... for a brighter future

Large Q Photon Correlation Spectroscopy

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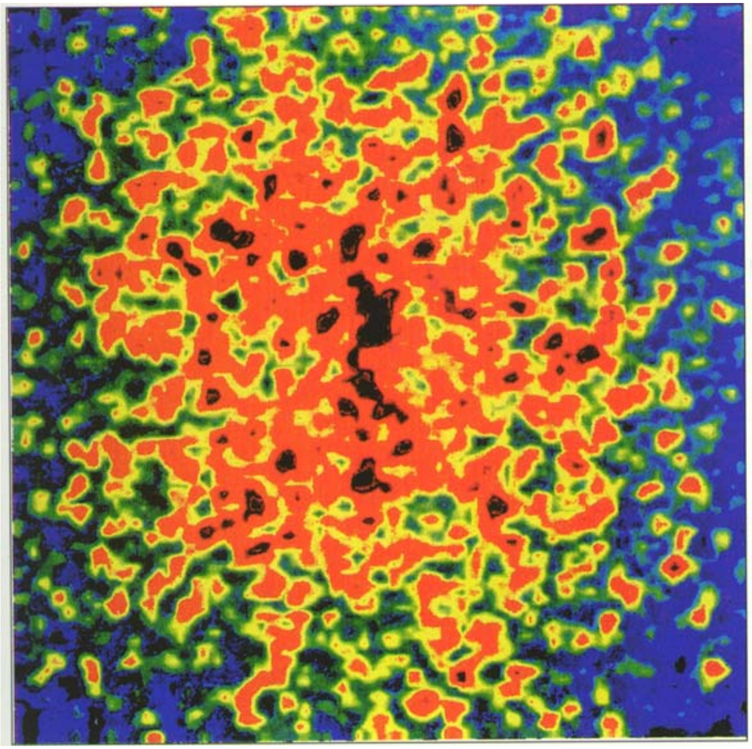
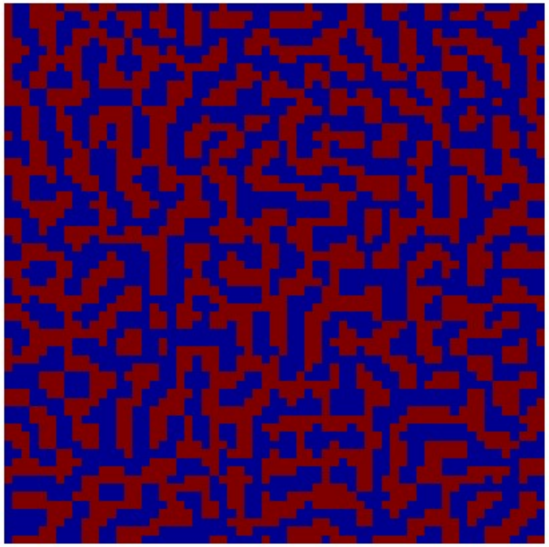
Outline

- Scientific Motivation for Large-Q XPCS
  - Fundamental Considerations
  - Examples, Current and Future
- Design of Large-Q XPCS Experiments at Pulsed Sources
  - Signal Rates and Beam Heating
  - Optimum photon energy, bandwidth, focusing
  - Detector considerations



Scattering from Disorder: Speckle

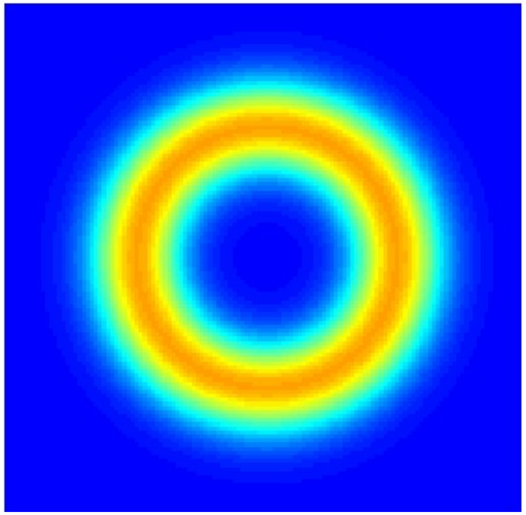
sample with disorder
(e.g. domains)

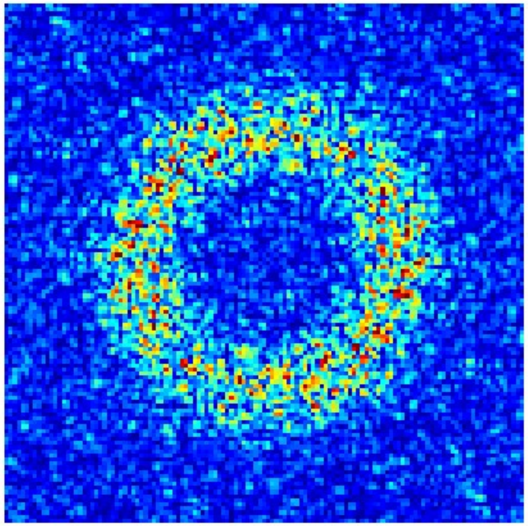


- ***Incoherent Beam: Diffuse Scattering***
  - **Measures averages, e.g. size, correlations**

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

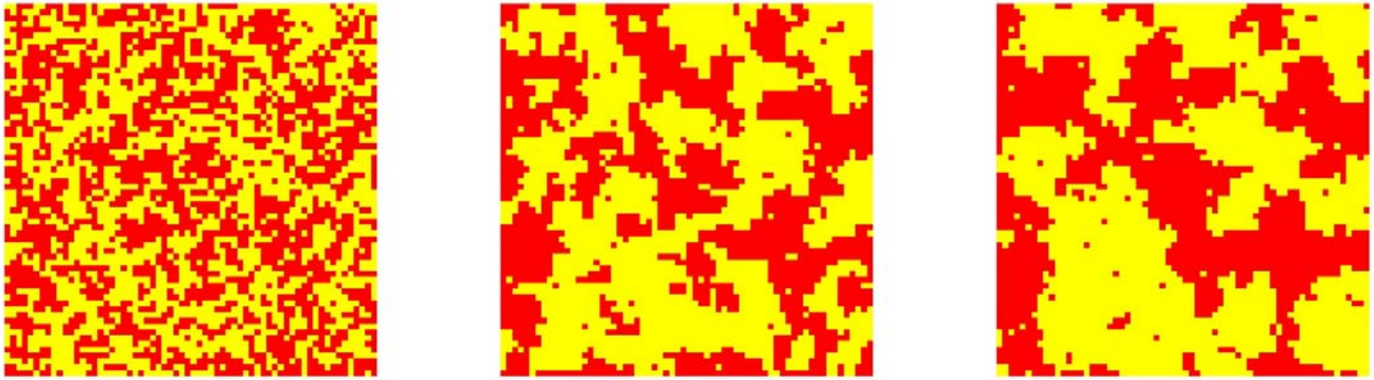
scattering





Speckle Reveals Equilibrium Dynamics

A. Non-equilibrium dynamics: average structure changes

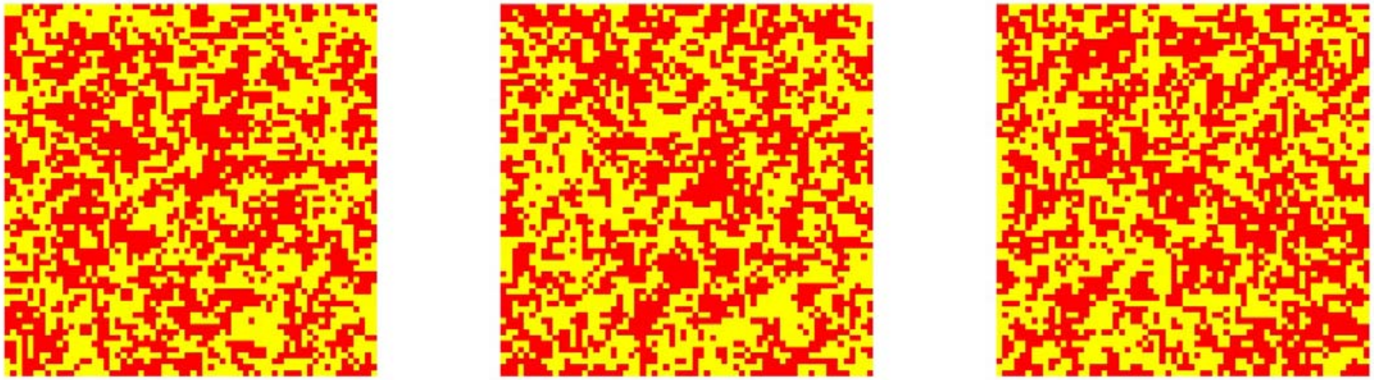


time = 0

time = 1

time = 4

B. Equilibrium dynamics: average structure is static



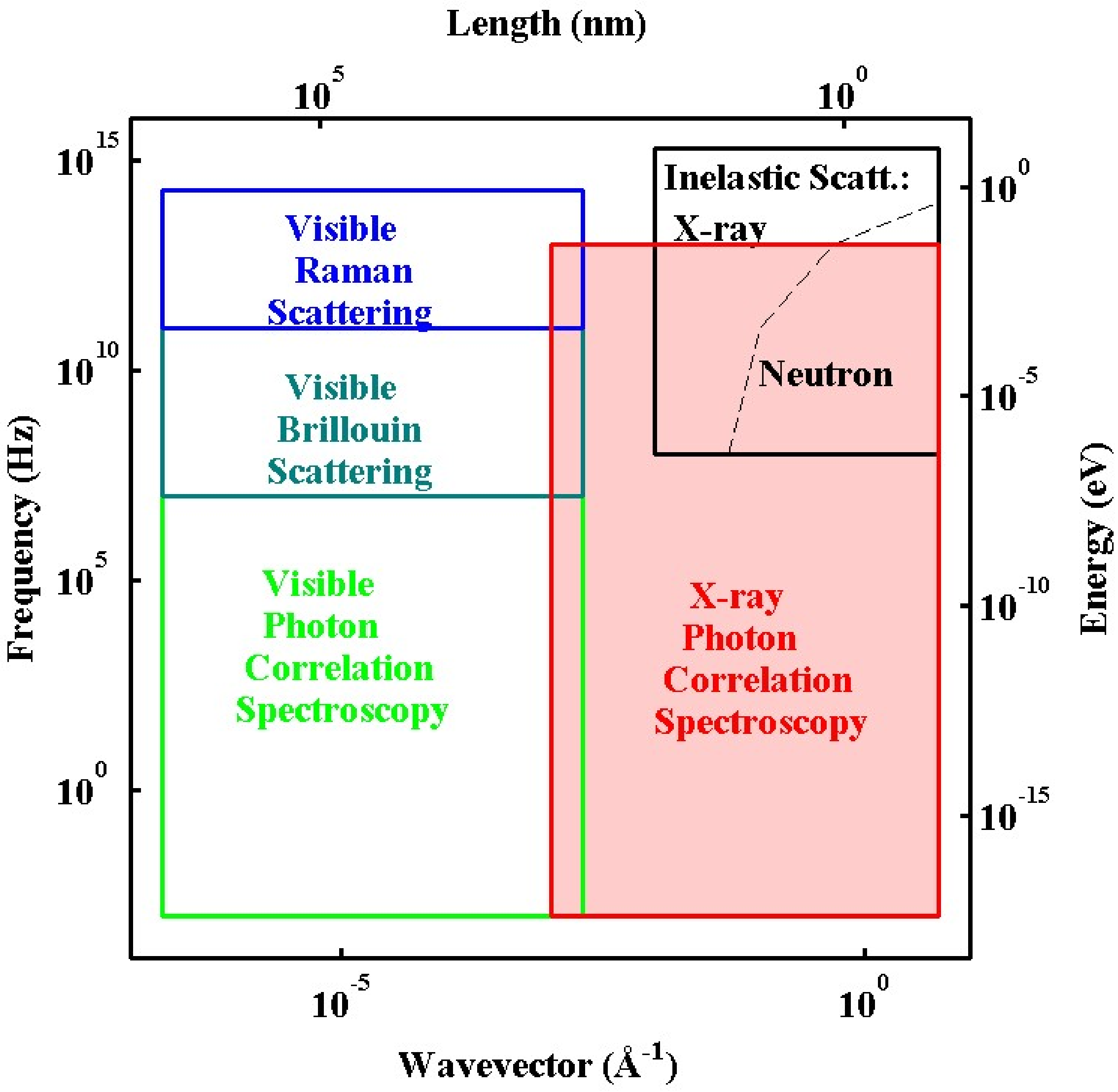
time = 0

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

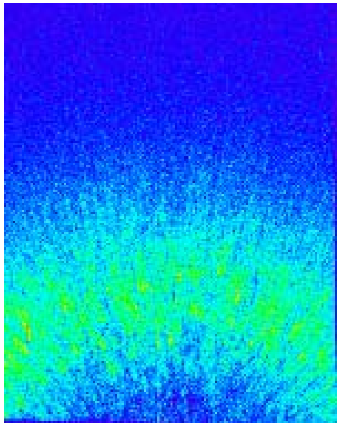
X-ray PCS Covers Larger Wavevector (Q) Than Visible PCS

Nanoscale Dynamics:
Small-Angle Scattering

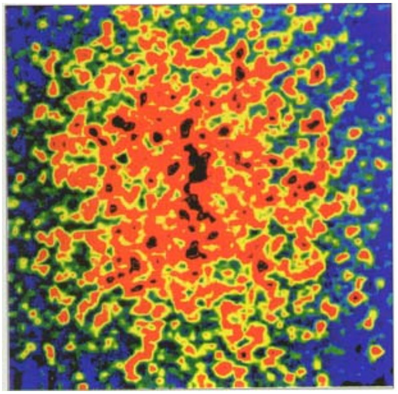
Atomic-scale Dynamics:
Wide-Angle Scattering

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



Phase Separation in Borosilicate Glass

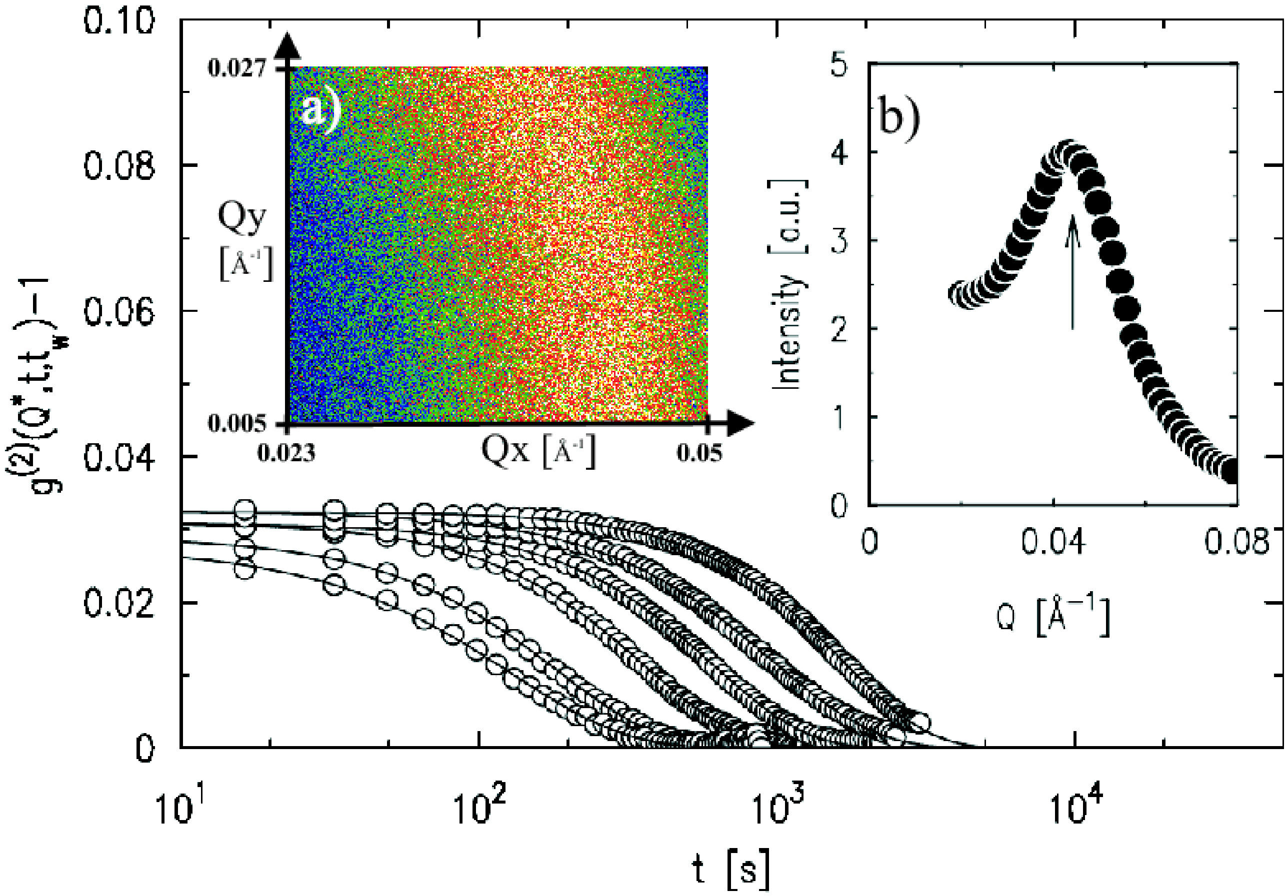


Ordering in Fe_3Al Alloy

XPCS Example: Dynamics in Ferrofluid

Small-angle scattering from magnetic particles

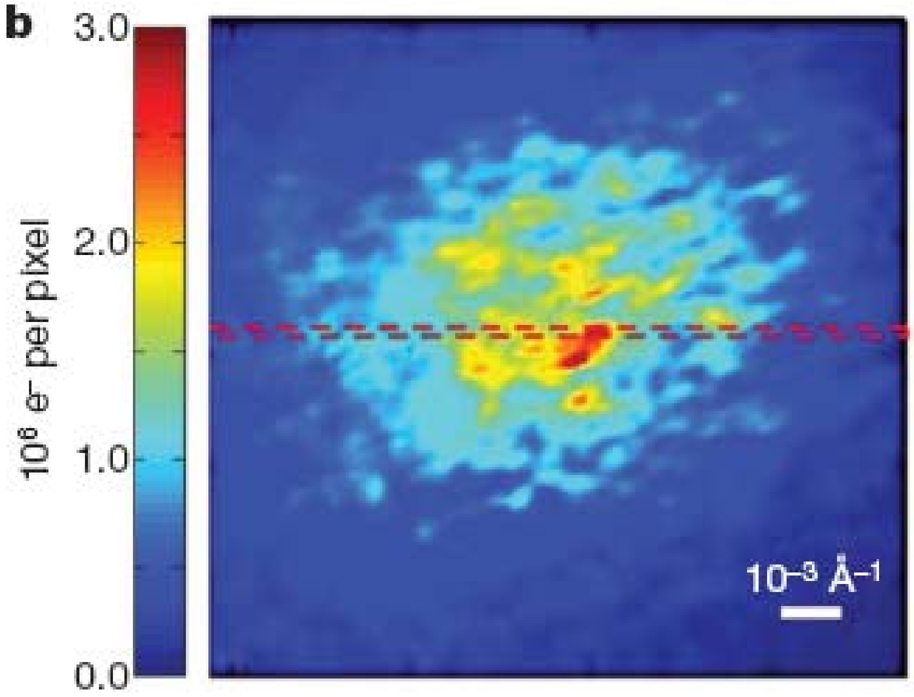
A. Robert et al., Europhys. Lett. ***75****, 764 (2006)*



XPCS Example: Antiferromagnetism

Wide-angle scattering from
charge density wave peak in Cr

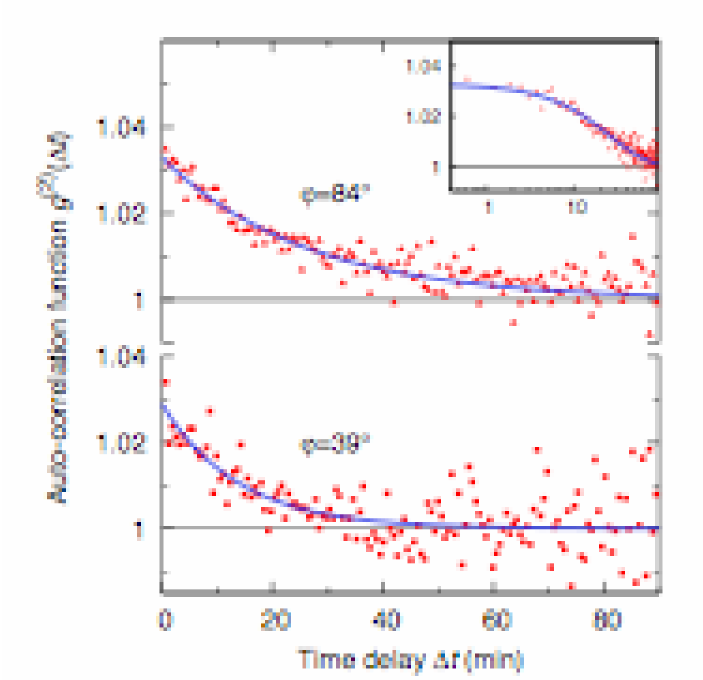
*O. Shpyrko et al., Nature
447, 68 (2007)*

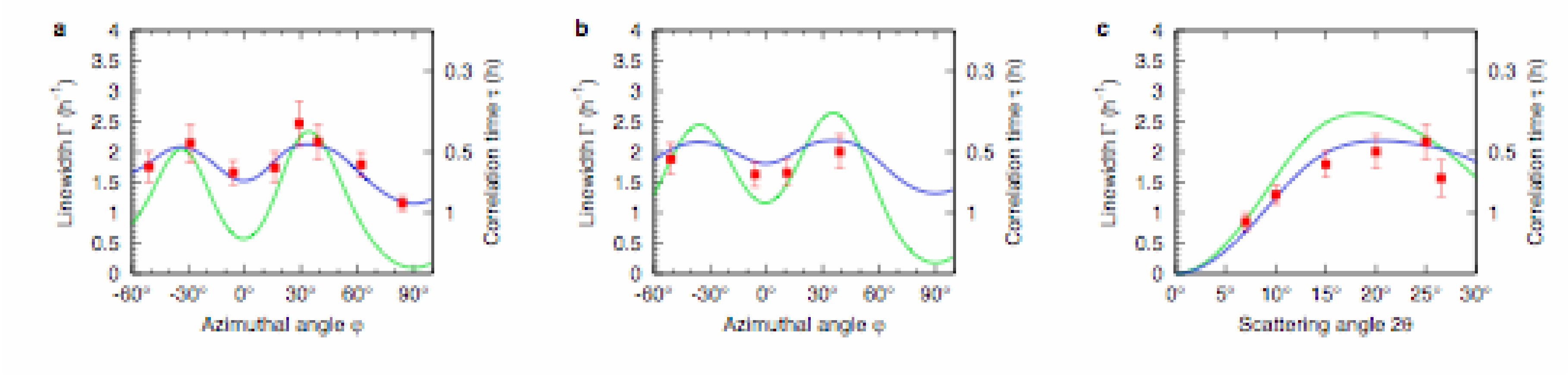


XPCS Example: Atomic Diffusion

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

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

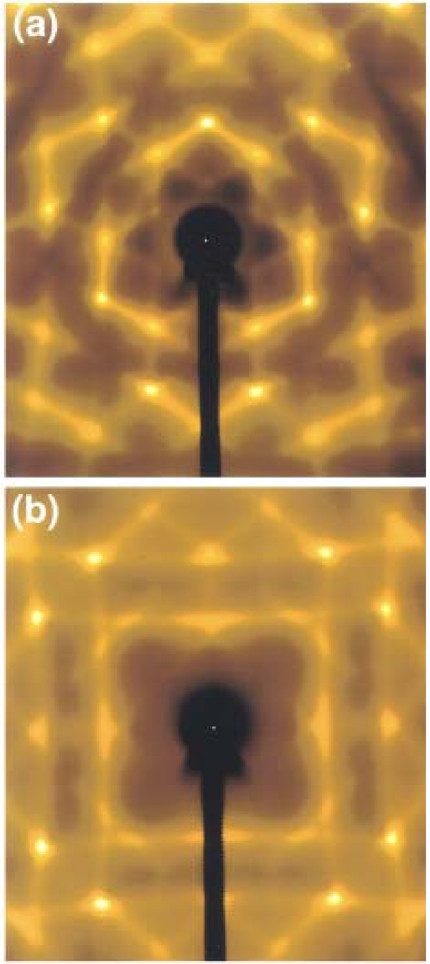




Dream for XPCS: Observe Dynamics in Any Diffuse X-ray Scattering

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

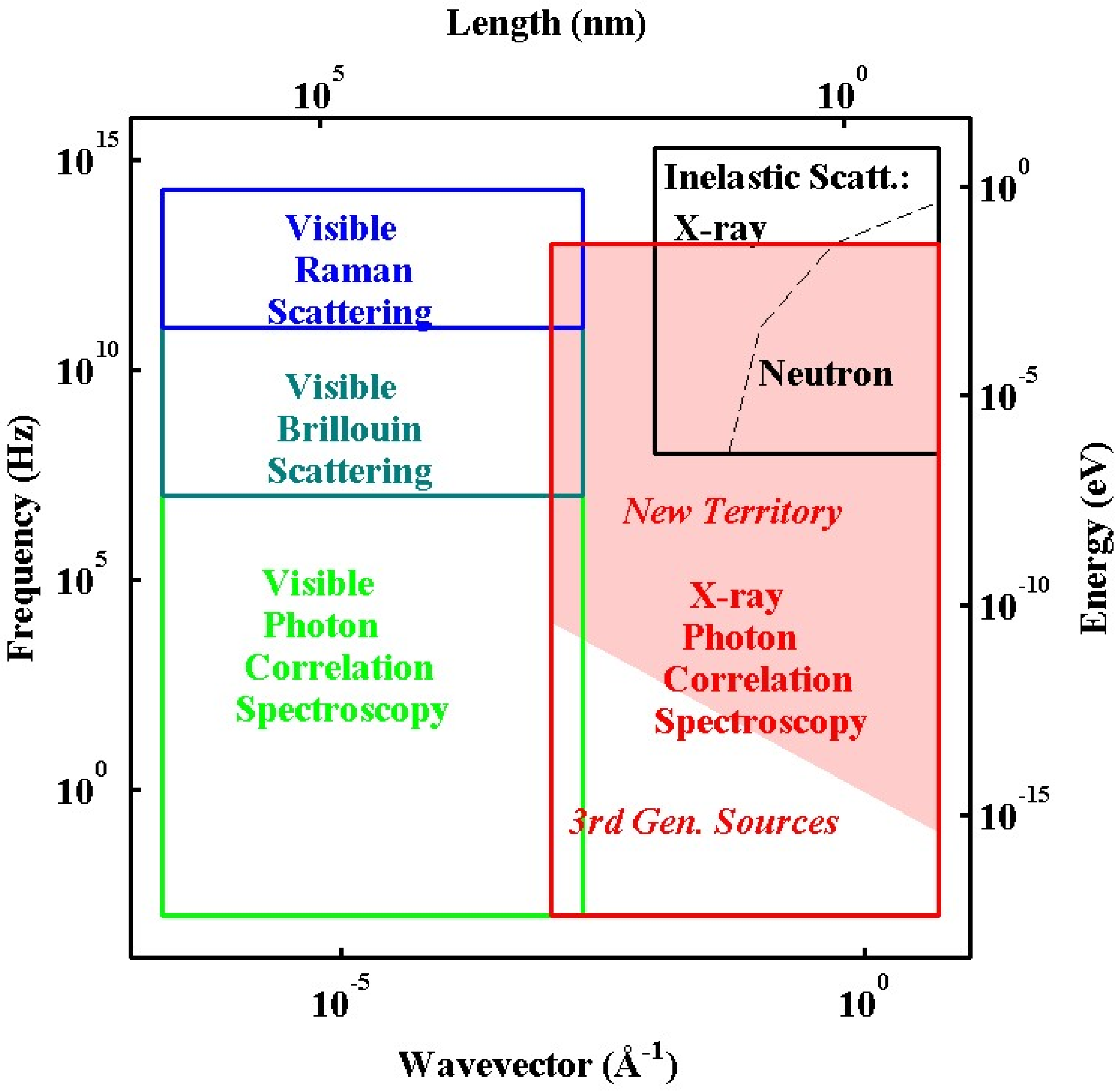
With higher coherent flux from XFEL, more weakly scattering systems and faster time scales can be investigated



Thermal Diffuse Scattering around Si 111 and 100

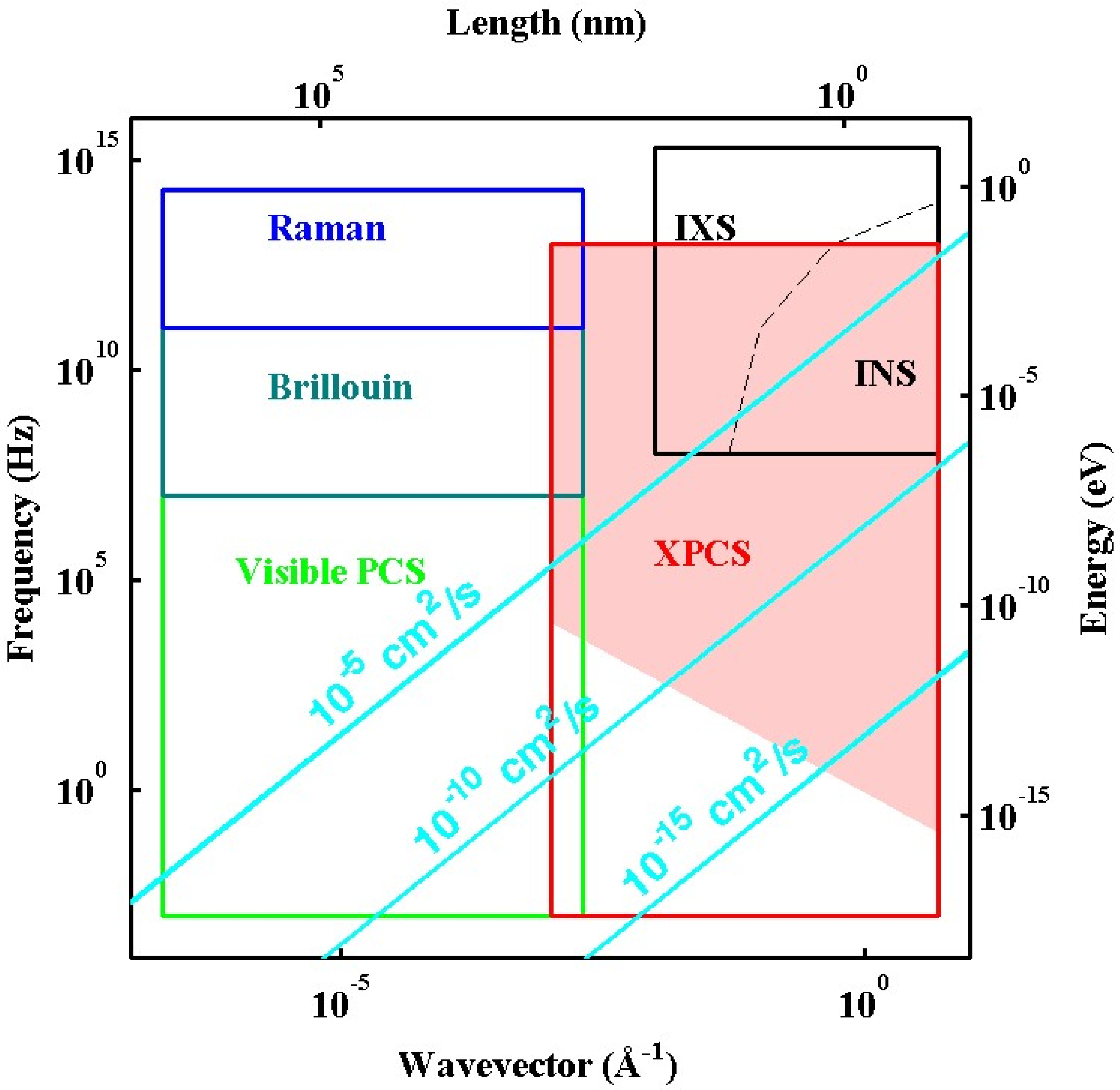
*M. V. Holt et al., PRL **83**, 3317 (1999)*

New Territory for XPCS at XFEL: Large Q



- 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

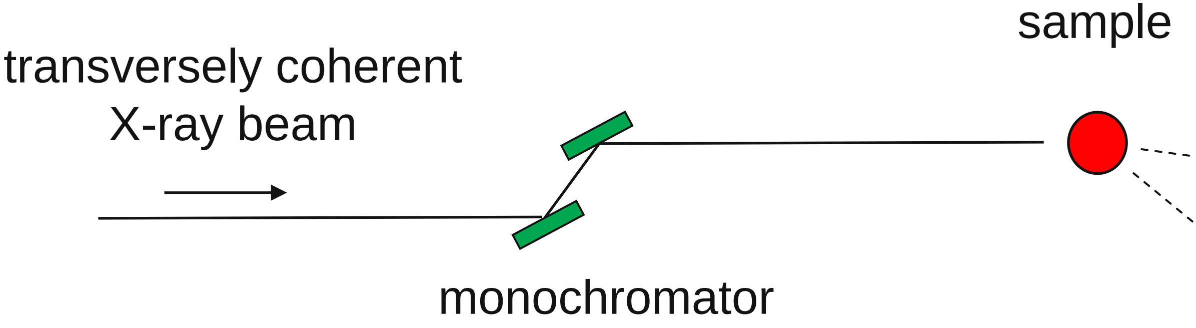
Large Q: Small Length Scales => Fast Time Scales

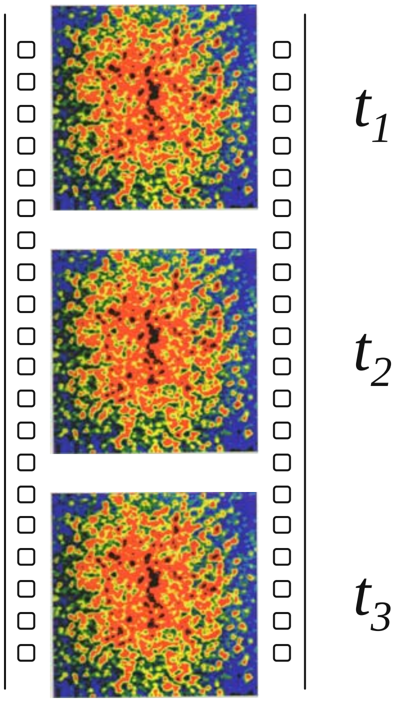


- Typical time scales of processes (e.g. mass diffusion) are faster at smaller length scales
- Mass diffusion time scales at molecular length scales are typically inaccessible by XPCS at third generation sources

XPCS using ‘Sequential’ Mode

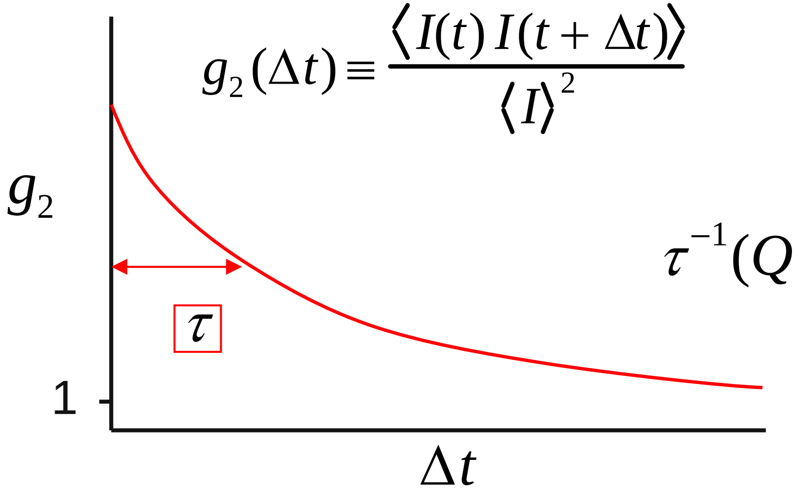
- Microseconds to seconds time resolution
- Uses high *average* brilliance





“movie” of speckle recorded by CCD

$$I(Q,t)$$



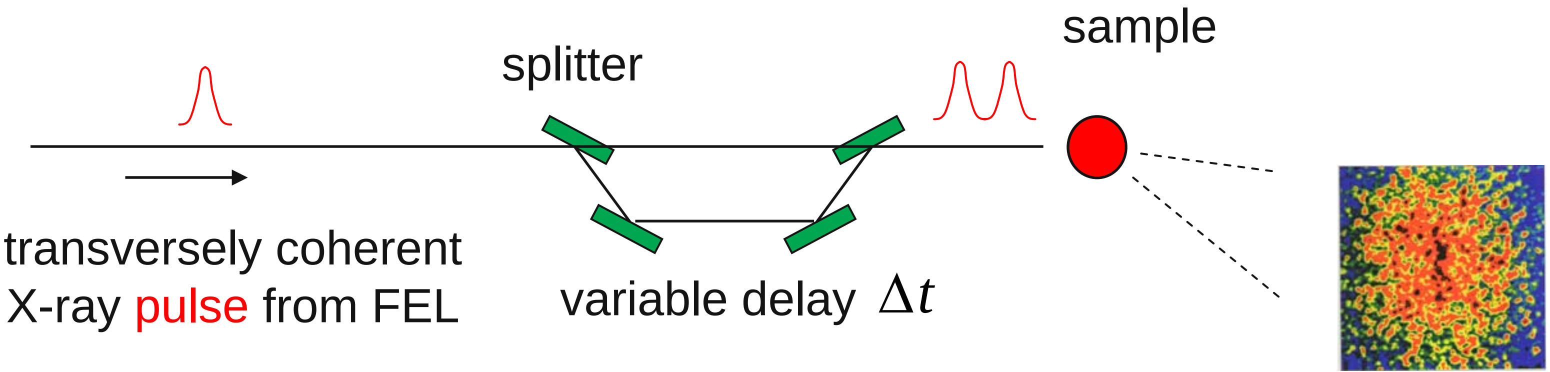
$$g_2(\Delta t) \equiv \frac{\langle I(t)\, I(t+\Delta t)\rangle}{\langle I\rangle^2}$$

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

Ultrafast XPCS using ‘Split Pulse’ Mode

Femtoseconds to nanoseconds time resolution

Uses high *peak* brilliance



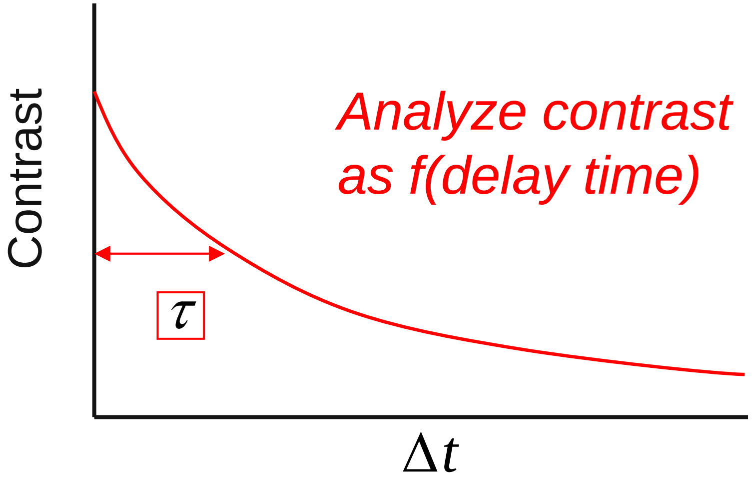
transversely coherent
X-ray pulse from FEL

variable delay Δt

$1ns \Leftrightarrow 300mm$

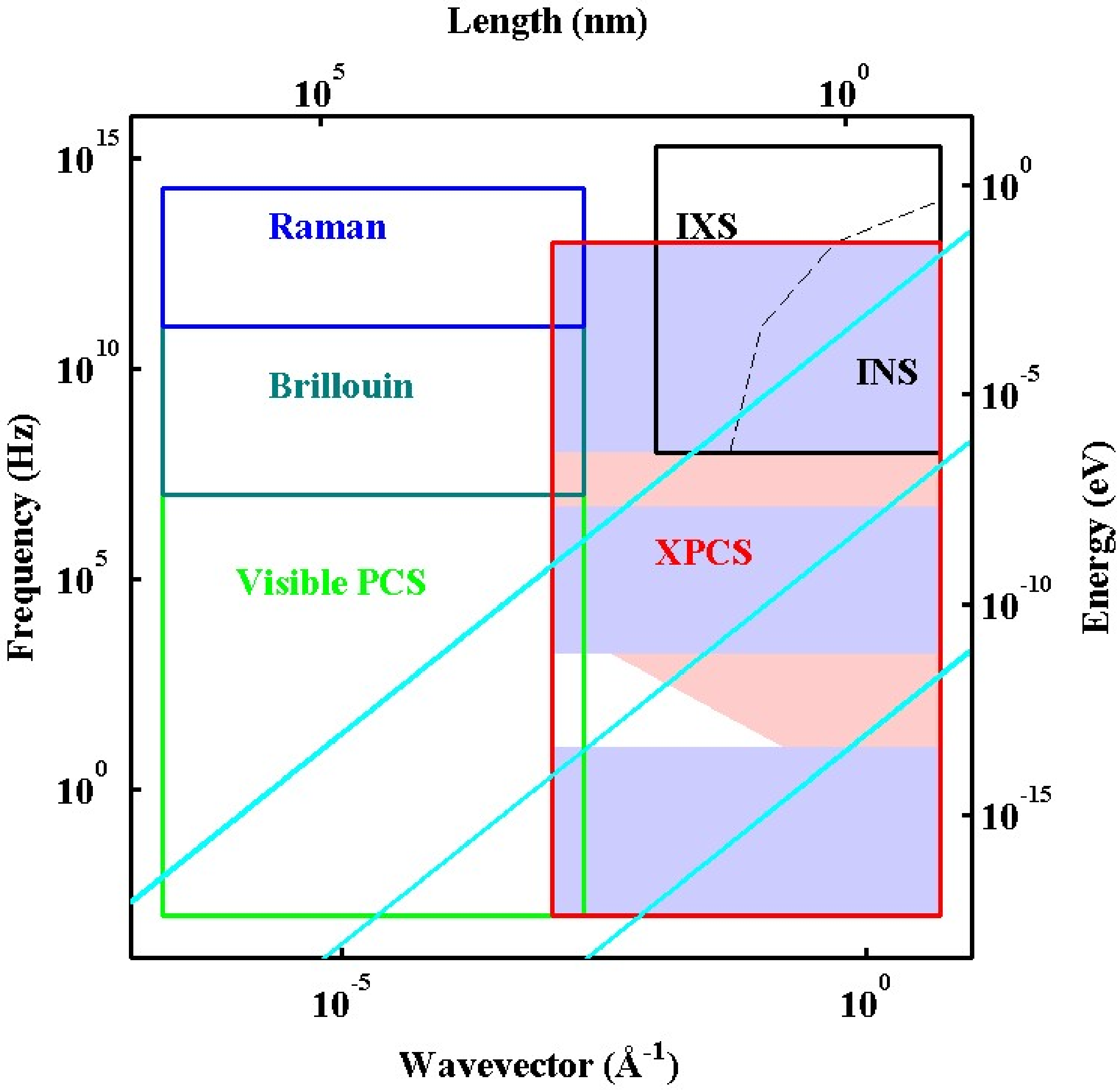
sum of speckle patterns
from prompt and delayed pulses
recorded on CCD

$I(Q, \Delta t)$



*Analyze contrast
as f(delay time)*

XFEL Pulse Structure Affects Accessible Times



- Current XFEL pulse structure covers much of time range, but leaves gaps
- Difficult to produce split-and-delay longer than ~10 ns
- Ability to have operational modes with pulse spacing down to 10 ns and train spacing down to 1 ms (or train length up to 100 ms) would fill gaps

Design of XPCS Experiments at XFEL

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

Longitudinal Coherence Requirement

Maximum path length difference should not be longer than longitudinal coherence length.

==> Bandwidth requirement becomes more stringent at large Q

For reflection geometry, limited by absorption:

$$\frac{\Delta\lambda}{\lambda} \leq \frac{16\pi^2}{\lambda\, l_{abs}\, Q^2}$$

For transmission geometry, limited by thickness:

$$\frac{\Delta\lambda}{\lambda} \leq \frac{8\pi^2}{\lambda\, t\, Q^2}$$

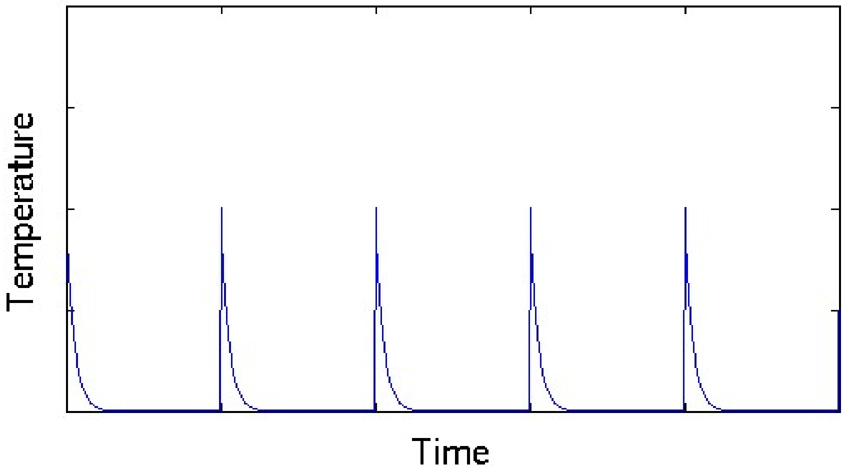
M. Sutton et al., Nature ***352****, 608 (1991)*

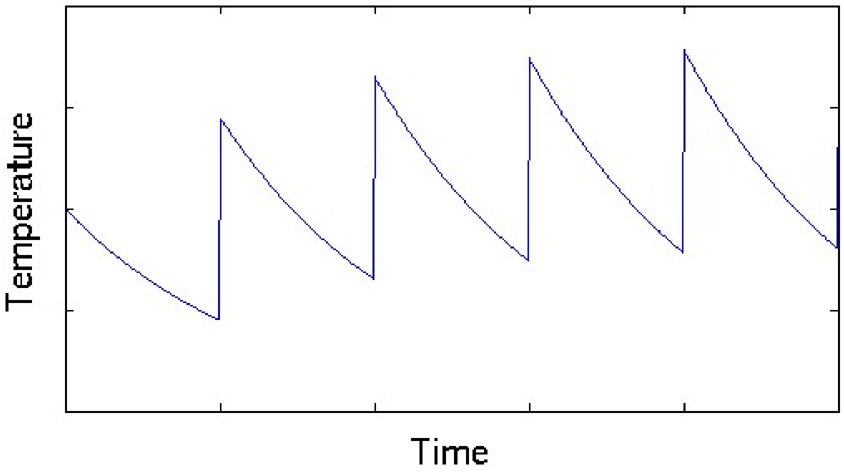
Heating by a Pulsed Beam

- 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





Thermal Time Constants (Cylindrical Geometry)

Thermal time constant depends on thermal diffusivity D_{th} and beam size *d*, weakly on diameter of hot zone d_0. Use $d_0 = 2/\alpha$.

$$\tau \approx \frac{d^2 \log(d_0/d)}{8D_{th}} \qquad D_{th} = \frac{\kappa}{C\rho}$$

Material	D_{th}	τ (*d* = 25 μm, E = 12.4 keV)	τ (*d* = 10 μm, E = 12.4 keV)
	cm^2/s	μs	μs
Au	1.32	0.40	0.063
Cu	1.12	0.46	0.074
Al	0.84	2.9	0.60
Al_2O_3	0.072	35	7.1
SiO_2 glass	0.0030	890	180
H_2O liquid	0.0014	3200	590

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:

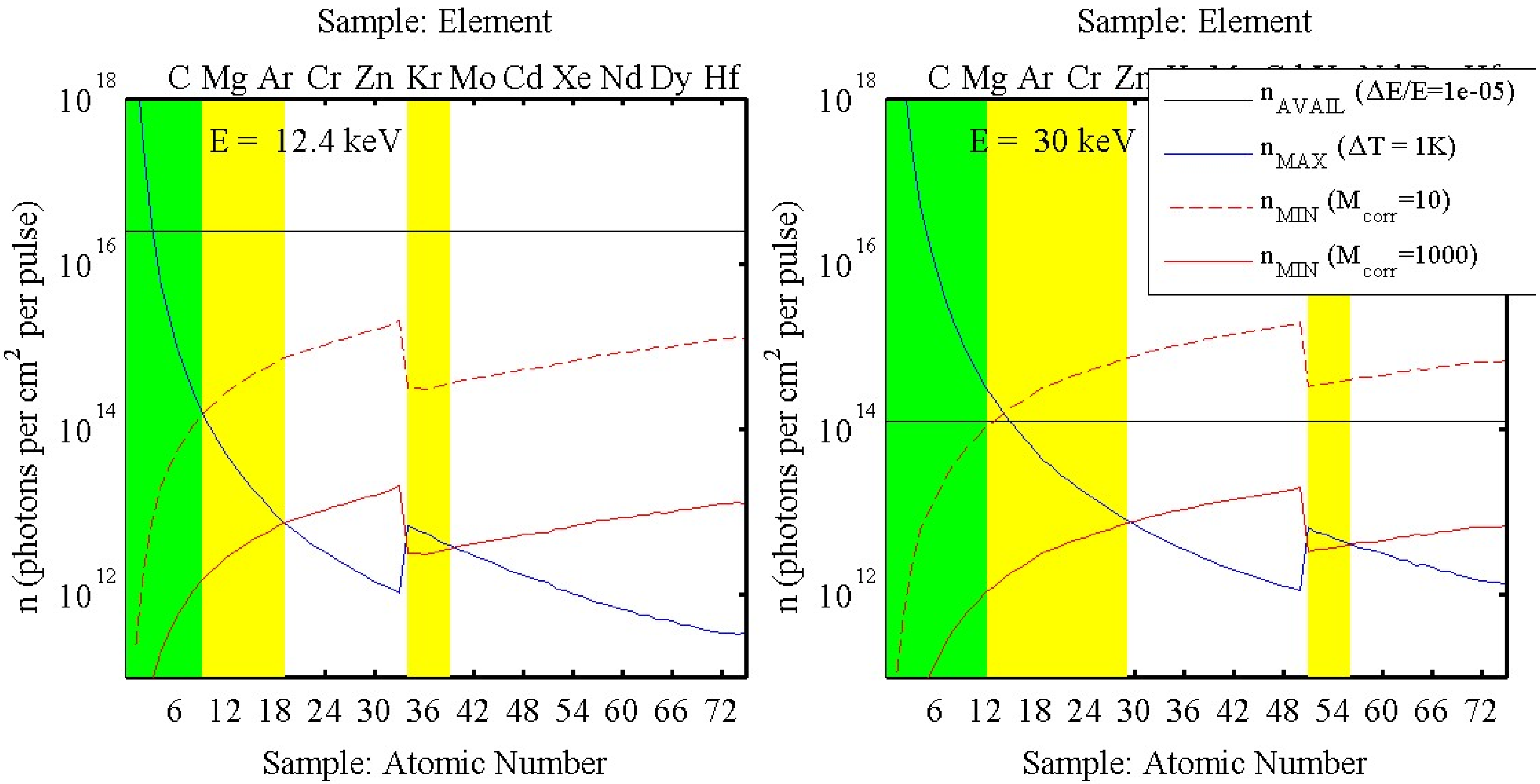
$$n_{MIN} = \frac{\Delta\lambda/\lambda Q^2}{4\pi\lambda\sigma_{el}\rho_a M_{corr}} N_{MIN}^{SPECKLE}$$

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

Available, Required, Tolerable Photon Densities

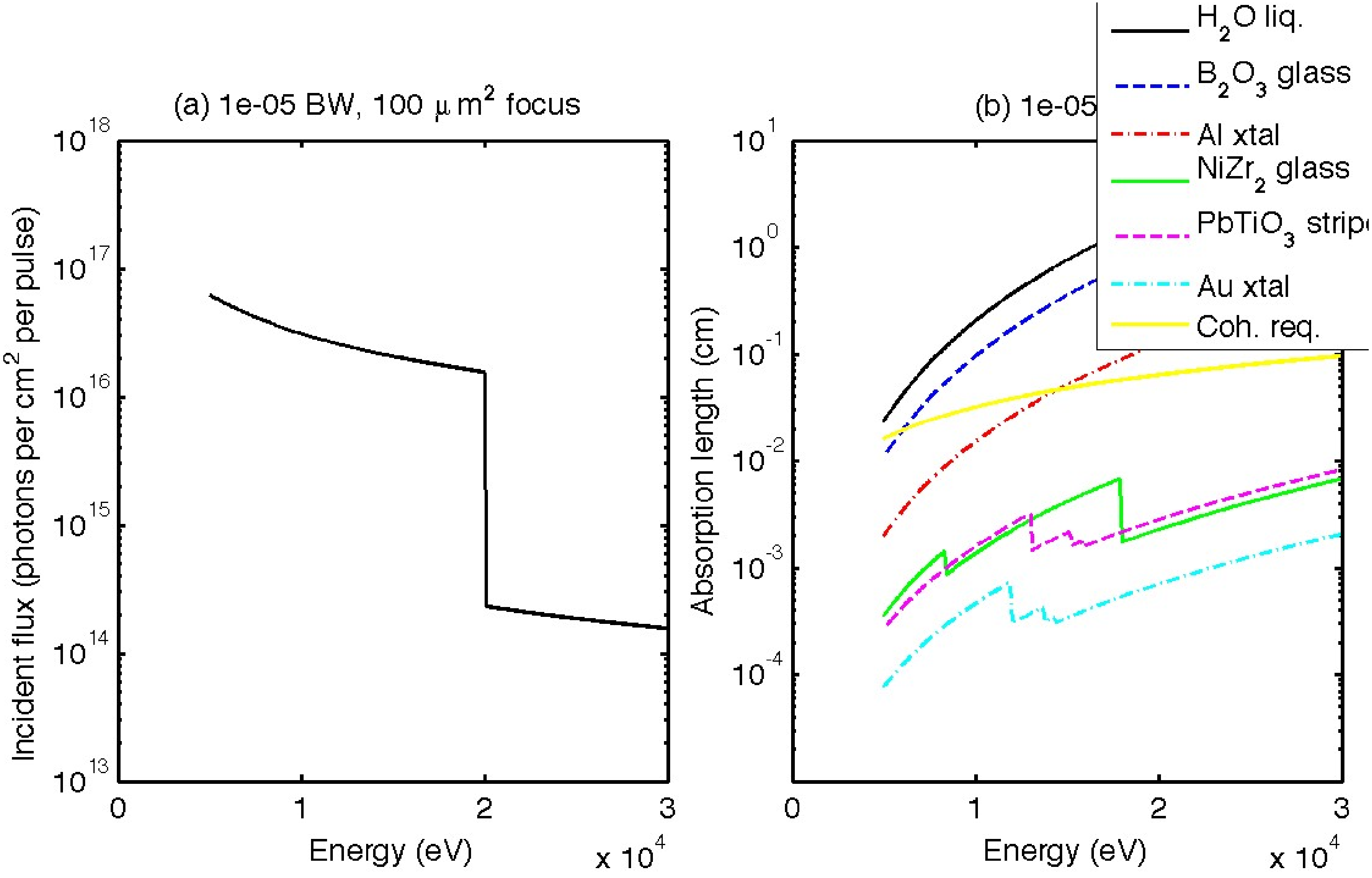


Shaded areas show feasibility regions e.g. for liquid or glass (green) or nanoscale cluster (yellow)

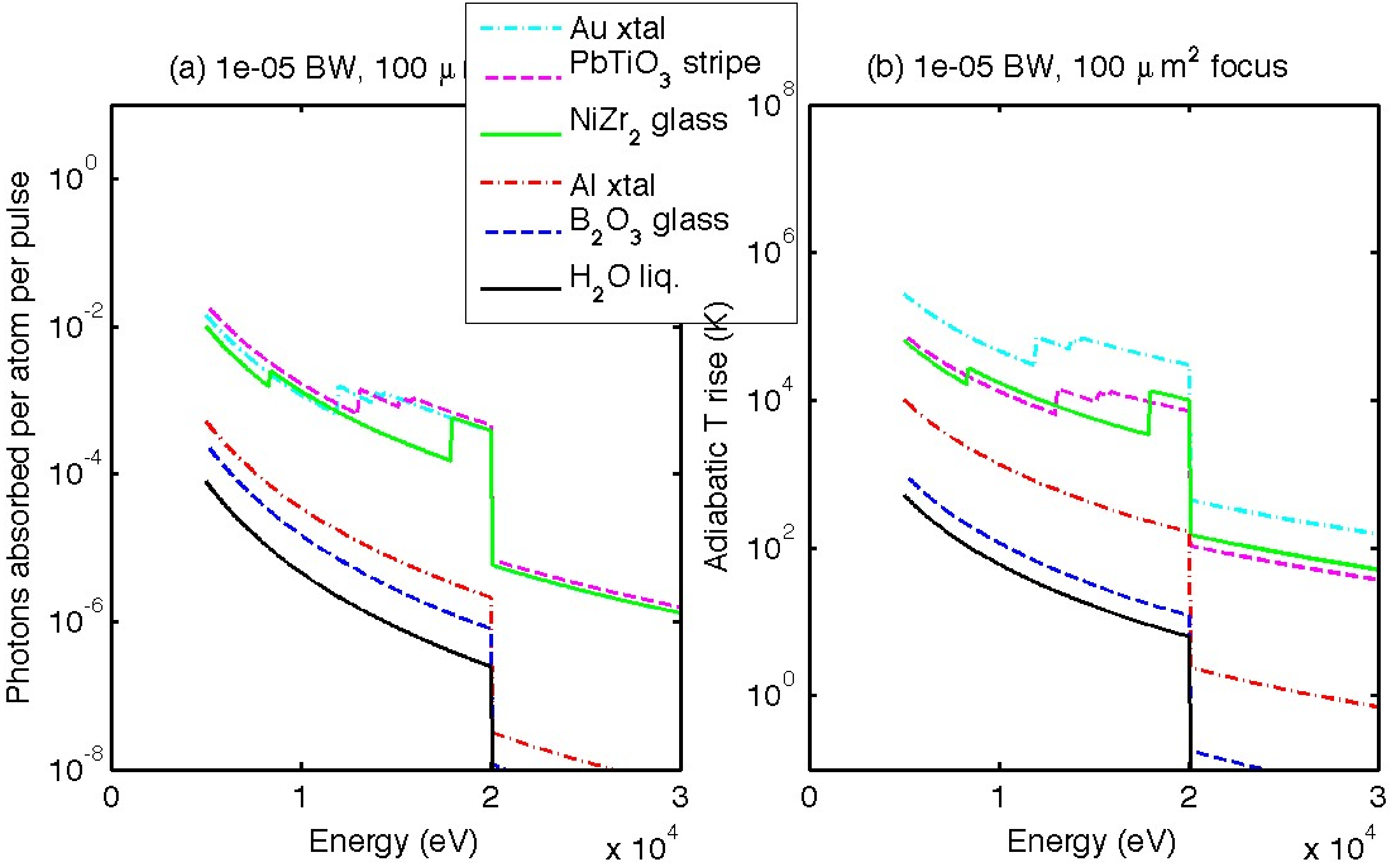
Focused to 10 μm diam.

See analysis in LCLS: The First Experiments

Calculations for Specific Samples: Assumptions

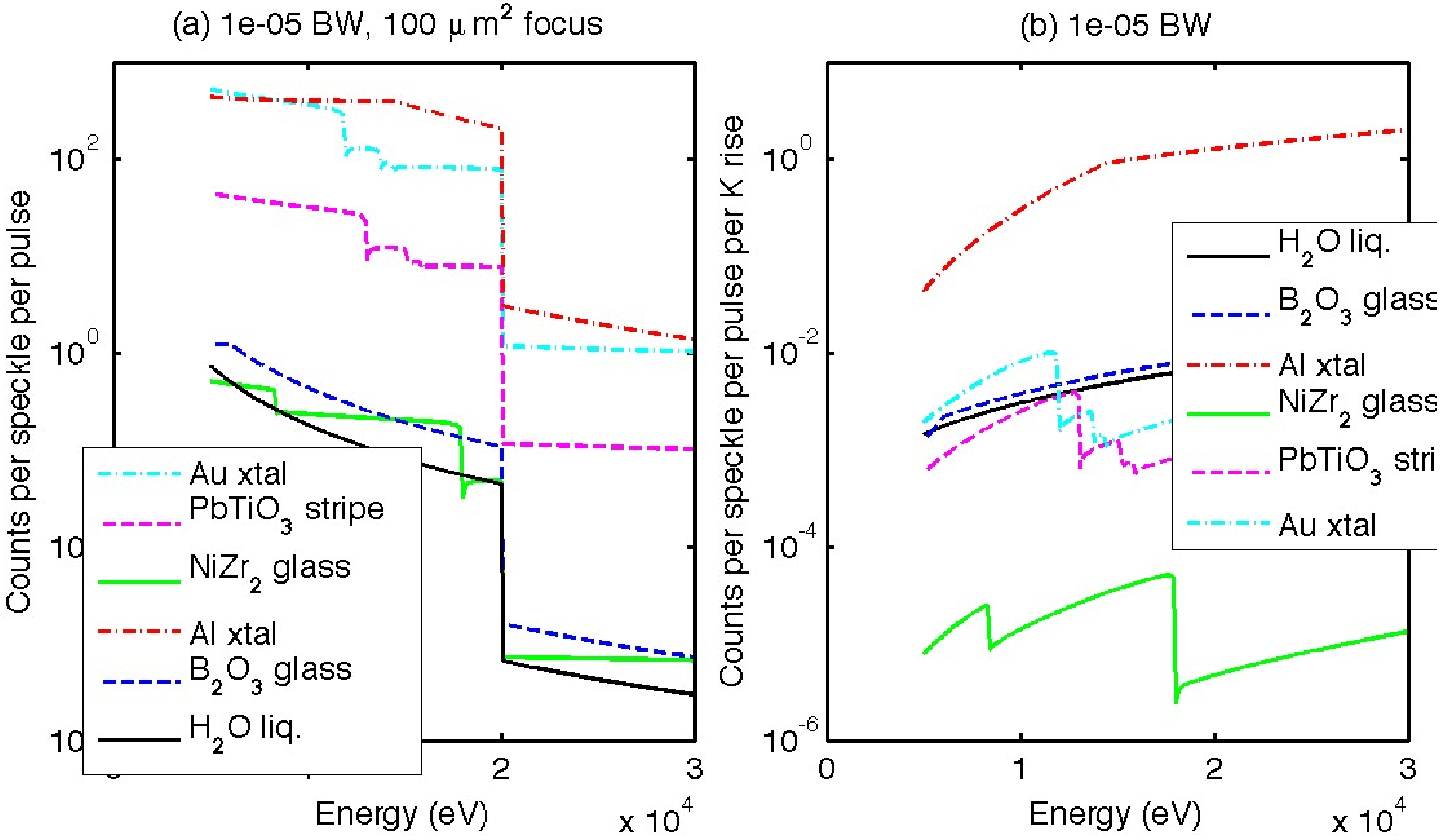


Calculations for Specific Samples: Heating



Need data on actual beam heating to refine analysis

Calculations for Specific Samples: Signal



Many experiments feasible, energy flexibility important

Area Detectors for Ultrafast 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:

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

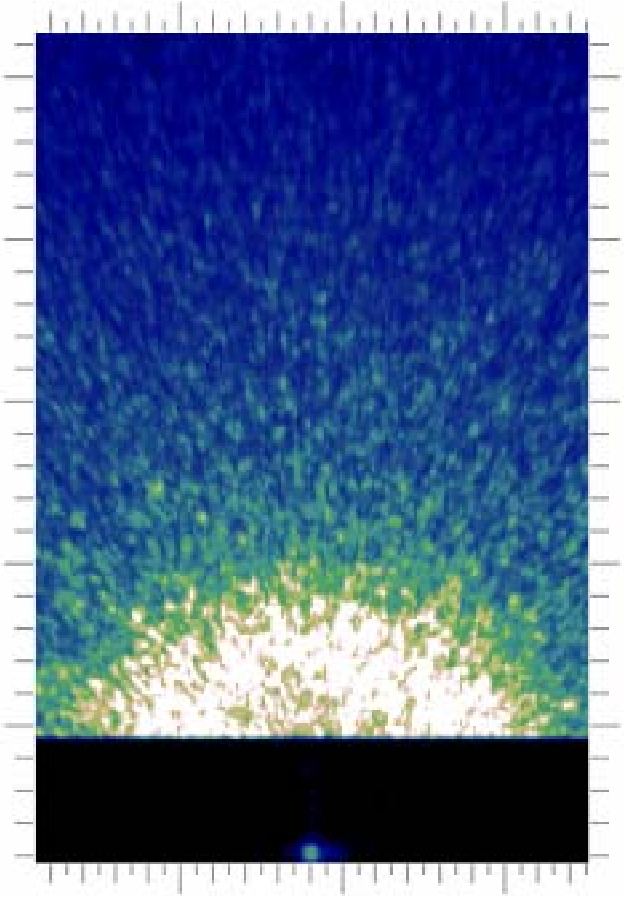
Required signal/noise: determine P_2 to a few %;

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

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

Summary

- XPCS - frontier is in large Q scattering, faster time scales
- The high average brilliance of XFEL will allow XPCS studies to push down to atomic length scales
- The high peak brilliance of XFEL will allow studies to sub-picosecond time scales
- Feasibility studies give strong dependences of optimum energy, focusing, and bandwidth on sample properties
- Flexibility in pulse structure, energy range, and energy bandwidth will maximize opportunities



Dawn of new era