Structural Analysis of Highly Disordered Materials Using Total Scattering

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Structural analysis of highly disordered materials (such as, liquids, glasses, molecules, and nanomaterials, etc.) using total scattering (X-ray, neutron, or electron), particularly pair distribution function (PDF) has been extremely fruitful in the past few decades. However, progress in operando studies of these materials has often been hindered by extremely low signal and instrumental difficulties. To meet the current demands for ex-situ and operando structural analysis of liquids, glasses, and highly disordered materials, this workshop aims to provide a forum for the PDF user community to circulate not only basic knowledge of PDF but also current cutting-edge frontier research in structural analysis of highly disordered materials. Also, this workshop will provide an opportunity to discuss currently available PDF modeling software and future development of PDF modeling software for highly disordered materials.

Thursday, April 27

Start Time (ET)	Title	Speaker (Affiliation)
09:00	Atomic Pair Correlations: Anisotropy and Atomic Dynamics	Takeshi Egami (University of Tennessee)
09:25	Water and amorphous ices – the structural evolution from high- to low-density	Katrin Amann-Winkel (Stockholm University)
09:45	Laboratory PDF – liquids and complexes in solution	Mirijam Zobel (RWTH Aachen University)
10:05	Atomic pair distribution function of liquids under extreme conditions	Janes W E Drewitt (University of Bristol)
10:25	Application of synchrotron total scattering and PDF analysis to mixtures of phases in natural and synthetic samples	Marc Michel (University of Virginia)
10:45	Experimental Method to Quantify the Ring Size Distribution in Silicate Glasses and Its Simulation Validation	Ying Shi (Corning)
11:05	New Insight into the Structure of Aqueous Salt Solutions by Adding Chemical and/or Environmental Dimensions to Pair Distribution Function Analysis	James Martin (North Carolina State University)
11:25	Double-difference PDF to investigate nanoparticle dispersions	Sabrina Thomä (RWTH Aachen University)

Friday, April 28

Start Time (ET)	Title	Speaker (Affiliation)
09:00	Structure-Function Characterization of Interfacial Catalyst Thin Films Using Operando Grazing-Incidence Total X-Ray Scattering and Pair Distribution Function Analysis	David Tiede (Argonne National Laboratory)
09:20	X-ray analysis and modeling of molecular liquids and glasses.	Chris Benmore (Argonne National Laboratory)
09:40	Structure of molten salts under extreme conditions	Alexandr Ivanov (Oak Ridge National Laboratory)
10:00	Data-Driven Extraction and Atomistic Modeling of Pair Distribution Functions from Complex Environments: Application to the Solvation Structure of Small Molecules	Niklas B. Thompson (Argonne National Laboratory)
10:20	Watching nanoparticles grow	Karena Chapman (Stony Brook University)
10:40	TOPAS PDF capability	Jue Liu (Oak Ridge National Laboratory)
11:05	Discussion of developing a new PDF software for amorphous materials/continuity issues on existing software	Gihan Kwon (Brookhaven National Laboratory)
11:30	Discussion of future development of experimental capabilities.	Jue Liu (ORNL), Leighanne Gallington (ANL), Gihan Kwon (BNL)

Thursday, April 27

Atomic Pair Correlations: Anisotropy and Atomic Dynamics

Takeshi Egami
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Atomic two-body correlation functions, such as the PDF, can be directly determined by x-ray or neutron scattering measurements, and is a powerful technique to characterize disordered matter, such as liquids, glasses and crystals with imperfections. Usually the samples are macroscopically isotropic, such as powder, and the PDF analysis is carried out assuming isotropic nature. However, it can readily be extended to anisotropic case using the spherical harmonics expansion. I show how such analyses helped understand the structure of metallic glasses under uniaxial stress. Often the response to the structure is more informative than the structure itself in characterizing the structure of glass. The PDF can also be extended to describe the dynamic correlations among atoms using inelastic x-ray or neutron scattering. The dynamic structure factor, $S(Q, E)$, where Q and E are the momentum and energy exchange in scattering, can be double Fourier-transformed into the Van Hove function, $G(r, t)$, to describe the dynamic correlation between an atom at $t = 0$ and another atom at time t. I discuss how it helped elucidate properties of liquid for water and other liquids. The Van Hove function is a powerful method to characterize the dynamics of

complex materials, and it is likely that a significant fraction of the results from inelastic scattering measurements will be displayed by this function.

Water and amorphous ices – the structural evolution from high- to low-density

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Water is ubiquitous and the most important liquid for life on earth. Nevertheless, various macroscopic properties of water are most anomalous, such as the density maximum at 4°C or the divergence of the heat capacity upon cooling. The fundamental origin of these anomalies is yet to be fully understood. Computer-simulations suggest the anomalous behaviour of ambient and supercooled water to be explained by a two state model of water [1]. An important aspect in this ongoing debate is the fact that water can form different amorphous solid states, namely high- and low-density amorphous ice, HDA and LDA [2]. What can we learn from X-ray scattering experiments regarding their structure? How are the amorphous ices connected to liquid water?

In my talk I will discuss our diffraction experiments obtaining O-O Pair-Distribution Functions (PDF) of different amorphous ices [3,4]. Further, we will look into time-resolved and dynamical information during the phase transition between different states [5-7].

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Laboratory PDF – liquids and complexes in solution

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Although the very first laboratory-based X-ray pair distribution function (PDF) analysis had been carried out in the 1930s [1], laboratory PDF studies have been pretty uncommon till a few years back. [2] We have significantly pushed instrumental resolution of PDF data in the laboratory by reducing air scattering and optimizing beamstop positioning for a diffractometer in transmission geometry, using a MYTHEN2 4K module to cover a large angular range. [3] The use of monochromatic Ag Kα_1 radiation permitted

laboratory PDF data to be fitted over interatomic distance ranges of several dozens of Angstroms. The structural characterization of ionic liquids remained challenging with this setup [3], while even difference-PDF data of heterogeneous catalysts can be retrieved with astonishingly high sensitivity [4]. Recently, we further showed that it is possible to measure laboratory PDF data on single crystal diffractometers, using high-energy X-ray detectors such as the HyPix-Arc series (Rigaku) or Photon III (Bruker) combined with high-flux microfocus sources. [5] An advanced data collection strategy on the Bruker D8 QUEST enabled us to characterize the local structure of polynuclear lanthanide complexes in the solid state and in particular in solution. While not being able to compare with the instrumental resolution of dedicated laboratory PDF powder diffractometers, the resolution is sufficient to monitor the self-assembly of tetranuclear species with $Ln_4(OH)_4$ cores in organic solvents with an overwhelming measurement time of only 30 minutes.

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Atomic pair distribution function of liquids under extreme conditions

Dr James Drewitt, HH Wills Physics Laboratory, University of Bristol.

The structural response of liquids under extreme conditions (high temperature and/or pressure) is important from technological, planetary science, and fundamental science perspectives. For example, understanding the structure and solidification pathways in liquid oxides and metals at extreme conditions can enable us to unravel the secrets of liquid-liquid transitions and glass formation, to develop new materials with novel physical properties, and to understand geophysical processes (e.g., magma genesis, planetary differentiation) in deep planetary interiors.

However, the disordered nature of liquids at the atomic scale makes characterising their structure challenging. For liquid oxides and metals this is exacerbated by their high melting temperatures. Measurements at simultaneous high pressure and temperature conditions are doubly challenging, requiring specialised instrumentation to generate these extreme conditions, whilst simultaneously allowing good accessibility to the sample.

In this talk, I will discuss developments in containerless levitation techniques at neutron and synchrotron x-ray facilities for *in situ* measurements of the atomic pair distribution function of high temperature liquids. I will also discuss recent advances in pressure cell technology for measuring the structure of liquids under high pressure and temperature conditions, as applied to planetary magmas and liquid metals, and interpreted with the aid of molecular dynamics simulations.

Application of synchrotron total scattering and PDF analysis to mixtures of phases in natural and synthetic samples

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Abstract

Pair distribution function (PDF) analysis of synchrotron total scattering data is a versatile and efficient technique for examining the atomic order of natural and synthetic samples. It can be applied to crystalline, poorly crystalline, and amorphous solids, including mixtures of phases with different degrees of crystallinity. The removal of parasitic background signal caused by the sample environment/reaction cell is critical to using the PDF method for in situ and operando experiments, as well as for measuring relatively dilute samples, such as nanoparticle suspensions in water. We have developed a method that uses mixed flow reactors and in situ PDF analysis to understand what chemical factors influence the early stages of a mineral growth process. This setup has been used successfully to observe the structures of molecular clusters (~ 1 nm) that are precursors to amorphous calcium phosphate (ACP), carbonate (ACC), and ferric hydroxides, as well as their crystalline transformation products. This talk will highlight the importance of background subtraction for total scattering experiments in which the parasitic signal is > 99% of the total scattering intensity. It will also demonstrate how we are using total scattering and PDF analysis to determine the identities and abundances of different crystalline, nanocrystalline, and amorphous phases in sediments collected from a surface water reservoir. These types of natural materials can be sensitive to processing steps such as filtering and drying. As such, synchrotron experiments are essential because samples can be measured in solution by removing the large parasitic background signal.

Experimental Method to Quantify the Ring Size Distribution in Silicate Glasses and Its Simulation Validation

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Silicate glasses have no long-range order and exhibit a short-range order that is often fairly similar to that of their crystalline counterparts. As such, the out-of-equilibrium nature of glasses is largely encoded in their medium-range order. However, the ring size distribution—the key feature of silicate glasses' medium-range structure—remains invisible to conventional experiments and, hence, is largely unknown. Here, by combining neutron diffraction experiments and force-enhanced atomic refinement simulations for two archetypical silicate glasses, we show that rings of different sizes exhibit a distinct contribution to the first sharp diffraction peak in the structure factor. Based on these results, we demonstrate that the

ring size distribution of silicate glasses can be determined solely from neutron diffraction patterns, by analyzing the shape of the first sharp diffraction peak. This method makes it possible to uncover the nature of silicate glasses' medium-range order.

Key words: neutron total scattering, ring size distribution, first sharp diffraction peak

New Insight into the Structure of Aqueous Salt Solutions by Adding Chemical and/or Environmental Dimensions to Pair Distribution Function Analysis

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Diffraction experiments have long been used to gain structural understanding of disordered materials such as liquids and glasses. Interatomic distances out to first to second nearest neighbor intermolecular contacts can be reasonably assessed through Pair Distribution Function (PDF) analysis. However, the random orientation of local structure in liquids reduces the measured structural information to a single radial dimension, in contrast to 3-D spatial information accessible for single crystal diffraction measurements. Analysis of 1-D PDF data is further complicated by the fact that for n possible atomic components there are (n+n(n-1)/2) types of atom-atom pair correlations, which are difficult to resolve, particularly when multiple pair correlations occur at similar distances. However, structural information that can be obtained from PDF analysis can be dramatically enhanced by adding chemical and/or environmental dimensions to the experiments.

Herein we recognize that intramolecular pair correlations should be relatively invariant with respect to changes in concentrations or temperature. By contrast, changes in molecular ion speciation and/or intermolecular pair correlations often exhibit substantial changes as a function of concentration and/or temperature. To access the chemical and/or environmental dimensions, we collect a substantial number of diffraction measurements across a perturbing variable, e.g., concentration or temperature. We then subtract the original signal from the signal of the perturbed sample to yield the differential PDF pattern. Examples of unique structural detail of aqueous salt solutions, revealed through such variable concentration (d-VC-PDF and variable temperature (d-VT-PDF), will be discussed.

Double-difference PDF to investigate nanoparticle dispersions

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Nanoparticles in dispersion are widely applied in many different areas like in biomedicine or for waste water treatment. In these dispersions the nanoparticles interact with the dispersion medium and an interfacial region with different structure from bulk exists. [1] In case of water, this region with enhanced ordering is called hydration shell. An understanding of the order in this interfacial region is crucial, since it affects the whole panoply of solvent-nanoparticle interactions.

Here we present how we investigate aqueous iron oxide nanoparticle dispersions of 6-7 and 15 nm in diameter with high energy X-ray total scattering. By double-difference pair distribution function (dd-PDF) analysis of the total scattering data from the dispersion minus bulk water minus the IONP powder tiniest signal contributions can be retrieved. Three years ago, we received a strong dd-PDF signal from IONP dispersions with particle concentration up to 0.5 wt%, freshly redispersed after purification. The signal,

with three sharp peaks within 3 Å and broad oscillations beyond up to 15 Å, was interpreted as hydration shell with an adsorbed water layer and weaker restructured water beyond, well agreement with literature. [2] Our recent investigations, however, trace these features back to ethanol impurities of ca. 6 vol%, which feature local structural motifs in the dilute aqueous dispersions that differ from motifs in bulk ethanol. [4] The ethanol concentration can be determined from the total scattering data. [3] Furthermore, this little ethanol amount has huge impact on beam-induced redox chemistry of the iron oxide nanoparticles in the highly brilliant X-ray beam of ESRF-EBS, even at energies of 60 keV.

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Thursday, April 28

Structure-Function Characterization of Interfacial Catalyst Thin Films Using Operando Grazing-Incidence Total X-Ray Scattering and Pair Distribution Function Analysis

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Understanding the relationship between the atomic structure and macroscopic properties for interfacial thin films is a cross-cutting challenge for a broad range of applications, including artificial photosynthesis, heterogeneous catalysis, and energy storage. Particularly for amorphous and mesoporous catalyst thin film materials, high energy X-ray scattering (HEXS) and pair distribution function analysis (PDF) offers unique opportunities to resolve structure features across inner and outer coordination shells (0.1 to 1 nm) and intermediate length (1 nm to 50 nm) ranges that can provide critical benchmarks for mechanistic modelling. We note that capabilities for tracking atomic structure within ultrathin films has been enhanced by the development of beamlines with micro-focused high energy X-rays, allowing PDF analyses from grazing incidence scattering (GI-PDF). Particularly for functional thin films at liquid-solid interfaces, the grazing incidence geometry offers opportunities for selectively enhancing detection of scatting from the interfacial film. In this presentation we demonstrate opportunities for utilization of GI-PDF for characterization of few-atom metal oxide clusters hosted within 100 nm thick organic polymer films and structure characterization of sub-40 nm thick water-splitting catalysts films of 1st row transition metal oxides during operando electrocatalytic function.

X-ray analysis and modeling of molecular liquids and glasses.

Chris J. Benmore

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PDF analysis of high energy x-ray diffraction data represents a powerful tool for investigating the structure of molecular liquids, glasses and amorphous materials. However, inadequacies in the currently available data analysis and modeling procedures have sometimes led to dubious structural interpretations of weakly scattering systems. The lack of periodic structure, often used as a starting point in the PDF modeling of crystalline systems, is not applicable for liquids. Data analysis methods require the appropriate corrections to be applied and sum rules to be met in order to obtain correctly normalized data, and for accurate coordination numbers to be extracted. For properly normalized x-ray structure factors, Monte Carlo modeling methods such as RMC and EPSR provide 3-dimensional atomistic models consistent with the measured data in Q-space, provided realistic chemical constraints are imposed. Empirical Potential Structure Refinement achieves this by using an approximate Lennard-Jones potential plus an empirical potential with partial charges to obtain representative atom-atom interactions. EPSR is particularly useful for x-ray studies of molecules because the scattering is dominated by the molecular backbones and orientations of aromatic rings. Examples of applications to aqueous solutions, polymers and pharmaceuticals will be presented.

Structure of molten salts under extreme conditions

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Enhancing the solar energy storage and nuclear power delivery afforded by emerging molten salt-based technologies requires a fundamental understanding of the complex interplay between structure and dynamics of the ions in the high-temperature media. This not only makes characterization difficult, but also renders it highly questionable whether conventional in-lab methods of analysis typically used for solids could be applied to the molten state. Our research seeks to provide atomic-level insights into the ionic correlations in high-temperature molten inorganic salts by applying synchrotron X-ray and neutron scattering coupled with ab initio molecular dynamics simulations and reverse Monte-Carlo modeling. A thorough analysis paints a more complex picture than previously understood, with the formation of ionic chains even at high temperatures and surprising similarities with aqueous solutions, suggesting a possible universal connection between local structural changes and physical properties of liquids despite the drastically different types of chemical bonding. We discuss how the total scattering approaches could help understand the aggregation phenomena and transport in molten salts, with pertinence to novel molten salt reactors and emerging concentrated solar power technologies.

Data-Driven Extraction and Atomistic Modeling of Pair Distribution Functions from Complex Environments: Application to the Solvation Structure of Small Molecules

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High-energy total X-ray scattering, complemented by real-space analysis via the pair distribution function (PDF), is an indispensable tool in determining the local atomic structure of amorphous and nanoscale

materials. While the application of PDF analysis to bulk systems is a mature field, there is burgeoning interest in extending its domain of application to more complex sample environments, such as thin films and dilute solutions, with an eye toward *in operando* measurements under realistic operating conditions. In this context, two complementary challenges emerge: (1) In settings where the background signal dominates, how can the desired scattering information be extracted from the raw data in a robust and reproducible fashion?; and (2) What are the best-practices to be employed when developing the models necessary to understand the structural information encoded by the PDF?

This talk will discuss each of these challenges in turn for the case of total scattering measurements performed on dilute solutions. A data-driven algorithm to extract the PDF from such measurements will be presented. By posing the (multi-component) background subtraction task as a rank minimization problem, we demonstrate, through simulations, that accurate PDFs can be reconstructed in a semi-automated fashion from noisy measurements in which the desired scattering represents a small fraction of the total scattered intensity. We will then apply this methodology to experimental measurements of dilute solutions of organometallic complexes relevant to solar energy conversion and explore the application of multi-scale atomistic modeling approaches to understand subtle details regarding the solvation structure of these molecules. These include direct detection of solvation shells about the solute, as well as specific non-covalent interactions, such as H-bonding.

Watching nanoparticles grow

Bryan A. Sanchez Monserrate, Michelle L. Beauvais, Peter J. Chupas, John B. Parise, and Karena W. Chapman

Understanding and controlling how nanomaterials evolve dynamically during synthesis is critical to deliberately controlling their physicochemical properties and accessing new states. However, probing how nanomaterials form and evolve in solution, to develop a mechanistic understanding, is an experimental challenge owing to the dilute nature of the species and the time scales on which they change. This presentation will describe our recent efforts to explore solution-phase nanoparticle synthesis using X-ray Pair Distribution Function analysis and developments of new in-situ capabilities to enable these studies.