X-ray photon correlation spectroscopy study of dynamics in colloidal suspensions

X-ray photon correlation spectroscopy (XPCS) is a well established technique to study the equilibrium dynamics in soft and hard matter systems. XPCS has been successfully applied to study dynamics in colloidal suspensions, nanoparticle dispersion in polymers, polymer thin films, etc. XPCS uses the partially coherent nature of the synchrotron beam to probe speckles and its fluctuations in time. By using a 2-D detector such as a CCD, the dynamics over a range of length scales in the range of 100 nm - 10 nm can be probed simultaneously.

In the demonstration experiment, a colloidal suspension of latex spheres in the size range of 100 nm dispersed in a viscous solvent like glycerol will be studied. By varying the particle concentration, single particle Brownian diffusion and the effect of particle interactions will be studied.

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People

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- Slides contributed by Prof. Larry Lurio (Northern Illinois University) and Qingteng Zhang (APS).

Scientific Motivation

- Length scales probed by SAXS correspond to interesting length scales in a variety of nanomaterials and soft condensed matter
  - Polymers
  - Colloidal suspensions
  - Microemulsions
  - Colloidal Glasses
  - Nanocomposites

- Dynamics on these length scales are also interesting as they provide information on the relaxation mechanisms and energy scales of these same materials
  - X-ray photon correlation spectroscopy (XPCS)

XPCS

- Dynamic Light Scattering but with X-Rays
  - Fluctuations about equilibrium
  - Fluctuations about (non-equilibrium) instantaneous average
- Key advantages
  - Dynamics at small – nanoscale – length scales
  - Weak scattering – optically turbid and opaque samples can be studied
- Key disadvantages
  - Limited signal because coherent x-rays required
  - Challenging detector requirements

Coherent X-Ray Beams

- Coherence-based x-ray experiments are routinely performed at 3rd generation synchrotron x-ray sources even though the source is incoherent. How?

- What is coherence?
  - A measure of the lateral and longitudinal extent of a photon wave packet

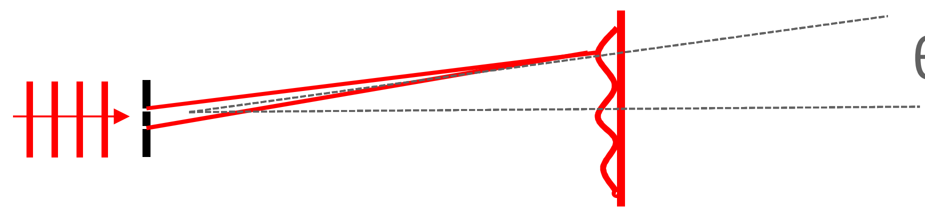
- XPCS in the small angle geometry is mostly concerned with lateral or transverse coherence

Lateral or Transverse Coherence

- Lateral or Transverse Coherence
  - A small source far away is coherent over a coherence length typically called ξ

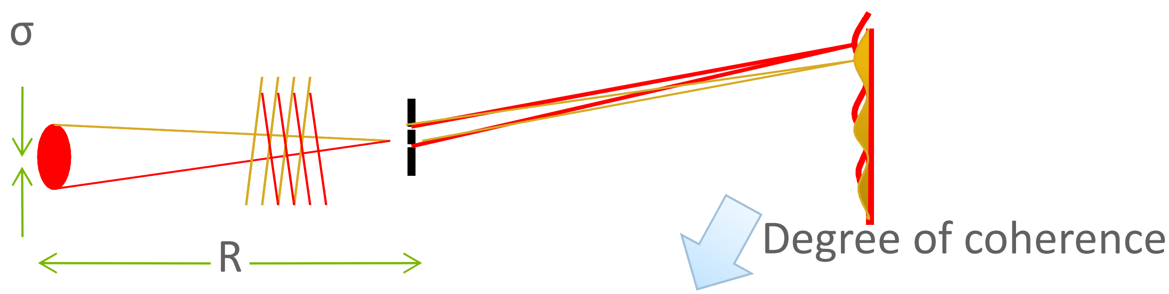
$$\xi_{x,y} = \lambda R/(2\pi\sigma_{x,y})$$

Perfect Young's double slit experiment



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

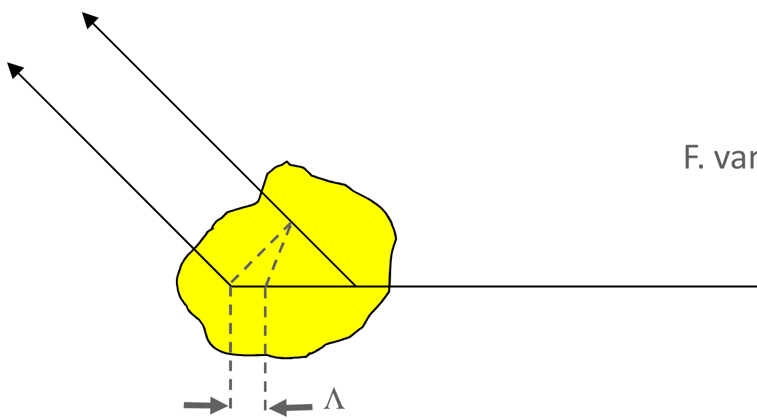
Young's double slit experiment using an incoherent source



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

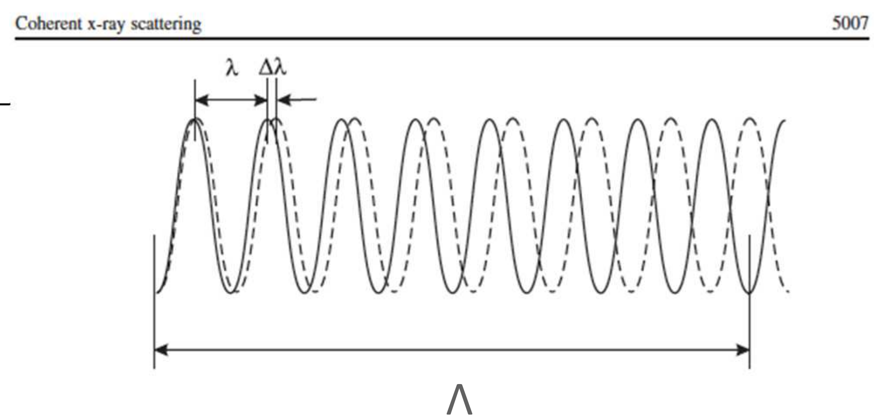
Longitudinal Coherence

- 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 $T_c = \Lambda/c$



$$\Lambda \approx \lambda(E / \Delta E)$$

F. van der Veen and F. Pfeiffer, J. Phys.: Cond. Matter **16**, 5003 (2004)



Coherent X-Ray Beams

- APS numbers:
  - Transverse Coherence

$$\xi_{x,y} = \lambda R / (2\pi\sigma_{x,y})$$

- λ is the x-ray wavelength ≈ 1.7 Å,
  R is the source to pinhole distance ≈ 65 m
  σ is the 1-sigma Gaussian source size
  ≈ 270 μm horizontal (x) ≈ 9 μm vertical (y)

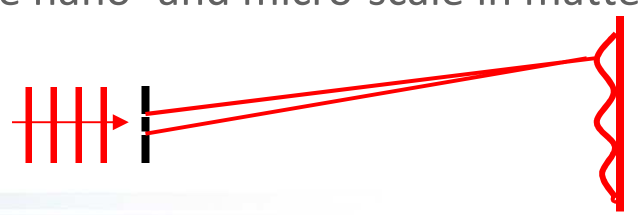
$$\xi_x = 7\,\mu m \qquad \xi_y = 200\,\mu m$$

  - Micrometer-sized pinholes used to select coherence area of the beam

  - Longitudinal Coherence

≈ 2 μm for Si(111)
≈ 0.5 μm for Ge(111)
≈ 10 nm for First Harmonic – "Pink" Beam

- X-ray coherence yields interference effects on the nano- and micro-scale in matter

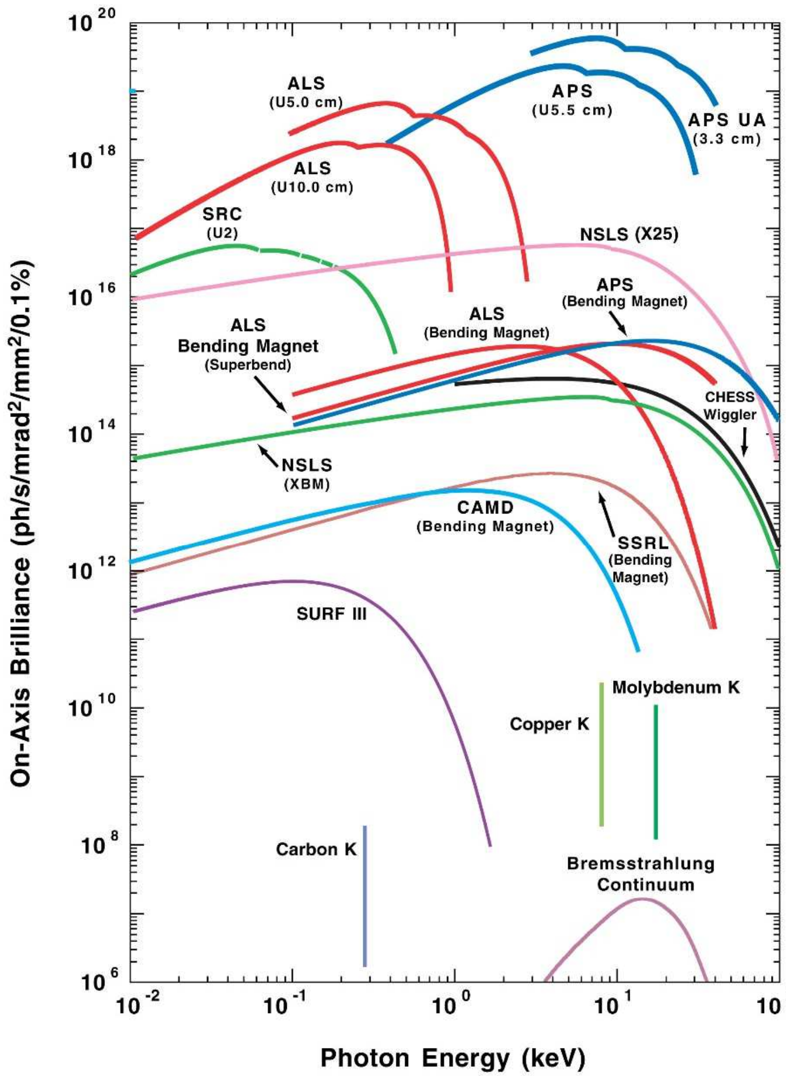


Coherent X-Ray Beams

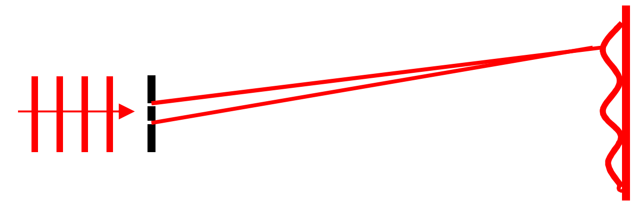
- Brilliance of 3rd generation synchrotron sources provides sufficient flux for coherence-based experiments

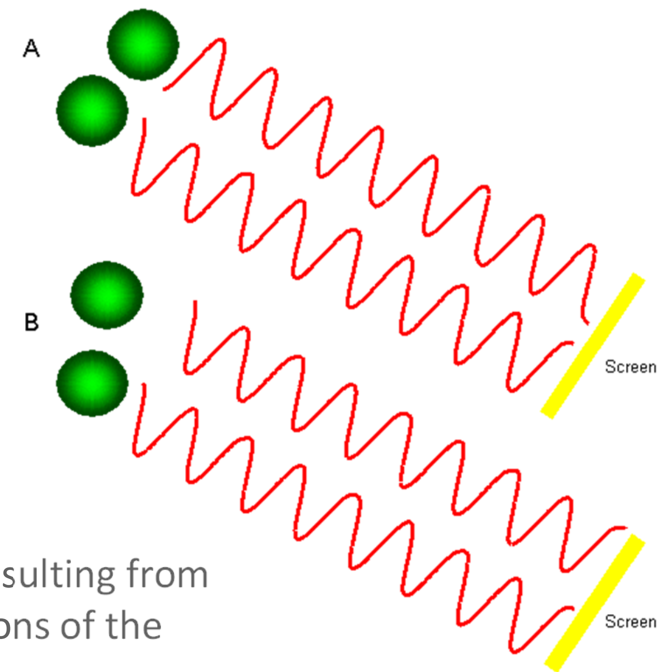
$$F_c = B(\lambda/2)^2$$

➔ $O(10^{11})$ monochromatic photons/sec



Coherent X-Ray Beams



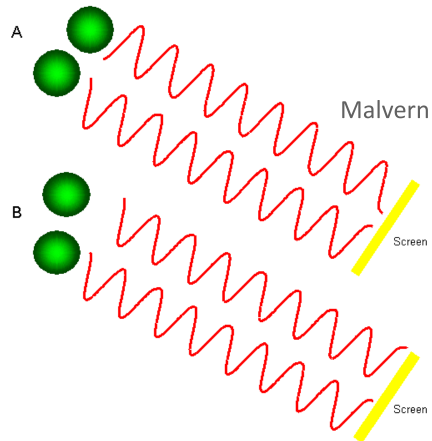


- Coherent x-ray scattering
  - Scattering or diffraction but without the simplifying assumption of ensemble averaging
  - Constructive and destructive interference at the detector creates a speckled scattering pattern

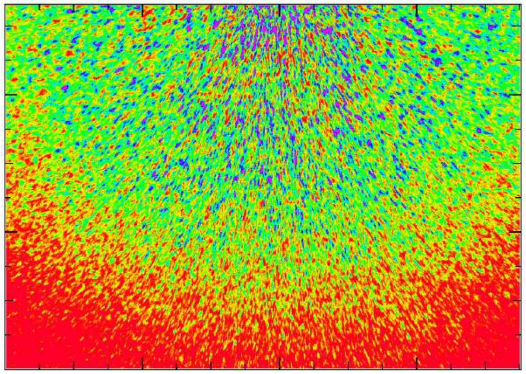
- How are coherent x-ray beams useful?
  - Exact arrangement of scatterers in aperiodic samples via phase inversion techniques
  - Analyze statistical fluctuations of scattered intensity resulting from spontaneous re-arrangements or equilibrium fluctuations of the scatterers
    - I.e., Brownian motion
    - X-ray photon correlation spectroscopy (XPCS)
      - Same as PCS or DLS with visible laser light but using x-rays instead

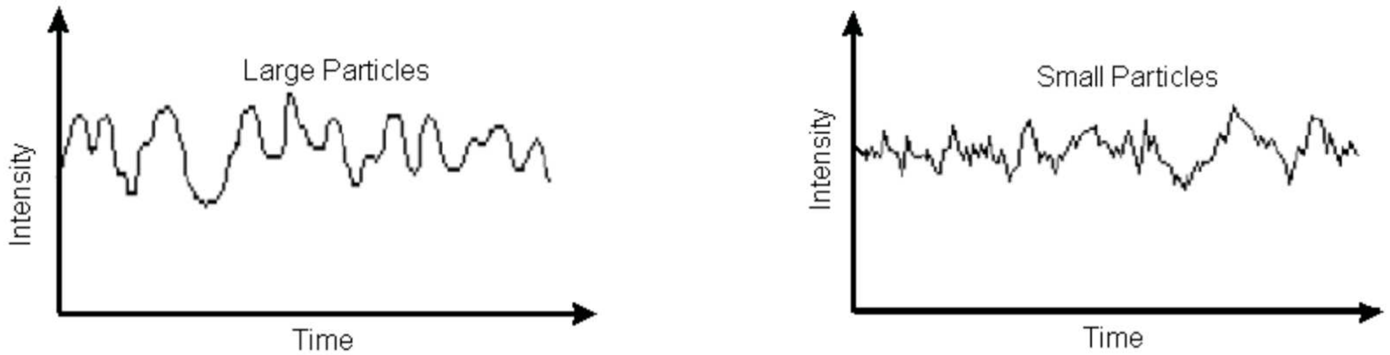
XPCS

- Dynamic light scattering (DLS) or photon correlation spectroscopy (PCS) but with x-rays rather than laser light:
  1. Illuminate a disordered sample with a (partially) coherent x-ray beam
  2. Collect the speckled scattered beam with a high resolution detector
  3. Monitor speckle pattern as a function of time so that changes in the speckle pattern can be observed



Malvern Technical Note MRK-656-01





Malvern Technical Note MRK-656-01

Speckle statistics

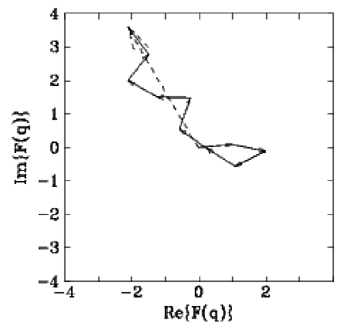


Figure 2.10: The complex scattering amplitude $F(\vec{q}) = \sum_i f_i e^{-\vec{q}\cdot\vec{r}_i}$ for ten atoms for a given $\vec{q}$, based on Fig. 4.2 in Ref [39]. As the number of atoms goes to infinity, the real and imaginary parts of $F(\vec{q})$ become independent Gaussian random variables. The dashed line is the resulting scattering amplitude, and the square of its magnitude is the structure factor $S(\vec{q})$.

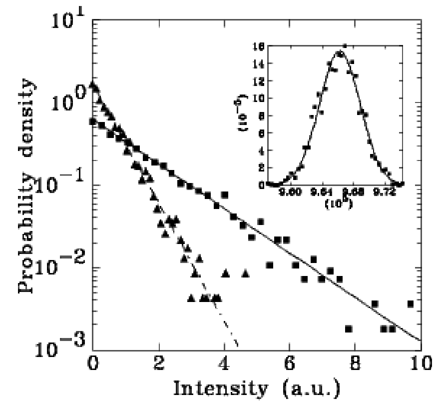


Figure 2.12: The probability density of the scattered intensity $S(\vec{q})$ for a binary alloy in equilibrium below T_c. $S(\vec{q})$ was simulated with model A. The squares and triangles are respectively the probability density of $S(\vec{q})$ for the smallest and largest $\vec{q}$ in Fig 2.11. The simulation results are in perfect agreement with the exponential distributions drawn with solid and dot-dashed lines, discussed in the text. An exponential distribution implies that $S(\vec{q})$ is non-self-averaging. The inset shows that the probability density of $S(\vec{q}=0)$ is nearly Gaussian, showing the scattered intensity self-averages for $\vec{q}=0$.

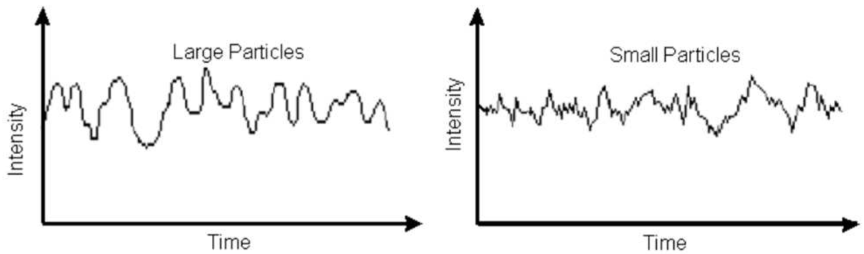
The scattered field E(q) is a random sum of scattered waves from atoms in the illuminated volume. In the thermodynamic limit, the real and imaginary part of E(q) are Gaussian random variables. $P(I=E^2)$ can be shown to be an exponential distribution.

P(I) for several Qs in an Ising-like 2D system. (simulations).

N.B. For exponential distribution variance/(mean)^2 = 1 !

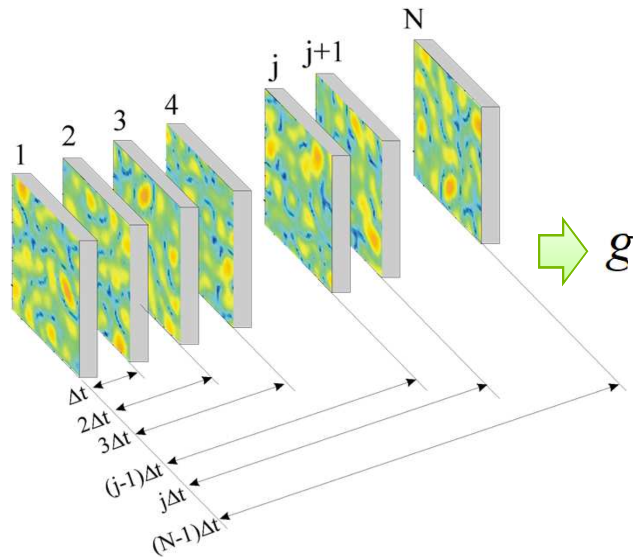
XPCS

3. Monitor speckle pattern as a function of time so that changes in the speckle pattern can be observed

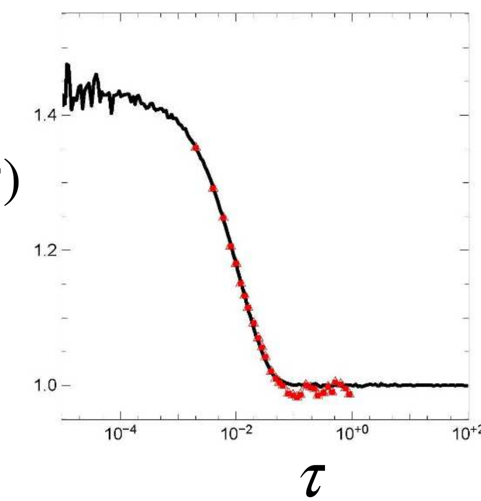


3. Calculate the time auto-correlation of the fluctuating signal at a particular wave vector to yield information about the nature and time scale of sample fluctuations at that length scale

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

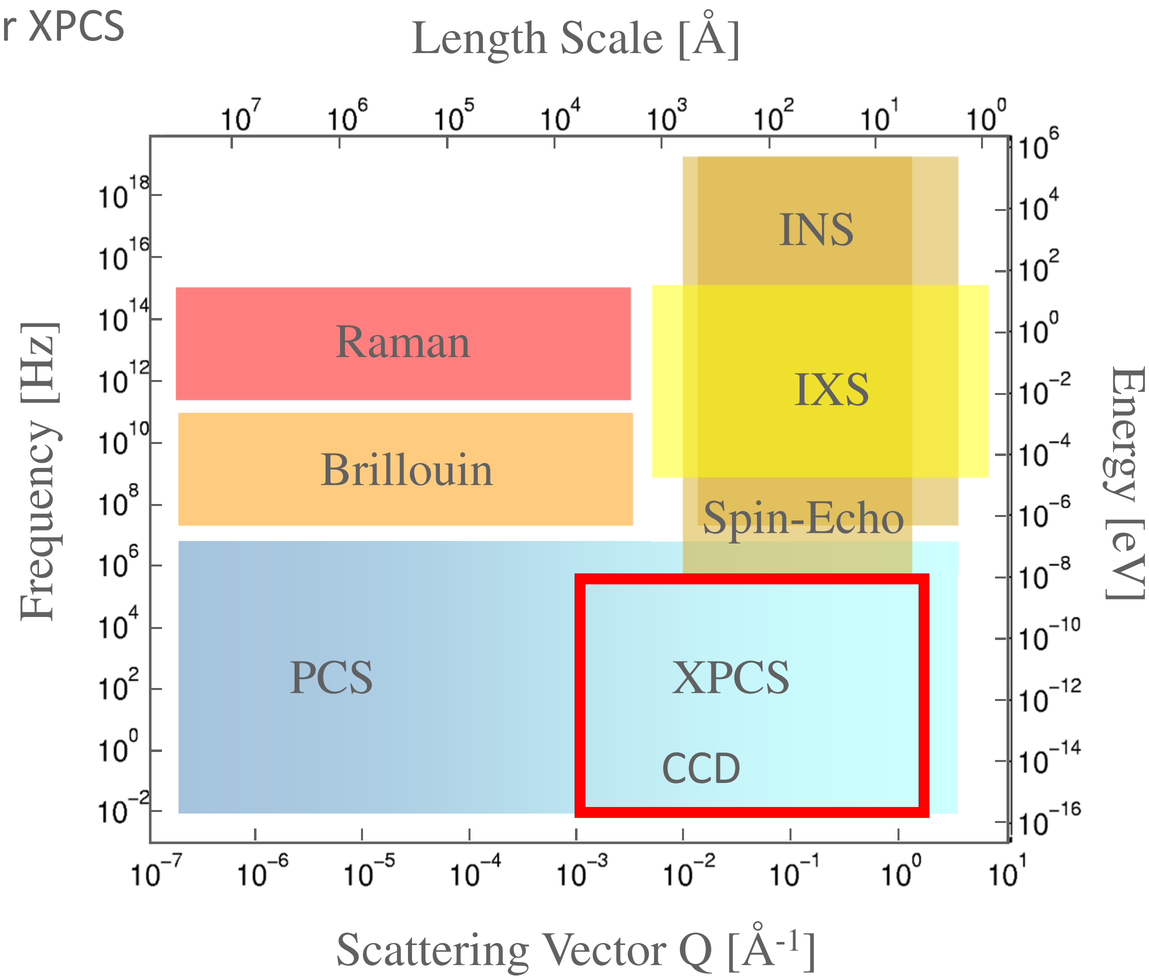


$$g_2(Q,\tau)$$



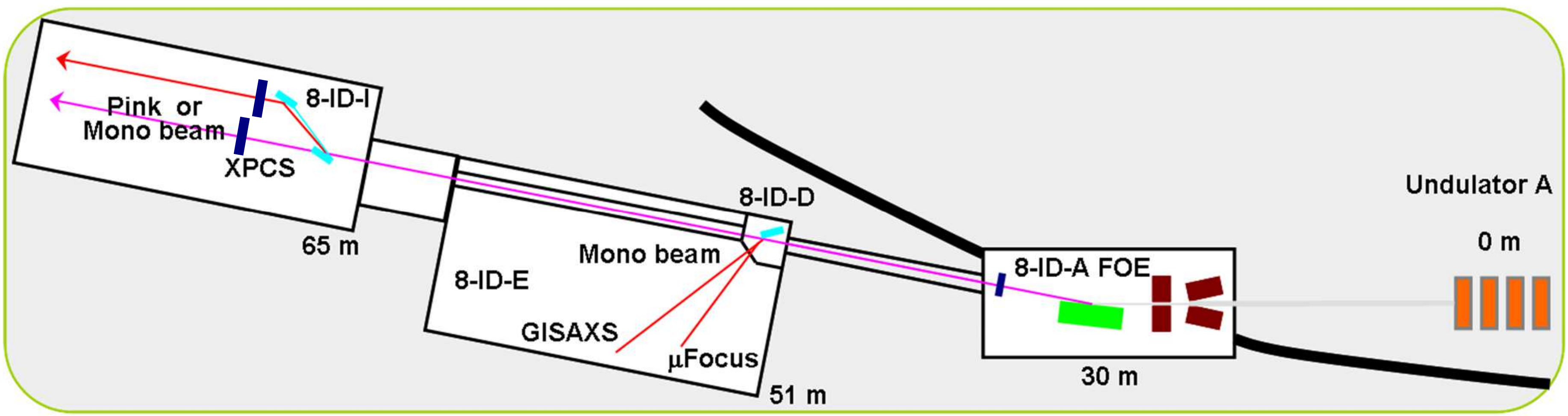
XPCS

- Phase space for XPCS



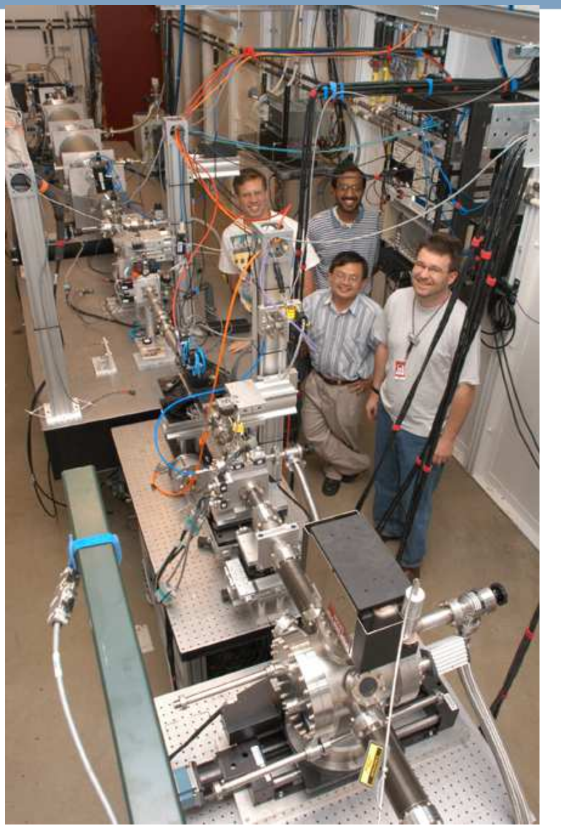
Small-Angle XPCS at 8-ID

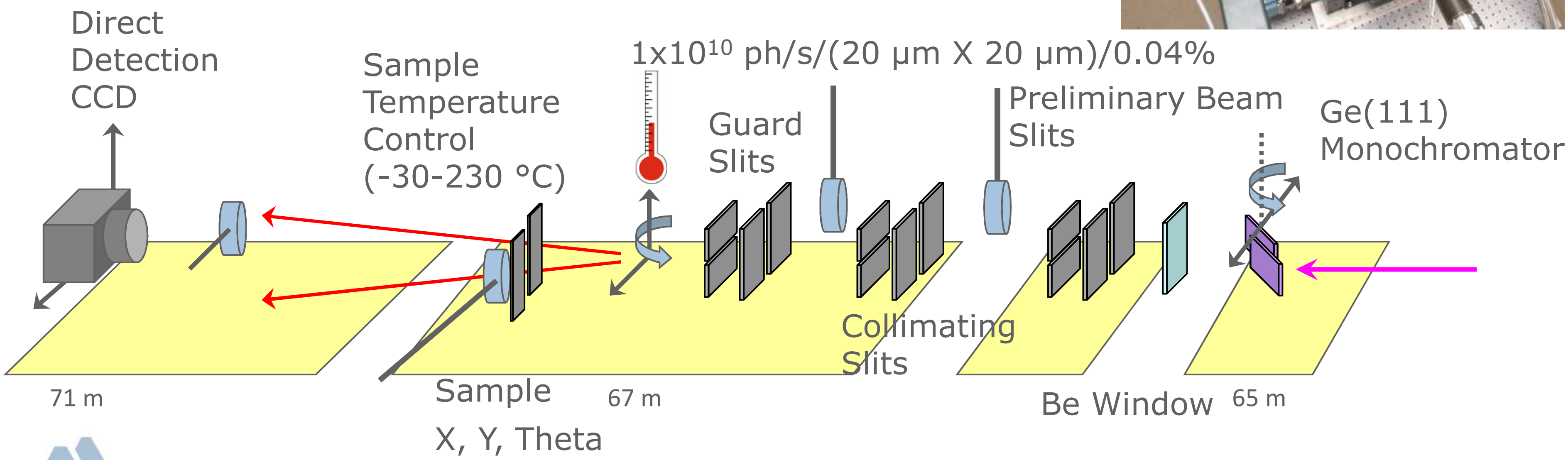
- How is XPCS realized at 8-ID?
  - Simple undulator beamline → improved stability
  - Minimal beam size – only central cone into optics enclosure
  - 2 phased undulator A using the full straight section



Small-Angle XPCS at 8-ID

- 8-ID-I Station Features
  - Ge(111) monochromator
  - Polished Be window
  - In-vacuum slits- preliminary, collimating and guard slits (X2)
  - In-vacuum sample “oven”
  - In-vacuum alignment detectors and beam stops
  - Direct-detection CCD, and Pixel-Array Detectors





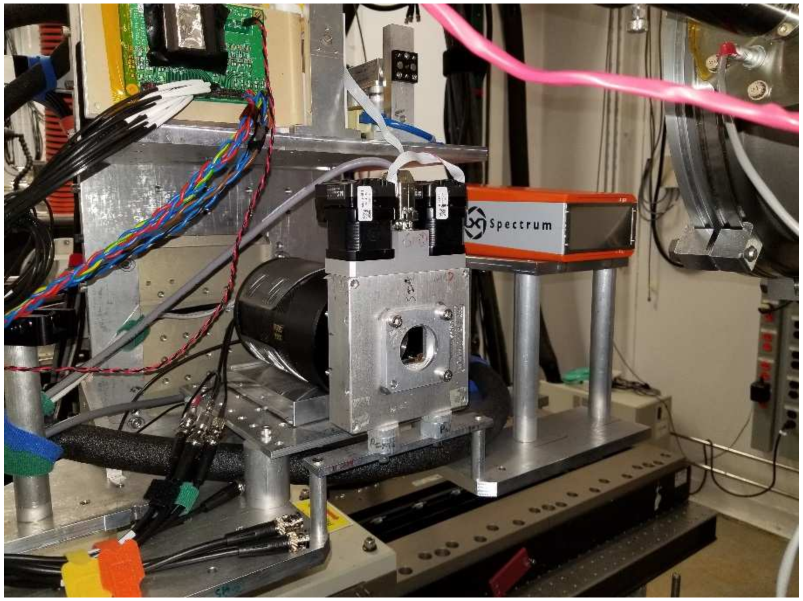
XPCS Area Detectors

- Need to be able to resolve individual speckles
  - Required detector resolution (@ Rdet ≈ 5 m)
  - Here L is 20 μm.

$$\Delta\Omega = (\lambda / L)^2$$

$$\approx R_{\mathrm{det}}\lambda / L \approx O(10\mu\mathrm{m})$$

- Few scattering events so require:
  - High efficiency
  - Large photon signal compared to dark current
  - Limited dynamic range (<≈ few 100 photons per pixel (for CCD))
  - Deep depletion X-ray sensitive CCD were key detectors in the first two decades of XPCS.
  - Recent advances in Pixel-Array Detector promises much higher time resolution and timing patterns.



Dual counter PADs enables new modes of operation such as dead-time free operation, two-frame mode

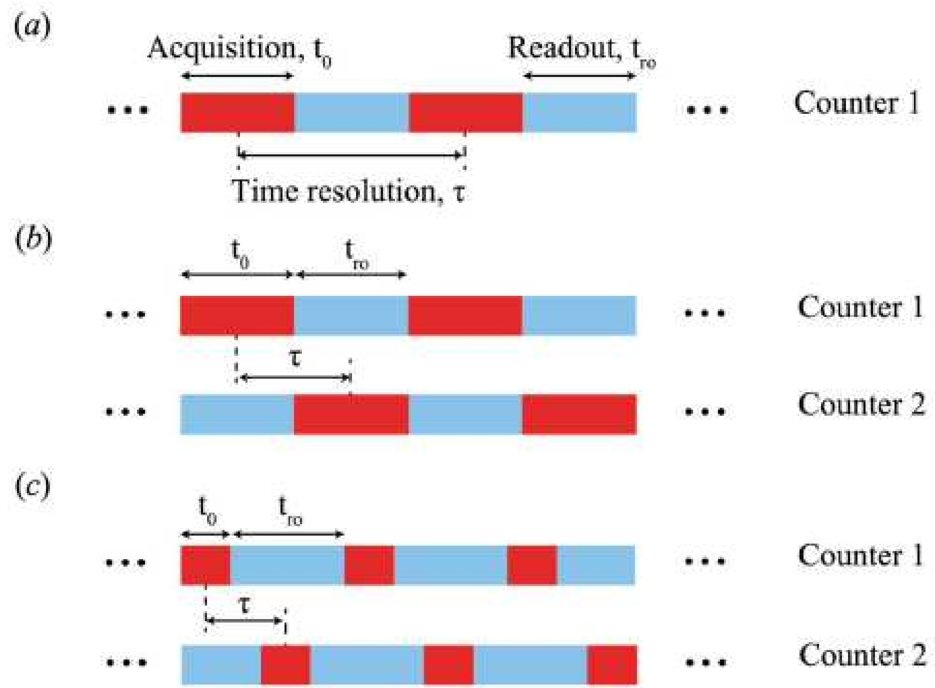
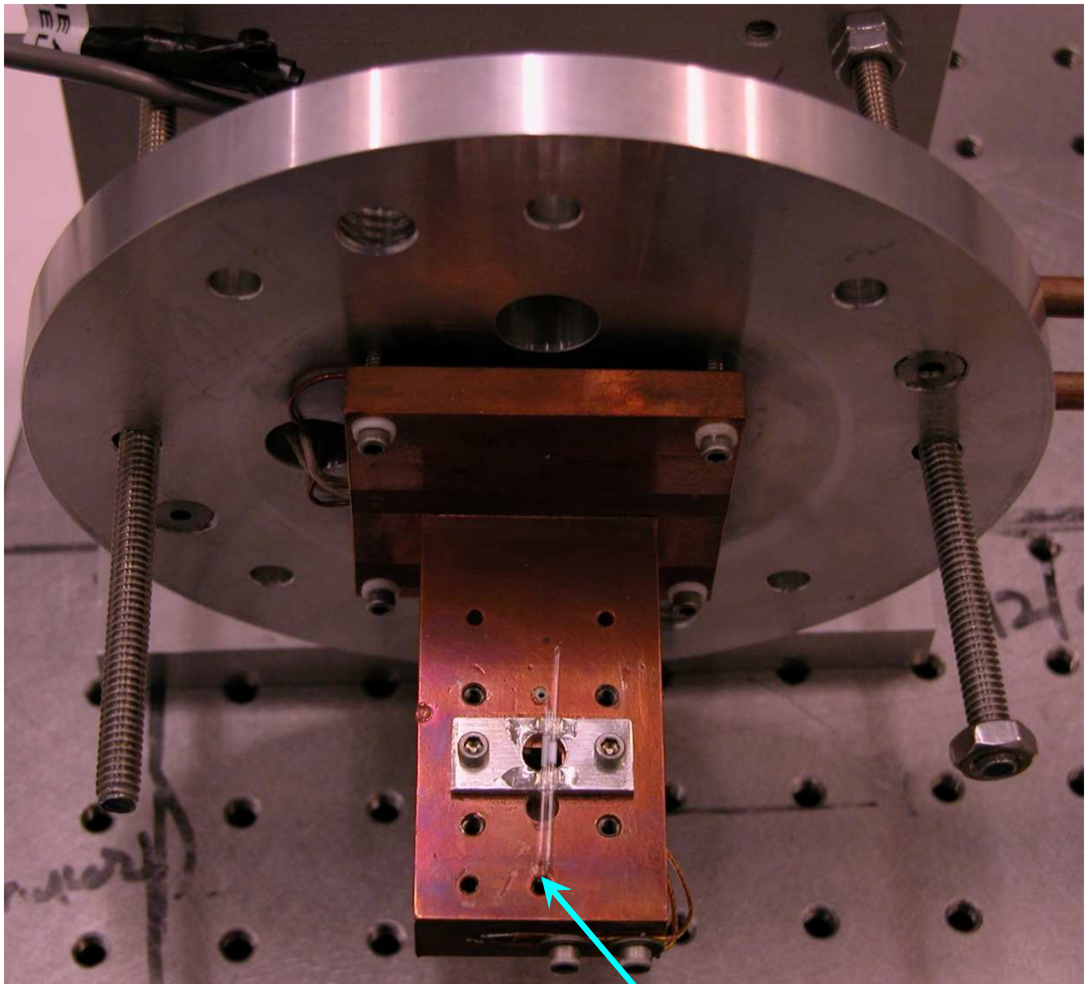


Figure 1
Time infrastructure of (*a*) continuous acquisition with one counter per pixel, (*b*) dual counter acquisition discussed in this study with no readout dead-time between the frames and (*c*) future upgrade of dual counter acquisition where the separation between the frames is smaller than the digitization time associated with each counter.

Q. Zhang et al., J. Synchrotron Rad. 23, 679-684 (2016)

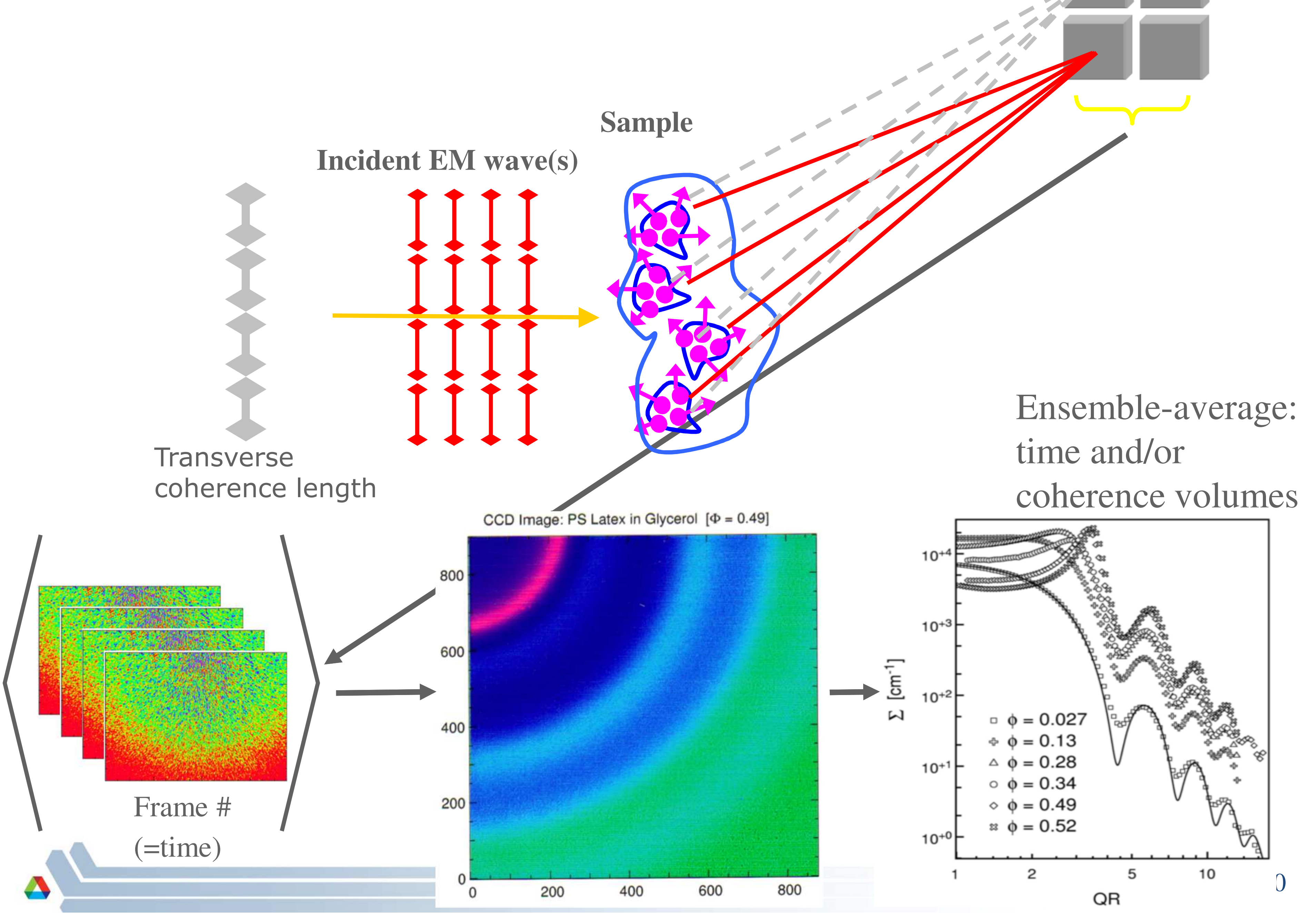
Samples



Capillary

- 67 nm radius latex spheres
- 2 concentrations in glycerol (to slow dynamics) in 2 glass capillaries on separate mounting plates
- ≈ 2% vol. frac.
- ≈ 40% vol. frac.
- Cooled to ≈ -10 °C
- Equilibrium/ergodic system

Measuring Static/Time-Averaged Properties



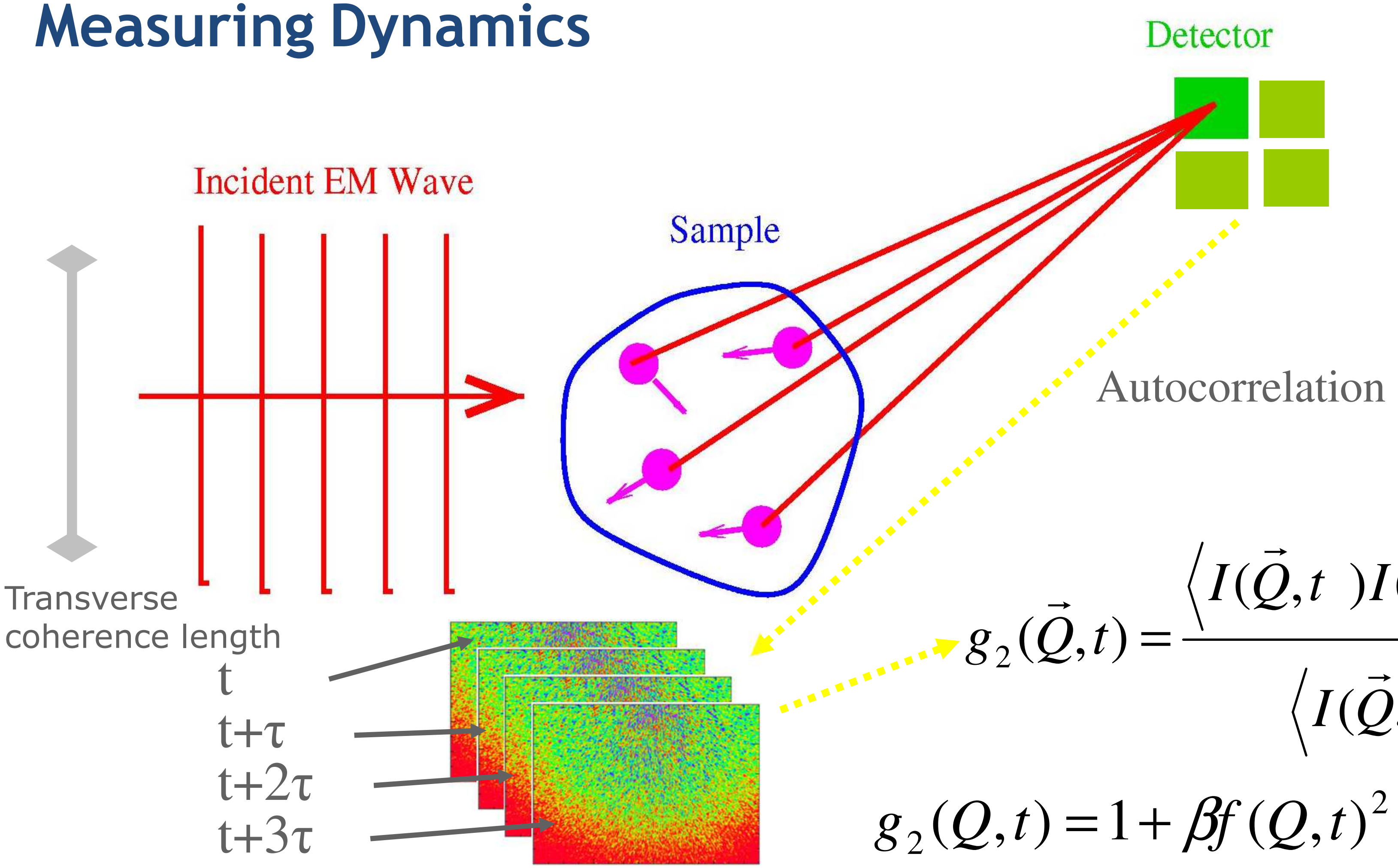
Experiment Part 1: Static/Time-Averaged Analysis

1. Determine the time-/ensemble-averaged* structure factor [S(Q)] for a concentrated suspension of latex spheres in glycerol:
   a) Measure the ensemble-averaged scattering** from a dilute suspension—$I_d(Q) \propto \langle F(Q) \text{ x } S_d(Q) \rangle$
   b) Measure the ensemble-averaged scattering** from a concentrated suspension— $I_c(Q) \propto \langle F(Q) \text{ x } S_c(Q) \rangle$
   c) Determine $S_c(Q)$ by evaluating the ratio I_c/I_d which is $\propto S_c(Q)$ because $S_d(Q)$ is unity

*Particle radius is ≈ 67 nm (Q ≈ 0.01 Å-1) so small-angle x-ray scattering (SAXS) measurements

**We will use (partially) coherent incident x-ray beam (so ensemble average will be determined from a time average of the scattered intensity)

Measuring Dynamics



$$g_2(\vec{Q},t) = \frac{\left\langle I(\vec{Q},t\ )I(\vec{Q},t\ +\tau)\right\rangle_\tau}{\left\langle I(\vec{Q},\tau\ )\right\rangle_\tau^2}$$

$$g_2(Q,t) = 1 + \beta f(Q,t)^2$$

$$f(Q,t) = S(Q,t)/S(Q,0)$$

- S(Q,t) is the dynamic structure factor
- Γ is proportional to the diffusion constant and has a Q^2 dependence (dilute)
- β, varying from 0 →1, expresses how coherent the incident beam is

$$= e^{-\Gamma t}$$

$$\Gamma = DQ^2 = (k_B T / 6\pi\eta R)Q^2$$

Dilute suspension-"Brownian" motion

UFXC32k tests on 8-ID-I (cont)

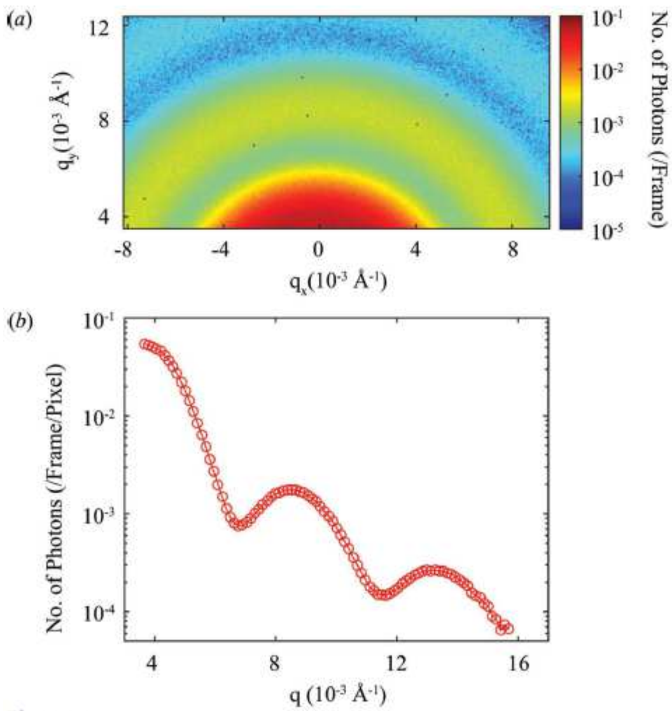


Figure 5
(*a*) Time-averaged scattering from the latex nanoparticle suspension. The scattering intensity is indicated by the logarithmic color bar. (*b*) Azimuthal average of Fig. 5(*a*).

70nm latex spheres
In glycerol

Prototype detector tested successfully at 50kHz.

**We recently sparsified the data saving, and used the detector in a novel burst mode with 0.8 and 2.6 µs frame period.

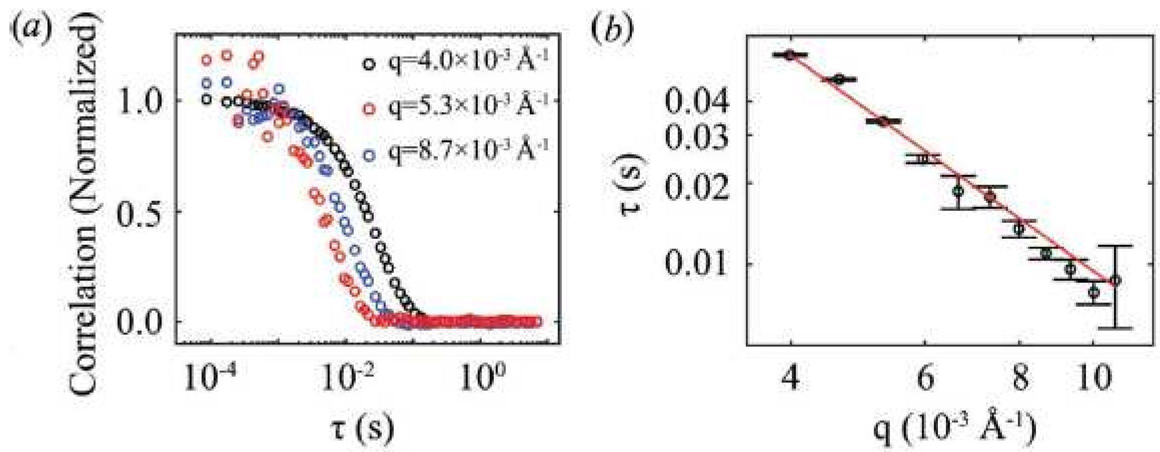


Figure 6
(*a*) Dynamics of latex nanoparticles indicated by $g_2(\tau)$ at different q. (*b*) Decorrelation time $\tau(q)$ *versus* q. The red line shows the inverse-square decay of the correlation time.

Q. Zhang et al., J. Synchrotron Rad. 23, 679-684 (2016) and **Q. Zhang et al., to appear in J. Synchrotron Rad (2018).

Experiment Part 2: Equilibrium Dynamics Analysis

2. Measure the diffusion of the latex spheres in dilute and concentrated suspensions:
   a) Measure time-series of "instantaneous" scattering from a dilute suspension—scattering will display "speckle" because the sample will be illuminated with a partially coherent beam
   b) Measure time-series of "instantaneous" scattering from a concentrated suspension—scattering will display "speckle" because the sample will be illuminated with a partially coherent beam
   c) Calculate pixel-by-pixel autocorrelations
   d) Compare dilute and concentrated suspension autocorrelation decays
      i. Dilute suspension shows "Brownian" dynamics
      ii. Concentrated suspension shows anomalously slow dynamics at the same wave-vector transfer of the peak of S(Q) → long-lived particle configurations (called "de Gennes Narrowing")

Experiment-fastest dynamics in colloids (continued)

- We will measure two Silica colloids in water with different particle diameter.
- We will use the Rigaku camera for this experiment. The Rigaku camera is a new camera with 16 UFXC modules operating at the same frequency but capturing a similar area as the Lambda camera.
- The two colloids diffuse in water and are loaded in capillaries with 2.5% concentration by volume, with 50 and 100 nm diameters.

Future Opportunities at an MBA Source

- Coherent flux: $F_c = B(\lambda/2)^2$

- Signal-to-noise (SNR) ratio of $g_2(\tau)$ guides improvements and enables new science

$$SNR = Contrast \times Intensity \times \sqrt{T \tau N}$$

  - Contrast is speckle contrast or speckle visibility (0 ➔ 1)
  - Coherent Intensity ≈ Source Brilliance
  - T = measurement duration
  - τ = delay time ≈ (detector acquisition or frame rate)$^{-1}$
  - N = number of detectors (pixels)

Accessible delay times go like the square of the coherent intensity

Two beamlines for SAXS and Wide-Angle XPCS have recently been selected as part of a suite of instruments included in the APS MBA upgrade.

Archived slides next

XPCS Area Detectors

$$\Delta\Omega = (\lambda / L)^2$$
$$\approx R_{\text{det}} \lambda / L \approx O(10\mu\text{m})$$

- Need to be able to resolve individual speckles
  - Required detector resolution (@ Rdet ≈ 5 m)
- Few scattering events so require:
  - High efficiency
  - Large photon signal compared to dark current
  - Limited dynamic range (<≈ few 100 photons per pixel)