X-ray Photon Correlation Spectroscopy

Anders Madsen, ESRF

- Coherence
- X-ray Speckle
- Photon Correlation Spectroscopy
- Applications of XPCS
Coherence?

- Quantum mechanics → probability amplitudes (waves)
- Optics → Young’s double slit experiment, interference
- X-ray (and neutron) scattering

It’s all about probability amplitudes and interference !!!

Example: Young’s double slit experiment (Thomas Young, 1801)
[wave-character of quantum mechanical particles (photons)]

\[ P = |\sum_j \Phi_j|^2 \]
\[ \Phi_j \sim \exp[-i(\omega t-k l_j)] \]
\[ \omega = ck, k = 2\pi/\lambda, l_j(L,y) \]
\[ P(y) \sim \cos^2(\pi y d/\lambda L) \]
\[ \Delta y = \lambda L/d \]

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Reasons for loss in (visibility/interference/coherence):

1) Incoherent superposition of probability amplitudes \( P = \sum_j |\Phi_j|^2 \) (distinguishable alternatives, uncertainty principle)

2) Intensity interference is only observed if event is repeated many times; repetition under non-ideal conditions washes out the visibility

*Using a (partially) coherent X-ray source 2) is a major limitation*

Non-ideal conditions:

- \( E_{in}, E_{out}, k_{in}, k_{out} \) not well defined in the experiment
- Disorder in the scattering sample
- Limited detector resolution (temporal and spatial)
- The source is chaotic……..

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Light sources

- Chaotic sources (spontaneously emitted photons)
  - Lab. X-ray generators
  - Synchrotron and Neutron sources
  - Radioactive nuclei

- One-mode sources (stimulated emission, Glauber light)
  - Unimodal lasers

Important parameter: \( N_C = \text{photons pr. coherence volume} \)

\( N_C \approx 10^{-3} \) for typical ESRF undulator
\( N_C \approx 10^7 \) for typical optical laser

Coherence volume \( V_c : \pi l_h l_v l_l / 4 \)

horizontal, vertical and longitudinal (temporal) coherence length
**Chaotic source (ESRF undulator)**
(spontaneous, independent emission in all modes)

**Longitudinal (or temporal) coherence**
At times $\gg \tau_0$ the field amplitudes from a chaotic source are no longer correlated due to the wavelength spread.

\[
g^{(1)}(\tau) = \frac{\langle E^*(t)E(t+\tau) \rangle}{\langle |E(t)|^2 \rangle} \propto e^{-\tau/\tau_0} \]
(Gaussian 1st order time-correlation function)

\[
\tau_0 = \frac{1}{(\pi \Delta \nu)} = \frac{\lambda^2}{(c\pi \Delta \nu)} \approx 3\text{fs}
\]

Longitudinal coherence length $l_1 = c\tau_0 = \frac{\lambda}{(\pi \Delta \nu)} \approx 1\mu m$

**Spatial coherence**
Analogy with Young’s double slit experiment:
Transverse coherence length $(v,h)$:
\[
l_{v,h} = \frac{\lambda L}{\pi d_{v,h}} \approx 2-150\mu m
\]
**Important source parameters**

Brilliance $B = \text{photons/sec} / [\text{source area} \times \text{solid angle} \times \text{bandwidth}]$

Lateral coherence area $A_t = \pi l_h l_v / 4 = (\lambda L)^2 / (4\pi d_h d_v)$  ($\sim 200 \ \mu\text{m}^2$)

$N_c = \text{photons in } V_c (V_c = A_t \times l_l)$

Coherent solid angle $\Omega_C = A_t / L^2 = \lambda^2 / (4\pi d_h d_v) = \lambda^2 / 16A_s$

$N_c = B \times \tau_0 \times A_s \times \lambda^2 / 16A_s \times \Delta\nu / \nu = B \lambda^3 / (16\pi c)$

Coherent intensity $I_c = \left( N_c / V_c \right) \times c \times A_t$

$= B \times (\lambda / 4)^2 \times (\Delta\lambda / \lambda)$  ($\sim 10^{10} \ \text{ph/s}$)

Coherent intensity decreases with decreasing $\lambda$ (increasing energy)!

Coherent scattering is very Brilliance-hungry!

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Coherence lengths

Example: Young’s double slit experiment with X-rays

\( \lambda = 2.1\,\text{Å}, \quad d = 11\,\mu\text{m} \)
Visibility(\(\beta\)) \(\sim\) 80%

\( \lambda = 0.9\,\text{Å}, \quad d = 11\,\mu\text{m} \)
Visibility(\(\beta\)) \(\sim\) 30%

\( \Delta y = \frac{\lambda L}{d} \)


Transverse coherence length \((v,h)\): \( l_{v,h} = \frac{\lambda L}{\pi d_{v,h}} \) (~5-250 \(\mu\text{m}\))

Longitudinal coherence length \(l_l = c\tau_0 = \frac{\lambda^2}{(\pi \Delta \lambda)} \) (~1\(\mu\text{m}\))

Contrast \(\beta \approx \frac{(\text{coherence volume})}{(\text{scattering volume})}\)

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Setup for coherent X-ray scattering

\[ I_C \propto B \times \lambda^2 \]

Coherence parameters:
- Transverse coherence length \( l_{h,v} = \frac{\lambda L}{\pi d_{h,v}} \)
- Longitudinal coherence length \( l_l = \frac{\lambda^2}{\pi \Delta \lambda} \)
- Contrast (degree of coherence) \( \beta = \beta (\Delta \lambda / \lambda, ...) \)

ID10A:
- \( I_c \sim 2 \times 10^8 \) ph/s (1997)
- \( I_c > 1 \times 10^{10} \) ph/s (2008)

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Fraunhofer diffraction from slit

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Coherent scattering: What is the information we gain?

If coherent light is scattered from a disordered system it gives rise to a random (grainy) diffraction pattern, known as **speckle**. A speckle pattern is an interference pattern and related to the **exact spatial arrangement** of the scatterers in the disordered system (no averaging).

\[
I(Q,t) \propto S_c(Q) \propto |\sum e^{i Q R_j(t)}|^2
\]

\( j \) in coherence volume \( V_c = l_v l_h l_l \)

Aerogel SAXS
\( \lambda = 1\text{Å} \)
CCD (22 μm pixels)
10 micron beamsize

**speckle size \( \sim \lambda/d \)**

D. Abernathy *et al*,

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Longitudinal coherence length and scattering geometry

PLD: Path Length Difference $< l_l$

SAXS:
$PLD = t + BC - AC \approx d \tan(2\theta)$

Bragg geometry:
$PLD \approx 2(\mu^{-1})\sin^2\theta$

Grazing Incidence:
$PLD \approx 2\Lambda \sin\alpha_i$

Condition: $PLD < l_l$ !!!

SAXS: $d=10\mu m$, $\lambda=1.55\AA$, $\Delta \lambda/\lambda=1.4 \times 10^{-4} \rightarrow \theta_{\text{MAX}} \approx 1^\circ \rightarrow Q_{\text{MAX}} \approx 0.15\text{Å}^{-1}$

Reflection: $\mu^{-1}_{\text{Cu}} = 22\mu m$, $\lambda=1.55\AA$, $\Delta \lambda/\lambda=1.4 \times 10^{-4}$
$\rightarrow \theta_{\text{MAX}} \approx 5^\circ \rightarrow Q_{\text{MAX}} \approx 0.7\text{Å}^{-1}$

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What is the contrast of the setup?

Statistical speckle analysis

Princeton Instruments CCD
1 Photon gives 879 adu
2 Photons give 1758 adu

Gamma-Poisson distribution of intensity coming from $M$ statistically independent superimposed speckle patterns

$$P_M(I) = (M/<I>)^M\Gamma^{-1}\exp(-MI/<I>)/\Gamma(M)$$

$$\sigma^2 = <I^2>/M, \ 1/M = \beta$$

Static speckle pattern

Coherent SAXS, 8keV
10 micron beam

Vycor™ silica glass

$$M \sim V_{\text{scattering}}/V_{\text{coherence}}$$

contrast $\beta = 1/M = 1/2.81 = 35.6\%$

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What is the shape of a speckle?

Pink beam ID10C ($\Delta\lambda/\lambda=1.5\%$)
$E=8$keV, $20\mu m$ beamsize
$I_{\text{coherent}} > 1 \times 10^{11}$ ph/s

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**XPCS: What is the information we gain?**

- Real space
- **Reciprocal space**
  - Non-coherent
  - Coherent

$I(Q)$  \[\langle I(Q) \rangle\]

**Kinetics**

$I(Q,t)$  \[I(Q,t)\]

**Dynamics**

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What do we measure?

Temporal intensity auto-correlation function

\[ g^{(2)}(Q, \tau) = \frac{\langle I(Q,t)I(Q, t+\tau) \rangle}{\langle I(Q) \rangle^2} \]

\[ g^{(2)}(Q, \tau) = 1 + (\text{Re}\{S(Q, \omega)\})^2 = 1 + |f(Q, t)|^2 \]

\[ |f(Q, t)| \propto \int \int b_n(Q)b_m(Q) \exp(iQ \cdot [r_n(0) - r_m(t)]) \]

Dynamic structure factor (Lorentzian shape)

\[ S(Q, \omega) \sim \frac{1}{[\omega - \omega_0(Q)]^2 + \Gamma(Q)^2} \]

\[ g^{(2)}(Q, \tau) = 1 + \exp(-2\Gamma \tau) \cos^2(\omega_0 \tau) \quad \text{(propagating waves)} \]

\[ g^{(2)}(Q, \tau) = 1 + \exp(-2\Gamma \tau) \quad \text{(Brownian motion, overdamped waves)} \]

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Challenges

Non-ergodicity i.e. $<>_t \neq <>_\phi$
(time average different from ensemble average)

systems that do not sample the entire allowed set of spatial configurations

Typical example:
samples with some degree of (quasi) static disorder (gels, glasses, etc)

To properly calculate $g^{(2)}$ the ensemble averaging $<>_\phi$ must be performed explicitly


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Challenges

Non-ergodicity i.e. $<>_t \neq <>_\phi$
(time average different from ensemble average)

systems that do not sample the entire allowed set of spatial configurations

Solution: move the beam around and average $g^{(2)}$ over many exposures

or (much better)

Use a 2D detector and catch many pixels with same $|Q|$

$$g^{(2)}(Q, \tau) = \frac{\left< \left< I_p(t)I_p(t+\tau) \right>_\phi \right>_t}{\left< \left< I_p(t) \right>_\phi \right>_{0 \leq t \leq T-\tau} \left< \left< I_p(t) \right>_\phi \right>_{\tau \leq t \leq T}}$$

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Challenges

Non-equilibrium i.e. not all $\Delta t$ are equivalent $g^{(2)}$ depends on both $\Delta t$ and the absolute time (age)

Solution: calculate the correlation function without time averaging (two-time correlation function)

$$G(Q,t_1,t_2) = \frac{\left\langle I(Q,t_1)I(Q,t_2)\right\rangle_\phi}{\left\langle I(Q,t_1)\right\rangle_\phi \left\langle I(Q,t_2)\right\rangle_\phi}$$

age: $t_a = (t_2 + t_1)/2$

lag time: $\tau = t_2 - t_1$

Only with a 2D detector several Qs at same age can be recorded

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2d detectors for multi-speckle XPCS

Advantages: More efficient data-taking (Mpixels) with 2d detector
Beam induced sample damage minimized

Drawbacks: 2d detectors are slow, noisy, have limited dynamic range,
are not always photon counting, have limited resolution,
radiation hardness can be a problem........

Princeton Instruments  Dalsa  Medipix/ Maxipix

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Limitations

- s/n ratio (more flux)
- Speed and area of 2D detectors
- Beam damage (minimize exposure)

Medipix-II detector, 1kHz ff

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Depletion gel

Complex phase diagram
\( r_g/R (0.1) , \phi (20\%) , c_p (4.3\text{mg/cm}^3) \)

- Mixture of Poly(MethylMethacrylate) PMMA particles (spherical, \( R \approx 1000 \text{ Å} \)) coated with poly-12-hydroxystearic acid and free polymer (polystyrene) in cis-decalin
- Entropic forces between the polymer coatings layers → infinite repulsion
- Depletion effect due to the free polymer → attractive potential

Inter-particle interaction potential

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The gel phase is transient.....


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...but the structure is constant in the accessible Q-range
Two time analysis

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

Kohlrausch-Williams-Watts (KWW):

\[ g^{(2)}(\tau) = 1 + \exp(-2(\Gamma \tau)^\gamma) \]


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A jamming transition?


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Jamming

**Micro-collapses**

Kohlrausch-Williams-Watts (KWW):
\[ g^{(2)}(t) = 1 + \exp(-2(\Gamma t)^\gamma) \] with \( \gamma \sim 1.5 \)

Bouchaud & Pitard, EPJE 6, 231 (2001)

**Characteristic features**

- crowded media
- intermittent dynamics
- \( \langle \Delta x^2 \rangle \propto t^2 \) (or \( Q \propto \Gamma \))
- cooperative behavior
- aging

V. Trappe *et al*,
Nature 411, 772 (2001)

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The Glass Transition
(solid like behavior of liquids)

- Characterized by several distinct relaxations in the super-cooled state $T<T_m$
- Non-Arrhenius behavior of the viscosity
- Form glasses below $T_g$ depending on the cooling rate

From Pablo G. Debenedetti and Frank H. Stillinger, Nature (2001)

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Recent results on surface dynamics

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

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Grazing incidence XPCS

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

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

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**CW dynamics on supercooled poly-propylene glycol (PPG)**

All functions are simple exponential decays

$$g^{(2)}(Q, \tau) = 1 + \exp(-2\Gamma \tau)$$

Characteristic times change 5 orders of magnitude from 280 to 214K (T_g \sim 205K)

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CW dynamics on supercooled poly-propylene glycol (PPG)

\[ \Gamma = \frac{\gamma}{2\eta} q \]

Newtonian liquid

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Models for viscoelasticity

Liquids near the glass transition
Viscosity and elasticity become important \(\rightarrow\) viscoelasticity

Maxwell-Debye model
(viscoelastic liquid)

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

\[
\eta(\omega) = \frac{\eta_0}{1 + i\omega\tau}
\]

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

\[
\Gamma(0) = 0
\]

Over-damped capillary waves
Newtonian liquid

\[
G(\omega) = i\omega\eta_0 + E
\]

\[
\eta(\omega) = \eta_0 + \frac{E}{i\omega}
\]

\[
\Gamma = \frac{\gamma q}{2\eta_0} + \frac{E}{\eta_0}
\]

\[
\Gamma(0) = \frac{E}{\eta_0}
\]

Kelvin-Voigt model
(viscoelastic solid)

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Models for viscoelasticity

Liquids near the glass transition
Viscosity and elasticity become important \( \rightarrow \) viscoelasticity

Combined Maxwell-Debye and Kelvin-Voigt model

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

\[
\eta(\omega) = \frac{\eta_0}{1 + i\omega\tau}
\]

Maxwell Debye

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

Elasticity from Voigt-Kelvin

\[ q_0 = 2E/\gamma \]

\[ \Gamma \rightarrow E/\eta \text{ for } q \rightarrow 0 \]

\[ \Gamma \rightarrow G(\infty)/\eta \text{ for } q \rightarrow \infty \]

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CW dynamics on poly-propylene glycol (PPG)

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

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Viscoelasticity of poly-propylene glycol (PPG)

XPCS of CWs is a genuine way to measure low frequency response of glass forming liquids

Low frequency elasticity of (supercooled) liquids is an extremely controversial topic in the literature and non-invasive experimental methods are missing

\[ \eta \sim \exp(A/(T-T_0)) \] VTF law

\[ E \sim \exp(A/(T-T_0)) \] VTF law

Chushkin, Caronna and Madsen, EPL (in press)

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Next topic: Nano-particles in supercooled liquids

Or should I stop here.........?
Dynamics of nano-particles in a glass forming solvent

Samples

Nano-spheres in a glass forming solvent

Silica, R=250nm

Solvent: Propanediol ($T_G \sim 170K$)
Liquid at elevated temp. ($\eta \sim 0.1$ Pa·s @ 290K)


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Simple Diffusion and Hyper-Diffusion

Ballistic motion: \( x = v \cdot t \) \( \Rightarrow \langle [x(t)-x(0)]^2 \rangle = \Delta x^2 = v^2 t^2 \) \( \Rightarrow \quad Q \propto 1/x \propto 1/t = \Gamma \)

Brownian (random walker) motion: \( \langle [r(t)-r(0)]^2 \rangle = 6D_0 t \) \( \Rightarrow \quad Q^2 \propto \Gamma \)

\( D_0 : \) self-diffusion constant

\( D_0 = k_B T / 6\pi \eta R \) (Einstein, 1905)

\[ g^{(2)} \sim 1 + \exp(-2\Gamma t) \]

\( \Gamma = D_0 Q^2 \) for Brownian motion

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Dispersion relations

Silica nano-particles (1% vol.) in supercooled propanediol

\[ \Gamma [s^{-1}] \]

QR

\( n=2 \) (Brownian motion)

\( n \rightarrow 1 \) (Hyper diffusion?)

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Correlation functions

Results: QR=6.75

240K: simple exponential decay

205K: decay faster than exponential

γ≈1.7

Fits with empirical model (KWW): \( g^{(2)} = 1 + \exp(-2(\Gamma t)^\gamma) \)

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XPCS results

Lines are guides to the eye

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Model for particle dynamics

Continuous time random walk model

\[ g^{(2)}(Q,t) = 1 + |f(Q,t)|^2 \]

\[ f(Q,t) = \sum_{N=0}^{\infty} P_t(N) h(Q,N) \]

\[ P_t(N) = \frac{\exp(-\Gamma_0 t)(\Gamma_0 t)^N}{N!} \]

\[ h(Q,N) = \left\langle \exp(-iN^\alpha \mathbf{Q} \cdot \mathbf{R}) \right\rangle \]

\[ \alpha = 1: h(N+1) = h(N)h(1) \text{ (ballistic motion)} \]

\[ \alpha = 1/2: \text{Brownian motion (simple diffusion)} \]

\[ \alpha < 1/2: \text{sub-diffusion} \]

\[ \alpha > 1/2: \text{hyper diffusion} \]

P(\mathbf{R}) : distribution of \mathbf{R} (Gaussian)

\[ <|\mathbf{R}|> = \delta \]

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The fits with the KWW form $f(t) = \exp(-\Gamma t^\gamma)$ are perfect:

The model explains the KWW exponent $\gamma$!
Results

Caronna, Chushkin, Madsen, and Cupane
PRL 100, 055702 (2008)

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Results

Tg=170K (by DSC)

The transition from simple diffusion into event dominated hyper-diffusion is caused by elastic relaxations of the solvent “kicking” the particles.

Those excitations become more important than diffusion at around 1.2*Tg

This again shows that the solid like response of supercooled liquids dominates as the viscosity gets high close to Tg (to be continued........)

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Further reading


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


**General conclusion on XPCS**

XPCS is the X-ray counterpart to PCS (DLS) with the obvious advantages of X-rays over visible light:

* Larger Q-range
* Surface sensitivity
* Penetration power
* No (or only little) multiple scattering

Difficulties arise from the fact that the synchrotron is a chaotic source and intensity is lost when a coherent beam is defined

Brilliance hungry technique but samples are often radiation sensitive.........

Interesting perspectives with X-ray lasers coming on-line but XPCS at storage ring based sources (quasi DC) will remain competitive

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