How can x-ray intensity fluctuation spectroscopy push the frontiers of Materials Science

Mark Sutton
McGill University
Coherent diffraction

(001) Cu₃Au peak

Coherence allows one to measure the dynamics of a material (X-ray Intensity Fluctuation Spectroscopy, XIFS).

\[
\langle I(\vec{Q}, t)I(\vec{Q} + \delta \vec{k}, t + \tau) \rangle = \langle I(Q) \rangle^2 + \beta(\vec{k}) \frac{k^8}{(4\pi R)^4 V^2 I_0^2} \left| S(\vec{Q}, t) \right|^2
\]

where the coherence part is:

\[
\beta(\vec{k}) = \frac{1}{V^2 I_0^2} \int_V \int_V e^{i\vec{k} \cdot (\vec{r}_2 - \vec{r}_1)} \left| \Gamma(\vec{0}, \vec{r}_2^\perp - \vec{r}_1^\perp, \frac{\vec{Q} \cdot (\vec{r}_2 - \vec{r}_1)}{\omega_0}) \right|^2 d\vec{r}_1 d\vec{r}_2
\]

and \( \beta(\vec{0}) \approx \frac{V_{coherence}}{V_{scattering}} \) with widths \( \lambda/V^{1/3} \)

Define correlation function:

\[
g^{(2)}(\vec{Q}, \tau) - 1 = \frac{\langle I^2(\vec{Q}, t) \rangle - \langle I(\vec{Q}, t) \rangle^2}{\langle I(\vec{Q}, t) \rangle^2} \\
= \beta \left| g^{(1)}(\vec{Q}, \tau) \right|^2 \\
= \beta e^{-2\tau/\tau_O}
\]
Two-time correlation functions

Au in polystyrene

Cu$_3$Au

![Graphs and images related to two-time correlation functions for Au in polystyrene and Cu$_3$Au.](image-url)
Scientific Case for an Energy-Recovery Linac at Cornell University

X-Ray Photon Correlation Spectroscopy

Detlef-M. Smilgies, CHESS

Scientific Applications

Frontiers of the technique are compiled in the following subsections:

- Phase Transitions and Domain Wall Dynamics
- Dynamics of Complex Fluids
- Dynamics at Surfaces
- Dynamics of Lattice Defects and Disordered Systems
- Ultrasoft Modes in Soft Condensed Matter and Biological Systems
“Real” Equation of Everything

Langevin dynamics (Models A through J):

\[ \frac{\partial \Psi_\mu(\vec{x}, t)}{\partial t} = \left\{ F, \Psi_\mu(\vec{x}, t) \right\}_{PB} - M_{\mu\nu} \frac{\partial F}{\partial \Psi_\nu} + \eta_\mu(\vec{x}, t) \]

\[ = - \int \left\{ \Psi_\mu(\vec{x}, t), \Psi_\nu(\vec{x}', t') \right\}_{PB} \frac{\partial F}{\partial \Psi_\nu} d\vec{x}' - M_{\mu\nu} \frac{\partial F}{\partial \Psi_\nu} + \eta_\mu(\vec{x}, t) \]

\[ = V_\mu(\vec{x}, t) - M_{\mu\nu} \frac{\partial F}{\partial \Psi_\nu} + \eta_\mu(\vec{x}, t) \]

where

\[ \langle \eta_\mu(\vec{x}, t) \rangle = 0 \]

and (generalized Einstein-Stokes/fluctuation-dissipation)

\[ \langle \eta_\mu(\vec{x}, t) \eta_\nu(\vec{x}', t') \rangle = -2M_{\mu\nu}k_bT \delta(\vec{x} - \vec{x}') \delta(t - t') \]

Equilibrium Time Dependence

In equilibrium $F$ has no linear term in $\Psi$ so equation of motion becomes:

$$\frac{\partial \Psi(\vec{x}, t)}{\partial t} = -M \left( \frac{\partial^2 F}{\partial \Psi^2} \right)_{eq} \Psi + \eta(\vec{x}, t)$$

or

$$\frac{\partial \Psi(\vec{Q}, t)}{\partial t} = -\frac{Mk_bT}{S(\vec{Q})} \Psi + \eta(\vec{Q}, t)$$

Where the structure factor is:

$$S(\vec{Q}, t) = \langle \Psi^\dagger(\vec{Q}, t)\Psi(\vec{Q}, t) \rangle = k_bT / \left( \frac{\partial^2 F}{\partial \Psi^2} \right)_{eq}$$
Phase Separation of AlZn

\[
\frac{1}{2Mq^2} \frac{\partial S(q,t)}{\partial t} = - \left( \kappa q^2 + \frac{\partial^2 f}{\partial c^2} \right)_{c_0} S(q,t) + \frac{1}{6} \left( \frac{\partial^4 f}{\partial c^4} \right)_{c_0} S_4(q,t) + k_b T
\]


Signal to Noise

Signal is \( g_2 - 1 = \beta \) and variance of is \( \text{var}(g_2) \sim 1/(\bar{n}^2N) \). So:

\[
\frac{s}{n} = \beta \bar{n} \sqrt{N} \\
= \beta I \tau \sqrt{\frac{t_{\text{total}}}{\tau}} N_{\text{speckles}} \\
= \beta I \sqrt{\tau t_{\text{total}} N_{\text{pixels}}}
\]

Note 1: This is linear in number of photons (as opposed to \( \sqrt{\bar{n}} \)).
Note 2: For fixed \( s/n \sim \alpha I \sqrt{\tau/\alpha^2} \). Thus an \( \alpha \)-fold increase in intensity is an \( \alpha^2 \)-fold increase in time resolution. Need very fast detectors.

Signal to Noise

More explicitly:

\[
\frac{s}{n} \approx \beta B_0 dx dx' dy dy' \frac{\Delta E}{E} \frac{1}{V} \frac{d\sigma}{d\Omega} L \sqrt{N_{sp}} \\
\approx \beta B_0 f_x f_y \lambda^2 \frac{\Delta E}{E} \frac{1}{V} \frac{d\sigma}{d\Omega} f_z \frac{\lambda^2}{\Delta \lambda} \sqrt{N_{sp}} \\
\approx \frac{1}{\max(1, f_i)^3} B_0 f_x f_y f_z \lambda^2 \frac{\Delta \lambda}{\lambda} \frac{1}{V} \frac{d\sigma}{d\Omega} \frac{\lambda^2}{\Delta \lambda} \sqrt{N_{sp}} \\
\approx B_0 \lambda^3 \frac{1}{V} \frac{d\sigma}{d\Omega} \sqrt{N_{sp}} \\
\approx f B_0 \lambda^3 \frac{1}{V} \frac{d\sigma}{d\Omega} \sqrt{N_{sp}} \quad (i f \ a n y f_i < 1).
\]

Note: should be a \(\lambda^3/8\) as normally use \(\lambda/2\).
Detector Resolution

Speckle size (width of $\beta(\vec{\kappa})$) is given by diffraction limit of beam:

$$\Delta \theta \approx \frac{\lambda}{d_{coh}} \approx \frac{d_{coh}}{R_{det}}$$

to resolve on detector. Thus

$$R_{det} = \frac{d_{coh}^2}{\lambda}$$

Problem if horizontal and vertical lengths are too different or if any coherence length is too long. Similarly, don’t want too large a mismatch between speckle size and the “diffraction width” of sample peak.

Focus for a virtual source, for $1.5\,\AA$ , a $100\mu\text{m}$ source at $10\text{m}$ gives $d_{coh} = 15\mu\text{m}$.

Ideally optics could tune coherence lengths.
Order-disorder phase transitions in $Cu_3Au$

Disorder:

$\mathit{f} = 0.75\: f_{Cu} + 0.25\: f_{Au}$

Order:

$f_{Cu}, f_{Au}$
Scattering from Cu₃Au

S(q,t) Movie

Scattering from Cu$_3$Au
Two-Time Correlation Functions

Non-stationary so autocorrelate \( \frac{I(q,t_1) - \langle I(q,t_1) \rangle}{\langle I(q,t_1) \rangle} \)
Upgrades to the beamline allow us to obtain better data, especially important for the early time region.

Cross-section of several slices
New Data
Quench from 425°C to 383°C

Two-$\vec{Q}$ two-time
Particle Size Effects

Q and $\phi$ dependence
Non-Gaussian Nature

Intensity related to Fourier transform of density-density correlation function. For non-zero correlations, must have pair of points within a correlation length $\xi$.

$$\langle \delta \rho (\vec{r}_1, 0) \delta \rho (\vec{r}_2, 0) \delta \rho (\vec{r}_3, \tau) \delta \rho (\vec{r}_4, \tau) \rangle \sim \langle \delta \rho (\vec{r}_1, 0) \delta \rho (\vec{r}_2, 0) \rangle \langle \delta \rho (\vec{r}_3, \tau) \delta \rho (\vec{r}_4, \tau) \rangle$$

$$+ \langle \delta \rho (\vec{r}_1, 0) \delta \rho (\vec{r}_3, 0) \rangle \langle \delta \rho (\vec{r}_2, \tau) \delta \rho (\vec{r}_4, \tau) \rangle$$

$$+ \langle \delta \rho (\vec{r}_1, 0) \delta \rho (\vec{r}_4, 0) \rangle \langle \delta \rho (\vec{r}_3, \tau) \delta \rho (\vec{r}_2, \tau) \rangle$$

This overcounts the volume when all four $\vec{r}_i$ are within the same correlation length. When Fourier transformed, this correction is of order $(\xi^3/V)^2$. 

\[
\langle I(\vec{q}, t_1)I(\vec{q}, t_2) \rangle_T = \langle \Psi^*(\vec{q}, t_1)\Psi(\vec{q}, t_1)\Psi^*(\vec{q}, t_2)\Psi(\vec{q}, t_2) \rangle_T \\
= \langle \Psi^*(\vec{q}, t_1)\Psi(\vec{q}, t_1) \rangle_T \langle \Psi^*(\vec{q}, t_2)\Psi(\vec{q}, t_2) \rangle_T \\
+ \langle \Psi^*(\vec{q}, t_1)\Psi(\vec{q}, t_2) \rangle_T \langle \Psi^*(\vec{q}, t_2)\Psi(\vec{q}, t_1) \rangle_T \\
+ \langle \Psi^*(\vec{q}, t_1)\Psi^*(\vec{q}, t_2) \rangle_T \langle \Psi(\vec{q}, t_1)\Psi(\vec{q}, t_2) \rangle_T \\
= [1 + \delta(\vec{q})]S^2(\vec{q}, t_1, t_2) + \langle I(\vec{q}, t_1) \rangle_T \langle I(\vec{q}, t_2) \rangle_T \\
\]

Where: \( S(\vec{q}, t_1, t_2) = \langle \Psi^*(\vec{q}, t_1)\Psi(\vec{q}, t_2) \rangle_T \) and \( I(\vec{q}, t) = S(\vec{q}, t, t) \)

FIG. 4 (color online). The measured major loop microscopic correlation coefficients for the 12 mT sample. The circles and squares (the triangles) represent the correlations between the first and the second (eleventh) loop.
Experimental Setup

Scattering geometry

X-rays

Reference

Sample

CCD
Scattering of model rubber
(EPR with carbon black)
\[ G_2(\vec{q}, t) = I_r^2 + \langle I_s(t) \rangle_t^2 (1 + \beta |g_1(t)|^2) + 2I_r\langle I_s(t) \rangle_t (1 + \beta \text{Re}(g_1(t))) + 2I_r\langle I_s(t) \rangle_t \beta \text{Re}(g_1(t)) \]

Moving at constant velocity gives phase factor

\[ e^{i\vec{q} \cdot \vec{v} t} = e^{i\omega t} \]

So correlation becomes \((x = I_s / (I_s + I_r))\)

\[ g_2(q, \phi, t) = 1 + \beta (1 - x)^2 + x^2 \beta \gamma^2 \left( t / \tau \right) + 2x(1 - x) \beta \cos(\omega t) \gamma \left( t / \tau \right) \]
Rubber

Q and φ dependence
\[ qv \cos(\omega) \]

\[ \omega \text{ vs } \cos \psi \text{ @ } q = 14.10^{-3} \text{A}^{-1} \]

\[ \omega \text{ vs } q \text{ for } \psi = 123 \text{ deg.} \]

Azimuth dependence    Wavevector dependence
velocity relaxation

\[ v \text{ (in Å/s)} \]

\[ \text{time} \]

\[ 10^3 \quad 10^4 \quad 10^5 \]
Wave vector dependence

$\tau$ for var. $\psi$ vs $q$

$\tau (s) \quad 10^3$

$10^2$

$10^1$

$q (A^{-1}) \quad 10^{-3}$

$10^{-2}$

$10^{-1}$
Hydrodynamics

For instance given density $\rho(\vec{x}, t)$ and momentum density $\rho(\vec{x}, t)\vec{v}(\vec{x}, t)$:

$$\{\rho(\vec{x}, t), \rho(\vec{x}', t')v_i(\vec{x}', t')\}_{PB} = \nabla_i(\rho(\vec{x}, t)\delta(\vec{x} - \vec{x}')).$$

Thus

$$\frac{\partial \rho}{\partial t} = -\vec{\nabla} \cdot (\rho \vec{v})$$

and (linearizing for simplicity)

$$\frac{\partial (\rho \vec{v})}{\partial t} = \vec{\nabla} \left[ \left( \frac{\partial p}{\partial \rho} \right)_S \delta \rho(\vec{x}) \right] + \vec{\eta},$$

($p$ is pressure and $S$ is entropy).

These are the linearized hydrodynamic equations.

Conclusions

1. Understanding the time evolution of the microstructure is key to understanding Materials Science.

2. XIFS is a powerful and direct way to measure this dynamics, both in and out of equilibrium.

3. This dynamics is controlled by the thermodynamic fluctuations of the system and XIFS directly measures these.

4. Did not show many examples, but has been done in SAXS, Diffuse Reflectivity, Short-range quasi-Bragg peaks. Essentially all forms of diffuse scattering

5. Can heterodyne. This will give access to understanding how microscopic structure controls visco-elastic properties (rubber). Can separate advection from dissipation effects in the equation of motion.
6. Can use speckle to obtain high resolution structural information from “very disordered” materials. (Thermal expansion of a glass, reversible and irreversible hysteresis effects in magnetic domains).