Coherent X-ray Scattering and X-ray Photon Correlation Spectroscopy

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Outline

• Theory of X-ray Photon Correlation Spectroscopy
• Some examples of work done using XPCS
• Experimental tricks of the trade
• The future of XPCS
XPCS and Dynamics in Soft Matter

Liquid Surface Capillary Waves

Colloidal Diffusion
Grübel et. al. in Slow Dynamics in Complex Systems

Protein Diffusion
Debartolo et. al. (unpublished)

Atomic Diffusion in CuAu Alloy
What is Coherence?

Ideal Young’s double slit experiment

Intensity varies as

\[ I = 2I_0 \left[ 1 + \cos \left(2\pi d \sin(\theta) / \lambda \right) \right] \]

Real Young’s double slit experiment

Intensity varies as

\[ I = 2I_0 \left[ 1 + \beta \cos \left(2\pi d \sin(\theta) / \lambda \right) \right] \]

\(\beta\) is the contrast, determined by the angular size of the source
Coherence Length and Contrast

It is generally convenient to assume the source has a Gaussian intensity profile

\[ I(x) = \frac{I_0}{\sqrt{2\pi \xi}} \exp\left[-\frac{(x-x_0)^2}{2\sigma^2}\right] \]

One can then define a coherence length

\[ \xi = \frac{\lambda R}{2\sigma \sqrt{\pi}} \]

This characterizes the distance over which two slits would produce an interference pattern, or more generally the length scale over which any sample will produce interference effects.

A more rigorous theory can be found in e.g. Born and Wolf
Longitudinal coherence

\[ \Lambda \approx \lambda \left( \frac{E}{\Delta E} \right) \]

e.g. the number of wavelengths that can be added before the uncertainty adds up to a full wavelength.

Can also be viewed as a coherence time \( T_c = \Lambda / c \)
Speckle Size and Contrast

The speckle widths are approximately the size of the diffraction pattern from a slit the size of the sample:

$$\Delta \theta \sim \frac{\lambda}{L}$$

The contrast is given by the ratio of the scattering volume to the coherence volume, $\Lambda \xi_x \xi_y / MLW \sin(\theta)$

Exact numbers require integrals over the sample volume and electric field spatial correlation function. For small angles, the scattering volume is much smaller than the sample volume.
How Practical is it to Make X-rays Coherent?

Consider a point 65 meters downstream of an APS Undulator A

\[ \lambda = 0.2\text{nm}, \quad \Delta \lambda/\lambda = 3 \times 10^{-4} \]

\[ \sigma_x = 254\mu\text{m}, \sigma_y = 12\mu\text{m} \]

\[ \xi_x = \frac{\lambda R}{2\sigma_x \sqrt{\pi}} = 14\mu\text{m} \]

\[ \xi_y = \frac{\lambda R}{2\sigma_y \sqrt{\pi}} = 306\mu\text{m} \]

\[ \Lambda = 0.66\mu\text{m} \]

\[ \sim 3 \times 10^{10} \text{Photons/Coherence Area} \]
Fraunhofer X-ray Diffraction from a Slit

B. Lin et. al. RSI 67, (9) (1996)

Narrow slit, coherent scattering

Wide slit, incoherent scattering
Setup for XPCS at Sector 8 of the APS
Optics must preserve coherence

Image of x-ray beam reflected from channel cut monochromator (left) vs. artificial channel cut which allows better polish of interior faces.

S. Naryanan, A. Sandy, M. Sprung, D. Shu and J. Sullivan
Scattering of Coherent X-rays

\[ I(Q) \sim \int \int e^{iQ \cdot \vec{r}} \rho_e(\vec{r} + \vec{r}') \rho_e(\vec{r}') \, d\vec{r} d\vec{r}' \]

For incoherent x-rays the measured scattering represents a statistical average over many incoherent regions within the sample and one obtains:

\[ \rho_e(\vec{r} + \vec{r}') \rho_e(\vec{r}') \Rightarrow \langle \rho_e(\vec{r} + \vec{r}') \rho_e(\vec{r}') \rangle \]

For coherent x-rays one measures the Fourier transform of the exact density distribution, not the average. What one observes is a speckle pattern superposed on the average scattering pattern.
Speckle from a Silica Aerogel
What to do with coherent x-rays?

- Try to invert the speckle to get information about the exact structure factor. (--- phase retrieval x-ray imaging---) Generally too slow to obtain dynamics information.

- Ignore the details of the exact structure factor, but use the time fluctuations of the pattern to study dynamics of the material (XPCS)
Measuring Dynamics

\[ g_2(q,t) = \frac{\langle I(q,t')I(q,t'+t) \rangle}{\langle I(q,t') \rangle^2} \]
The Intensity-Intensity Correlation Function

\[
g_2(Q, \tau) \equiv \left\langle I(Q, t) I(Q, t + \tau) \right\rangle / \langle I \rangle^2
\]

\[
g_2(Q, \tau) = \frac{V (\hat{e}_f \cdot \hat{e}_i)^2 r_0^4}{R^4} \int \int \int \int d \vec{r}_1 d \vec{r}_2 d \vec{r}_3 d \vec{r}_4 \exp \left( -i \left( (\vec{Q} + \vec{s}_1) \cdot (\vec{r}_1 - \vec{r}_2) + (\vec{Q} + \vec{s}_2) \cdot (\vec{r}_3 - \vec{r}_4) \right) \right) \\
\left\langle \rho_e(\vec{r}_1, t) \rho_e(\vec{r}_2, t) \rho_e(\vec{r}_3, t + \tau) \rho_e(\vec{r}_4, t + \tau) \right\rangle \\
\left\langle E_i \left( x_1, 0, z_1, t - \frac{(\vec{Q} + \vec{s}_1) \cdot \vec{r}_1}{\omega} \right) \right\rangle E_i^* \left( x_2, 0, z_2, t - \frac{(\vec{Q} + \vec{s}_2) \cdot \vec{r}_2}{\omega} \right) \\
\left\langle E_i \left( x_3, 0, z_3, t + \tau - \frac{(\vec{Q} + \vec{s}_1) \cdot \vec{r}_3}{\omega} \right) \right\rangle E_i^* \left( x_4, 0, z_4, t + \tau - \frac{(\vec{Q} + \vec{s}_2) \cdot \vec{r}_4}{\omega} \right) \\
\left\langle E_i \left( x_3, 0, z_3, t + \tau - \frac{(\vec{Q} + \vec{s}_1) \cdot \vec{r}_3}{\omega} \right) \right\rangle E_i^* \left( x_4, 0, z_4, t + \tau - \frac{(\vec{Q} + \vec{s}_2) \cdot \vec{r}_4}{\omega} \right)
\]
How to calculate $g_2$

(skipping most of the equations)

• Calculate electric field intensity correlation function at the observation point:

$$G_2(Q, \tau) = \int \exp(iQ \cdot r') <E_f^2(r, t) E_f^2(r+r', t+t)>_{r,t} dr'$$

• The fourth order correlations in E, can be reduced to pairs of second order correlation functions

• Assume correlation lengths are smaller than sample size, and the scattering can be factored into independent space and time parts.
Final Result

\[ G_2(\vec{Q}, \tau) = \langle I \rangle^2 \left[ 1 + \beta f(Q, \tau)^2 \right] \]

The contrast factor, \( \beta \), is related to the degree of coherence and can be between 0 and 1

\[ f(\vec{Q}, \tau) = \frac{S(\vec{Q}, \tau)}{S(\vec{Q}, 0)} \]

\[ S(\vec{Q}, \tau) = \left\langle \int e^{i\vec{Q} \cdot \vec{r}} \rho_e(0,0) \rho_e(\vec{r}, \tau) d\vec{r} \right\rangle \]
Typical Applications

The average structure is constant, but the local structure fluctuates.

- Diffusion of particles in solution
- Concentration fluctuations in binary liquids
- Fluctuations of order parameter in a crystal
- Thermally driven surface height fluctuations in a viscous fluid
- Vibrations of a membrane
- Aging: evolution of the “equilibrium” dynamics with time.
A dilute colloidal suspension
(71 nm Latex in Glycerol)
To theoretically calculate the dynamic scattering factor one has to take the correlation functions for a collection of point scatterers diffusing in the liquid.

\[
f(\vec{Q}, \tau) = \frac{1}{N} \sum_{i,j} \left\langle \exp(i\vec{Q} \cdot (\vec{r}_i(t) - \vec{r}_j(t + \tau)) \right\rangle
\]
For Brownian motion, this can be reduced to an exponential decay proportional to the diffusion coefficient.

\[ f(Q, \tau) = e^{-DQ^2\tau} \]

Here, the diffusion coefficient is related to the viscosity, \( \eta \) and the radius \( a \), via the Stoke-Einstein relation:

\[ D = k_B T / 6 \pi \eta a \]
Wavevector Dependence

\[ \tau = \frac{1}{DQ^2} \]
Short Time Diffusion Constants in

Concentrated Suspension

1. Structural correlations lead to a slowing down of dynamics

2. Hydrodynamic interactions further modify the dynamics at high concentration

3. These effects can be calculated for the initial decay rate of the correlation function, but the $f(Q,t)$ will not generally be an exponential at long times.

$$D(Q) = D_0 H(Q) / S(Q)$$
Deviations for Stokes-Einstein Diffusion

\[ \phi = 0.34 \]
Example 2

Atomic Diffusion in Metal Alloys

Example 3 Concentrated Polymeric Vesicles

Concentrated Block Copolymer Vesicles
Falus et. al. PRL 94, 16105, 2005

In Liquid State, Near Tg Exponential Decays Become Stretched
Example 4
Antiferromagnetic Domain Fluctuations


Note that although the length scale of the fluctuations is large (>10 nm) they require x-rays with wavelengths ~0.1 nm in order to be visible.
Example 5: Dynamics of Liquid Surfaces

- Polystyrene films on Si wafers (Kim, PRL 2003) are highly viscous and show exponential decay.
- Thin liquid crystal membranes (Sikharulidze, PRL 2002) show transition from oscillatory to overdamped behavior.
From Jiang et. al. PRL, 246104, 2008
Limitations of XPCS

• Too much flux (X-ray damage)
  – Radiation can cause cross linking of polymers and charging of colloids.
  – A reasonably radiation resistant polymer (PS) in vacuum can absorb around $\sim 10^7$ Gy. (10 min in surface reflection geometry)
  – Protein in water can absorb $\sim 10^5$ Gy (10 sec in transmission geometry)

• Too little flux (Poor signal to noise)
Some tricks of the trade …
Multispeckle Detection

• Falus, Borthwick, Mochrie, RSI (2004)
• SNR increases as $\sqrt{N}$
• Limitations:
  • Readout rate presently around 60 Hz
  • Efficiency < 50%
• New Camera under development at LBL and APS ~500 Hz at 100% efficiency. (John Weizeorick and Alec Sandy) Should see first light this cycle.
Focusing
Khalid Laaziri and Mark Sutton

• Focusing the x-ray beam down to a small spot (~1 µm) maintains flux, but increases the speckle size. SNR ~ photons/speckle, so SNR goes up. Disadvantage is that radiation damage goes up as well.

• Fluctuations in Fe$_3$Al
Heterodyne Detection
Livet. et. al. JSR (2006)

- Mix a static signal with a weaker dynamic signal.
- For diffusive motion relaxation times are longer: \( \exp(-\Gamma t) \) instead of \( \exp(-2\Gamma t) \).
- Constant flow can be detected, which is invisible to homodyne. (example aerosil + carbon-black rubber)
What is in the Future for XPCS?

X-ray Free Electron Lasers

LCLS at Stanford

European Free Electron Laser Laser at Hamburg

Ultrafast XPCS using ‘Split Pulse’ Mode

Femtoseconds to nanoseconds time resolution
Uses high peak brilliance

Sample

Transversely coherent X-ray pulse from FEL

Variable delay $\Delta t$

$10\text{ ps} \Leftrightarrow 3\text{ mm}$

Sum of speckle patterns from prompt and delayed pulses recorded on CCD

$I(Q, \Delta t)$

Analyze contrast as $f$(delay time)
References

• **This talk:** http://www.niu.edu/~llurio/coherence/

• **XPCS:**

• **Dynamic Light Scattering:**

• **Coherence:**

• **X –ray Free Electron Lasers**