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X-ray Photon Correlation Spectroscopy Studies of Dynamics in Condensed Matter

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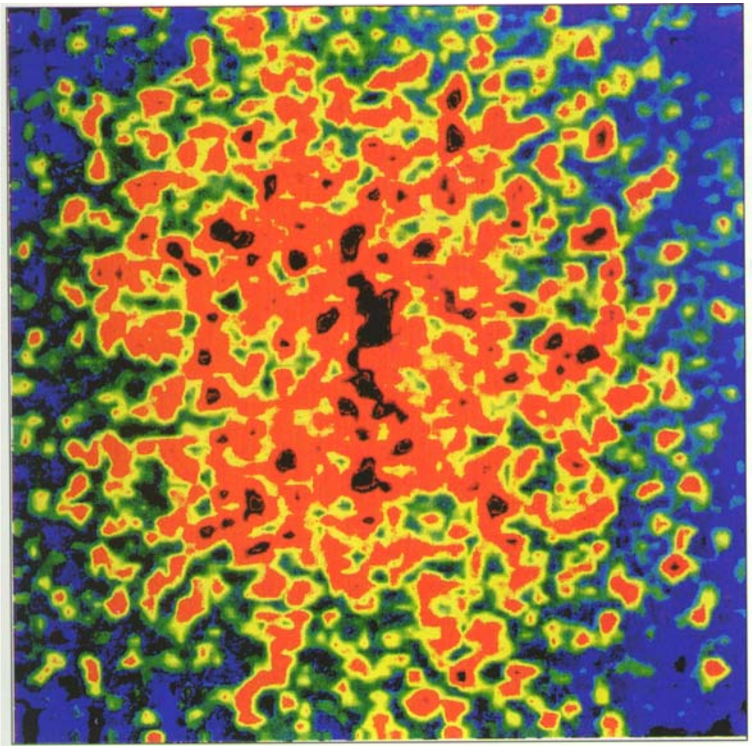
X-ray Science in the 21st Century
Kavli Institute for Theoretical Physics, Santa Barbara, CA, August 2-6, 2010

Outline

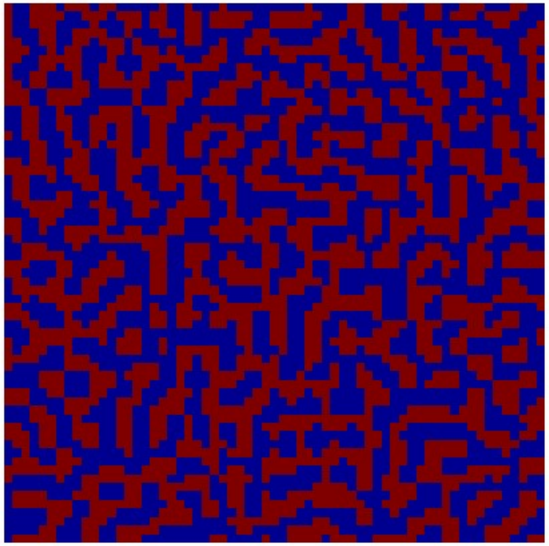
X-ray Photon Correlation Spectroscopy (XPCS) with New Coherent X-ray Sources

- Opportunities
  - Overview
  - Science Examples, Current and Future
- Challenges
  - Experimental Design: Avoiding Disturbing the Sample Dynamics
  - Analysis in Low Signal Limit
- Outlook



Scattering from Disorder: Speckle

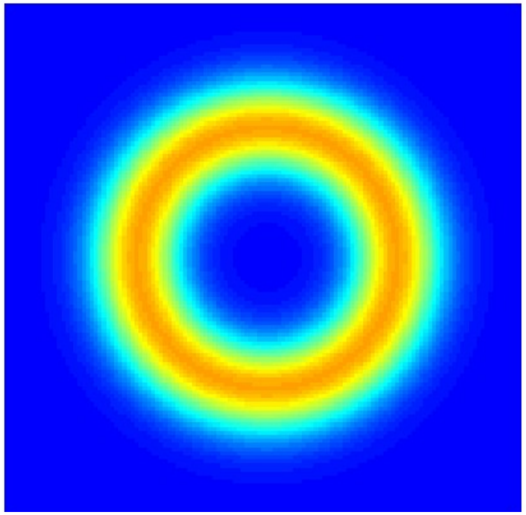
sample with disorder
(e.g. domains)

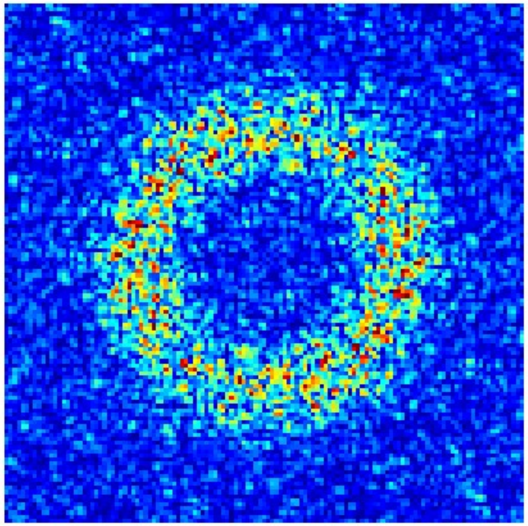


- ***Incoherent Beam: Diffuse Scattering***
  - **Measures averages, e.g. size, correlations**

- ***Coherent Beam: Speckle***
  - **Speckle depends on exact arrangement**

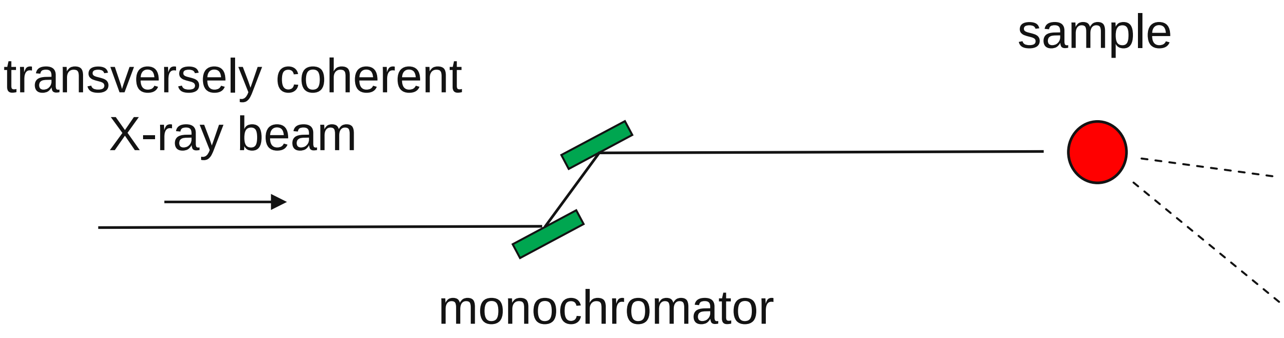
scattering

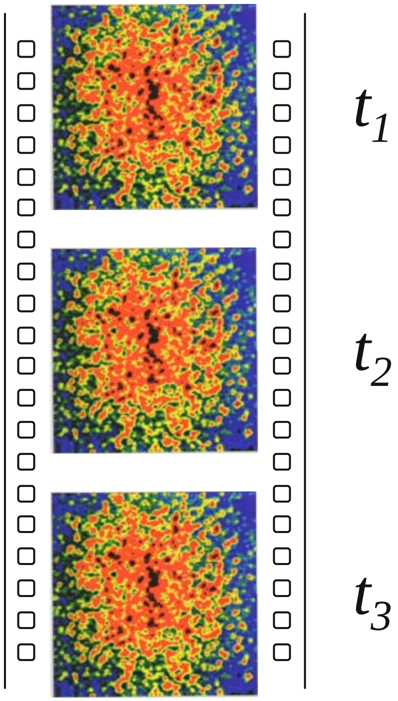




Typical Current XPCS Method

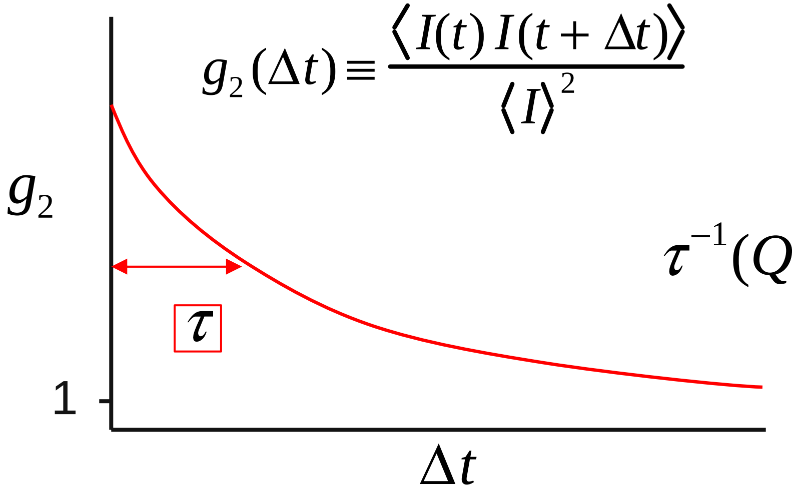
- Microseconds to seconds time resolution
- Uses high *average* brilliance





“movie” of speckle recorded by CCD

$I(Q,t)$

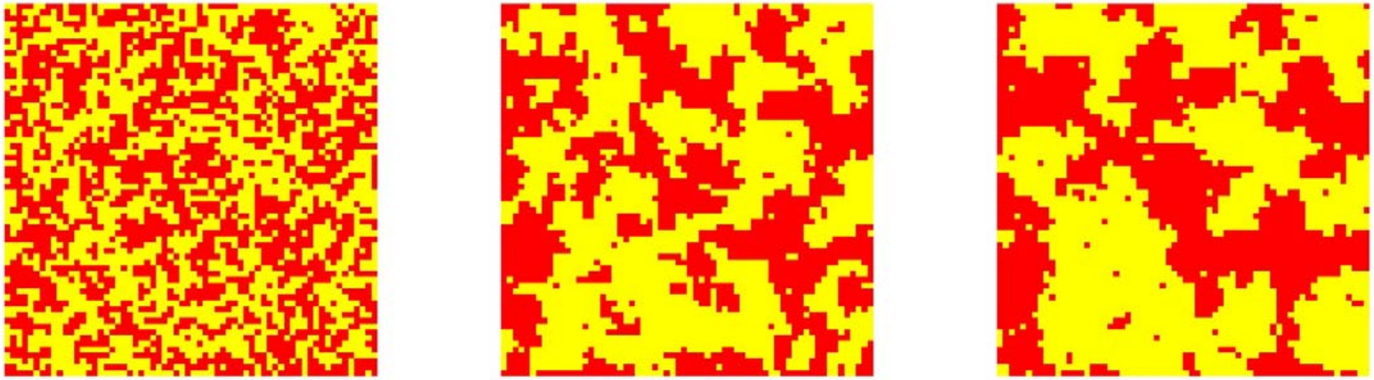


$$g_2(\Delta t) \equiv \frac{\langle I(t)\, I(t+\Delta t)\rangle}{\langle I \rangle^2}$$

$$\tau^{-1}(Q) = Rate(Q)$$

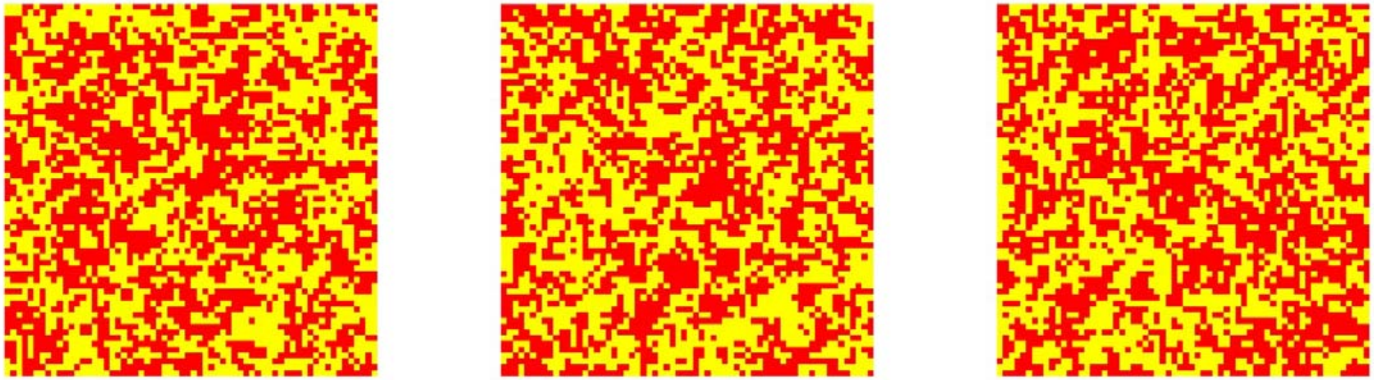
Speckle Reveals Equilibrium Dynamics

A. Non-equilibrium dynamics: average structure changes



time = 0 time = 1 time = 4

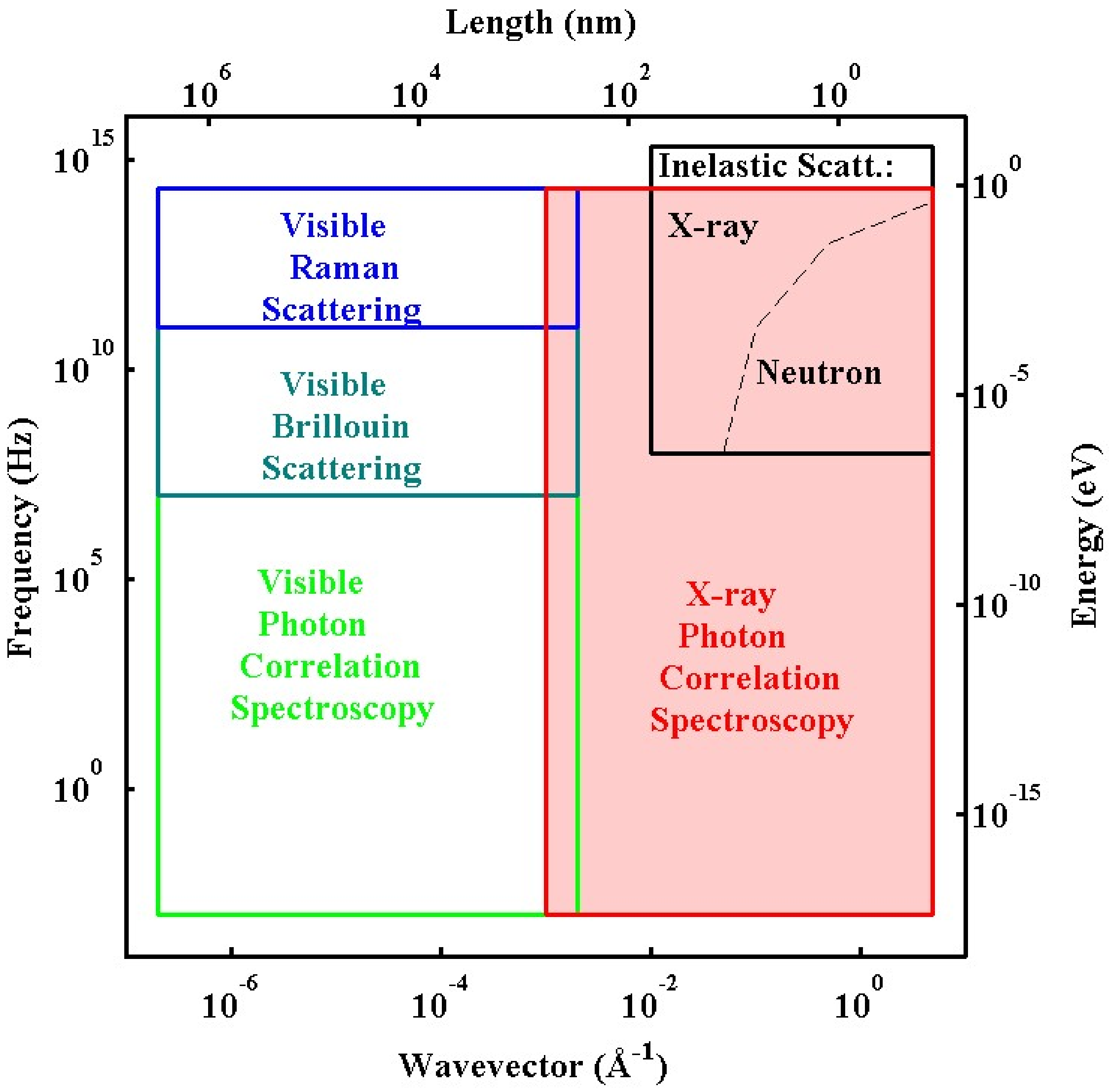
B. Equilibrium dynamics: average structure is static



time = 0 time = 1 time = 4

G.B. Stephenson, A. Robert, G. Grübel, Nature Mater. ***8****, 702 (2009)*

X-ray Photon Correlation Spectroscopy



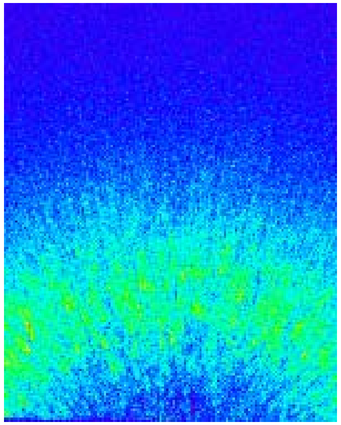
Allows observation of equilibrium (and non-equilibrium) dynamics down to atomic scale

Time domain complementary to energy domain

Frontier for XPCS: Atomic-Scale Dynamics

Nanoscale Dynamics:
Small-Angle Scattering

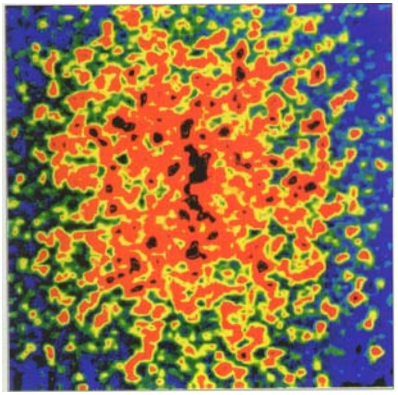
Atomic-scale Dynamics:
Wide-Angle Scattering



Phase Separation in Borosilicate Glass

Most XPCS experiments to date have been small-angle scattering, since signal typically decreases as Q increases (weaker scattering, more stringent coherent illumination criterion)

==> True power of XPCS is still awaiting exploitation



Ordering in Fe_3Al Alloy

Wide Potential Impact of XPCS

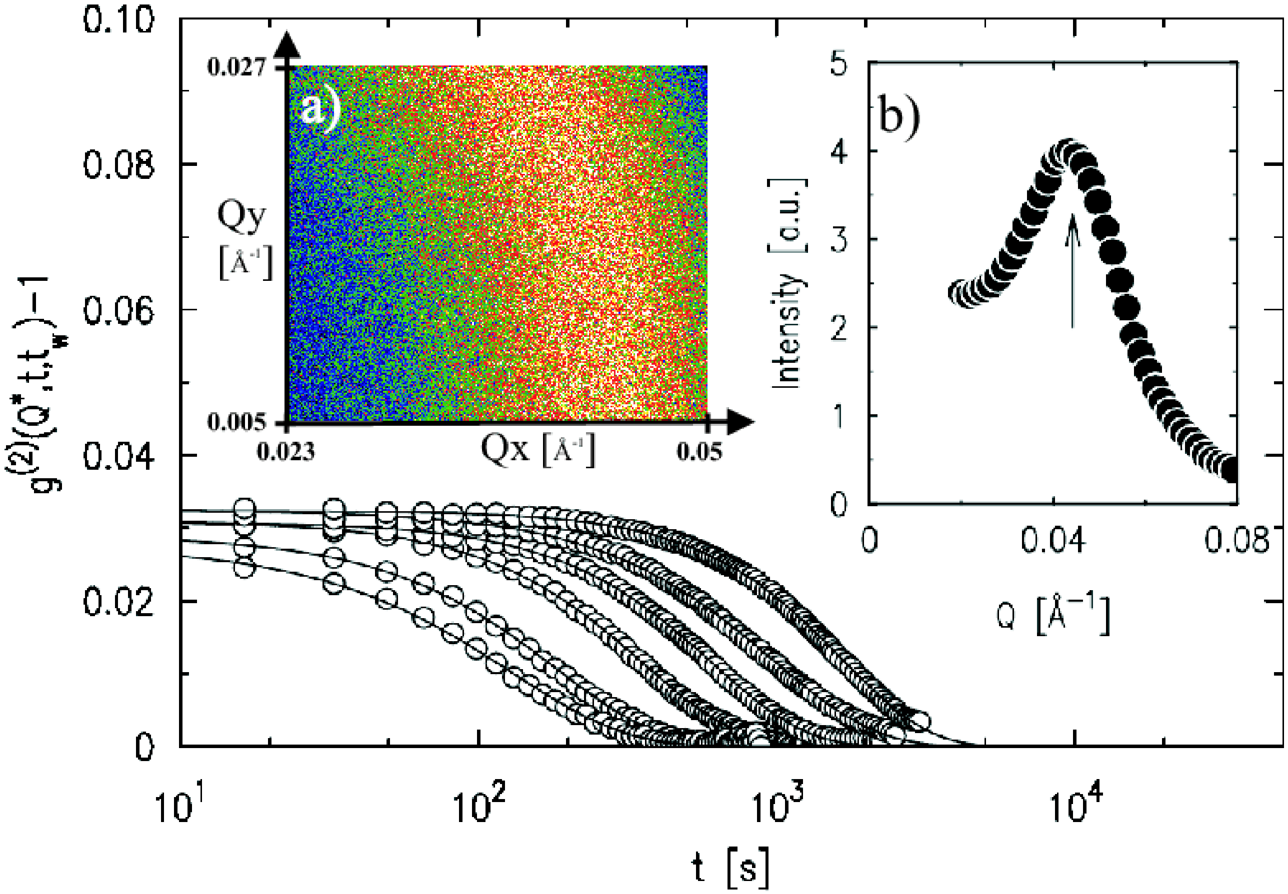
XPCS in Scientific Cases for New Coherent X-ray Sources:

- ***Simple Liquids* –** Transition from the hydrodynamic to the kinetic regime.
- ***Complex Liquids* –** Effect of the local structure on the collective dynamics.
- ***Polymers* –** Entanglement and reptative dynamics.
- ***Proteins* –** Fluctuations between conformations, e.g folded and unfolded.
- ***Glasses* –** Vibrational and relaxational modes approaching the glass transition.
- ***Phase Transitions* –** Order fluctuations in ferroelectrics, alloys, liquid crystals, etc.
- ***Charge Density Waves* –** Direct observation of sliding dynamics.
- ***Quasicrystals* –** Nature of phason and phonon dynamics.
- ***Surfaces* –** Dynamics of adatoms, islands, and steps during growth and etching.
- ***Defects in Crystals* –** Diffusion, dislocation glide, domain dynamics.
- ***Soft Phonons* –** Order-disorder vs. displacive nature in ferroelectrics.
- ***Correlated Electron Systems* –** Novel collective modes in superconductors.
- ***Magnetic Films* –** Observation of magnetic relaxation times.
- ***Lubrication* –** Correlations between ordering and dynamics.

XPCS Example: Dynamics in Ferrofluid

Small-angle scattering from magnetic particles

“Glassy dynamics and aging in a dense ferrofluid,” A. Robert et al., Europhys. Lett. ***75****, 764 (2006)*



Dynamics depend on aging time after mixing

XPCS Example: Atomic Diffusion

Wide-angle diffuse scattering from short-range order fluctuations in Cu-Au alloy

$\Gamma = \tau^{-1}$

M. Leitner et al., Nature Mater. 8, 717 (2009)

111

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Small-Q limit: $\Gamma = D\,Q^2$

110

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

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Nearest-neighbor jumps (blue) vs 2nd neighbor jumps (green)

11-1

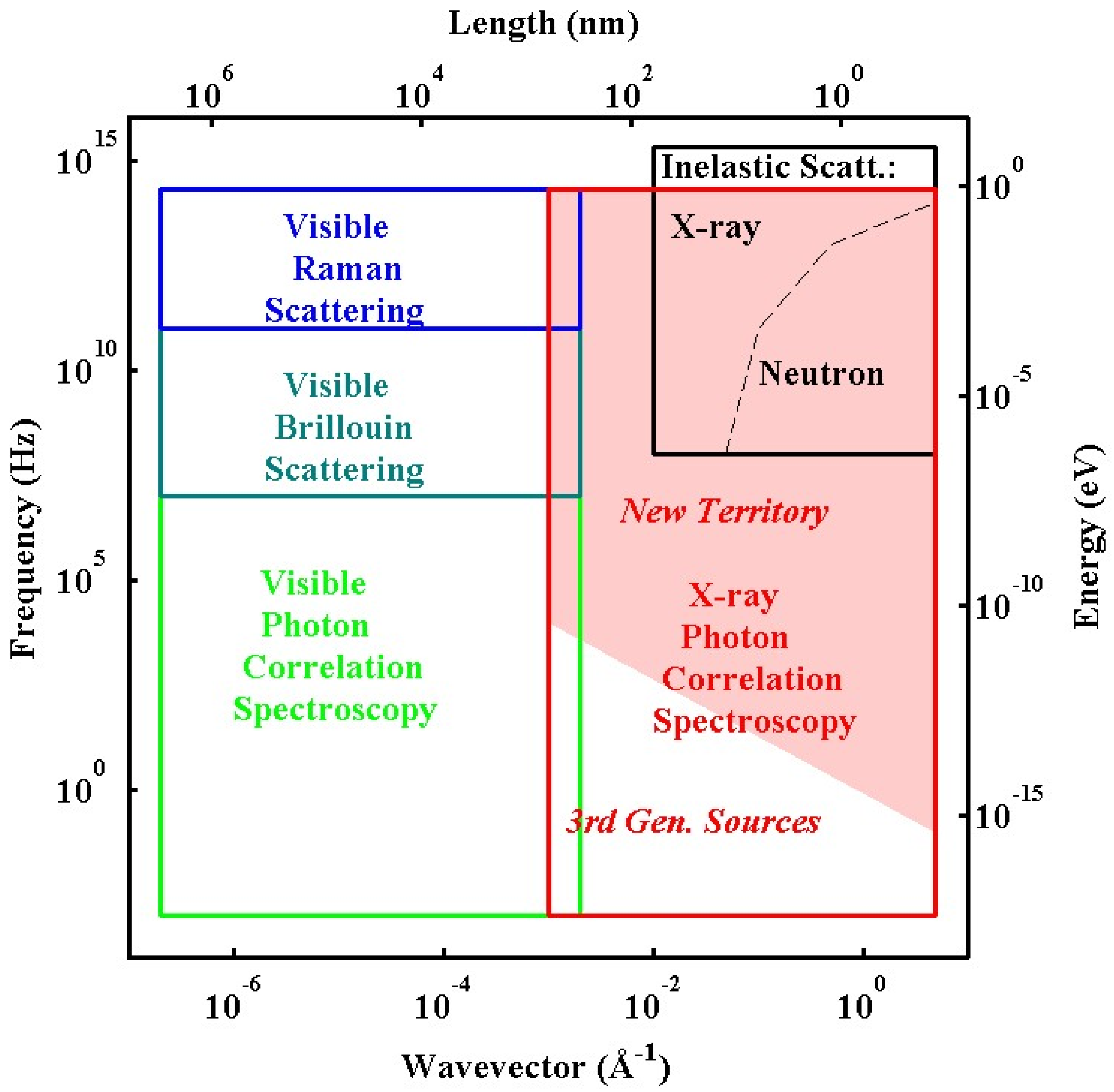
QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Impact of New X-ray Sources

Coherent flux, pulse width, rep rate:

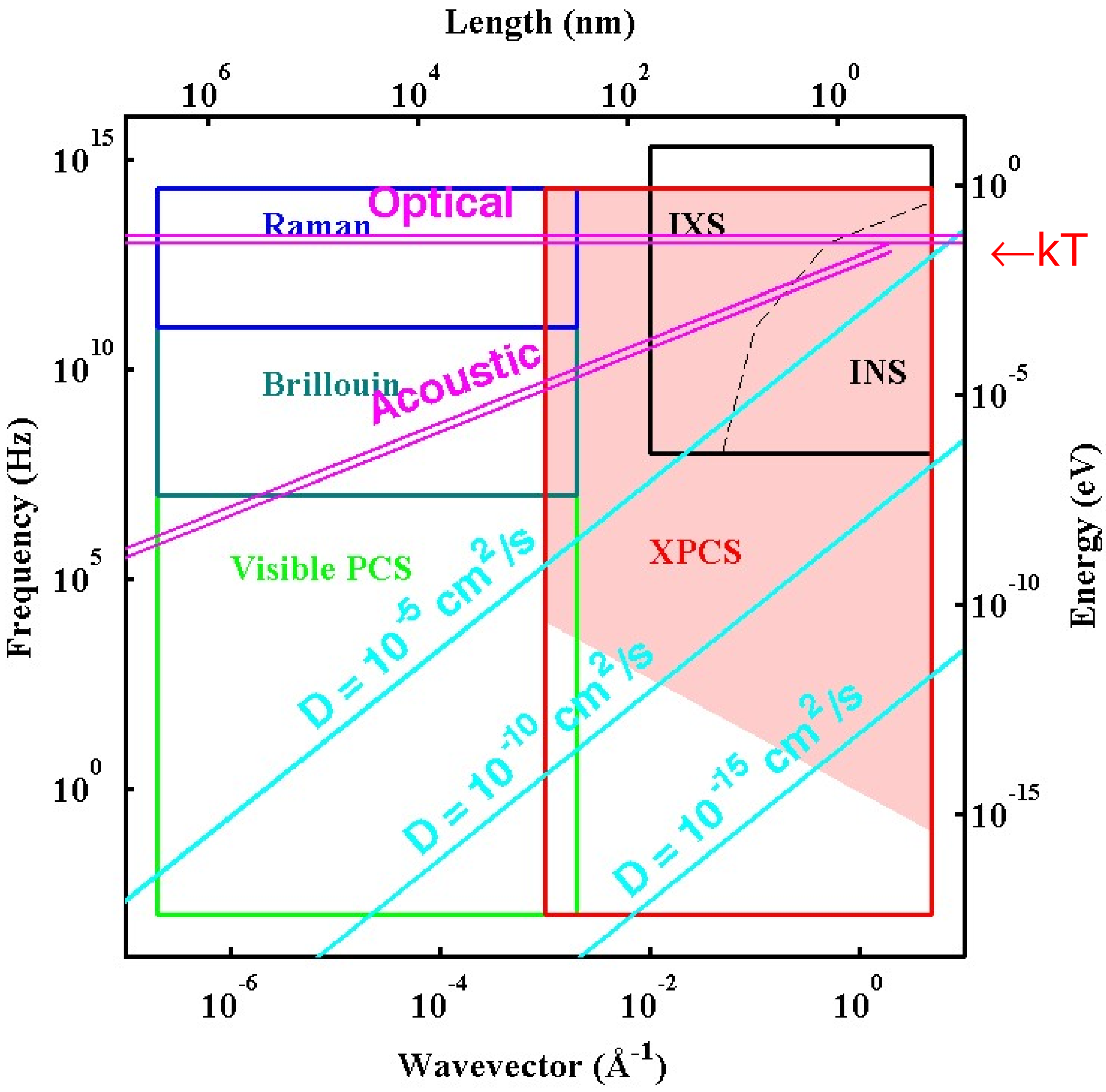
at 8 keV:	Avg. Trans. Coherent Flux (/s /0.1% BW)	Pulse FWHM (ps)	Eff. Rep. Rate (Hz)	Transversely Coherent Photons / Pulse
Storage Rings:				
ESRF, APS, Spring-8	4×10^{11} to 3×10^{12}	50 to 100	2×10^{6} to 3×10^{8}	4×10^{3} to 5×10^{5}
NSLS-II	1×10^{13}	25	4×10^{8}	2×10^{4}
ERLs:				
Cornell	2×10^{14}	2	1×10^{9}	1×10^{5}
FELs:				
LCLS	2×10^{14}	0.01	1×10^{2}	2×10^{12}
European XFEL	7×10^{16}	0.01	3×10^{4}	2×10^{12}

New Territory for XPCS: Large Q, Small τ



- To date, most XPCS experiments have been small-angle scattering in order to obtain sufficient signal
- Higher coherent flux from new sources will allow large-angle scattering studies of atomic scale dynamics, and studies at faster time scales

Large Q: Small Length Scales => Fast Time Scales



- Typical time scales of processes (e.g. mass diffusion) are faster at smaller length scales
- Mass diffusion time scales at molecular length scales are typically inaccessible by XPCS at third generation sources
- kT at 1000K: hν = 86 meV or 1/ν = 48 fs; will be able to study all thermally excited equilibrium fluctuations

Relaxor Ferroelectrics

Dielectric relaxation times span picoseconds to milliseconds near phase transition

Polar nanoregions are believed responsible

DC field:

E = 0

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

E = 20
kV/cm

10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2}

J. Macutkevic et al., Phys. Rev. B **74**, 104106 (2006)

G. Xu et al., Nature Materials **5**, 134 (2006)

Heterogeneous Dynamics at Glass Transition

Diffusion relaxation times near the glass transition predicted to split into α and β modes, with separate dependences on Q and T

Ideally need many orders of magnitude of time scale at high Q to map transition between liquid and solid

“Anomalous diffusion in heterogeneous glass-forming liquids: Temperature-dependent behavior,” J. S. Langer, *Phys. Rev. E* **78**, 051115 2008

Predictions and INS data for orthoterphenyl at 293 K

β:
liquid-like

$Q = 1.2$ Å^{-1}

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

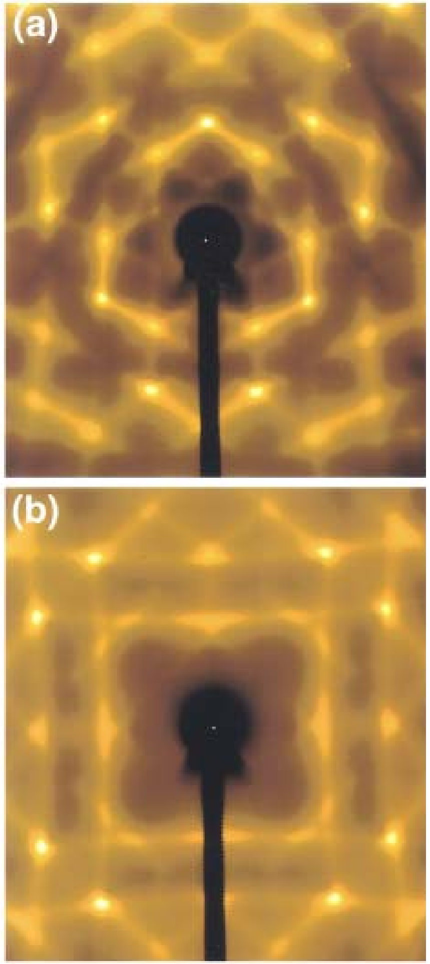
$Q = 2$ Å^{-1}

α: glass-like

Dream for XPCS: Observe Dynamics in Any Diffuse X-ray Scattering

To date, the main experimental issue with XPCS measurements has been obtaining sufficient signal

With higher coherent flux from FEL, more weakly scattering systems and faster time scales can be investigated



Thermal Diffuse Scattering around Si 111 and 100

M. V. Holt et al., PRL ***83****, 3317 (1999)*

Thermal Diffuse Scattering from Phonons in Si

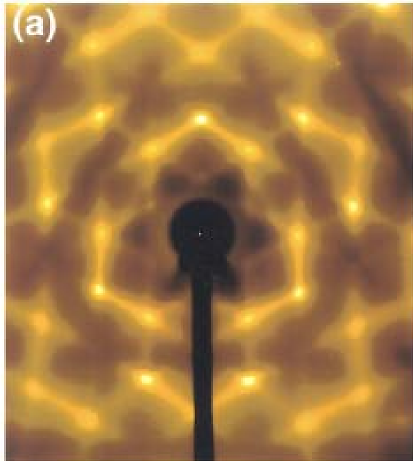
M. V. Holt et al., PRL ***83****, 3317 (1999)*

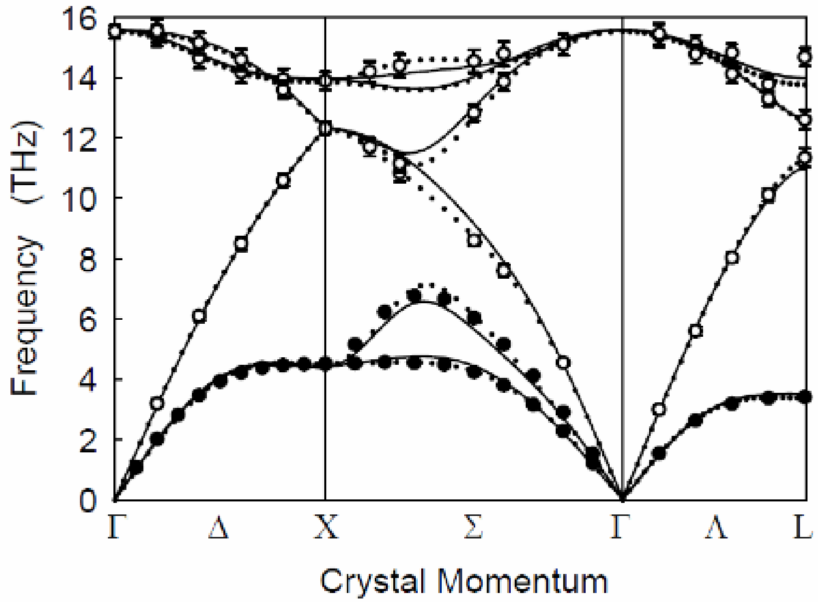
Demonstrated that intensity distribution of TDS can be analyzed using a model that includes dynamics, and obtain full phonon dispersion curves from a few images

=> phonon studies in nanostructures

Using XPCS, can we directly measure the dynamics as a function of Q?

Observing speckle dynamics would be critical to sorting out behavior in disordered systems, where TDS overlaps scattering from static structure

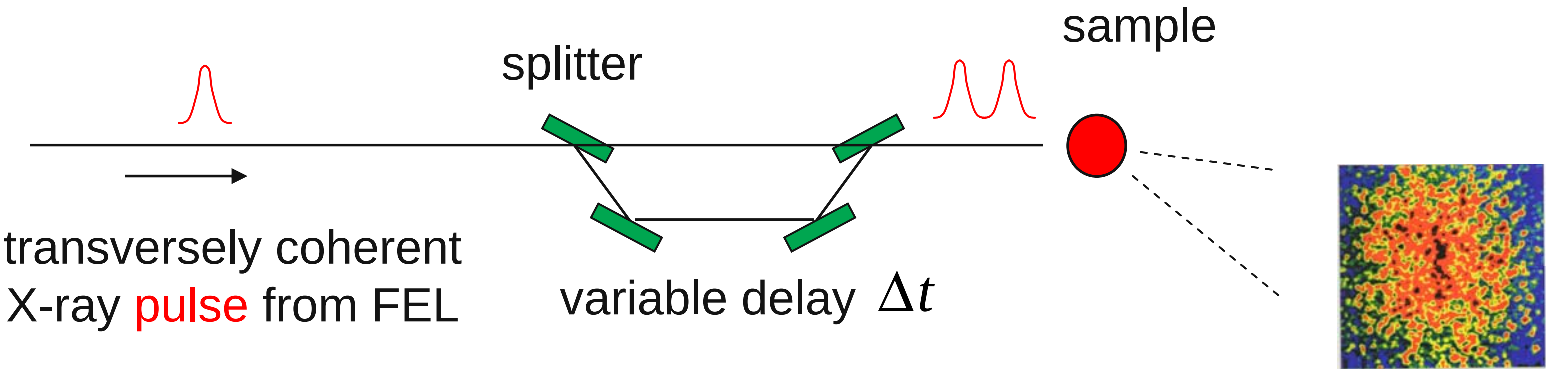




Ultrafast XPCS using 'Split Pulse' Mode

Femtoseconds to nanoseconds time resolution

Uses high *peak* brilliance



sample

splitter

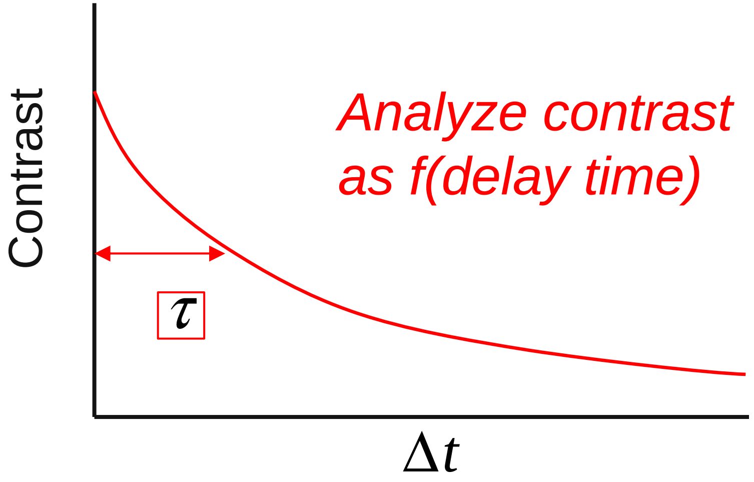
transversely coherent X-ray pulse from FEL

variable delay Δt

$1ns \Leftrightarrow 300mm$

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

$I(Q,\Delta t)$



Analyze contrast as f(delay time)

Split, Delay, Recombine

Initial hard x-ray split and delay system recently built and tested by DESY group

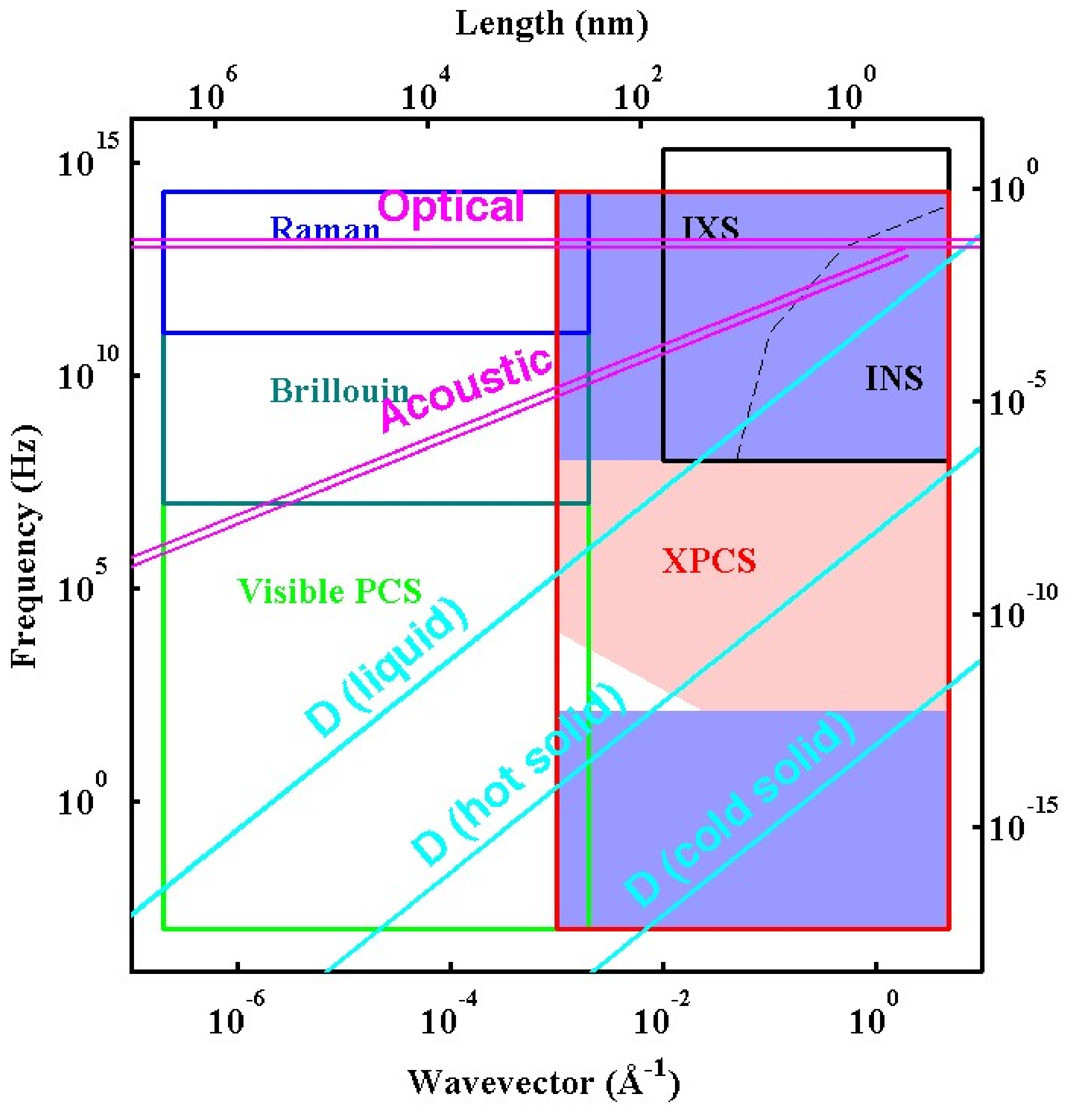
Maximum delay 2.7 ns

Fixed energy determined by 90° crystal diffraction (e.g. Si (511) at 8.39 keV)

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

“Performance of a picosecond x-ray delay line unit at 8.39 keV”, W. Roseker, H. Franz, H. Schulte-Schrepping, A. Ehnes, O. Leupold, F. Zontone, A. Robert, and G. Gruebel, *Optics Letters* **34**, 1768 (2009)

FEL Pulse Structure Affects Accessible Times



- Current LCLS pulse structure leaves gap
- Difficult to produce split-and-delay longer than ~10 ns
- New operational modes with multiple pulses in same RF train could narrow gap

Ultrafast Pulses - Opportunity and Challenge

- Ultrafast pulses provide opportunity to explore new time domains
- For experiments which do not require such time resolution, ultrafast pulses may limit usable coherent flux due to disturbance of the sample
- This affects optimum source characteristics and beamline configurations for XPCS

Design of XPCS Experiments at FEL

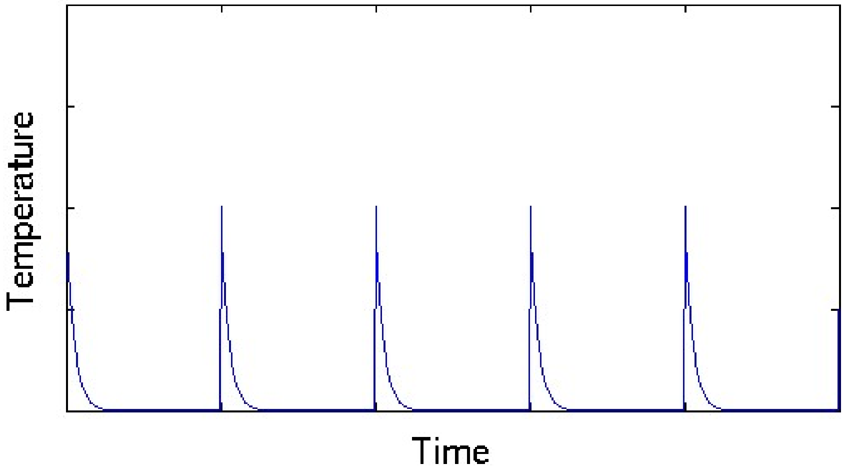
Driven by analysis of sample heating by beam

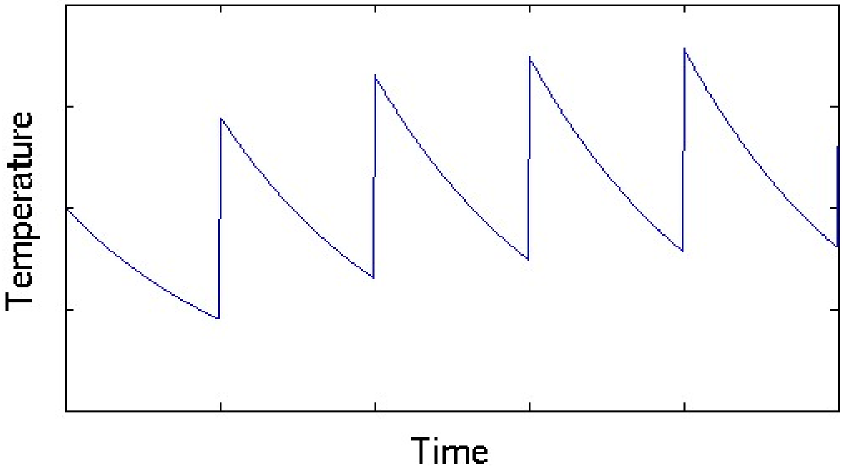
For these studies of dynamics, we must avoid changing the behavior of the sample by the beam (e.g. < 1K heating)

Design beamline to allow work at low signal rates (e.g. 0.01 counts per pulse per speckle), collect signal from many speckles

Heating by a Pulsed Beam

- Adiabatic (single pulse) heating - no heat flow, *T* rise given by heat capacity
- Steady-state heating - *T* rise given by balance of energy deposition and conduction, averaged either within pulse train or overall
- Ratios of thermal time constant to pulse spacings determine whether single-pulse or steady-state *T* rise is limiting





Sample Heating and Signal Level

Is there enough signal from a single pulse?
Is sample heating by x-ray beam a problem?

Maximum available photon density per pulse:

$$n_{AVAIL} = \frac{N_0}{A} \frac{\lambda(\Delta\lambda/\lambda)}{\lambda_0(\Delta\lambda/\lambda)_0} \qquad A \equiv \text{beam area}$$

Minimum required photon density per pulse to give sufficient signal:

If limited by absorption:

$$n_{MIN} = \frac{2\pi\sigma_{abs}}{\lambda^2\sigma_{el}M_{corr}} N_{MIN}^{SPECKLE}$$

If limited by longitudinal coherence:

$$n_{MIN} = \frac{\Delta\lambda/\lambda Q^2}{4\pi\lambda\sigma_{el}\rho_a M_{corr}} N_{MIN}^{SPECKLE}$$

Maximum tolerable photon density per pulse due to temperature rise:

$$n_{MAX} = \frac{3k_B}{E\sigma_{abs}} \Delta T_{MAX}$$

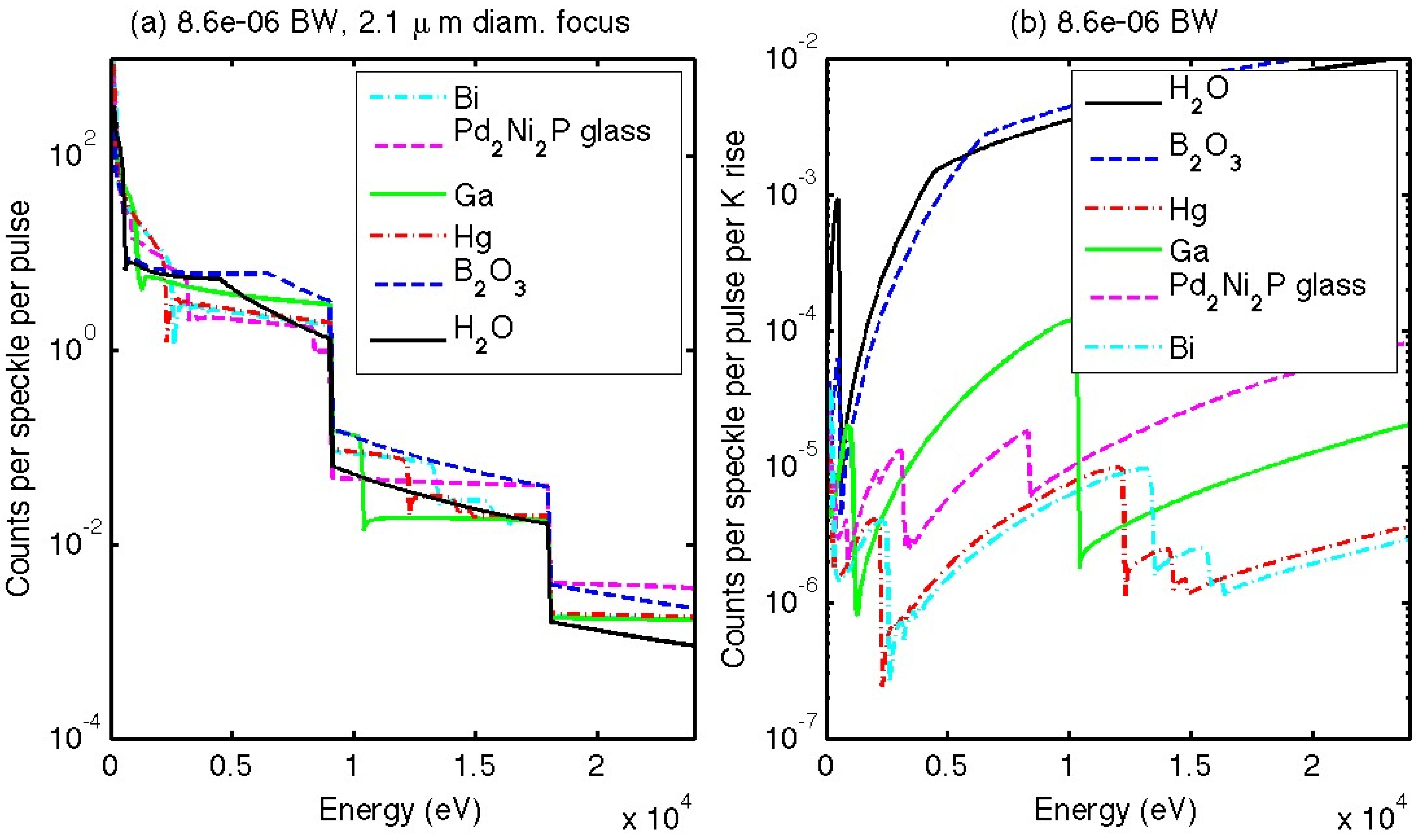
See analysis in LCLS: The First Experiments

Adiabatic Heating vs Focusing

LCLS at 8.4 keV, Si (111) resolution ($\Delta E/E = 1.4e-4$)

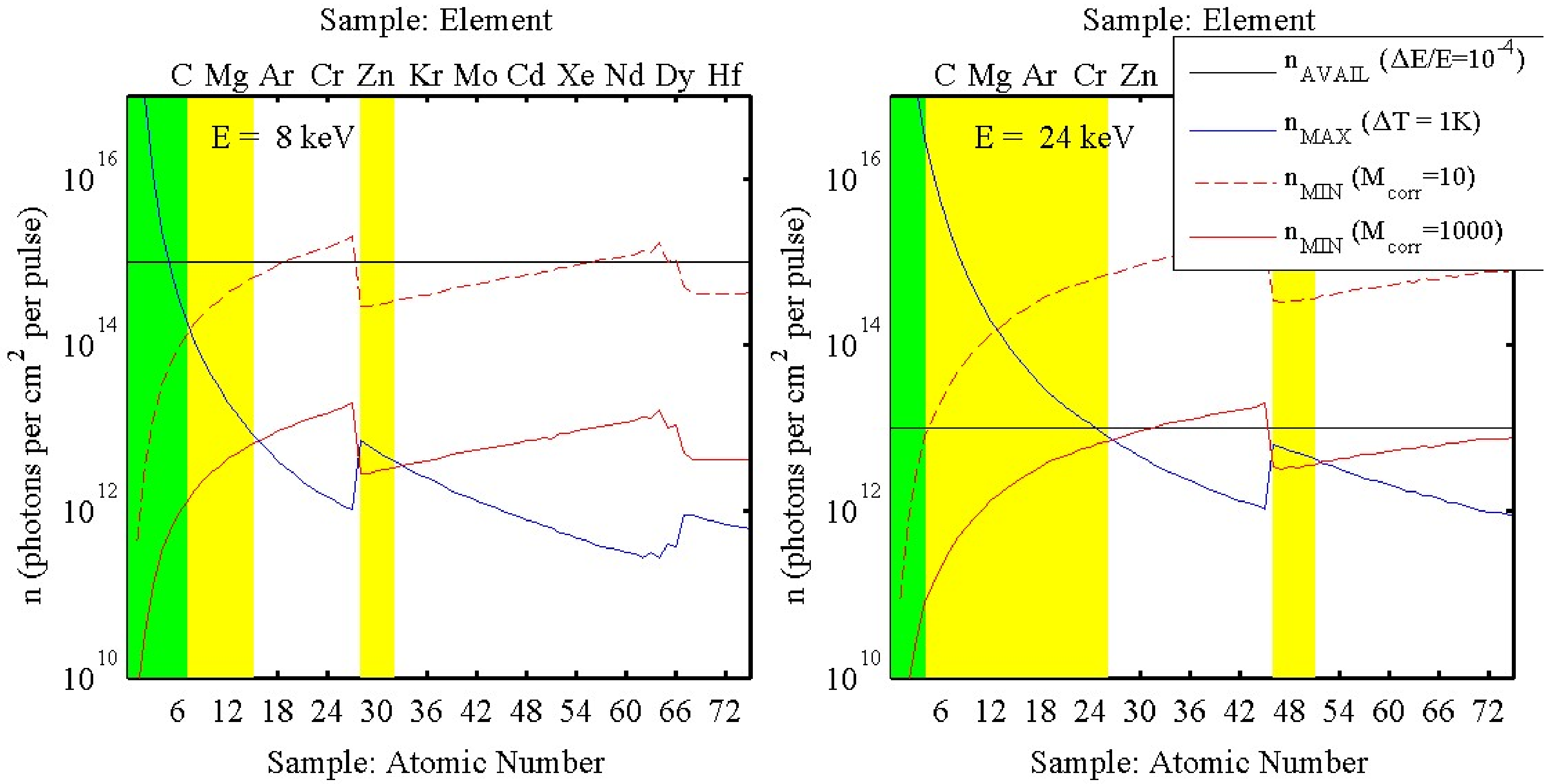
Focal diam.	220 (μm) (unfocused)	2 (μm)	0.01 (μm)
Material:	ΔT (K):	ΔT (K):	ΔT (K):
Be	0.08	1.1e3	3.9e7
H_2O	0.76	8.4e3	2.9e8
B_2O_3	1.5	1.6e4	5.6e8
Si	22	2.4e5	8.4e9
Ga	55	6.1e5	2.1e10
W	400	4.4e6	1.5e11
Bi	640	7.1e6	2.4e11

Calculations for Specific Samples: Signal



Many experiments feasible, energy flexibility important

Available, Required, Tolerable Photon Densities



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

Focused to 100 μm diam.

See analysis in LCLS: The First Experiments

Low-Signal Limit for XPCS

Speckle:

Negative binomial distribution

Mean counts per pixel $\bar{k}$

Inverse contrast M

Probability of k counts:

$$P_k = \frac{\Gamma(k+M)}{\Gamma(M)\Gamma(k+1)} \left(1 + \frac{M}{\bar{k}}\right)^{-k} \left(1 + \frac{\bar{k}}{M}\right)^{-M}$$

Low count rate limit $\bar{k} \approx 0.01$

$$P_1 = \bar{k}$$

$$P_2 = \frac{M+1}{2M} \bar{k}^2$$

To reduce adiabatic heating, expect to operate area detector in low count rate limit (e.g. average of one count per 100 pixels per pulse)

Contrast will be determined from ratio of double to single hits:

$$1/M = 2P_2/P_1^2 - 1$$

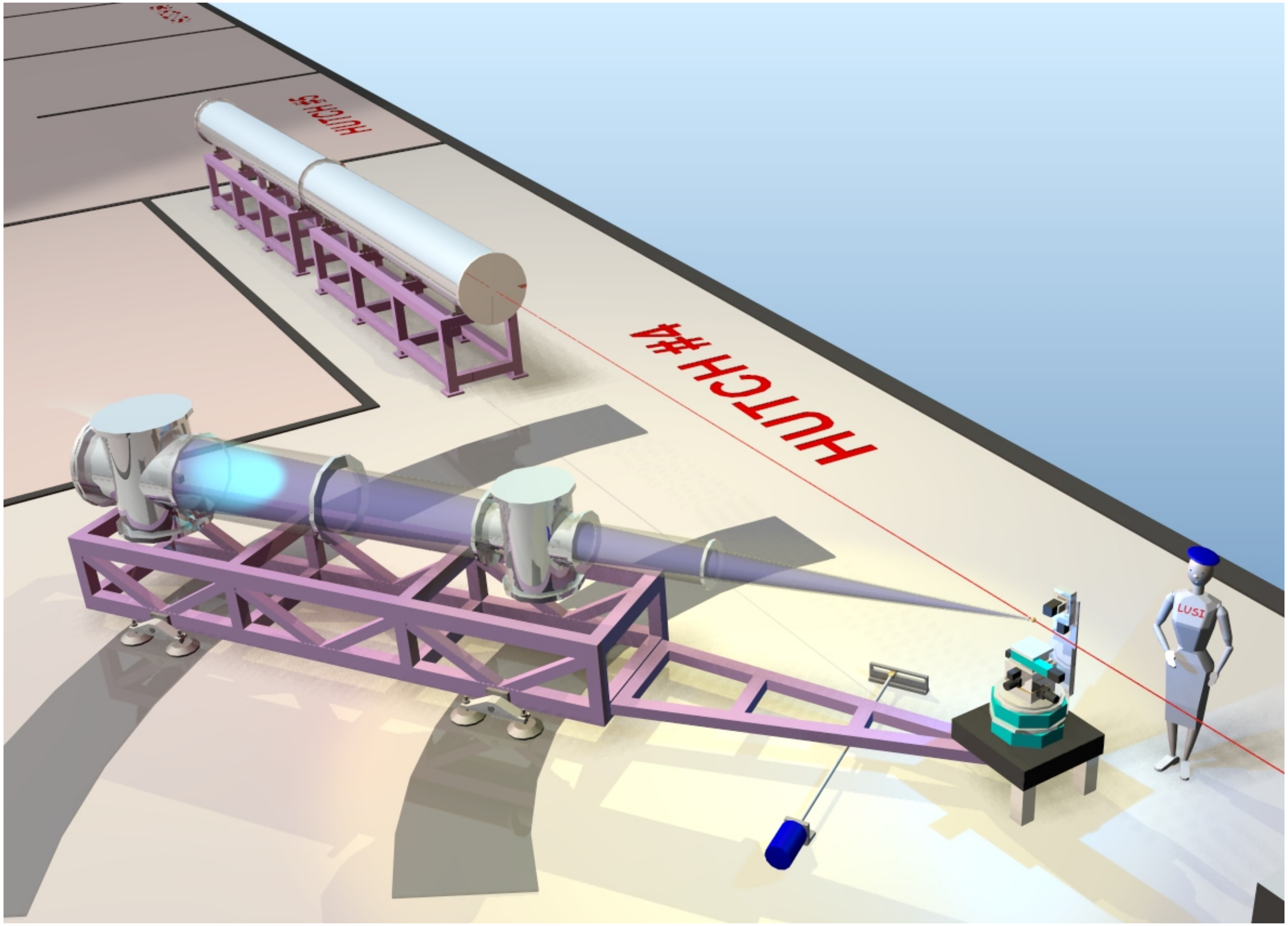
Required signal/noise: determine P_2 to a few %;

need $N_2 \sim N_{tot}\, k^2 > 1000$

Required N_{tot} (number of pixels at “same” Q): 10^6 to 10^8

XPCS Station at LCLS

Operational mid-2011



Upcoming XPCS Experiments at LCLS

(Using XPP station)

Proposal	Lead PI	Dates
Coherent X-ray Observation of Atomic Structure and Dynamics in Liquids and Glasses	G. B. Stephenson	Nov 11 - 16, 2010
Detecting Order in the Disorder – Investigating Local Symmetries in Liquids and Glasses via Speckle Correlation	C. Gutt	Nov 18 - 23, 2010
X-ray Split-Pulse Experiments	G. Gruebel	Jan 20 - Feb 1, 2011

Optimum Source for XPCS

- FELs produce much higher peak brilliance and are well-suited for ultrafast studies (e.g. picosecond range) e.g. using split-pulse mode
- ERLs produce similar average brilliance, and spread the x-ray energy over many smaller pulses. This can lead to a higher usable average coherent flux for longer timescale XPCS when adiabatic heating of the sample is an issue. The more uniform time structure is also a benefit.

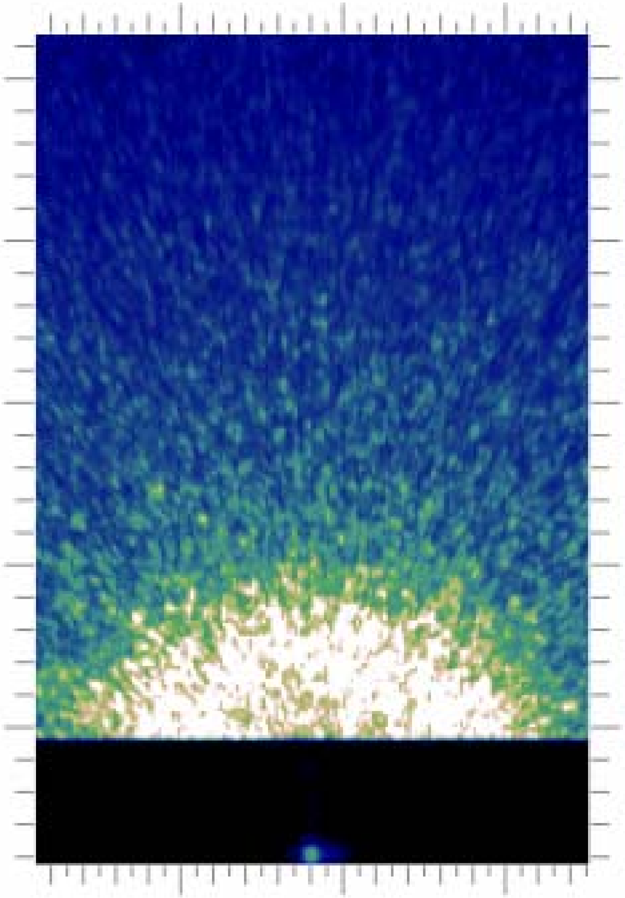
Summary

- XPCS - frontier is in atomic scale dynamics, on time scales down to femtoseconds
- Coherent, ultrafast x-ray sources allow observation without ensemble averaging
- Flexibility in pulse structure, energy range, and energy bandwidth will maximize opportunities
- Key theory developments:

  - equilibrium dynamics in time domain

  - higher-order correlations

  - extracting maximum information in the low-signal limit



Dawn of new era