X-ray Photon Correlation Spectroscopy (XPCS) and Coherent X-ray Diffraction Imaging (CXDI)

Examples from ESRF and Perspectives for X-ray Lasers

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Outline:

• XPCS history

• Current capabilities and forthcoming upgrades at ESRF

• CXDI at ESRF

• XPCS at synchrotrons vs. X-ray lasers

• Concluding remarks
XPCS history

First ESRF paper in 1995 (Troika, Fe₃Al)
First SAXS paper 1995 (X25 NSLS, Au colloids in glycerol)

Dedicated XPCS beamlines: Troika ID10A/C (ESRF)
                        8-ID (APS)

Total output: 40-50 papers/year

Keywords: physics oriented, specialist’s technique

Competitors/colleagues arrive(d): Diamond Light Source, Swiss Light Source, Petra III, NSLS-2,…….

What about LCLS and X-FEL ???
Troika (ID10): One of the first operational beamlines at ESRF (1992)

Troika I: Open undulator beamline (general purpose, UM since 1994)
Later, the Troika I branch specialized in XPCS

ID10B (Troika II): Independent side branch for GID & XR (since 1998)

Troika III: End-station (since 2001). Specialized in coherent SAXS/XPCS
Recent developments of CXDI
Source

2 U27 (27mm period, 11mm min. gap) and 1 U35 undulator. 4.8m in total

Brilliance

Coherent intensity
CRLs in white beam at ID10A

B. Lengeler et al

Unit 1: 2 CRLs with 200µm radius (Troika I, ~1:3@8keV);
Unit 2: 2 CRLs with 300µm radius (Troika III, ~1:1@8keV);
Unit 3: 1 CRL with 300µm radius (Troika III, ~1:1@7.2keV);

Set n.1: Troika I@8keV

Set n.2: Troika III@8keV

Set n.3: Troika III@7.2keV

FWHM: 20µm
Gain factor: ≈8

FWHM: 21µm

Gain factor: ≈10
Maxipix-2 detector

Medipix detector: 256 x 256 pixels, 55 \( \mu \)m pixel size
Photon counting, Upper and lower energy threshold, 30Hz readout

(C. Ponchut, ESRF)
Maxipix-2 detector

>1kHz full-frame readout, 65k pixels, 55µm pixel size, photon counting

now with 2 chips, soon with 4…..

Wish: Faster, more pixels, hardware correlator via FPGA (smart detector)
Maxipix-2 detector

SAXS pattern, 1kHz

Current max. speed: 1200 frames/s
675 shifts/year requested on average
385 shifts/year provided on average
Over-subscription: 1.75

Main request from soft-matter (SC) and hard-condensed matter (HE+HS)


**Dynamical heterogeneity in colloidal gels**: *Phys. Rev. E* 76, 051404 (2007)

**Transient gelation**: *Phys. Rev. E* 76, 010401(R) (2007)


**Bulk fluctuations in a lamellar phase**: *Phys. Rev. E* 74, 031706 (2006)


**Grazing incidence XPCS**: *J. Sync. Rad.* 12, 786 (2005)

Dynamics of Nanoparticles in a Supercooled Liquid

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The dynamic properties of nanoparticles suspended in a supercooled glass forming liquid are studied by x-ray photon correlation spectroscopy. While at high temperatures the particles undergo Brownian motion the measurements closer to the glass transition indicate hyperdiffusive behavior. In this state the dynamics is independent of the local structural arrangement of nanoparticles, suggesting a cooperative behavior governed by the near-vitreous solvent.

DOI: 10.1103/PhysRevLett.100.055702
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coherent X-rays

Low T SAXS chamber

The European Light Source
From diffusive motion to cooperative ballistic behavior near $T_g$

Nanoparticles in 1,2-propanediol

KWW: $g^{(2)}(t) = \beta \exp(-2(\tau t)^{\gamma}) + 1$

Fundamental changes at $\sim 1.2T_g$

$$\text{SNR} \propto B \tau^{1/2} S(q)$$

The goal is to achieve faster times and larger $Q$ to investigate the dynamic properties of e.g. supercooled liquids ($\alpha$, $\beta$ relaxations) on “molecular” length scales (necessitates: higher Brilliance, larger and faster 2d detector)
Capillary waves on highly viscous liquids: \[ \Gamma = \frac{2\gamma}{\eta} Q \]

What happens as \( \eta \to \infty \) i.e. at the transition from a supercooled liquid to a glass?

What happens with the shear response as the liquid solidifies?

RHEOLOGY (modulus=stress/strain)

Liquid: deforms cont. under stress
Solid: equilibrium deformation under stress

Liquid: stress relaxes under a constant strain
Solid: constant stress level under constant strain
Grazing incidence XPCS

Intensity fluctuations of the speckle pattern reflect the dynamics of the sample

\[ g(q,t) = \frac{\langle I(q,0)I(q,t) \rangle}{\langle I(q,t) \rangle^2} \]

monochromatic synchrotron beam

deflecting mirror

\[ \alpha_i < \alpha_c \]

sample (liquid or solid)

pinhole aperture

slits

2D detector

beamstop

Speckle pattern

The European Light Source
CW dynamics on poly-propylene glycol (PPG)

\[
\Gamma = \frac{\gamma (q + q_0)}{2\eta_0} \left( 1 + \frac{\gamma (q + q_0)}{2G(\infty)} \right)^{-1}
\]

\[G(\omega) = i\omega \eta(\omega) + E\]

\(\Gamma \rightarrow \frac{E}{\eta} \text{ for } q \rightarrow 0\)
Elastic behavior of supercooled liquids is an extremely controversial topic in the literature and non-invasive experimental methods are missing.

Viscoelasticity of poly-propylene glycol (PPG)

\[ \eta \sim \exp\left(\frac{A}{T-T_0}\right) \quad \text{VTF law} \]

\[ E \sim \exp\left(\frac{A}{T-T_0}\right) \quad \text{VTF law} \]

Towards faster XPCS at larger Q and on weaker signals
PURPLE BOOK CDR: XPCS-CXS

1) Faster and better 2d detectors for the $\mu$s regime:
   - Pixel detectors
   - APD arrays
   - Smart detectors

2) Higher coherent flux:
   - Coherence preservation
   - No undulator sharing
   - No semi-transparent diamond beam-splitter

3) Reduce beam damage:
   - XPCS at higher energy?
   - Work further away from the source
   - Optimized sample environments

Large pixels necessitate longer sample-detector distance i.e. **larger hutches**

Separate ID10A and B

Optimized beam tailoring (size, bandwidth) in the range 7-20keV.
**Larger source-sample distance** and **larger hutches**
Idea: separation of the Troika beamlines

Coherent scattering and XPCS moves to ID22

Advantages: higher brilliance, beamsplitter diamond out, large dev. potential
On-line data reduction/data analysis

Crucial point for a state-of-the-art XPCS beamline

With increasing data-rates on-line calculation of correlation functions becomes challenging but very important

The multi-tau algorithm (K. Schätzel) can be “parallelized” to run in multiple processor (cluster) environments

Ensemble averaging (non-ergodic samples); equilibrium (one-time) or non-equilibrium (two-time) correlation functions

Speed can be increased by use of FPGAs (intelligent detector)
On-line data reduction/data analysis

\[ g^{(2)}(Q,\tau) = \frac{\left\langle I_p(Q,t)I_p(Q,t+\tau) \right\rangle_\phi}{\left\langle I_p(Q,t) \right\rangle_\phi} \left\langle I_p(Q,t) \right\rangle_{\tau \leq t \leq T} \]

\[ G(Q,t_1,t_2) = \frac{\left\langle I_p(Q,t_1)I_p(Q,t_2) \right\rangle_\phi}{\left\langle I_p(Q,t_1) \right\rangle_\phi \left\langle I_p(Q,t_2) \right\rangle_\phi} \]

Higher order correlation functions
Beam damage

Huge problem for soft condensed matter, increasing problem with higher flux

Possible ways to minimize beam damage:
- Right choice of X-ray energy
- 2D detection with shutter in front of sample
- Intelligent sample environment (flowing liquid samples)
- Working in a low-flux mode (large sample-source distance)

But in some cases the problem persists, and may create effects that mimic e.g. aging in soft glasses and gels
Sample environments

droplet generator

flow cell

J.-B. Salmon, CNRS-Rhodia, Bordeaux


flow

no flow
Coherent X-ray Diffraction Imaging

Logo physics

Phase retrieval and FFT\(^{-1}\)

SEM image

Phase retrieval and FFT\(^{-1}\)

SEM image

E. Lima, F. Glassmeier, F. Zontone, and A. Madsen
Towards bio-CXDI at Troika

- on-axis microscope mirror
- on-axis microscope lens
- cells on a vitreous membrane

Cryo-jet (100K)

Cells: ~2µm
Towards bio-CXDI at Troika

Deinococcus Radiodurans speckle pattern (hydrated, unstained)

8 keV

HIO/ER+shrink wrap

Reconstruction not shown...

E. Lima, L. Wiegart, P. Pernot, F. Zontone, M. Mattenet, E. Papillon, J. Timmins, and A. Madsen
Towards bio-CXDI at Troika

3D bio-CXDI, in progress.............

-70° … 70° rotation

array of DR cells
Hard X-ray Holographic Diffraction Imaging

(a) hologram
(b) FT(hologram)
(c) 3D reconstruction

Troika III beam → hologram → FT(hologram) → CCD
Running the phase retrieval algorithm with the FT result as support one can refine the structure and reconstruct the structure AND the reference dots.

Resolution ~25nm (close to diffraction limit)

Advantage: Very fast convergence of algorithm due to good starting conditions

CXDI with nano-beam

Beam size 100x100nm

ID13 – ESRF
E=15.25 keV

Au colloids

10 min exposure
Reconstruction with
5nm resolution

Is XPCS big enough for both X-ray Lasers and Synchrotrons?

Yes, because
• we address different length and timescales

Work at APS and ESRF paved the road but

• The scientific case for XPCS needs to be further developed and broadened

• The technique must be improved

• We can’t continue being an ‘experts only’ technique i.e. the community needs to grow
Brilliance considerations...

**ESRF:**

\[ I_c = B \frac{\lambda^2}{4} = 1.5 \times 10^{20} \times 1 \times 10^6 \times (1.5 \times 10^{-7} \text{mm})^2 / 4 \times 0.14 = 1.2 \times 10^{11} \text{ph/s} \]

\[ A_c = (\lambda D / r_{h,v})^2 = 265 \mu m (v) \times 7 \mu m (h) \]

1 pulse (73 fs) of LCLS contains 1.1e12 ph
120 pulses/s = 1.3e14 ph/s
10^{12} \text{ph/pulse}

Inter image correlations: \langle C(I_N, I_M) \rangle

Scheme will probably work for some samples. It is recommended to foresee high quality (no scattering, coherence preserving) beam attenuators.

What could be done with 1e12ph on 10ms timescales compared to today (10^9 \text{ph/10ms @ ESRF}) i.e. factor 10^3
factor $10^3$

**SAXS**: study dynamics (ms-s) of ultra dilute weakly scattering systems. Higher order correlations. Improve existing XPCS capabilities in slow dynamics (buried interfaces, solid surfaces, polymers, proteins, binary fluids, glasses, ….). High energy?

$$\frac{d\sigma}{d\Omega} \propto n V^2 (\Delta\rho)^2$$

Further out in Q, but $Q^{-n}$ power laws eat $10^3$ very fast

10nm particle diffusing in H$_2$O, can LCLS study that?

$$D_0 = k_B T / 6\pi \eta R, \Gamma = 120\text{Hz} \rightarrow Q_{\text{max}} = 2.4 \times 10^{-3} \text{ nm}^{-1} \text{ (USAXS)}$$
factor $10^3$

**WAXS:** critical fluctuations, order-disorder transitions, amorphous materials (metallic glasses), charge or spin dynamics in correlated materials, polarization effects, out of equilibrium dynamics, dynamical scaling,…..

All these experiments are today flux limited, i.e. **large potential gain with LCLS**

Inter-image correlation spectroscopy can be seen as the natural extrapolation of XPCS to AC X-ray laser sources

Issues for inter-image correlation spectroscopy: beam damage, stability, longitudinal coherence, normalization,…
10^{10} photons in split pulse

Split and delay of the pulses

**Intra image correlations:** \( <C(I, \Delta t)>_N \)

Contrast analysis of double exposures will give access to ps-ns timescales

Drawback: efficiency of split delay \( \sim 1\% \)
Averaging difficult, individual images must have statistical significance

What could be done with \( 1e10 \) ph on 1ns timescales?

\[ \Delta t = 1\text{ns} \]
\[ \Delta t = 500\text{ps} \]
\[ \Delta t = 100\text{ps} \]
\[ \Delta t = 50\text{ps} \]
10nm particle diffusing in H₂O, can LCLS detect that?

1ns $\rightarrow 10^9$ Hz $\rightarrow Q=7\text{nm}^{-1}$. Is there enough intensity?

Example (1% vol. Au particles, 100micron pixel size, 1m distance)

$\Gamma=1\text{ns}, \: Q=7\text{nm}^{-1}$

$2\times 10^{-3}$ ph/pixel/image
1nm particle diffusing in H$_2$O, can LCLS detect that?

1ns $\rightarrow$ $10^9$ Hz $\rightarrow$ Q=2.1nm$^{-1}$. Is there enough intensity?

Example (1% vol. Au particles, 100micron pixel size, 1m distance)

- Within reach! (many pixels in detector)
- Detector must be noise free, 2d, 100% eff., 120Hz rep. rate
- Speckle size, sample-detector distance (need for spatial filter?)
- Important that split-delay line has high throughput
Nano/picosecond dynamics on nanoscale in condensed matter

- Molecular excitations (vibrational, rotational)
- Brillouin scattering (phonons)
- Chemistry
- Magneto dynamics
- Polymers and bio-materials

Dynamics of functional biomolecules
all length scales and timescales matter

a cell can quasi-instantaneously switch on or off its permeability for a protein over the whole surface;
that can only be understood as a collective dynamical phenomenon

Movie: Theoretical and Computational Biophysics group, University of Illinois
Concluding remarks:

XPCS at LCLS and 3rd generation machines will to a large extent be complementary. 
0.01-1000 $\mu$s will be difficult to cover with the laser.

$10^{12}$ ph/pulse seems a lot, but not enough to saturate the detector at the relevant Qs.

Conceptual difference between inter- and intra image correlation schemes.

Both schemes provide new possibilities and challenges.

Pump-probe XPCS experiments will become feasible.  
(maybe all experiments will inevitably be pump-probe)

Possible that CXDI and XPCS techniques could merge in the future.

Very demanding detector development ahead…….