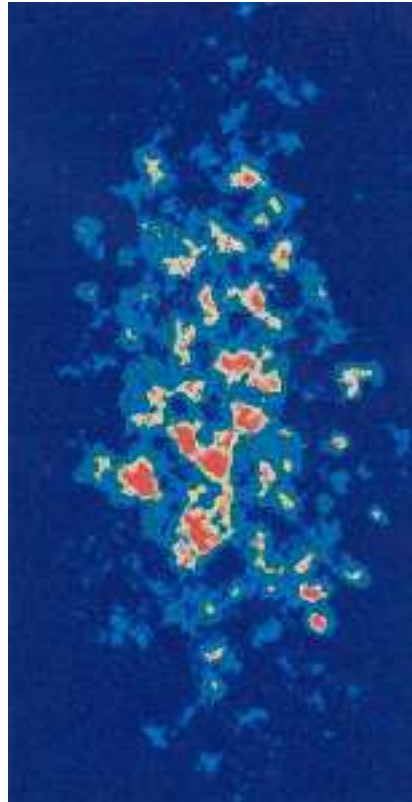


**Potential for Ultrafast
X-ray Intensity
Fluctuation Spectroscopy**

Mark Sutton
McGill University

Coherent diffraction

(001) Cu_3Au peak



Sutton et al., The Observation of Speckle by Diffraction with Coherent X-rays, *Nature*, **352**, 608-610 (1991).

Why Coherence?

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

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

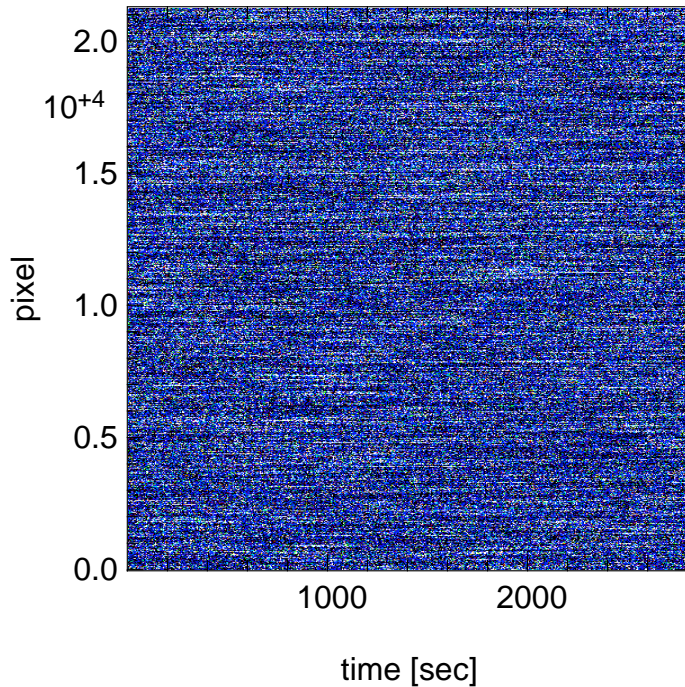
where the coherence part is:

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

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

Reference: M. Sutton, Coherent X-ray Diffraction, in **Third-Generation Hard X-ray Synchrotron Radiation Sources: Source Properties, Optics, and Experimental Techniques**, edited by. Dennis M. Mills, John Wiley and Sons, Inc, New York, (2002).

SAXS of Au particles in PS



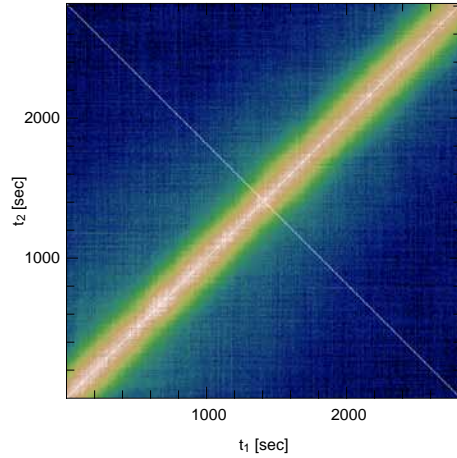
Define correlation function:

$$\begin{aligned} g^{(2)}(\vec{Q}, \tau) - 1 &= \frac{\langle I^2(\vec{Q}, t) \rangle - \langle I(\vec{Q}, t) \rangle^2}{\langle I(\vec{Q}, t) \rangle^2} \\ &= \beta \left| g^{(1)}(\vec{Q}, \tau) \right|^2 \\ &= \beta e^{-2\tau/\tau_Q} \end{aligned}$$

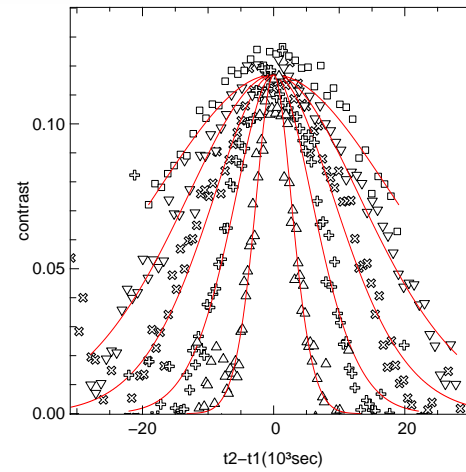
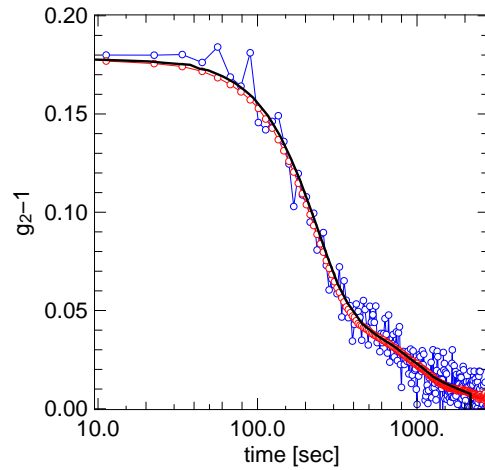
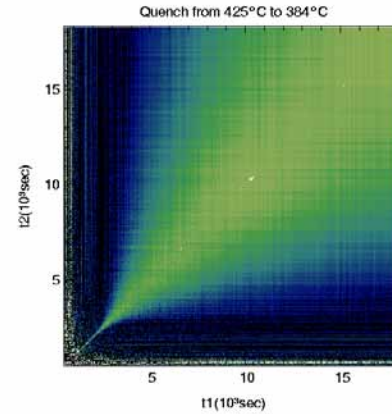
Time fluctuations in coherent scattering.

Two-time correlation functions

Au in polystyrene



Cu_3Au



Brightness

Conventionally brightness has the form:

$$B(\vec{r}, \hat{s}, \mathbf{v}) = \frac{1}{4\pi^2} \frac{I_0 H(\mathbf{v})}{\sigma_{s_h} \sigma_{s_v} \sigma_h \sigma_v} e^{-\left(\frac{x^2}{2\sigma_h^2} + \frac{y^2}{2\sigma_v^2}\right)} e^{-\left(\frac{s_x^2}{2\sigma_{s_h}} + \frac{s_y^2}{2\sigma_{s_v}}\right)}$$

where $\hat{s} = (s_x, s_y, 1) = (x/z, y/z, 1)$, the σ 's are the beam sizes and angular spreads and $H(\mathbf{v})$ is frequency spectrum.

Brightness is coherence:

$$B(\vec{r}, \hat{s}, \mathbf{v}) = k^2 \frac{1}{(2\pi)^2} \int \Gamma(\vec{v}) e^{ik\hat{s}_\perp \cdot \vec{v}} d\vec{v}$$

So mutual coherence function is:

$$\Gamma(\vec{r}_1, \vec{r}_2, \mathbf{v}) = \frac{I_0 H(\mathbf{v})}{2\pi\sigma_h\sigma_v} e^{-\left(\frac{(x_1+x_2)^2}{8\sigma_h^2} + \frac{(y_1+y_2)^2}{8\sigma_v^2}\right)} e^{-\left(\frac{(x_2-x_1)^2}{2\rho_h^2} + \frac{(y_2-y_1)^2}{2\rho_v^2}\right)}$$

where ρ_i are coherence lengths and $\rho_i = 1/(k\sigma_{s_i})$.

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):

$$\begin{aligned}\frac{\partial \Psi_\mu(\vec{x}, t)}{\partial t} &= \{F, \Psi_\mu(\vec{x}, t)\}_{PB} - M_{\mu\nu} \frac{\partial F}{\partial \Psi_\nu} + \eta_\mu(\vec{x}, t) \\ &= - \int \{ \Psi_\mu(\vec{x}, t), \Psi_\nu(\vec{x}', t') \}_{PB} \frac{\partial F}{\partial \Psi_\nu} d\vec{x}' - M_{\mu\nu} \frac{\partial F}{\partial \Psi_\nu} + \eta_\mu(\vec{x}, t) \\ &= V_\mu(\vec{x}, t) - M_{\mu\nu} \frac{\partial F}{\partial \Psi_\nu} + \eta_\mu(\vec{x}, t)\end{aligned}$$

where

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

and (generalized Einstein-Stokes/fluctuation-dissipation)

$$\langle \eta_\mu(\vec{x}, t) \eta_\nu(\vec{x}', t') \rangle = -2M_{\mu\nu} k_b T \delta(\vec{x} - \vec{x}') \delta(t - t')$$

Reference: Section 8.6.3 *Principles of condensed matter physics*, Chaikin and Lubensky (1995).

Equilibrium Time Dependence

In equilibrium F has no linear term in Ψ 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:

$$\begin{aligned} S(\vec{Q}, t) &= \langle \Psi^\dagger(\vec{Q}, t) \Psi(\vec{Q}, t) \rangle \\ &= k_bT / \left(\frac{\partial^2 F}{\partial \Psi^2} \right)_{eq} \end{aligned}$$

Signal to Noise

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

$$\begin{aligned}\frac{s}{n} &= \beta \bar{n} \sqrt{N} \\ &= \beta I \tau \sqrt{\frac{t_{total}}{\tau} N_{speckles}} \\ &= \beta I \sqrt{\tau t_{total} N_{pixels}}\end{aligned}$$

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 α -fold increase in intensity is an α^2 -fold increase in time resolution. **Need** very fast detectors.

Reference: Area detector based photon correlation in the regime of short data batches: data reduction for dynamic x-ray scattering, D. Lumma, L.B. Lurio, S.G.J. Mochrie, and M. Sutton, Rev. Sci. Instr. **71**, 3274-3289 (2000).

Signal to Noise

More explicitly:

$$\begin{aligned}
 \frac{s}{n} &\approx \beta B_0 dx dx' dy dy' \frac{\Delta E}{E} \frac{1}{V} \frac{d\sigma}{d\Omega} L \sqrt{N_{sp}} \\
 &\approx \beta B_0 f_x f_y \lambda^2 \frac{\Delta E}{E} \frac{1}{V} \frac{d\sigma}{d\Omega} f_z \frac{\lambda^2}{\Delta\lambda} \sqrt{N_{sp}} \\
 &\approx \frac{1}{\max(1, f_i)^3} B_0 f_x f_y f_z \lambda^2 \frac{\Delta\lambda}{\lambda} \frac{1}{V} \frac{d\sigma}{d\Omega \Delta\lambda} \lambda^2 \sqrt{N_{sp}} \\
 &\approx B_0 \lambda^3 \frac{1}{V} \frac{d\sigma}{d\Omega} \sqrt{N_{sp}} \\
 &\approx f B_0 \lambda^3 \frac{1}{V} \frac{d\sigma}{d\Omega} \sqrt{N_{sp}} \quad (\text{if any } f_i < 1).
 \end{aligned}$$

Note: should be a $\lambda^3/8$ as normally use $\lambda/2$.

Detector Resolution

Speckle size (width of $\beta(\vec{k})$) 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 10m gives $d_{coh} = 15\mu\text{m}$.

Ideally optics could tune coherence lengths.

Scattering strengths

For a small crystal:

$$\frac{1}{V} \frac{d\sigma}{d\Omega} = r_0^2 \frac{|\bar{F}|^2}{v_c} N \left[\frac{\sin(N_x q_x a/2)}{N_x \sin(q_x a/2)} \frac{\sin(N_y q_y b/2)}{N_y \sin(q_y b/2)} \frac{\sin(N_z q_z c/2)}{N_z \sin(q_z c/2)} \right]^2$$

For a correlation volume:

$$\frac{1}{V} \frac{d\sigma}{d\Omega} = r_0^2 \frac{|\bar{F}|^2}{v_c^2} \xi^3 \frac{1}{1 + (\xi q)^2}$$

Typical values of $\frac{|\bar{F}|^2}{v_c}$ are ($e^2/\text{\AA}^3$):

Si(111)–18 Ge(111)–100 Pb(111)–400

NaCl(002)–38 Fe₃Al(1/2 1/2 1/2)–.5

For a TDS of 3 μm NaCl:

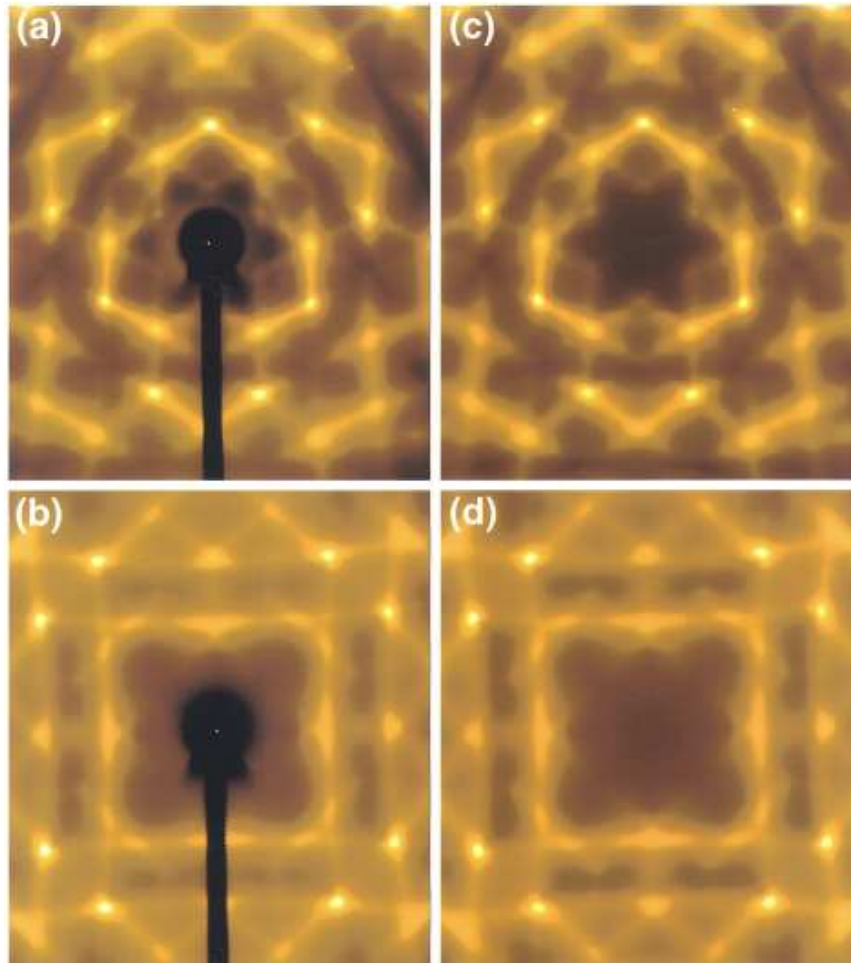
$$\begin{aligned}L \frac{1}{V} \frac{d\sigma}{d\Omega} &= .001 d\Omega \\ &= 4 \times 10^{-13} \text{ for } 22\mu\text{m pixel at a meter} \\ &= 10^{-11} \text{ for } .1 \text{ mR}\end{aligned}$$

(1)

But potentially have $4\pi/ (.1\text{mR})^2 = 10^9$ speckles.

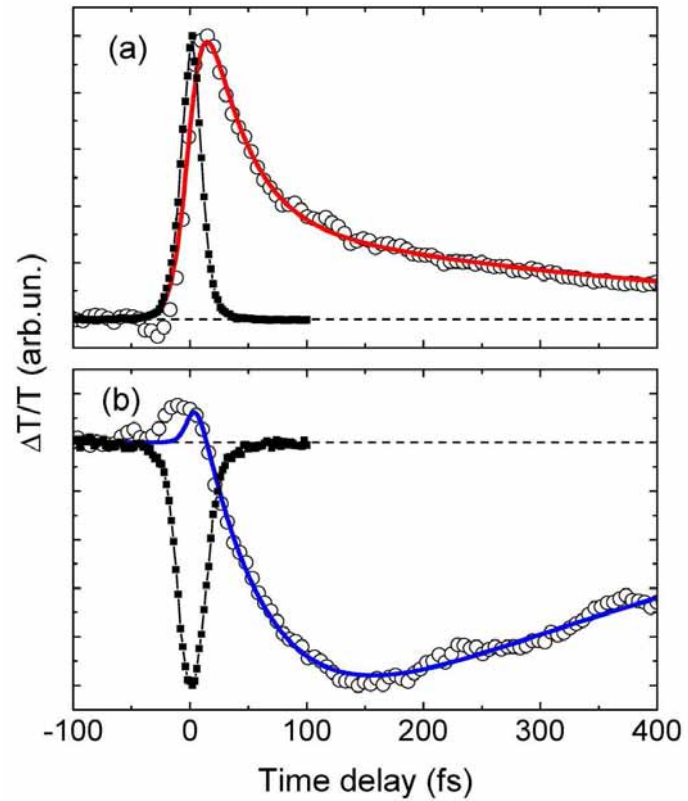
Reference: *Theory of X-ray Diffraction in Crystals*, W.H. Zachariasen, Dover (1994).

TDS of Si



Holt et al. PRL **83** 3317 (1999).

SW Carbon Nanotubes

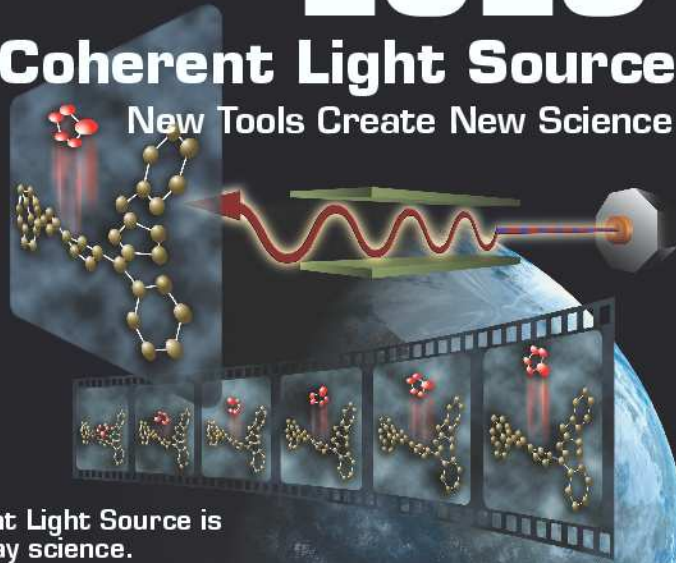


Manzoni et al., PRL **94** 207401 (2005).

LCLS

Linac Coherent Light Source

New Tools Create New Science



The Linac Coherent Light Source is a revolution in x-ray science.

Just as the invention of x-ray machines a century ago astonishingly revealed the inside of our bodies and began new sciences, the world's first x-ray laser will open up unprecedented opportunities.

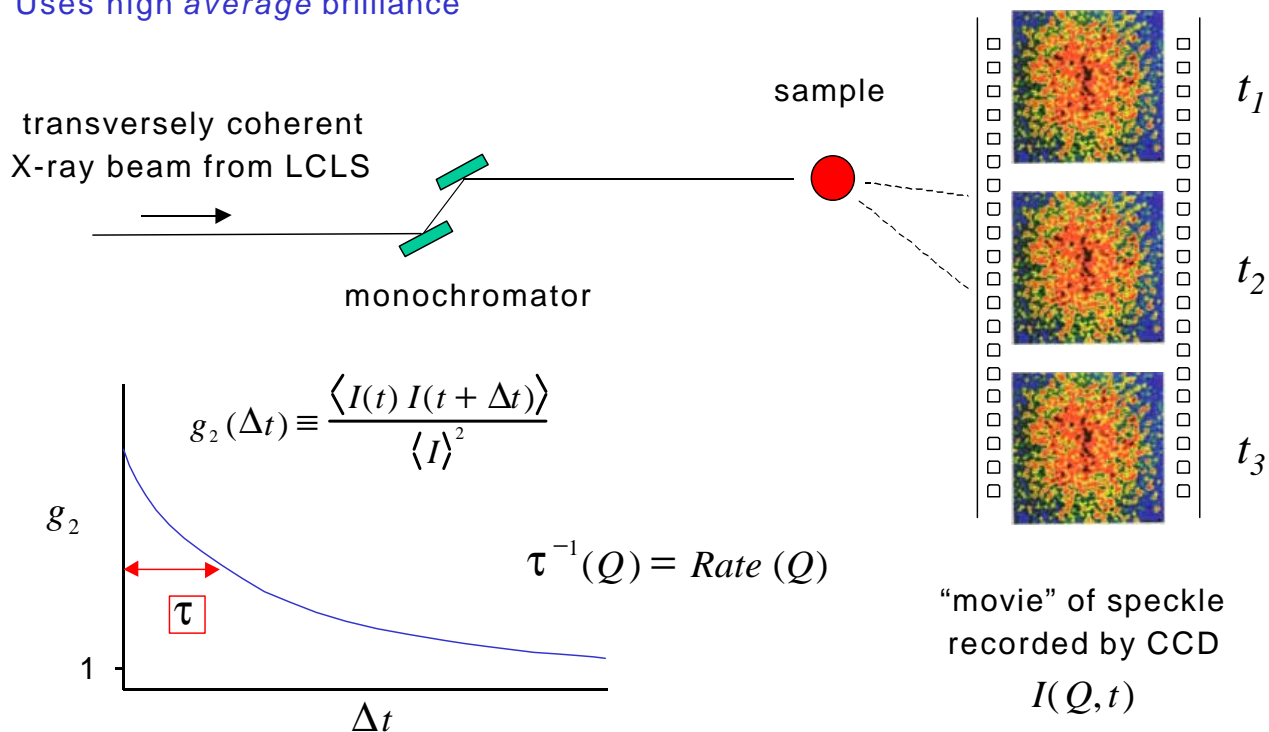
Pioneering experiments will advance our understanding of everything from the hidden physics inside planets, to how proteins function as the engines of life, to building nanotechnology devices for the backbone of future industry and technology.

The applications are legion: medicine, electronics, biology, solid-state physics, nanotechnology, energy production, industry and fields that do not yet exist.

Experiment 1:
X-ray Photon Correlation Spectroscopy (XPCS)

LCLS

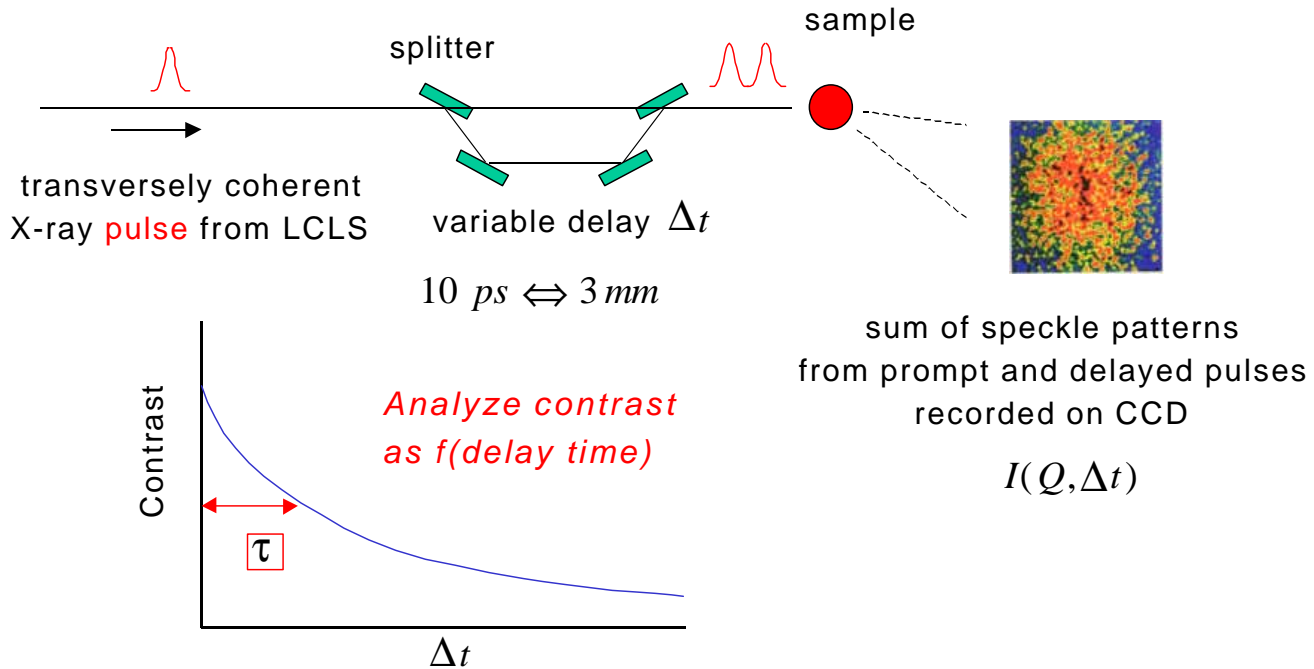
In milliseconds - seconds range:
Uses high average brilliance



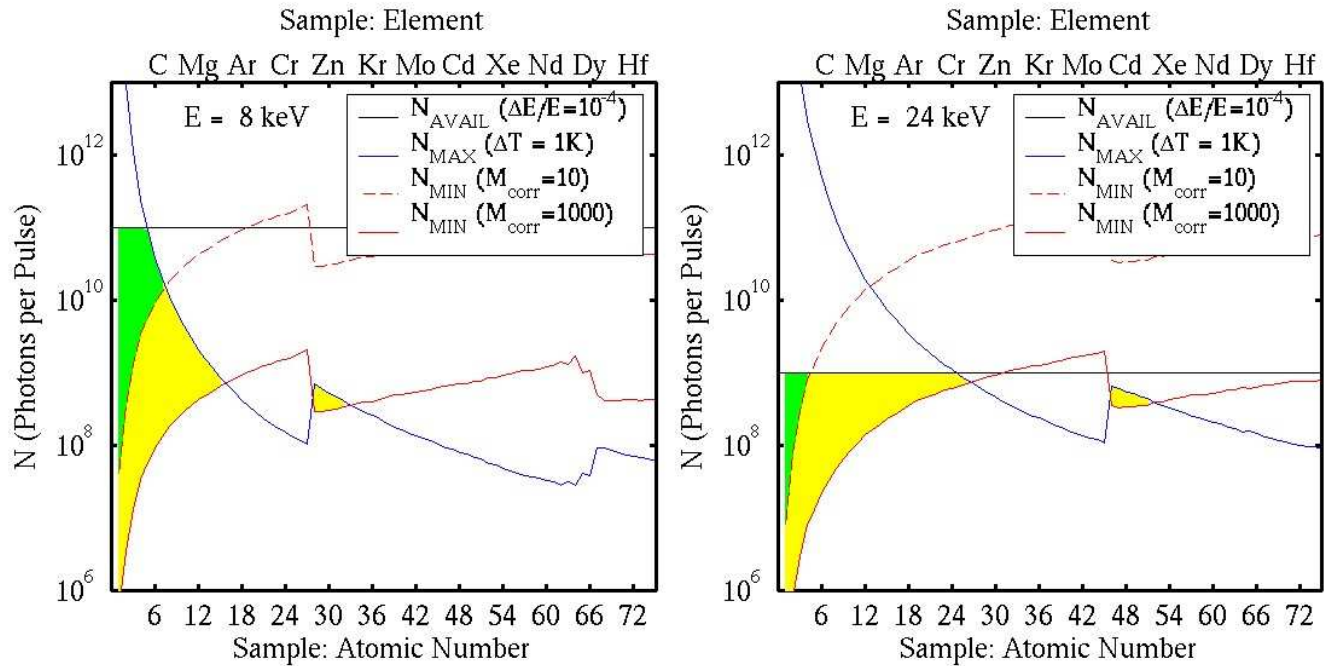
Experiment 2: XPCS Using Split Pulse

LCLS

In **picoseconds - nanoseconds** range:
Uses high *peak* brilliance



Heating and XPCS Signal from Single Pulse



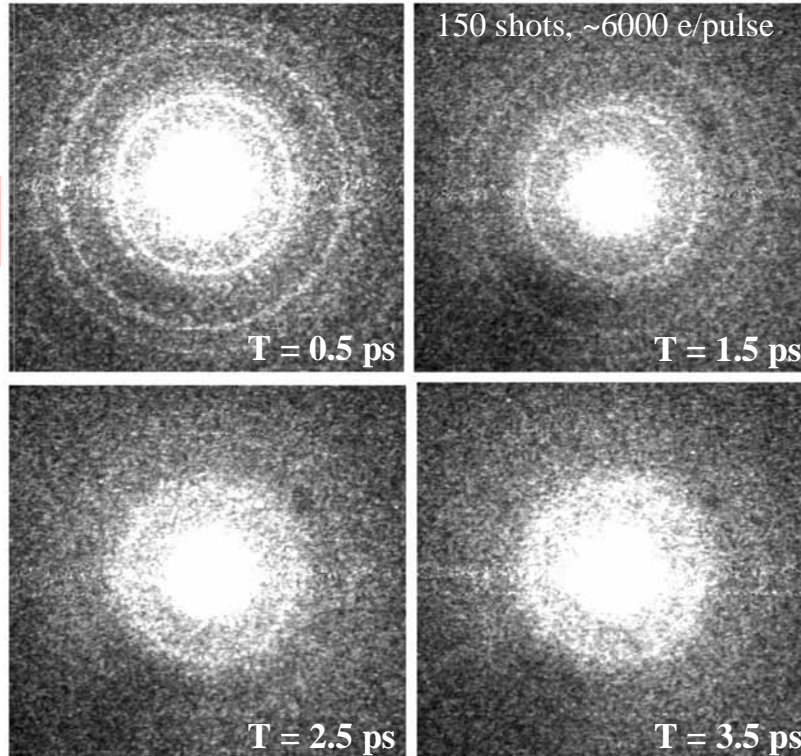
Shaded areas show feasibility regions e.g. for liquid or glass (green) or nanoscale cluster (yellow)

See analysis in LCLS: The First Experiments

Strongly-Driven Solid-To-Liquid Phase Transition in Aluminum

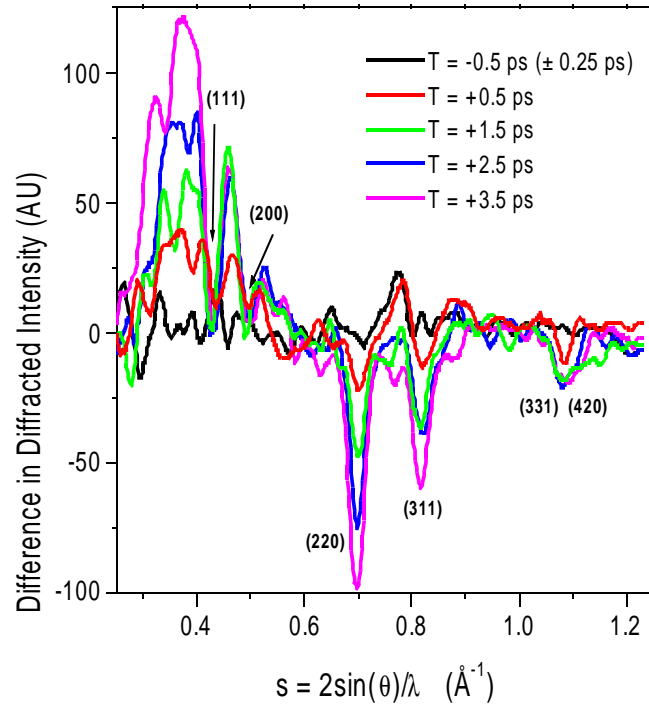
70 mJ/cm²
Incident Laser
Intensity

$$n_{\text{ex}} \sim 2 \times 10^{23} \text{ cm}^{-2}$$

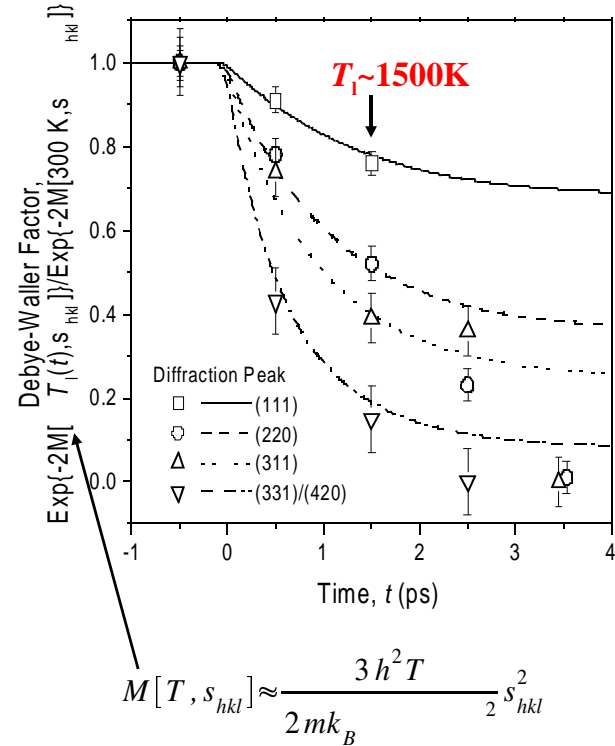


Phase Transition Dynamics: Thermal Activation

B. J. Siwick et al., Science **302** (2003) 1382.



B. J. Siwick et al., Chem. Phys. **299** (2004) 285.



Ultrafast Melting: An Atomic-Level Perspective

