp,Asn,His,Tyr . Queuosine (Q) occurs in both eukaryotes and bacteria and, located at the "wobble" position, modulates protein translation.[1,2]

Eukaryotic TGT is a heterodimer and we recently published its crystal structure in complex with a short RNA mimicking the anticodon stem loop.[3] Since then, a structure of the TGT heterodimer alone was also published.[4] While instructive, several questions were left unanswered due to the inherit limitations of protein crystallography: The two subunits of the dimer are angled differently in both crystal structures, suggesting that the dimer arrangement might be flexible in solution. In addition, no density was measured for one of the N-terminal regions (10 amino acids) and a 30 amino acid loop, most likely because both regions are inherently disordered in solution. Using small angle X-ray scattering in combination with multi-angle light scattering and dynamic light scattering, all coupled to size exclusion chromatography, we characterized the TGT heterodimer in solution and analyzed its conformational spread.

**Keywords**
Protein Structure, SEC-SAXS, RNA-binding protein, flexibility

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POSTER

# 380 - CHARACTERIZATION BY SAXS OF THE POROUS STRUCTURE OF LA0.75SR0.25CR0.50MN0.50O3 SYNTHESIZED BY THE MICELLAR SOL-GEL METHOD AND CALCINED AT 1000 °C

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Producing and characterizing the porous structure of materials is extremely important.The use of these materials in electrodes of solid oxide fuel cell (SOFC) is advantageous. This device supplies electrical energy most efficiently and is an environmentally friendly. The electrode materials need to have porous and an optimized porous structure for the insertion of fuel and oxidant gases and for materials to provide a greater number of active sites for the electrocatalytic reactions of these gases.

For all these reasons, this work aims to produce and characterize the material La0.75Sr0.25Cr0.50Mn0.50O3. The material was produced by the micellar sol-gel method with structure - directing (Pluronic® P123) and - expanding agents (1,3,5-triisopropylbenzene - TIPB)[1]. It is characterized by the technique of small angle X-ray scattering (SAXS).

First, it was added Pluronic® P123 and TIPB (mass ratio 1:1) in the acid dispersant ([HCl] = 2M). Then the reagents of the cations of interest were added and then the pH control with NH4OH ($3 < pH < 4$). Subsequently, the mixture in an autoclave underwent hydrothermal treatment (80 °C/48 h). Then, the material was dried (60 °C/24 h) and calcined (1000 °C/4 h).

The SAXS equipment is the Nanostar model (Bruker). It has a Genix 3D microfocus source (Xenocs) and a two-dimensional X-ray detector, Vantec 2000 (Bruker). The instrument covers the scattering vector range between 0.01 and 0.35 Å-1. The measurement was performed at room temperature.

Both the synthesized and calcined sample SAXS curves have a large slope for small values of the scattering vector (q) (Fig. 1). That indicates the presence of particle agglomerates. Furthermore, another characteristic of the synthesized curve is the presence of a peak (q = 0.054 Å) that indicates the ordering of the pores filled by the agents. However, this peak is not observed in the calcined curve. In other words, the act of calcining collapses this ordering.

Moreover, the Porod region of the calcined sample is delimited by . Thus, it encompasses objects of nanometric dimensions (~ 4 and 5 nm), that is, dimensions of mesopores. Furthermore, the value of the Porod coefficient is –4 which means that the material is a two-phase system with an abrupt interface between the two phases.

Through the invariant (Q = 1.7.10-4 arb. u. Å-3) and the Porod constant (Kp = (2.4 ±0.1).10-6 arb. u. Å-4 ), it was calculated the specific area (S/V) of the material (S/V = Π.Kp/Q) which is (4.4±0.2).10-2 Å-1 . As the calcined material is in fact a two-phase system with an abrupt interface (inorganic material with porosity), the specific area represents the area of the mesopore-material boundary per unit volume.

The material was produced and characterized. A porous material was obtained, with mesopores and with a specific area around 0.04 Å-1.

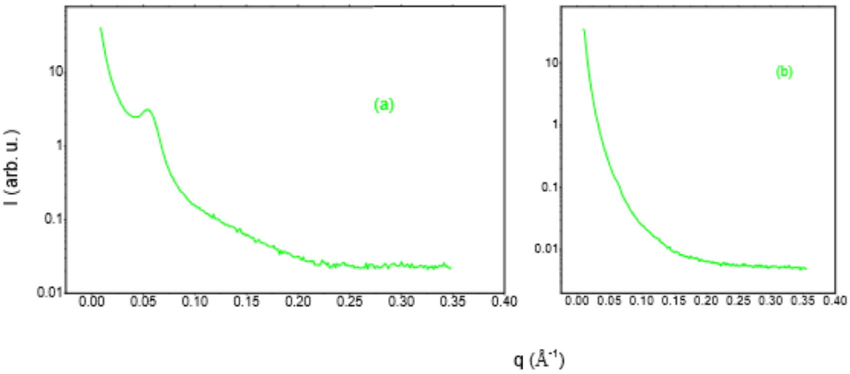

Figure 1 – SAXS graphs. (a) As-synthetized and (b) calcined sample.

## Keywords

Micellar Sol-Gel Method, Porous Structure, Pluronic® P123, SAXS, SOFC.

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## Acknowledgements

I thank FAPESP (process: 2013/03257-2) for the financial support.

POSTER

# 296 - COMPOSITES OF BACTERIAL CELLULOSE AND LAPONITE AS CONTROLLED DELIVERY SYSTEMS OF CIPROFLOXACIN

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Bacterial cellulose (BC) is formed by nanocellulose with three-dimensional network-like structures at the nanometer scale and presents interesting properties for biomedical use such as high purity and biocompatibility, large porosity and high surface area [1], [2]. In drug delivery systems, the BC exhibits burst release behavior releasing about 70-80% of the drug in less than 15 minutes [3]. Obtaining composites with layered matrices, such as laponite, can modify the structure of BC films and influence characteristics such as intumescence and direct interaction with the drug, through the surface charges of its layer, which can result in a more gradual release profile [4]. Laponite (Lap) is a layered clay of synthetic origin, belong to the smectite family, and has good dispersion in water and a small crystallite size, ideal for obtaining nanocomposites [5]. The main objective of the work is to obtain and characterize nanocomposites using BC and Lap, with different contents of the clay, to study the structure/release correlation of the drug ciprofloxacin. SEM results (Fig 1.) show that the BC fibers have an average diameter of 59.8 nm (± 14.0 nm) and in the BC/Lap 15% composite the fibers are also in this magnitude (72.5 ± 23.7 nm). On the surface of the BC films and after the addition of different clay ratios (15, 30 and 50%) small granules are superficially observed on the surface, indicating a dispersion of the clay throughout the fibers and the formation of aggregates as the clay content increases. The Ultra Small Angle X-ray Diffraction (USAXS) patterns were used to determine the dimensions of the fibrils in the cellulose. The measurements were performed at Cateretê beamline (Sirius). Information about the cross-section of the fibrils bundles was obtained using the Guinier approximation considering scattering for long rods (Fig2). The critical radius of the scattering element was obtained from the slope of the ln(qI(q)) x q 2. Two populations of fibrils were identified, the cross-sectional dimensions increased with the introduction of laponite [6]. The obtained dimensions were 6 nm x 52 nm and 10 nm x 74 nm for BC and BC/Lap 50% respectively. In the FTIR (Fig3) it is possible to note bands at 2900 cm-1 in all materials and at 1010 cm-1 in the composites corresponding to -CH2 groups present in the cellulose and Si-O groups present in the Laponite [7]. Cell viability tests (Fig4) indicate that all the materials obtained in the present work present viability above 70%, thus indicating that the films obtained do not present cytotoxic behavior [8]. In the water vapor permeability tests (Fig5) a reduction in permeability is observed due to the addition of clay, the BC/Lap 5-50% composites show a significant difference compared to BC, indicating that the presence of clay can clog the pores of the films and hinder the passage of water vapor through the material. Finally, results of adsorption kinetics (Fig6) indicate that the BC/Lap composites have a higher affinity for the drug compared to BC and consequently increase the adsorption capacity of the material.

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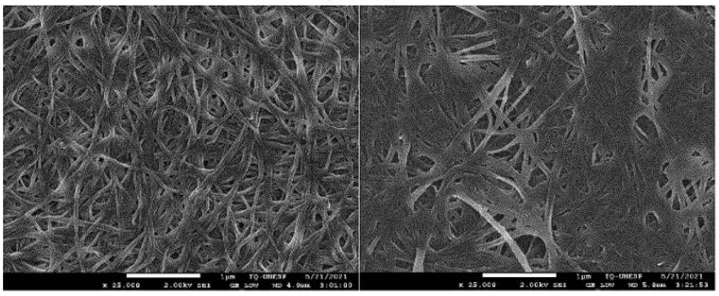

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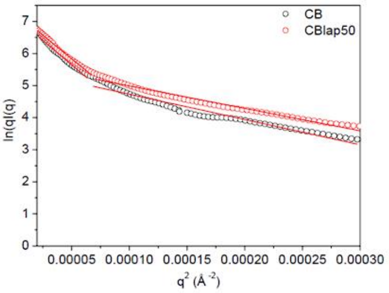

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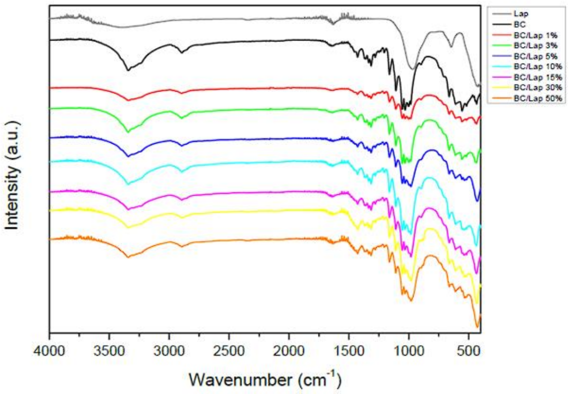

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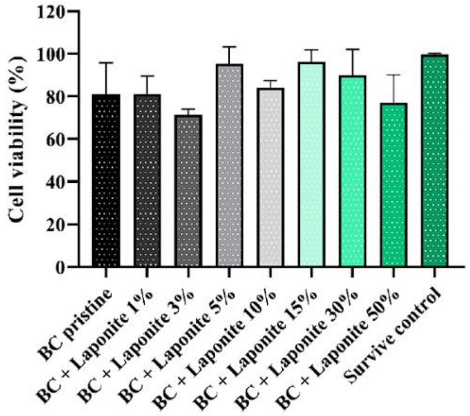

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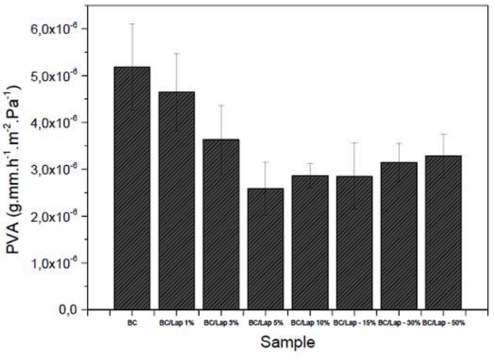

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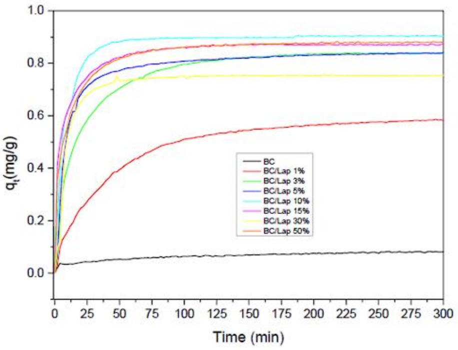

Fig 1. Scanning Electron Microscopy images BC film (left) and BC/Lap 15% (right).
Fig 2. Guinier plots for bacterial cellulose (Black) and BC/Lap 50% (Red).
Fig 3. Infrared Spectrum of Lap (Grey), BC (Black), BC/Lap 1% (Red), BC/Lap 3% (Green), BC/Lap 5% (Blue), BC/Lap 10% (Cyan), BC/Lap 15% (Magenta), BC/Lap 30% % (Yellow), and BC/Lap 50% (Orange).
Fig 4. Cytotoxicity evaluation of different BC/Laponite biocomposites on HDFa cells.

Cell viability (%) was determined by colorimetric assay using MTT.
Fig 5. Water vapor permeability (WVP) values of control and nanocomposite films using different amounts of BC, BC/Lap 1-50%.
Fig 6. Adsorption kinetics of the drug Ciprofloxacin on BC, BC/Lap 1-50%.

**Keywords**
Bacterial cellulose, laponite, nanocomposites, drug delivery system

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POSTER

# 410 - SIMULTANEOUS SAXS/WAXS INVESTIGATION OF 3D PRINTED PLURONIC-BASED HYDROGELS

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3D printing has revolutionized the fabrication of polymer-based devices in several industrial fields. However, in the biomedical area, 3D printing has not yet reached its full potential due to limitations regarding the printable materials available. Several aspects, such as biocompatibility, mechanical performance, and chemical composition should be considered simultaneously when selecting a printable material. Pluronic, which is a block copolymer surfactant made up of poly(ethylene glycol) (PEO) and poly(propylene glycol) (PPO) is a promising material for printing flexible biomedical devices due to the formation of a supramolecular micellar nanostructure. However, the leaching out of Pluronics from the devices might lead to toxicity. One interesting alternative to overcome this matter is functionalizing the Pluronic chain-ends to produce crosslinked supramolecular networks.

In this work, we investigated by simultaneous SAXS/WAXS the supramolecular structure of 3D printed hydrogels formed by chain-end functionalized Pluronic F127. The experiments were performed at the CoSAXS beamline, at MAXIV laboratory (Lund, Sweden), using a wavelength of 1Å and a sample-detector distance of 3.5 m for the SAXS detector and 0.5 m for the L-shaped WAXS detector. The q-range covered was $0.05 \leq q \leq 18$ nm-1. The 3D printed objects were scanned in a 1x1 cm2 area with an x-ray beam of 150 x 150 mm2. The exposure time was 100 ms.

Initially, dimethacrylate-terminated Pluronic (F127-DMA) hydrogels were 3D printed via semi-solid extrusion using 30 wt % solutions, and photocrosslinked using visible light afterwards. The SAXS (Figure 1a) and WAXS (Figure 1b) results show that the PEO phase of the hydrogels are semicrystalline, and a lamellar structure is produced. By increasing the methacrylation degree, from 57 to 98 mol%, both the degree of crystallinity and the periodicity of the lamellar structures are reduced. Moreover, the shearing caused by the extrusion during printing seems to induce more ordered supramolecular structures.

Subsequently, hybrid poly(2-hydroxyethyl methacrylate) (PHEMA)-based hydrogels containing 10 wt% of ditriethoxysilyl-terminated Pluronic (F127-DTES) were 3D printed using digital light processing. The SAXS (Figure 1c) curves showed two wide and overlapped correlation peaks with q-maximum values of 0.45 nm-1 and 0.83 nm-1. However, WAXS (Figure 1d) data clearly show that samples are amorphous, suggesting the occurrence of isotropically distributed micelles. The addition of 1 3-mercaptopropyltrimethoxysilane (1 wt%) to introduce thiol groups onto the hydrogels (PHEMA-SH) has led to the formation of randomly distributed thiol-containing silsesquioxane aggregates. Moreover, the substitution of F127-DTES by F127-DMA resulted in a similar isotropic distribution of micelles, however, with a reduced correlation distance, which suggests that methacrylate-based crosslinking modifies the intermicellar distances.

In conclusion, these results show that irrespective of the printing method, the use of low concentrated solutions allow the retainment of the micellar structure upon crosslinking. On the other hand, with increasing concentrations, from 10 wt% to 30 wt%, the extensive crosslinking density disrupts the micelles and the supramolecular arrangement, leading to typical semicrystalline lamellar structures in the dried 3D printed hydrogels. Further studies are under development to understand the effect of extrusion-based printing on the supramolecular structure of 3D printed F127-DMA hydrogels in both hydrated and dried states.

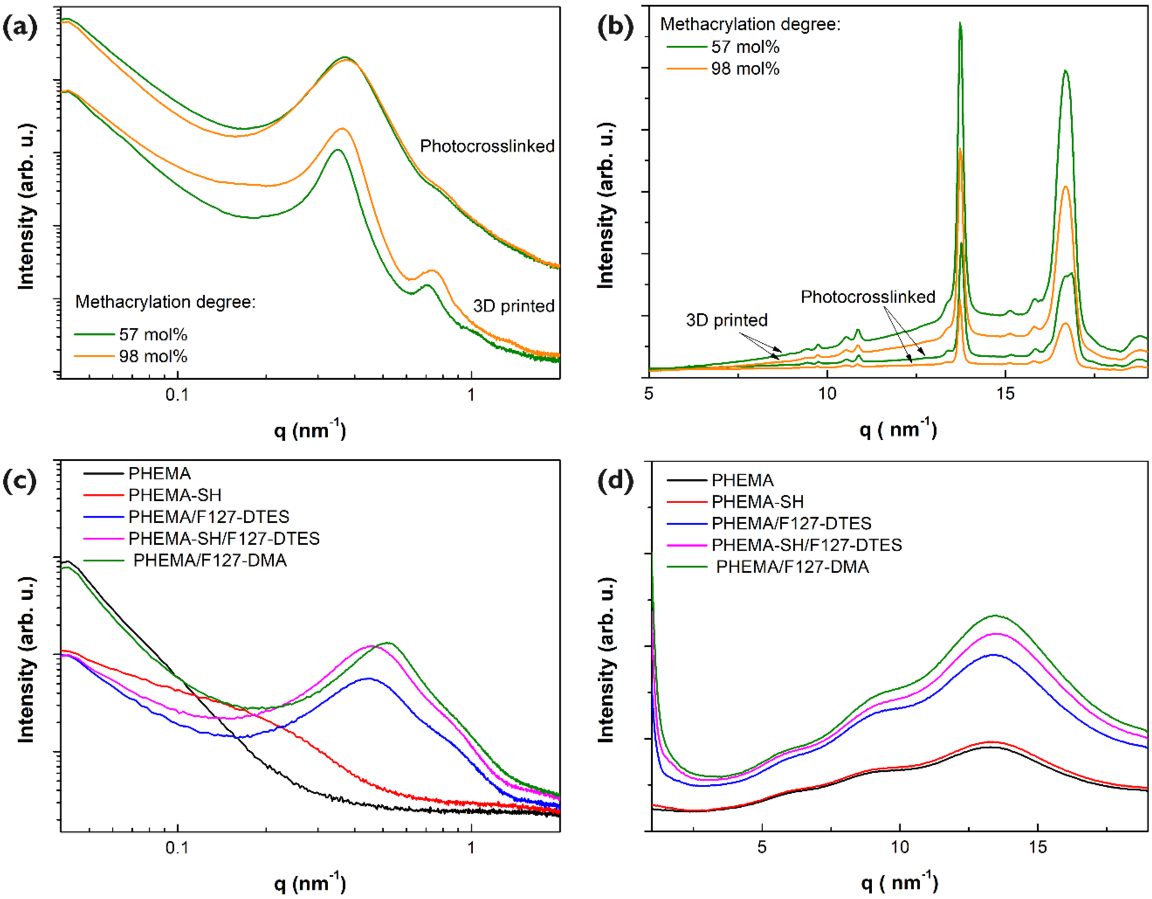

**Figure 1 –** (a) SAXS and (b) WAXS curves of 3D printed hydrogels obtained by semi-solid extrusion of 30 wt% dimethacrylate-terminated Pluronic (F127-DMA) solutions. (c) SAXS and (d) WAXS curves of 3D printed hydrogels obtained by digital light processing of poly(2-hydroxyethyl methacrylate) (PHEMA)-based hybrid resins containing 10 wt% ditriethoxysilyl-terminated Pluronic (F127-DTES).

## Keywords

Biomaterials, 3D printing, Pluronic, micelles, hydrogels

POSTER

# 393 - SAXS STUDY OF NANOSTRUCTURAL CHANGES IN SILOXANE-PEO-PLA HYBRIDS BEFORE AND AFTER RELEASE OF PENICILIN G INCORPORATED IN THESE SYSTEM

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Recently, a new PLA-Siloxane-PEO hybrid presenting covalent bonds between polymers chains and siloxane nodes has been developed in our group1. In addition to the absence of brittleness due to the low crystalline character of PLA, this biocompatible material exhibits a fantastic resistance to PLA degradation in aqueous medium. In this work, a Small-Angle X-ray Scattering investigation of the nanostructural changes occurring after release in aqueous medium of the water-soluble Penicilin G (Pen G) incorporated in this system has been performed. The study has been done by changing the PLA:PEO weight ratio (30-70, 50-50 and 70-30). Lorentz-corrected Small-Angle X-ray Scattering patterns of hybrids before immersion in aqueous medium showed the presence of two convoluted peaks. The peak centered at lower q-values has already been observed at similar position for siloxane-PEO hybrids (0.15 Å-1) and originates from the spatial correlation between the siloxane nodes located at polymer chains extremities 2. From comparison with the SAXS curve of neat PLA it is possible to attribute the peak centered at larger q-values to the long period of lamellae located inside PLA crystallites. In order to obtain information associated to the long period of PLA crystalline phase, we used the classical method of investigation of crystalline polymers which consists of determining, from the Fourier-transform of the Lorentz-corrected SAXS peak, the structural parameters such the thicknesses of crystalline lamellae (Lc) and amorphous layers (La), the values of the most probable long period Lp, the dispersion parameter D and the thickness I of the interface between crystalline and amorphous phases of lamellas. SAXS patterns after the drug release process showed for all hybrids a pronounced shift of the peak related to siloxane particles towards lower q-values, due to disentanglement of hydrophilic PEO chains promoted by water penetration. For the 30-70 hybrid, this process leads to rapid release of PenG by anomalous mechanism in which swelling of PEO chains plays an important role. The release mechanisms of the hybrids prepared with the greater and medium PLA content (70-30 and 50-50) are different, since the significant presence of PLA crystallites in these samples inhibit PEO swelling. The peak associated to PLA long-period in SAXS patterns quite disappears after drug release, revealing that progressive and slower water penetration in the hydrophobic PLA matrix leads to destruction of the ordering between PLA lamellas. Since XRD results show that crystallinity inside lamellas is preserved during the process, we conclude that PenG molecules released in 70-30 and 50-50 hybrids were located in the PEO-PLA interpenetrated phase between PLA lamellas. This interpretation is consistent with the Fickian diffusion mechanism detected for Pen G release in both samples and with the more extended time period of such release regime in the 50-50 hybrid, in which the volume fraction of the "ideal" interpenetrated PEO-PLA phase is greater.

**Keywords**
PLA-PEO, sol-gel, Lamellar, drug delivery

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POSTER

# 334 - IN-SITU SAXS STUDY OF TEMPERATURE DEPENDENCE IN THE SYNTHESIS OF AG2S NANOPARTICLES

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Great efforts have been made during recent years to enhance the photovoltaic performance of the quantum dots-sensitized solar cells (QDSSCs) to meet the increasing demands of clean energy. In the third generation of solar cells, QDs play the role of sensitizer due their novel optical properties such as appropriated energy band gap, high absorption coefficient and multiple exciton generation. In this context, Ag2S nanoparticles are a promising material for this devices because of their low toxicity, the high absorption coefficient (∼104 cm-1) [1] and relatively narrow energy band gap (Eg ∼ 1.0 eV) [2], which can extend the light absorption spectrum to near-infrared regions.

In order to achieve a fine tuning of the optical properties of this material, a fine control over the shape and size is crucial as well as a deep understanding of their process of formation. In this regard, non-invasive in situ characterization techniques, such as small angle x-ray scattering (SAXS), allow to study the process of nucleation and growth by following the shape and sizes of the products and sub-products during the reaction.

For the synthesis, the Ag precursor, silver diethyldithiocarbamate (Ag(DDTC)), is reacted with a surfactant, 1-dodecanethiol (DCT), in a hot solution at 210 ºC under vigorous stirring and N2 atmosphere, forming sub 5 nm Ag2S nanoparticles [3]. In this work, we follow the synthesis process of Ag2S nanoparticles by in-situ temperature dependent SAXS measurements using the previously mentioned wet-chemistry method with slight modifications adapted to our set up. We also study the effect of the synthesis temperature on the final product of the reaction. Transmission electron microscopy (TEM) images and UV-vis measurements were performed for a complementary characterization.

For the synthesis performed at 210 ºC we found that a Ag-DDT metal-organic polymeric lamellar phase with a lattice parameter of 3.5 nm is formed at the beginning of the reaction, as previously reported [4]. After few minutes at 210 ºC, ∽ 1 nm nanoparticles are formed and grow up to an average size of 5 nm . No significant difference was observed between the final product obtained during in situ experiment, without stirring, with respect to the ex-situ synthesis.

**Keywords**
SAXS, in-situ, Ag2S, photovoltaics

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POSTER

## 217 - ADVANCES IN DATA ACQUISITION AND ANALYSIS AT I22, DLS

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Advances to Diamond Light Source's Generic Data Acquisition (GDA) software have moved the architecture away from a strictly coupled client-server model to a more loosely coupled framework facilitated by an ActiveMQ message bus.

Such advances have not only allowed for greater flexibility in data acquisition but also in how other programs, or services, can interact with ongoing scans. For example, the DAWN software package takes advantage of these messages to conduct data processing in near-real time.

Since deploying these new technologies on I22 is now possible to view, within GDA, visually how far through a scan you are, how much remains and the results of your data processing unified in one interface. However, this is just one use case for this architecture. As we look forward to the future, the ability to inspect and evaluate both raw and processed data after reduction provides a mechanism for automated near real-time data analysis driven scanning on the beamline.

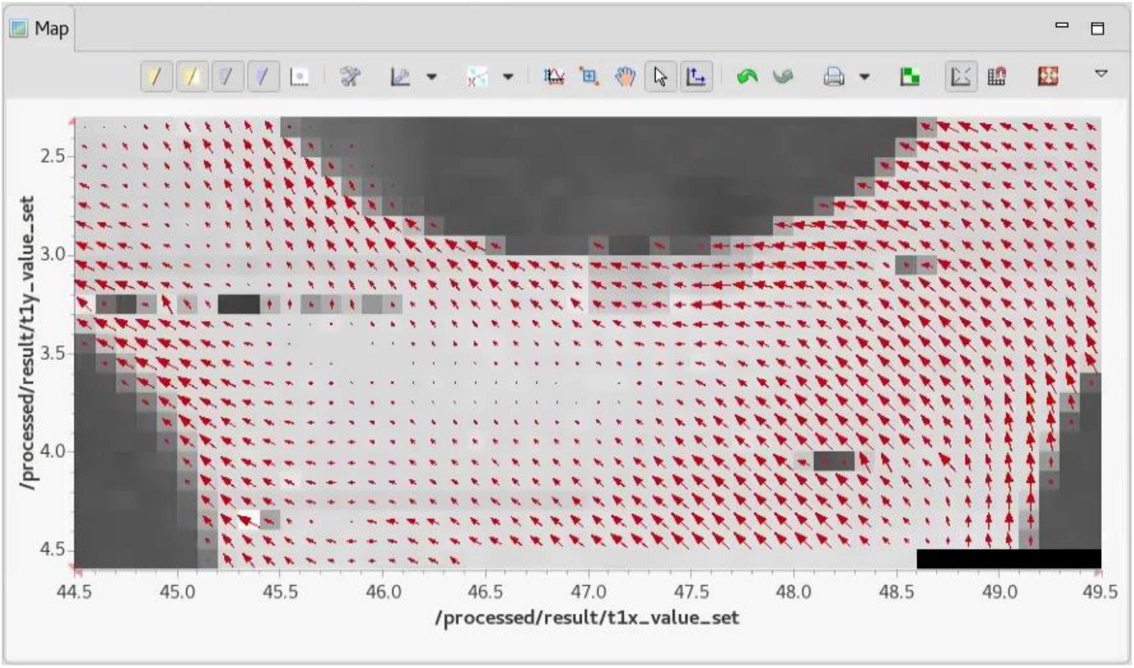

Figure 1 - The primary user interface within the GDA client showing live feedback view during a scan. The final line demonstrates data yet to be acquired, the black region, data that has been acquired but not processed, in greyscale, and data that has been acquired and processed, where vector arrows are shown highlighting orientation present within the sample scanned.

**Keywords**
Data Acquisition, Data Analysis, Adaptive Scanning

POSTER

# 431 - REVEALING THE NUCLEATION AND GROWTH MECHANISMS OF MOFS IN THE AQUEOUS PHASE THROUGH COMBINING MOLECULAR DYNAMICS SIMULATIONS AND SMALL/WIDE-ANGLE X-RAY SCATTERING

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This study combines molecular dynamics simulations with in situ small/wide-angle X-ray scattering (SAXS/WAXS) to reveal the mechanism of metal-organic frameworks (MOFs)-encapsulated enzymes in aqueous solutions. We extend our prior research published in Nano Letters 2020, 20 (9), 6630-6635, indicating freestanding catalase has less chemical interaction with the MOF than confined catalase. However, the interaction between MOF and enzyme isn't clarified very well. In this study, Molecular dynamics simulations of the self-assembly process are respectively run under vacuum state and water solution state. The presence and amount of water significantly affected the growth of MOFs, and we found that this was the result of competition between ligands and water for the coordination bonding rate of metal ions. To confirm the observed phenomenon in the simulation, the time-resolved SAXS/WAXS measurement has been explored at beamline TPS13A of the National Synchrotron Radiation Research Center (NSRRC) with the q-range 0.006-2.0 Å-1. In situ SAXS/WAXS monitors the full self-assembly process of MOFs in the aqueous state and shows the dynamic process of MOFs assembly. The results also echo the coordination binding rate selection in our simulation. This research is expected to be applied to improve the ratio of MOFs-encapsulated enzymes to increase the opportunity for related materials.

**Keywords**
Molecular Dynamics Simulation, small/wide-angle X-ray scattering, metal-organic frameworks, MOFs, nucleation and growth mechanisms.

POSTER

# 398 - SAXS/WAXS CHARACTERIZATION OF SWOLLEN LYOTROPIC LIQUID-CRYSTALLINE LIQUID EMULSIONS FOR CONTROLLED DELIVERY OF ACTIVE PHARMACEUTICAL INGREDIENTS

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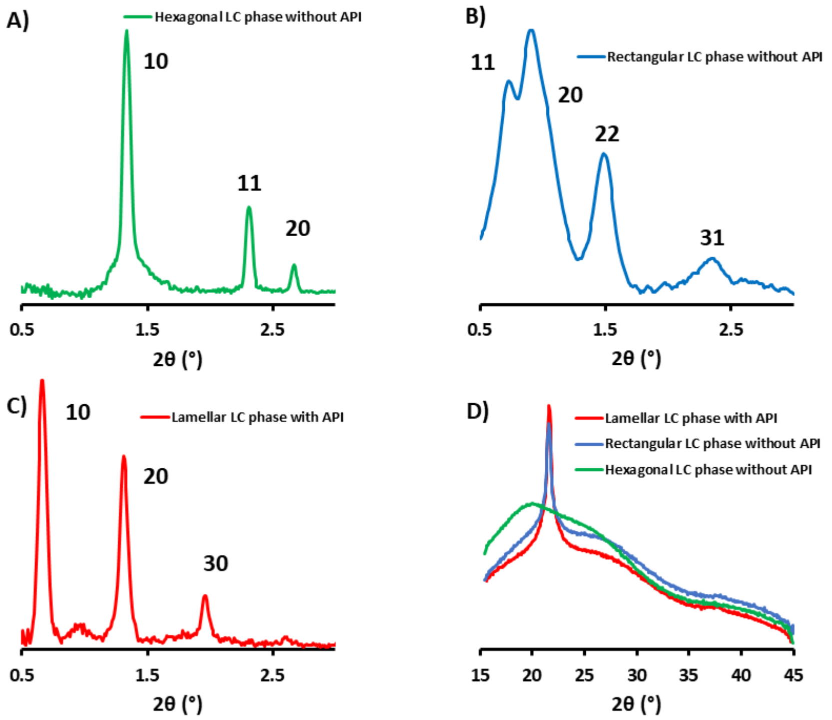
This work aims to develop a physicochemical understanding of how an emulsion-like liquid crystal (LC) matrix influence the percutaneous delivery of active pharmaceutical ingredients (APIs) for the treatment of infectious diseases (e.g., tuberculosis). The oral therapies have difficulties, such as drug-induced hepatotoxicity and treatment discontinuation. In this context, transdermal systems for anti-tuberculosis drug delivery are being explored.1 These systems are non-invasive and are administered by the patient himself, which improves treatment compliance, avoids the first-pass liver treatment, and can also provide drug release over long periods.2

On the other hand, it has been reported that emulsions stabilized by liquid crystal phases have unique rheologic properties. In addition, the structures formed by the different LC phases can act as a host to hydrophilic, hydrophobic, or amphiphilic molecules, locating themselves in different areas of the supramolecular structure,3 promoting the controlled release of active ingredients.4 In this work, we have fully explored a ternary water-oil-surfactant diagram. Here, we present small and wide-angle X-ray scattering (SAXS / WAXS) characterization of the lyotropic liquid crystal (LLC)-based emulsions, with and without active pharmaceutical ingredients (APIs). These experiments were carried out using a XENOCS Xeuss 2.0 HR SAXS/WAXS instrument at the Laboratorio de Cristalografía Aplicada, ITECA, UNSAM-CONICET, Argentina, equipped with two DECTRIS Pilatus detectors (200K for SAXS and 100K for WAXS).

Insert Figure

Figure – Small-angle X-ray scattering for A) Hexagonal (green), B) Rectangular (blue) and C) Lamellar (red) phase of lyotropic liquid crystal-based emulsions, and D) Wide-angle X-ray scattering of the same three samples, showing the characteristic board halo of LC phase between 2q = 20-30°. The corresponding Miller indexes are indicated.

At least, lamellar, mesh, rectangular/ribbon, and hexagonal LC phases have been found and characterized (see Figure for three examples), showing that the system under study has wide versatility. On the other hand, it has been shown that the incorporation of the analyte does not change the LC properties of the emulsions. Moreover, we have seen how some of the LC phases undergo a phase transformation over time. Between 15 and 20 days, we have seen, for example, how rectangular phases become lamellar. Finally, preliminary results show a dependence of the LC phase with the concentration of analyte diffused through a biological membrane.



## Keywords

Swollen, Lyotropic Liquid-Crystal, Emulsions, Drug Delivery, Active Pharmaceutical Ingredients.

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POSTER

# 306 - CHARACTERIZATION OF NONIONIC CUBOSOMES IN THE PRESENCE OF MODEL PROTEINS: A STRUCTURAL APPROACH

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Nanomedicine, with particular attention to drug delivery systems, has gained much attention in recent years; they are widely used to increase the effectiveness of diagnostic drugs, including anticancer, antimicrobial and antiviral drugs. In addition, they reduce the toxicity of existing drugs, minimizing drug interactions and overcoming systemic barriers. Cubosomes are nanostructured particles composed of a specific combination of some types of lipids, such as monolein and phytantriol. Lysozyme is an animal-produced antimicrobial enzyme that is part of the immune system, used as anti-inflammatory, antiviral, antiseptic, antihistamine and antineoplastic. In this project, we will highlight the systems formed by lipids and polymers, as cubosomes, studying the structural influence of a Lysozyme encapsulated by it. These systems will be composed of cubosomes in the absence and presence of the enzyme and will be analyzed using small angle X-ray scattering (SAXS). Cubossomes' preparation is made so that phytantriol (PHY) solution, anfifilic molecule wich forms a cubic structure in aqueous solution, and nonionic polymer are prepared. These solutions stay in 50° C bath and after, phytantriol solution is dripped in the polymer solution, forming cubosomes by agitation. When it's ready, the final solution passes through a machine that evaporates it until the sample final volume, 5 mL. The same procedure is made for multiple concentrations of the Lysozyme (1, 3 and 5 mg/mL).SAXS results indicates that cubosomes present a Pn3m in water solution (in samples made in buffer solution, we expect to find the same structure, or even a Im3m structure); The results also present a proper stability of the samples. In the samples made with water instead of buffer solution, the pH decreased over time, reaching the value of pH = 3, what isn't appropriate for some applications in human body; This indicates that cubosomes can be widely applicated in drug delivery systems with many other drugs due to its large internal volume, encompassing amphiphilic, hydrophilic and hydrophobic.

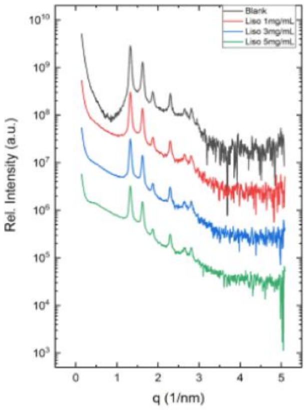
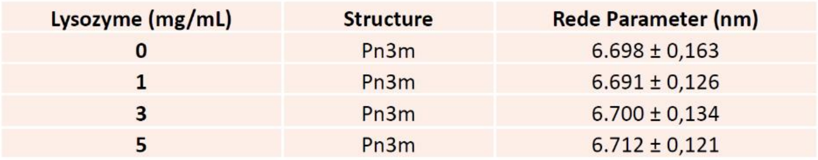


**Figure 1**. Results of SAXS tests in  samples with water.

**Table 1:** Crystallographic structure determined by SAXS for the phytantriol cubossomes.



| Lysozyme (mg/mL) | Structure | Rede Parameter (nm) |
|---|---|---|
| **0** | Pn3m | 6.698 ± 0,163 |
| **1** | Pn3m | 6.691 ± 0,126 |
| **3** | Pn3m | 6.700 ± 0,134 |
| **5** | Pn3m | 6.712 ± 0,121 |

**Keywords**
Lysozyme, Cubosomes, Nanostructured System

POSTER

# 428 - INTERACTION OF IONIC SURFACTANTS WITH EPOXY-BASED HYDROGEL INVESTIGATED BY SANS

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Stoichiometric amphiphilic epoxy network containing polyoxyethylene (POE) and polyoxypropylene (POP) was prepared by reaction of α, ω-diamino terminated POP and POE bis(glycidyl ether) of molar masses ca 4,000 and 526 g.mol-1. A series of hydrogels was obtained by swelling of the network in D2O and excess volume of solutions of two surfactants: myristyltrimethylammonium bromide (C14TAB) and sodium dodecylsulfate (SDS), respectively, in D2O. Composition and structure of hydrogels were investigated by gravimetry and small-angle neutron scattering (SANS). A two-phase structure with Bragg's distance in the range ca 86 - 110 Å was revealed in the hydrogels obtained by swelling in neat D2O, C14TAB solutions and subcritical SDS solutions. Details of the hydrogels structure were obtained by fitting experimental SANS profiles to two model scattering functions. Either water-poor polydisperse nanodomains or micelles dispersed in the mayor water-rich phase are considered in the models. SANS results shown that macroscopic observations are accompanied by significant change of the two-phase structure of hydrogels.

**Keywords**
hydrogels, swelling, surfactants, SANS

POSTER

## 230 - RECENT DEVELOPMENTS IN 3 D PRINTED MICROFLUIDIC DEVICES FOR BIOSAXS

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Some of the greatest achievements in science and engineering in recent times are associated with miniaturization. A reduction in the size of devices with additional improvements to their technical features. One of the most beneficial areas has been microfluidics.

At BM29, BioSAXS beamline we have embraced microfluidics in the development of new sample environments for our user community to widen the scope experiments performed at the ESRF. Where rapid prototyping methods that allow us to create a device within one day, and if necessary quickly modify it, are in high demand. Over the past few years to aid in the development of microfluidic research we have set up a dedicated laboratory fitted out with 2 direct laser printing (DLP) 3D printers (Asiga Pico2 HD & Asiga MAX X27) as part of the Partnership for Soft Condensed Matter (PSCM) and Structural Biology Groups.

**Keywords**
microfluidics, SAXS, BM29

POSTER

# 402 - BARRIER PROPERTIES OF NANOSTRUCTURED PMMA-SILICA COATINGS FOR CORROSION PROTECTION OF REINFORCEMENT STEEL

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Steel is a low-cost raw material widely used in civil construction in reinforced concrete structures (RCS). However, in the absence of preventive maintenance and exposure to aggressive environments, reinforcing steel will be susceptible to corrosion due to deterioration of the surface passive layer [1]. To overcome the problems caused by corrosion, current research efforts focus on developing efficient alternatives for corrosion protection of reinforcing steel. In this context, poly (methyl polymethacrylate) (PMMA)-silica hybrid nanocomposites have shown to be promising for the corrosion protection of steel surface [2]. Thus, the present study investigated the potential application of these hybrid coatings for corrosion protection of reinforcing steel. PMMA-silica nanocomposites were obtained by combining the polymerization reactions of methyl methacrylate (MMA) and 3-[(methacryloxy) propyl] trimethoxysilane (MPTS) in the presence of the thermal initiator benzoyl peroxide (BPO) and isopropanol as a solvent, with the sol-gel hydrolytic condensation of tetraethyl orthosilicate (TEOS). The molar proportions between the polymerization thermal initiator and the monomer (BPO/MMA) in the formation of the nanocomposites were evaluated in the range of 0.025-0.1. The structural characteristics of coatings with a thickness of a few micrometers, deposited by immersion on reinforcing steel, were studied by scanning electron microscopy (SEM), atomic force microscopy (AFM), infrared (FTIR), thermogravimetry (TG), X-ray photoelectron spectroscopy (XPS), and small-angle X-ray scattering (SAXS). The structural properties were correlated with the protective performance of the coatings obtained by electrochemical impedance spectroscopy (EIS) after exposure to 3.5 wt% NaCl solution and simulated concrete pore solutions (SCPS), which simulate the carbonate (pH 8) and alkaline (pH14) environment of concrete. Nanoscale dispersion of silica domains covalently conjugated to PMMA chains resulted in transparent, homogeneous, pore-free coatings. The formation of the PMMA-silica hybrid structure was confirmed by FTIR and XPS analyses. The mechanical, thermal, and surface analyzes showed a high adhesion of the coating to the substrate surface (15.9 MPa), low roughness, thermal stability of up to 256°C, and a contact angle of about 75°. The TG and SAXS results indicate that the variation of the BPO/MMA ratio is an important parameter in obtaining a nanostructure with improved anti-corrosion performance, indicating that there is a sensible balance between the reduction of the silica phase fraction and the reduction of the mean spacing between the silica nanodomains. Electrochemical tests for coatings exposed to 3.5 wt% NaCl solution and SCPS confirmed effective corrosion protection, with impedance modulus up to 100 GΩ cm2 (at 4 mHz) and a lifetime of up to 670 days. A similar performance with less durability was obtained in the SCPS (pH 8 and pH 14). Considering these results, PMMA-silica hybrid coatings proved to be a potential alternative for protecting reinforcing steel against corrosion.

## Keywords

organic−inorganic coating, sol-gel, reinforcing steel, corrosion protection, PMMA−silica hybrid

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POSTER

# 397 - PLURONIC/ACRYLIC ACID HYDROGEL: STRUCTURAL ANALYSIS AND PRINTABILITY

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3D printing of hydrogels has gained attention since it allows the construction of structures with shapes that are not possible using conventional manufacturing techniques. Recently, 4D printing has appeared, in which the fourth dimension arises from the ability of the printed structure to change its shape and/or functionality along time when exposed to a given environmental stimulus. In this project, we aimed at printing pH-responsive structures for applications in soft robotic. We developed precursor gels composed of Acrylic Acid (AA) and poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (Pluronic F127) triblock copolymer. The liquid AA monomers can be polymerized by free-radical polymerization after being printed. In solution, the F127 unimers can self-organize into micelles and the formation of a gel is associated with the formation of a liquid crystalline phase of F127 micelles. Thus, the F127 gelation is responsible for the printability of the AA/F127 formulation. However, the composition can influence the F127 organization, and impact rheological behavior. In this work, the influence of the AA/F127 proportion on the gel structure was evaluated by SAXS, by measuring the gelation temperature, and by Differential Scaning Calorimetry. The F127 concentration was set at 30 % (w/v) and the AA concentration was varied (16 - 20 %w/v). A 20.4 % AA concentration inhibited the gelation capacity of F127, which was confirmed by the absence of diffraction peaks on the SAXS pattern even if micelles were formed. Moreover, a decrease in the AA concentration led to a reduction of the gelation temperature, allowing printing at room temperature. SAXS measurements revealed that the addition of AA reduced the size, the aggregation number and the distance between micelles. The micelle network, when present, was determined to be a Simple Cubic structure. In all polymerized samples, a micelle network was formed in all compositions, and the conversion of AA into poly(acrylic acid) produced pronounced decrease in the measured parameters.

## Keywords

3d printing, printability, hydrogels, SAXS

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POSTER

# 400 - IN SITU SAXS UNDER TENSILE LOADING OF POLY(ACRYLIC ACID)/F127 SEMI-INTERPENETRATED NETWORK: EFFECT OF CROSSLINKING

**CONSTANTINO, Murilo Camargo (1); MENDES, Matheus (1); VIANA, Thiago Nunes (1); DE SOUSA JUNIOR, Rogério Ramos (1); CARASTAN, Danilo Justino (1); MENEAU, Florian (2); CHAMPEAU, Mathilde Julienne Gisele (1)**
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Because hydrogels exhibit similar properties to living tissues, they are interesting for biomedical applications but their brittleness limits their application range. Hybrid crosslinked hydrogels containing physical and chemical crosslinkers have shown improved elasticity. In this project, two hydrogels composed of poly(acrylic acid) (PAA) are polymerized in the presence of a network of Pluronic F127 micelles that act as physical crosslinkers. In the hybrid hydrogel, PAA is chemically cross-linked, whereas PAA is not chemically crosslinked in the physical hydrogel. SAXS patterns exhibit Bragg diffraction peaks characteristic of a face-centered cubic phase of F127 micelles, thus the ordered structure is maintained during PAA polymerization. The higher decrease of the lattice parameter observed in the hybrid hydrogel is accounted by greater network shrinkage provoked by the chemical crosslinker. Whereas pure chemically crosslinked PAA is brittle, the presence of micelles results in flexible materials. The ultimate tensile strength of the hybrid hydrogel is 2.5 times higher than the one of the physical gel but the chemical crosslinker limits its stretchability (elongation at break 290 % and 400 % in the hybrid and physical hydrogels). Energy-dissipation of the hydrogels was investigated by cyclic loading-unloading tests. The dissipated energy rises with strain and is higher in the hybrid gel, suggesting that higher damages occur. SAXS patterns were obtained while simultaneously deforming the hydrogels. The 2D patterns showed that the samples are initially isotropic but become anisotropic at 30 % of strain. Changes in intermicellar distance are observed during stretching, but this effect is restricted in the presence of a chemical crosslinker. Twelve hours after stretching, the hybrid hydrogel recovered its initial morphology whereas the physical one remained partially deformed. This set of results highlights that the presence of micellar physical crosslinks contributes to the stretchability of the sample and the chemical crosslinker hastens the recovery after deformation.

## Keywords

Hybrid Hydrogel, SAXS, Flexible Materials, Energy-dissipation

## References

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Zhao, X. Multi-scale multi-mechanism design of tough hydrogels: building dissipation into stretchy networks Soft Matter, 10, 672-687 (2014) https://doi.org/10.1039/C3SM52272E

POSTER

# 304 - SAXS INVESTIGATION ON THE STRUCTURE AND DYNAMICS OF RESPONSIVE HYDROGELS

**VILLARES, Matias (1); MÜLLER, Marcus (2); CEOLIN, Marcelo (1)**
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We have designed and studied acrylic hydrogels with thermal response capacity, focusing in both structural and dynamic properties. Our system of study is HEMA/NIPAAM hydrogels crosslinked with DEDGMA. It is known that NIPAAM's monomers experiments a transition from hydrophilic to hydrophobic behavior around 32°C. It is expected that the incorporation of NIPAAM into the polymer network will give rise to two different phases of the bulk material: a swollen state in which the gel retains the solvent inside and a shrinked state in which a portion of the solvent is expulsed. We are particular interested in investigate how can this thermal response be tuned by controlling the HEMA/NIPAAM relative concentrations, the amount of crosslinker and the lengths of the polymer chains.

Different synthesis methods have been explored in order to study how the gelation process and the network structure of the material influence its thermal response and mechanic behavior. With this purpose we perform Small Angle X-ray Scattering (SAXS) experiments that provides information about the local fluctuations of the electron density, the distance between the crosslinking points and the size of the pores. Although there are several models for the scattering spectrum of polymeric networks they lack generality and therefore a broader approach is necessary including complementary experimental techniques. The mechanic response is investigated using different implementations of oscillatory rheology (DMA) and the thermodynamics of the system is studied through differential thermogravimetry (DTG) and differential scanning calorimetry (DSC).

**Keywords**
hydrogel, structure, saxs

POSTER

# 190 - IN-SITU SAXS OF ELECTRODEPOSITED 3D NANOSTRUCTURED MATERIALS THROUGH A LIQUID CRYSTAL TEMPLATE.

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*1: University of Southampton, United Kingdom; 2: Diamond Light source; 3: ISIS Neutron and Muon Source*
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The emergence of synthetic strategies and fabrication technologies that afford control over the architecture of matter at nanometre length scales has provided a new tool kit for engineering functionality in materials. In particular, the three-dimensional (3D) nanostructuring of metals and semiconductors has resulted in enhanced optical, magnetic and electronic properties yielding new devices and device concepts. A synthetically attractive route to their preparation is electrochemical templating, which involves electrodeposition at the surface of an electrode around or through a pre-existing soft template. In particular, liquid crystal templating using lyotropic phases as soft templates has been shown to be an effective technique for the production of a range of nanostructured materials. The surfactant phytantriol self-assembles into an inverse bicontinous cubic phase ""double diamond"" in excess water. When materials are electrodeposited through this soft template the resulting structure has a single diamond phase. This allows the template and the resulting deposited material to be distinguised by SAXS.

The deposition of materials through these soft templates is challenging, however the ability to collect in-situ SAXS data during the electrochemical depostion is highly desirable in order to optimise depostion parameters and study the growth inside the template from start to finish. We have developed a novel in-situ electrochemical cell (figure.1) which allows both the deposited material and the template to be monitored during the deposition process while electrochemical data is also collected. The in-situ studies allow us to monitor the interplay between the template and the deposited material throughout the process. This poster will discuss the cell design, preliminary SAXS and electrochemical data on platinum and CdTe deposited through phytantriol and it's derivates along with in-situ SAXS data collected on the I22 beamline at The Diamond Light Source.

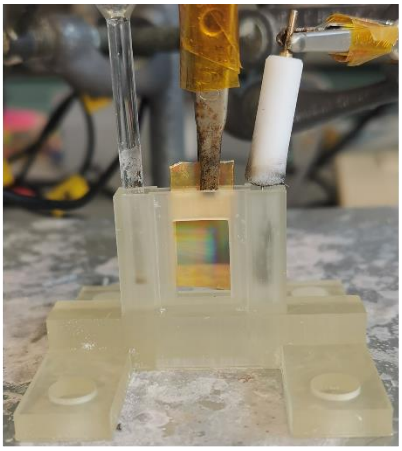

**Figure.1** In-Situ electrochemical cell

**Keywords**
materials, nano, SAXS, SANS, soft-matter, electrochemistry

POSTER

# 423 - NEUTRON TECHNOLOGY APPLIES TO THE STUDY OF POLYSTYRENE CHAINS BEHAVIOR IN PERFORATED LAYERS OF BLEND FILMS OF A SYMMETRIC POLYSTYRENE-BLOCK-POLY(METHYL METHACRYLATE)

**HUANG, Tzu-Yen (1); NELSON, Andrew (3); WU, Chun-Ming (1); SUN, Ya-Sen (2)**
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The distributions of dPS in PLs // can be probed by grazing-incidence small-angle neutron scattering (GISANS) and time-of-flight neutron reflectivity (ToF-NR). In this study, by finely tuning the composition (ϕPS+dPS = 63.8 vol%) of the total PS/dPS component and annealing temperature (230 and 270 °C), P(S-b-MMA)/dPS blend films mainly form perforated layers with parallel orientation (hereafter PLs //). Where basically follow up our previous studied segmental distributions of polymer chains in blend films of a weakly-segregated polystyrene-block-poly(methyl methacrylate) [P(S-b-MMA)] and deuterated polystyrene (dPS). The GISANS and ToF-NR results offer evidence that dPS chains are preferentially located at the free surface and within the PS layers for blend films that were annealed at 230 °C. Upon annealing at 270 °C, dPS chains distribute within PS layers and perforated PMMA layers. Nevertheless, dPS chains still retain a surface preference for thin films. In contrast, such surface segregation of dPS chains is prohibited for thick films when annealed at 270 °C.

**Keywords**
Neutron technology, GISANS, Thin film, PMMA-PS Block copolymer

POSTER

# 426 - STUDYING ON INTERACTIONS BETWEEN A-CRYSTALLIN AND MEMBRANE

**YANG, Ching-Hsun (1); LIU, Yu-Ting (1); WANG, Zong-Yan (1); LEE, Ming-Tao (1,2)**
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Cataract disease is caused by the aggregation of damaged γ-crystallin as well as b-crystallin without chaperone interaction with α-crystallin. One possible mechanism of chaperone function loss is the binding of α-crystallin to membrane. Therefore, it’s necessary to understand the disappearance of α-crystallin in solution through interacting with membrane, and the way to stop this tendency. We used DOPC as a model lipid to produce unilamellar vesicles circular dichroism (CD) as well as small angle X-ray scattering (SAXS) experiments and multilamellar thin film sample on substrate for lamellar X-ray diffraction (LXD). CD was used to detect the change of secondary structure induced by binding of protein to membrane. LXD was used to determine membrane structure to extract thickness change caused by protein interacting with 2D membrane surface. And combining SAXS data and model fitting, the structural change of bilayer induced by protein binding can be obtained. After preliminary analysis, we found that membrane thickness would become thinner first and then thicker in both LXD and SAXS cases for lipid-to-protein molar ratio (L/P) 500/1, 750/1, and 1000/1, respectively.

**Keywords**
Cataract, α-crystallin, vesicle, small-angle-scattering

POSTER

## 148 - BEAMLINE CONTROL USING PYTHON BASED GRAPHICAL USER INTERFACE

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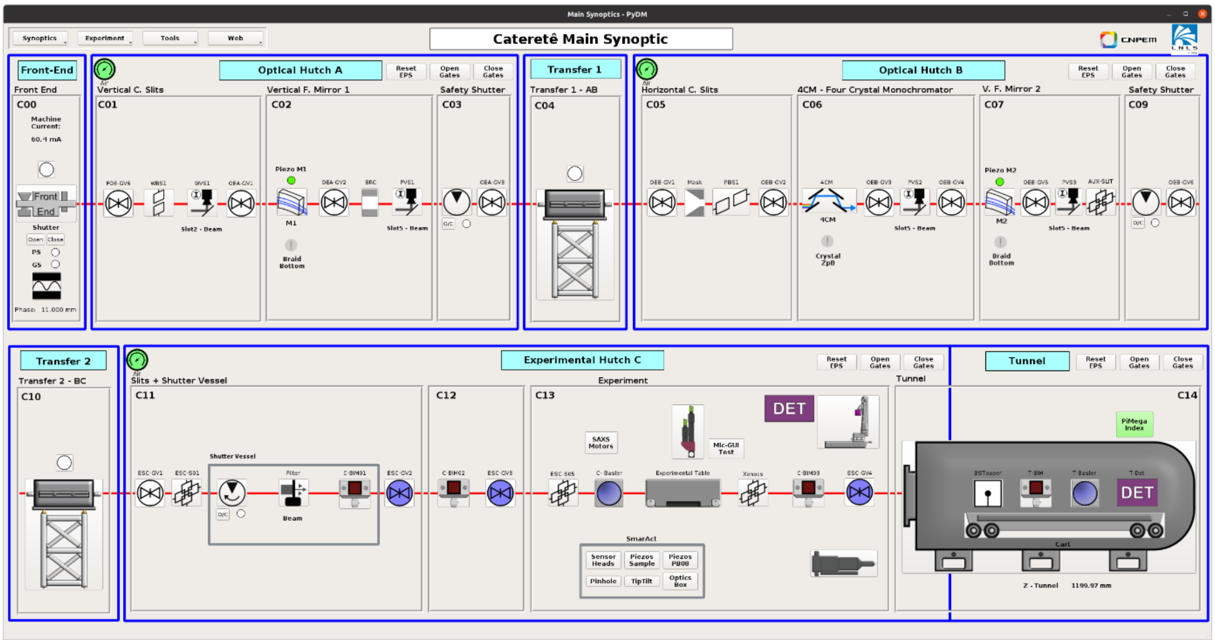
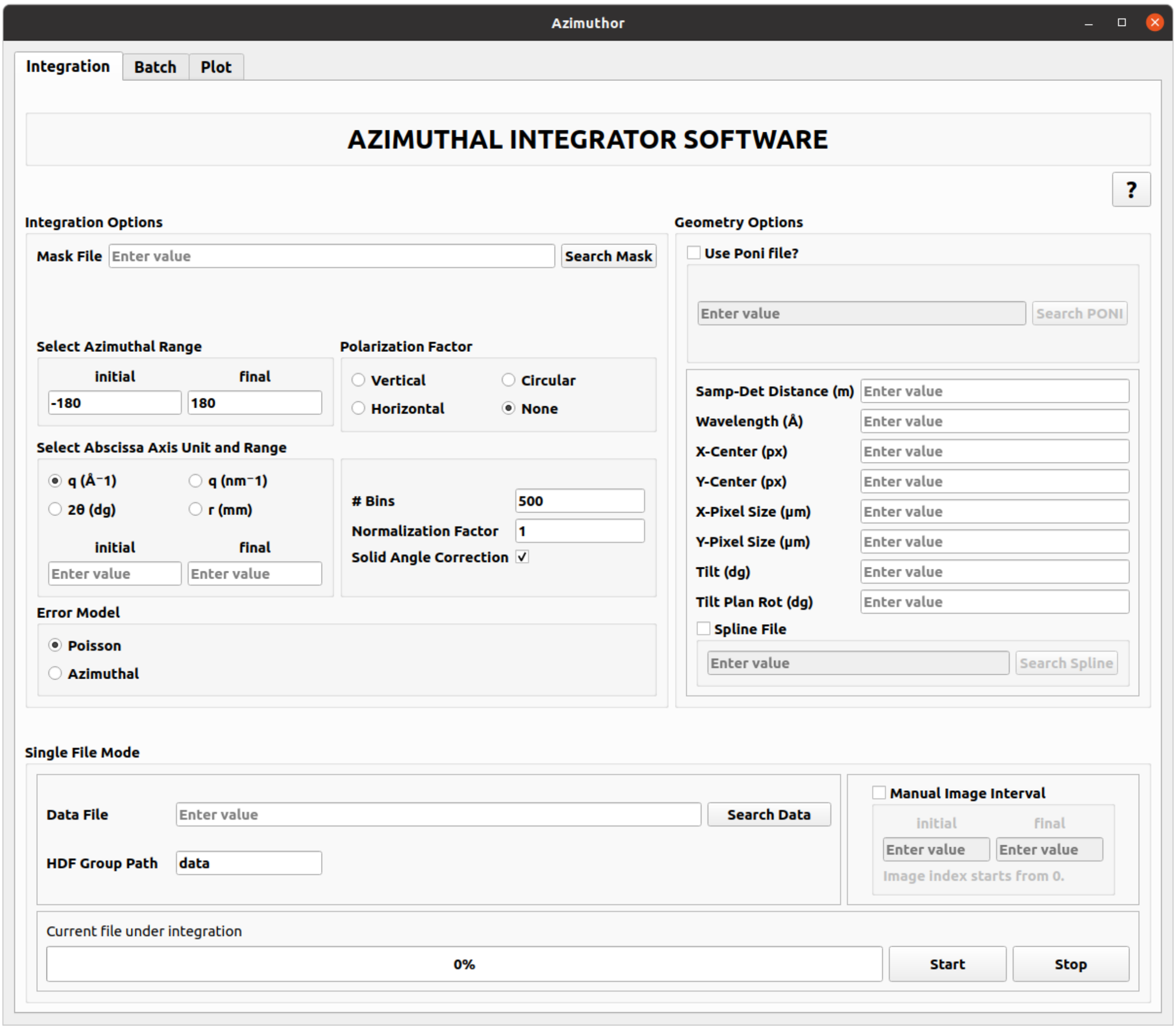
A beamline of a state-of-the-art synchrotron demands a huge number of variables for monitoring and control during its operation in experiments. This is how it works with the CATERETÊ beamline, which has a system of graphical interfaces based on Python and Epics for total control of the various equipment connected to the network such as motors, sensors and cameras, which facilitates operation and productivity in the various experiments and techniques performed in the lab. In this presentation I will show you how the main beamline control interface, the synoptic, works, and about the in-house developed Azimuthal integration interface based on pyFAI for SAXS and WAXS integration.



Machine Current: 60.4 mA

Phase: 11.000 mm

Z - Tunnel 1199.97 mm


Azimuthor

Integration | Batch | Plot

AZIMUTHAL INTEGRATOR SOFTWARE

?

Integration Options

Mask File: Enter value [Search Mask]

Select Azimuthal Range: initial -180, final 180

Polarization Factor: ○ Vertical ○ Circular ○ Horizontal ● None

Select Abscissa Axis Unit and Range: ● q (Å−1) ○ q (nm−1) ○ 2θ (dg) ○ r (mm)
initial: Enter value, final: Enter value

# Bins: 500
Normalization Factor: 1
Solid Angle Correction ☑

Error Model: ● Poisson ○ Azimuthal

Geometry Options

☐ Use Poni file?
Enter value [Search PONI]

Samp-Det Distance (m): Enter value
Wavelength (Å): Enter value
X-Center (px): Enter value
Y-Center (px): Enter value
X-Pixel Size (μm): Enter value
Y-Pixel Size (μm): Enter value
Tilt (dg): Enter value
Tilt Plan Rot (dg): Enter value
☐ Spline File
Enter value [Search Spline]

Single File Mode

Data File: Enter value [Search Data]
HDF Group Path: data

☐ Manual Image Interval
initial: Enter value, final: Enter value
Image index starts from 0.

Current file under integration
0% [Start] [Stop]

## Keywords

GUI, Python, PyQt5, PyDM, pyFAI

## References

G. S. Fedel, D. B. Beniz, L. P. Carmo, J. R. Piton. ""Python for user interfaces at SIRIUS"". ICALEPCS2017 Conference, Barcelona - Spain, 2017. doi:10.18429/JACoW-ICALEPCS2017-THAPL04

G. Ashiotis, A. Deschildre, Z. Nawaz, J. P. Wright, D. Karkoulis, F. E. Picca and J. Kieffer, ""The fast azimuthal integration Python library: pyFAI"". Journal of Applied Crystallography (2015) 48 (2), 510-519. https://doi.org/10.1107/S1600576715004306

POSTER

# 323 - SANS CHARACTERIZATION OF ALGINATE-CLAY NANOCOMPOSITE HYDROGELS WITH PEO-PPO-PEO COPOLYMERS

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Alginate-based hydrogels have the potential to be applied in multiple fields such as tissue engineering, cell encapsulation and wound dressings. Pluronic® F127 is a part of family of thermoresponsive copolymers made up of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO),which display sol to gel transition with temperature increase. Laponite® is a synthetic disc-shape smectite clay that can form clear gel when disperse in water. Mixture of alginate, Laponite® and Pluronic® F127 can form a nanocomposite gel with multiple gelation mechanism, which enhance the elasticity of hydrogels. This study presents a structure analysis of alginate-Laponite®-Pluronic® F127 (ALP) gels using small-angle neutron scattering and compared with rheology results. These measurements provide a more detailed study of the gel structure, describe possible interactions between the hydrogel components, and provide further insight into how Pluronic® F127 can help improve the elasticity of the hydrogel. Quantitative information of gel structure is obtained from spectra fitting. Alginate concentration do not show a significant influence on scattering intensity. However, alginate and Laponite® do affect the size of the micelles. Increase of Laponite® concentration caused an increase in the slope of spectra in the intermediate q range. Results from fitting the data show that the alginate network mesh sizes change significantly at vary temperature as F127 micelles presents stronger interactions at high temperature, while the distance between micelles are close at different temperature or concentration of Laponite/alginate.

**Keywords**
Alginate, SANS, hydrogels, F127

POSTER

# 359 - STRUCTURAL AND MORPHOLOGICAL MODIFICATIONS OF REGULAR CORN STARCH AFTER ACID HYDROLYSIS UNDER EXTERNAL ELECTRIC FIELD

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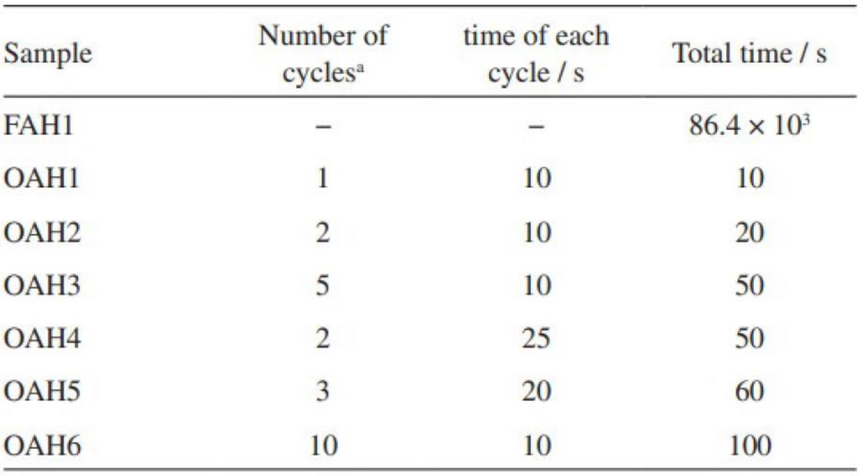
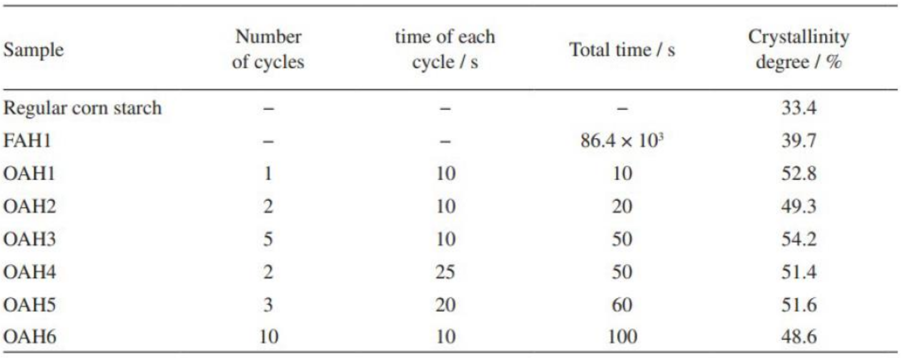
Corn starch is an abundant polysaccharide found in nature that presents itself in the form of semi-crystalline granules, which are predominantly composed of polymer chains of amylose (amorphous regions) and amylopectin (crystalline regions) associated by hydrogen bonds, forming a lamellar structure. The interest in improving starch physicochemical properties increases the search for physical or chemical techniques that allow modifying granular characteristics (such as size, porosity, or degree of crystallinity) in a fast and easy way. The goal of this project was to study a new method for starch acid hydrolysis, by evaluating the application of an external electric field during the hydrolysis process.[1] The method was named oriented acid hydrolysis (OAH), since the potential difference provides organization for the ions in solution. The hydrolysis method without coupling with electric field application was named free acid hydrolysis (FAH). X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Small angle X-ray scattering (SAXS) were applied to characterize the structural and morphological changes of the granules after the treatments. The experiments were carried out from dispersions of regular corn starch powder (amylose content of 18%) (5% (w/v) in 1.0 mol L-1 HCl. In the FAH methodology, a prepared dispersion was kept under hydrolysis for 24 h at room temperature (20 ± 3.0 °C). The resulting sample (FAH1) was neutralized, dried and grounded to powder. In the OAH methodology dispersions were prepared and then subjected to the electric field application (500 V m-1) in a 2 V fixed voltage, during different times and number of cycles (Table 1), followed by the same purification described for the FAH preparation. Figure 1 shows the representation of the device used for the electric field application experiments. The SEM images (Figure 2) showed the appearance of cavities at the surface of the granules after treatment. The XRD results (Figure 3) allowed to calculate[2] the crystallinity degree of the hydrolyzed starches, which enhanced as the hydrolysis time increased (Table 2). The SAXS profiles (Figure 4) and the related data fitting (Table 3) proved that the acid treatment affected the internal lamellar organization of the granules, what was observed through changes in the characteristic peak in q-value of 0,6 nm-1, that corresponds to the periodic arrangement of the lamellar structure of starch. The sample prepared by FAH method presented loss of lamellar organization, since the peak disappeared. The obtained changes in the treated starches are mainly due to the loss of amylose, since their chains are more susceptible to hydrolysis. The results showed that the acid hydrolysis combined with the external electric field application resulted in hydrolysis time reduction, due to the oriented ion migration.

Table 1 – Parameters of electric field application (time and number of cycles).



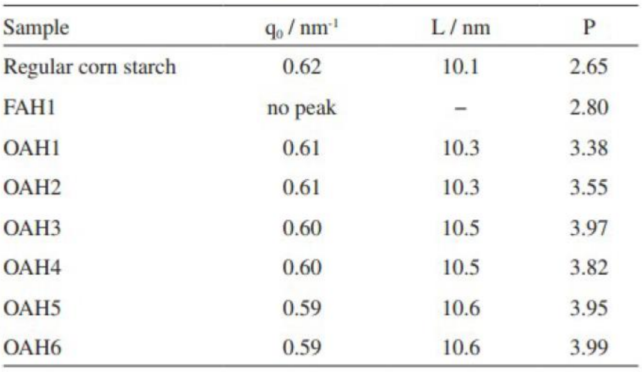
| Sample | Number of cycles[a] | time of each cycle / s | Total time / s |
|---|---|---|---|
| FAH1 | – | – | $86.4 \times 10^3$ |
| OAH1 | 1 | 10 | 10 |
| OAH2 | 2 | 10 | 20 |
| OAH3 | 5 | 10 | 50 |
| OAH4 | 2 | 25 | 50 |
| OAH5 | 3 | 20 | 60 |
| OAH6 | 10 | 10 | 100 |

Table 2 – Crystallinity degree of regular corn starch and hydrolyzed samples.



| Sample | Number of cycles | time of each cycle / s | Total time / s | Crystallinity degree / % |
|---|---|---|---|---|
| Regular corn starch | – | – | – | 33.4 |
| FAH1 | – | – | $86.4 \times 10^3$ | 39.7 |
| OAH1 | 1 | 10 | 10 | 52.8 |
| OAH2 | 2 | 10 | 20 | 49.3 |
| OAH3 | 5 | 10 | 50 | 54.2 |
| OAH4 | 2 | 25 | 50 | 51.4 |
| OAH5 | 3 | 20 | 60 | 51.6 |
| OAH6 | 10 | 10 | 100 | 48.6 |

Table 3 - SAXS data fitting, where $q_0$ is the peak center, L is the repeat distance ($2\pi/q_0$) and P is the power-law exponent.



| Sample | $q_0$ / nm$^{-1}$ | L / nm | P |
|---|---|---|---|
| Regular corn starch | 0.62 | 10.1 | 2.65 |
| FAH1 | no peak | – | 2.80 |
| OAH1 | 0.61 | 10.3 | 3.38 |
| OAH2 | 0.61 | 10.3 | 3.55 |
| OAH3 | 0.60 | 10.5 | 3.97 |
| OAH4 | 0.60 | 10.5 | 3.82 |
| OAH5 | 0.59 | 10.6 | 3.95 |
| OAH6 | 0.59 | 10.6 | 3.99 |

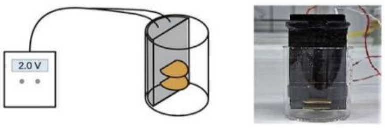


Figure 1 – Representation and real image of the experimental apparatus used for electric field application.

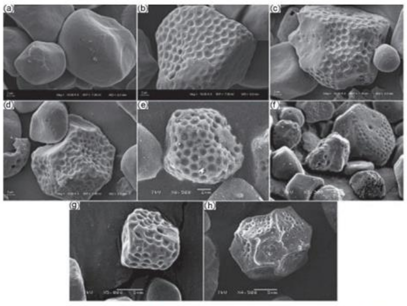


Figure 2 - SEM images of (a) regular corn starch; (b) FAH1; (c) OAH1; (d) OAH2; (e) OAH3; (f) OAH4; (g) OAH5; and (h) OAH6.

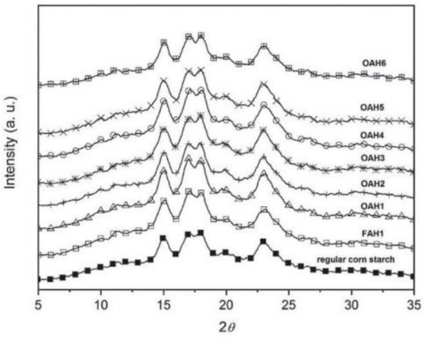


Figure 3 – XRD patterns of the samples.

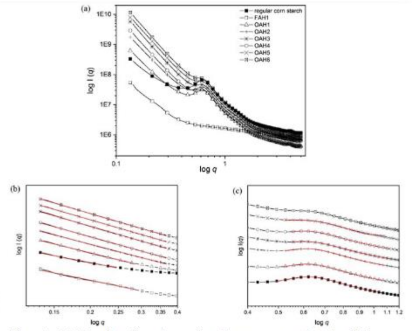


Figure 4 – SAXS profiles of samples covering all q-range measured (a); data fitting using a Power law model (b) and a Lorentz or a Gaussian function (c).

**Keywords**
acid hydrolysis, starch, electric field, crystallinity, SAXS

## References

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# *Guinier Prize*

## ***Congratulations Prof. Jill Trewhella***

*"Prof. Trewhella is a pioneer and acknowledged leader in the application of SAS to problems in structural biology as well as a tireless promoter of the technique in general, and to the structural biology community in particular. During her career, she has published over 180 original research papers, reviews, book chapters, essays, pedagogical articles, and reports. She has served on the editorial boards of the Biophysical Journal, Biochemistry, Biology and Medicine and others.*

*Her leadership in the development of and advocacy for well-defined standards for assessing data quality, model validation, publication and data archiving appropriate for the biosciences field culminated in the publication and wide acceptance of guidelines used by the bioSAS community today. Throughout her stellar career, she has also mentored generations of biomolecular SAS researchers. Prof. Trewhella's achievements, positive influence and strong contributions clearly make her a most deserving recipient of the Guinier Prize."*

Guinier Prize Selection Committee

# *Otto KratkyPrize*

***Congratulations Malina Jop***

*For your great contribution as a young scientist at SAS2022 with the work: “In-situ SAXS Investigation Of The Calcination Process During Synthesis Of Soft Templated Carbons With Ordered Cylindrical Mesoporosity“*

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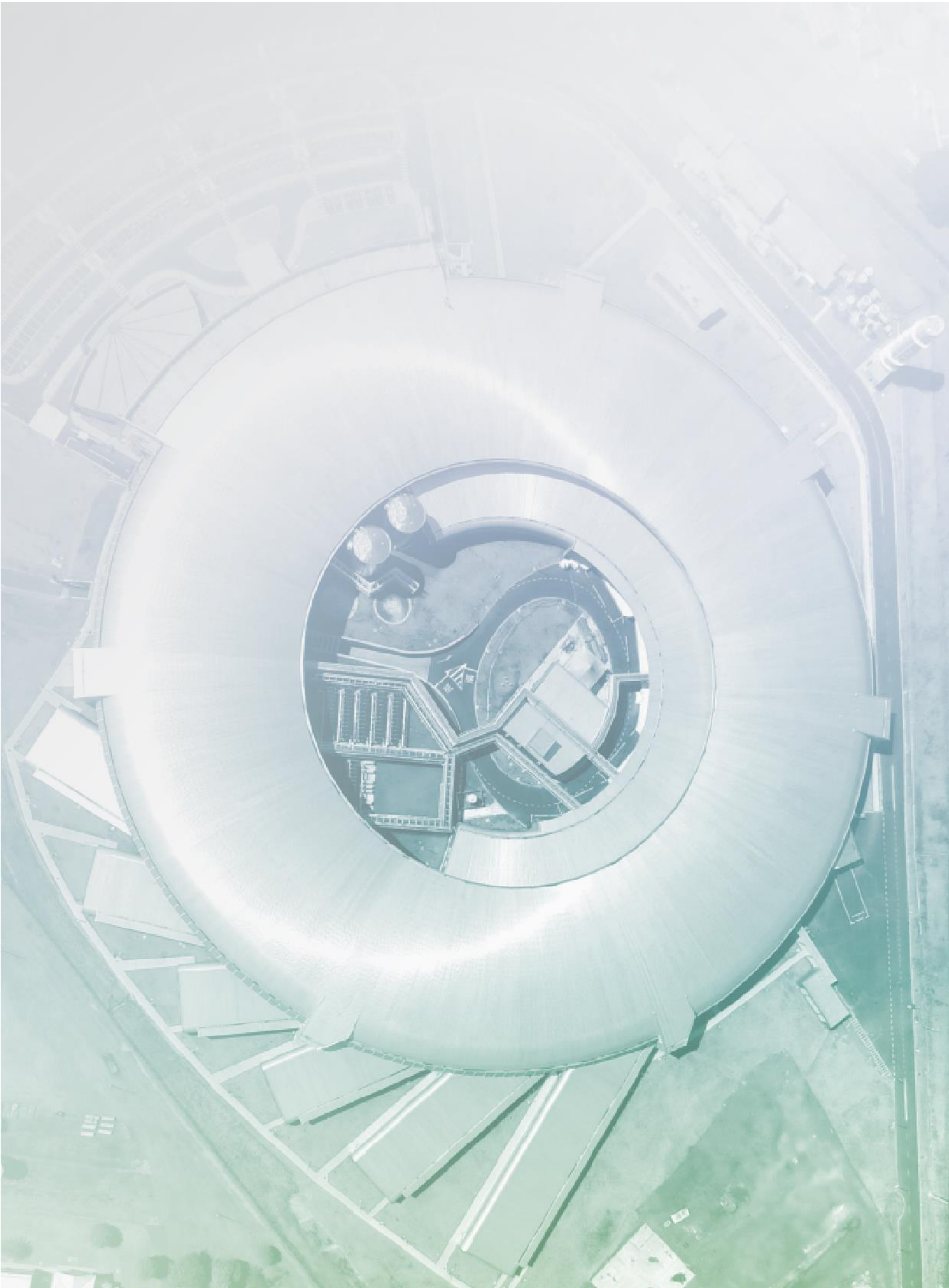

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