X-Ray Photon Correlation Spectroscopy

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Outline

I. Introduction

II. Coherence Properties of undulator radiation
   - Coherence lengths
   - Experimental Details

III. Disordered Systems under Coherent Illumination
    - Speckle
    - Speckle Statistics
    - X-Ray Photon Correlation Spectroscopy (XPCS)

IV. Structure and Dynamics of Complex Systems
    - Colloidal Fluids
    - (Surface Dynamics)
    - Magnetic Speckle

V. Perspectives with a FEL source

VI. Summary
If coherent light is scattered by a disordered system it gives rise to a random diffraction or "speckle" pattern. "Speckle" patterns are interference patterns and they are related to the exact spatial arrangement of the disorder.

If the spatial arrangement of the disorder changes as a function of time the "speckle" pattern will also change. A measurement of the temporal intensity fluctuations of a single or equivalent speckles is thus a measure of the underlying dynamics.

The temporal intensity fluctuations can be characterized by:

**Correlation Spectroscopy Techniques**

*Coherent visible light from a laser source (λ≈5300Å):*
  - Photon Correlation Spectroscopy (PCS) or Dynamic Light Scattering (DLS)

*Coherent light from a synchrotron source (λ≈1Å):*
  - X-Ray Photon Correlation Spectroscopy (XPCS)
Third generation synchrotron radiation sources
XPCS: Dynamic Light Scattering with X-Rays

- **Dynamics on short lengthscales**
  \[ Q_{\text{max}} = \frac{2\pi}{d} = (4\pi/\lambda) \sin \theta \]

- **No multiple scattering**
- **Opaque materials**

- **Dynamics of complex fluids**
  - colloidal suspensions (high \( \phi \), large \( Q \), ...)
  - polymer systems (internal modes, ...)

- **Slow dynamics: disordered systems**
  - domain formation phase separating ...systems (glasses, alloys, ...)
  - glass transition (3-D, 2-D)
  - time dependence of critical fluctuations

- **Domain wall dynamics in IC systems**
  - ferroelectrics, cdw systems, magnetic ...materials

- **2-D systems**
  - surfaces (liquid, solid), thin films, ...membranes, ...

- **Ultra-slow Dynamics**
  - jammed systems
  - Non-equilibrium Dynamics
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VI. Summary
Coherence Properties of Undulator Radiation

Machine parameters ESRF

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>GeV 6.03</td>
</tr>
<tr>
<td>Maximum Current</td>
<td>mA 200</td>
</tr>
<tr>
<td>Horizontal Emittance</td>
<td>nm 4</td>
</tr>
<tr>
<td>Vertical Emittance (<em>minimum achieved</em>)</td>
<td>nm 0.025 (0.010*)</td>
</tr>
<tr>
<td>Coupling (<em>minimum achieved</em>)</td>
<td>% 0.6 (0.25*)</td>
</tr>
<tr>
<td>Revolution frequency</td>
<td>kHz 355</td>
</tr>
<tr>
<td>Number of bunches</td>
<td>1 to 992</td>
</tr>
<tr>
<td>Time between bunches</td>
<td>ns 2816 to 282</td>
</tr>
</tbody>
</table>

Ultrafast X-ray Summer School 2011, DESY Hamburg, June 20-23, 2011
Coherence properties of undulator radiation

Coherent Flux:
\[ F_c = \left( \frac{\lambda}{2} \right)^2 \cdot B = 3.5 \cdot 10^{10} \text{ ph/s} \]
\[ B = 10^{20} \text{ ph/s/mm}^2/\text{mmrad}^2/0.1\% \text{bw} \]
\[ \Delta \lambda/\lambda = 10^{-4}; \lambda = 1\text{Å} \]

Temporal Coherence:
longitudinal coherence length:
\[ \xi_l = \lambda (\lambda/\Delta \lambda) = 1 \text{ μm} \]
\[ \Delta \lambda/\lambda = 10^{-4}; \lambda = 1\text{Å} \]

Transverse coherence length:
\[ \xi_t = \left( \frac{\lambda}{2} \right) (R/\Sigma) = 2.5\text{μm (h), } \Sigma_x = 1\text{mm} \]
\[ = 25 \text{ μm (v); } \Sigma_z = 0.1\text{mm} \]
\[ (\lambda = 1 \text{Å, } R = 50\text{m}) \]
A beamline for coherent scattering: P10 at PETRA-III

2-D detector
Direct illumination, deep depletion CCD
$10^6 \times 20 \mu m$ pixels, 1 MHz ADC, (1 Mbyte/s):
SLOW $\rightarrow$ PIXEL detectors

0-D detector
+ digital autocorrelator: FAST
speckle size: $(\lambda/\xi_t) \cdot L \approx 20-40 \mu m$
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VI. Summary
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.

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

\[j \text{ in coherence volume } c=\xi_t^2\xi_l\]

**Incoherent Light:**

\[
S(Q,t) = <S_c(Q,t)>_{V \gg c} \text{ ensemble average}
\]

Aerogel
\[\lambda=1\,\text{Å}\]
CCD (22 \,\mu m)

---

Abernathy, Grübel, et al.

J. Synchrotron Rad. 5, 37, 1998
Speckle Statistics

fully coherent illumination:

If the amplitude $f_n(Q)$ and phases $Q r_n$ are statistically independent and statistically distributed over $2\pi$:

$$P(I) = (1/\langle I \rangle) \exp(-I/\langle I \rangle)$$

Mean: $\langle I \rangle$
StdDev: $\sigma = \sqrt{\langle I^2 \rangle - \langle I \rangle^2} = \langle I \rangle$
Contrast: $\beta = \sigma^2/\langle I \rangle^2 = 1$

partially coherent illumination:

The speckle pattern is the sum of $M$ independent speckle patterns:

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

Mean: $\langle I \rangle$
StdDev: $\sigma = \langle I \rangle/M^{1/2}$
Contrast: $\beta = 1/M$

No information on:
Size and shape of individual speckles

Contrast: $\beta = \beta(\Delta\lambda/\lambda, Q, \ldots)$

Abernathy et al., J. Synchrotron Rad. 5,37 (1998)
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.

\[ I(Q,t) \propto S_c(Q,t) \propto |\sum e^{iQ\mathbf{r}_j(t)}|^2 \]

\( j \) in coherence volume \( c=\xi_2\xi_1 \)

**Incoherent Light:**

\[ S(Q,t) = \langle S_c(Q,t)\rangle_{\text{ensemble average}} \]

Aerogel

\( \lambda=1\text{Å} \)

CCD (22 μm)

Abernathy, Grübel, et al.

J. Synchrotron Rad. 5, 37, 1998
Speckle Reconstruction

Reconstruction (phasing) of a speckle pattern: “oversampling” technique

- Gold dots on SiN membrane (0.1 µm diameter, 80 nm thick)
- λ=17 Å coherent beam at X1A (NSLS), 1.3×10⁹ ph/s 10 µm pinhole
  24 µm x 24 µm pixel CCD
- Reconstruction “oversampling” technique

Miao, Charalambous, Kirz, Sayre, Nature, 400, July 1999

Other examples: nanocrystalline materials (Williams et al., PRL90,175501,2003; He et al., PRB67,174114,2003; Robinson et al., PRL87,195505-1)
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.

\[ I(Q,t) \propto S_c(Q,t) \propto | \sum_j e^{iQ \cdot R_j(t)} |^2 \]

\( j \) in coherence volume \( c = \xi_t \xi_l \)

**Incoherent Light:**

\[ S(Q,t) = < S_c(Q,t)>_{V>>c} \quad \text{ensemble average} \]

Aerogel
\( \lambda = 1 \text{Å} \)
CCD (22 \( \mu \text{m} \))

Abernathy, Grübel, et al.
J. Synchrotron Rad. 5, 37, 1998
Dynamics

Silica: 2610 Å, ΔR/R=0.03, 10 vol% in glycerol, T=-13.6°C, η ≈ 56000 cp

V. Trappe and A. Robert
Photon Correlation Spectroscopy

\[ G(Q,t) = \frac{\langle I(Q,0) \cdot I(Q,t) \rangle}{\langle |I(Q)|^2 \rangle} = a \, Re \{ g_1(Q,t) \} + \beta \, g_2(Q,t) + (1 - \beta) \]

- \( g_1(Q,t) = \langle \rho(Q,0) \cdot \rho^*(Q,t) \rangle \)
- \( g_2(Q,t) = \langle \rho(Q,0) \cdot \rho^*(Q,0) \cdot \rho(Q,t) \cdot \rho^*(Q,t) \rangle \)

Gaussian fluctuations \( (g_2 = 1 + |g_1|^2) \), no optical mixing \( (\alpha = 0) \):

- \( G(Q,t) = 1 + \beta(Q) \, |g_1(Q,t)|^2 \)
- \( g_1(Q,t) = f(Q,t) = F(Q,t) / F(Q,0) \):
  - normalized intermediate scattering function

\[ F(Q,t) = \frac{1}{N f^2(Q)} \sum_n \sum_m < f_n(Q) \cdot f_m(Q) \cdot \exp(iQ \cdot [r_n(0) - r_m(t)]) > \]

Diffusive Processes:

- Monodisperse, non-interacting scatterers:
  - \( F(Q,0) = 1, \langle |r(0) - r(t)|^2 \rangle = 6 \, D \, t \)

- \( f(Q,t) = \exp(-\Gamma \, t), \quad \Gamma = D(Q) \cdot Q^2 \)

Interacting scatterers:

- \( f(Q,t) = \exp(-\Gamma \, t), \quad \Gamma = D(Q) \cdot Q^2 \)
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Structure and Dynamics of Colloidal Fluids

Colloidal particles (paints, ink, clays, ……silica,……) suspended in a solvent (molecular fluid, ……). Stabilised against „van der Waals“ attraction.

„Hard Spheres“

„Soft Spheres“

Structure: \[ S(Q) = 1 + 4\pi \rho \int [g(r)-1] \frac{(\sin(Qr)/Qr)}{Qr^2} r^2 dr; \]

\[ g(r) = \exp\left[-\frac{V(r)}{kT}\right] \]

\[ \rho: \text{number density } N/V \]

\[ \Phi << 1\%: \quad S(Q) = 1 \]

\[ \Phi > 1\%: \quad V(r) = \begin{cases} 0 & r \geq d \\ \infty & r < d \end{cases} \]

\[ S = S(Q, \Phi) \quad \text{(Percus-Yevick)} \]

Dynamics: Interaction: colloid-solvent, colloid-colloid, hydrodynamics

Smoluchowski (many particle) diffusion equation:

\[ D_{\text{short}}(Q) = \frac{D_0}{S(Q)} * H(Q) \quad t << R^2/Do \]

\[ H(Q) \quad \text{(via } D_0, S(Q), D(Q)) \]
Dilute, non-interacting system

\[ I \sim |F(Q)|^2 S(Q) \]

\[ \sim [(\sin QR - QR \cos QR)/(QR)^3]^2 \]

\[ \Gamma = D_0 Q^2 \]

\[ D_0 = k_B T / 6\pi \eta R \]

\[ Q = k' - k \]

\[ Q = 2k \sin \theta \]

\[ k = 2\pi / \lambda \]

G. Grübel, A. Robert, D. Abernathy
8th Tohwa University International Symposium on "Slow Dynamics in Complex Systems", 1998, Fukuoka, Japan
Poly-methylmetacrylate  
37% volume fraction in cis-decaline  
sterically stabilized (hard-spheres)

Poly-octafluoropentylcrylate  
18% volume fraction in H₂O/glycerol  
charge-stabilized (soft-spheres)

\[ |F(Q)|^2 \]
\[ \Gamma = D_0 Q^2 \]
\[ S(Q) = I(Q)/|F(Q)|^2 \]
\[ \delta - \gamma \text{ expansion} \]
\[ H(Q) = S(Q)/[D_0/D(Q)] \]
\[ \text{no model} \]

QR=5.6

“caging” (deGennes narrowing)

\[ \delta - \gamma \text{ expansion} \]

Zontone, Moussaid, Robert, Grübel

Robert, Härtl, Wagner, Grübel
Magnetic Scattering with Coherent X-Rays

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.

\[ I(Q,t) \propto S_c(Q,t) \propto \sum |f_n^{\text{charge}} + f_n^{\text{magnetic}}| e^{iQR_j(t)}|^2 \]

\[ j \text{ in coherence volume } c = \xi_l^2 \xi_t \]

**Incoherent Light:**

\[ S(Q,t) = < S_c(Q,t) >_{V \gg c} \text{ ensemble average} \]

Aerogel
\[ \lambda = 1 \text{ Å} \]
CCD (22 μm)

Abernathy, Grübel, et al.
J. Synchrotron Rad. 5, 37, 1998
Magnetic Force Microscopy image and magnetic x-ray speckle from (meandering) magnetic stripe domains in a 350Å thick film of GdFe$_2$. Data from ID12B (ESRF) with $\lambda=11\AA$ (Gd-M$_v$).

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Perspectives with a coherent XFEL source

Brilliance x $10^{10}$

$\approx 10^{12}$ ph/pulse

Ultrashort pulses (< 100 fs)
Scientific applications using x-ray FELs

Atoms, ions, molecules, and clusters

- Multiple ionization and multiphoton events
- Creation and spectroscopy of excited states (hollow atoms, Rydberg states, Laser states, ...)
- Dynamics, electronic & geom. cluster properties

Plasma physics

- Generation of solid-density plasmas
- Plasma diagnostics

Condensed-matter physics

- Ultrafast (magnetic) dynamics
- Electronic structure
- Disordered materials & soft matter

Materials sciences

- Dynamics of hard materials
- Structure and dynamics of nanomaterials

Chemistry

- Reaction dynamics in solid, liquid systems
- Analytical solid-state chemistry
- Heterogenous catalysis

Structural biology

- Single molecule/particle imaging
- Dynamics of biomolecules

Optics and nonlin. Phen.

- Nonlinear effects in atoms and solids
- High field science
The VUV-FEL at DESY

\[ \lambda \geq 4.5 \text{ nm} \]

Commissioning: 2004/5
User experiments: 2005

Ultrafast X-ray Summer School 2011, DESY Hamburg, June 20-23, 2011
Femtosecond diffractive Imaging

Model structure in 20 nm SiN membrane

Speckle pattern recorded with a single (25 fs) pulse

Reconstructed image

*Incident FEL pulse: 25 fs, 32 nm, 4 \times 10^{14} \text{ W cm}^{-2} (10^{12} \text{ ph/pulse})*

Magnetic SAXS of CoPt multilayer at Co M_{II/III}

$\lambda = 20.8 \text{ nm (59 eV)}$: Co M_{2,3}

30 femtosecond pulse length
(4 $\mu$J/pulse $4 \times 10^{11}$ ph/pulse)
$\Delta E/E \approx 0.5-1\%$
250 $\mu$m beamsize
(5 Hz, single pulse)

Single-shot (30 fs)
magnetic SAXS pattern.

CoPt multilayer sample is not destroyed!

[Co(0.8nm)/Pt(1.4nm)]_{16} on 50nm Si$_3$N$_4$ substrate
2048x2048 13.5$\mu$m pixel CCD (40 mm from sample)

C. Gutt et al., PRB(Rapid), 2010
XPCS at FEL sources

1ps < t < 10 ns: "delay-line" mode
for "all" times: "pump-probe" mode

t > 0.1 s
200 ns < t < 600 µs: "movie" mode
Conclusion

Third generation, storage ring based, sources permit novel scattering and imaging techniques based on coherent X-rays. Among them is:

**X-Ray Photon Correlation Spectroscopy (XPCS).**
XPCS today covers timescales down to about 100 ns up to moderately large momentum transfers.

**Fields of activity:**
- Dynamics of complex fluids
- Critical Dynamics
- 2-D systems
- Non-equilibrium dynamics

**Exploit:**
- Anomalous scattering, polarization

**Develop:**
- 2-D detector technologies to reach atomic resolution and time scales down to 1 ns.

Future XFEL sources will provide (spatially) coherent beams with a time averaged coherent flux: \(<F_c> \approx 10^{16} \text{ ph/s and } 10^{12} \text{ photons/bunch} >

The high flux of photons/100 fs bunch will allow **single “shot” experiments.**

XPCS might be extended in the **ns - ps regime.**
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The End