Northern Illinois University

Introduction to X-ray Photon Correlation Spectroscopy

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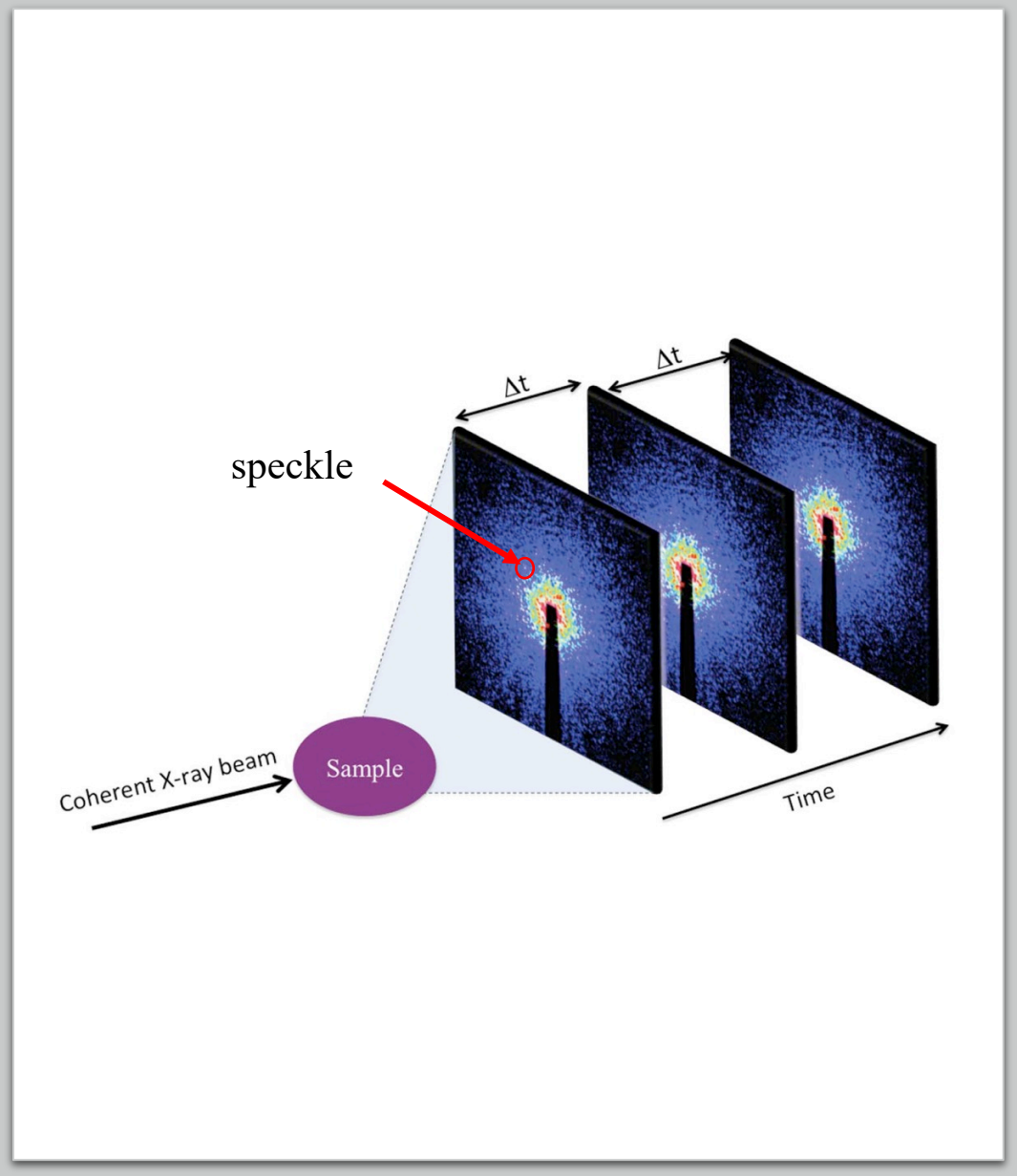
Outline

1. Overview of XPCS
2. The NX school XPCS experiment that we would have done if there was beam.
3. XPCS applications

XPCS in a Nutshell

- XPCS measures equilibrium density fluctuations in materials.
- It requires a coherent x-ray beam in order to produce a speckle pattern.
- The measured quantity, g_2, is the average correlation of the intensity within individual speckles over time.
- $g_2(q,\tau) = \langle I(q,t)I(q,t+\tau)\rangle / \langle I(q)\rangle^2$

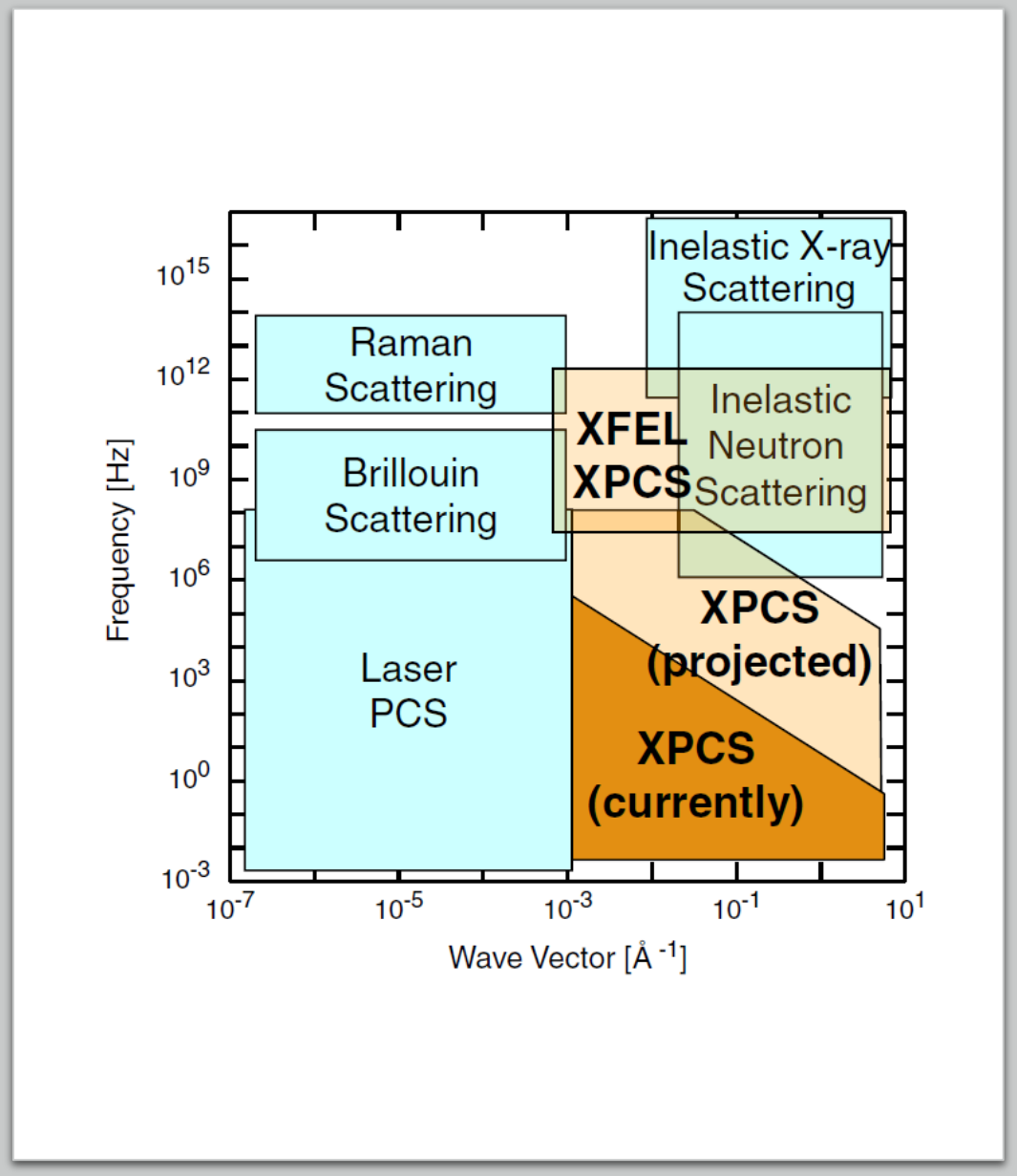
- This measured quantity is directly related to the dynamic structure factor of the material:
- $g_2(\vec{q},\tau) = 1 + \beta|f(\vec{q},\tau)|^2$
- $f(\vec{q},\tau) = S(\vec{q},\tau)/S(\vec{q},0)$
- $S(\vec{q},t) = \int e^{i\vec{q}\cdot\vec{r}} S(\vec{r},\tau)$
- $S(\vec{r},\tau) = \langle \rho(r,\tau), \rho(0,0)\rangle_{eq}$



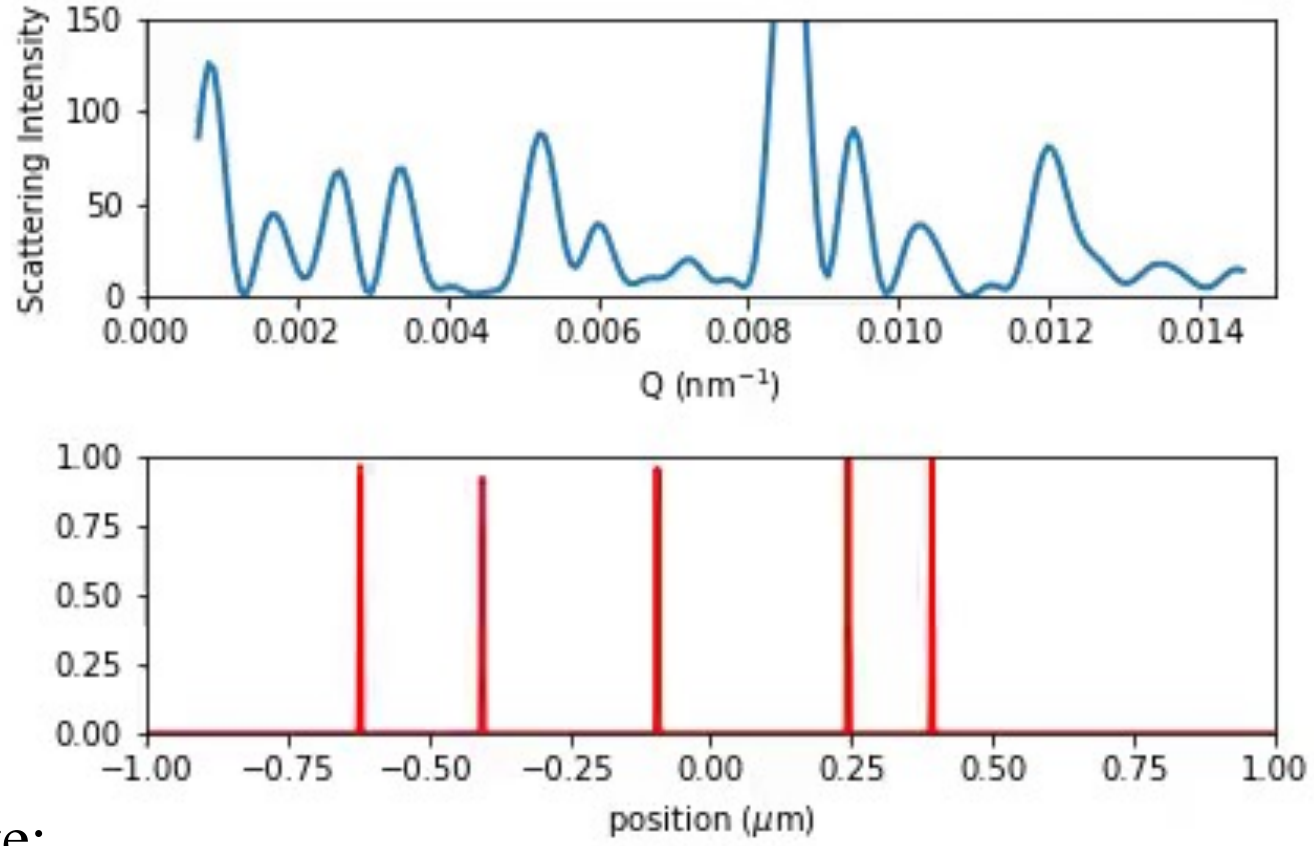
Uses of $f(q, \tau)$

- Brownian Motion and Diffusion
- Surface and Membrane Fluctuations
- Density Fluctuations
- Concentration fluctuations in a binary fluid or solid
- Fluctuations of the order parameter of a crystal.
- Atomic fluctuations about lattice positions
- Diffusion within sheer flow
- Magnetic domain fluctuations
- Aging of glasses
- Battery aging

Fluctuations about the average structure can be measured, which are invisible to incoherent x-rays.



$$I(q) \propto \sum_{m,n} e^{iq(x_m(t)-x_n(t))}$$



Note:

(1) Random intensity variations (speckle)

(2) Speckle intensity fluctuates with time

(3) Dynamics faster at higher Q

Why do you need coherence?

$$I(\boldsymbol{q}) \propto \iint \rho(\boldsymbol{r})\rho(\boldsymbol{r'})e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r'})}d\boldsymbol{r}d\boldsymbol{r'}$$

If the beam is incoherent, then this integral can be approximated as the average over a large number of independent parts of the sample so that:

$$I(\boldsymbol{q})_{incoherent} = \langle \iint \rho(\boldsymbol{r})\rho(\boldsymbol{r'})e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r'})}d\boldsymbol{r}d\boldsymbol{r'} \rangle_{ensemble} \sim g(r)$$

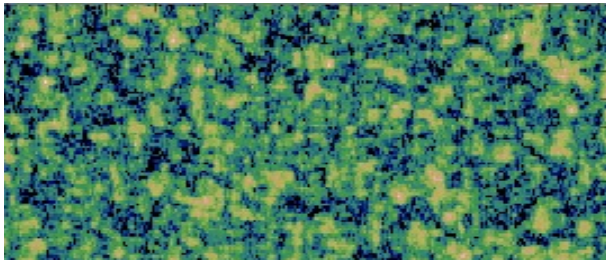
However, in this approximation, all time dependent information is lost.

Dynamics information can be obtained, but only by perturbing the system so that $g(r)$ changes in time. Equilibrium dynamics is invisible.

Coherent Beams

We still have:

$$I(\boldsymbol{q}) \propto \iint \rho(\boldsymbol{r})\rho(\boldsymbol{r'})e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r'})}d\boldsymbol{r}d\boldsymbol{r'}$$



Speckle Pattern

But … this is no longer equal to g(r)

The intensity depends on the exact distribution of density, not the statistically averaged correlation function of the intensity.

These two intensity functions are almost the same, but the difference results in a speckle pattern superimposed on top of the average scattering for the case of a coherent beam. The speckle pattern changes in time, even for an equilibrium system.

What do we mean by coherence?

- Plane electromagnetic waves are completely coherent

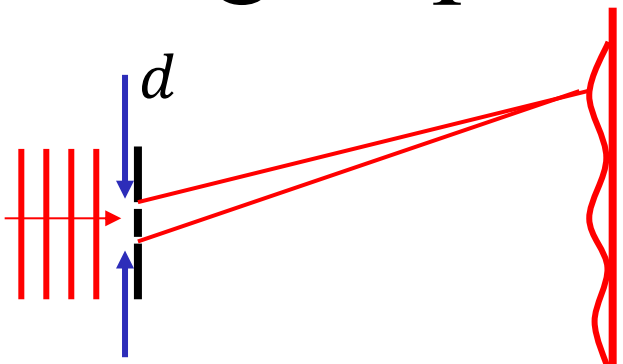
$$\vec{E} = \hat{\epsilon} E_0 e^{i\vec{k}\cdot\vec{r} - \omega t}.$$

- However, most sources emit x-rays over a range of angles and energies. This spread destroys coherence. The x-rays behave like a large number of independent modes.
- Coherence can be regained by collimation and monochromatization.
- New sources (e.g. APSU and FELs) are coherent or partially coherent without any modification. This means that coherent x-ray scattering will become the norm rather than the exception.

Transverse coherence and angle spread

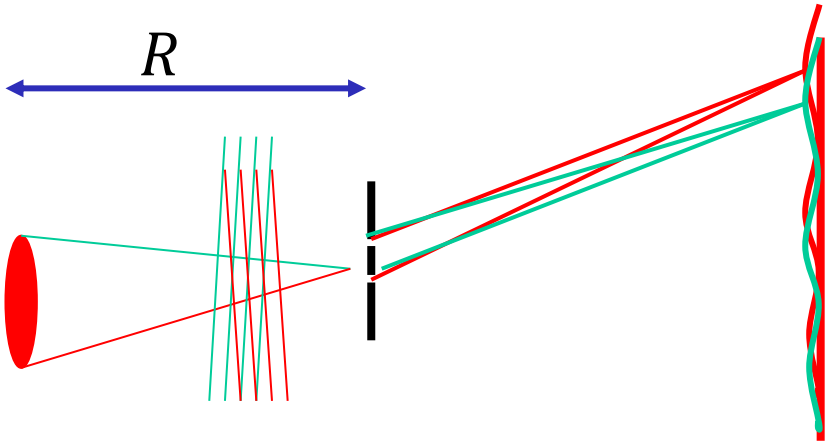
Ideal Young's double slit experiment

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



Real Young's double slit experiment

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

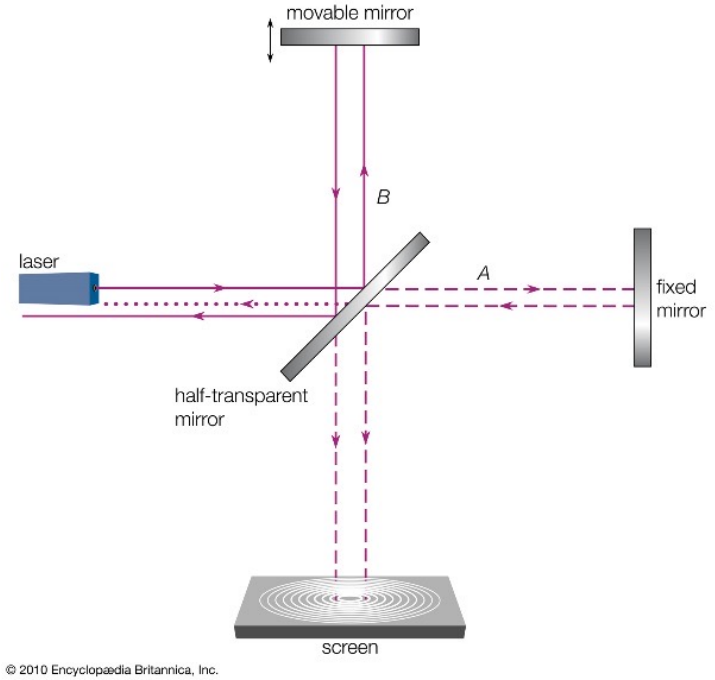


Transverse coherence length ξ, largest distance between slits which still yields interference pattern. For gaussian source distribution of width σ:

$$\xi = \lambda R/2\sqrt{\pi}\sigma$$

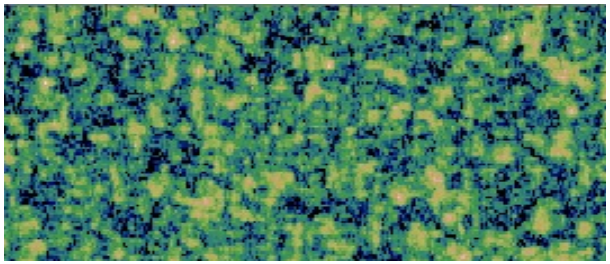
Longitudinal coherence and energy spread

In optics this is typically understood in the context of a Michaelson Interferometer. By how much can the path lengths in the two arms differ and still produce an interference pattern?



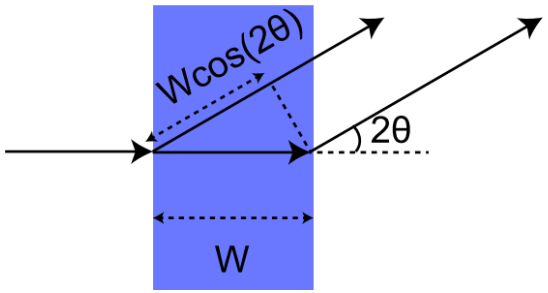
$$\Lambda \approx \lambda(E / \Delta E)$$

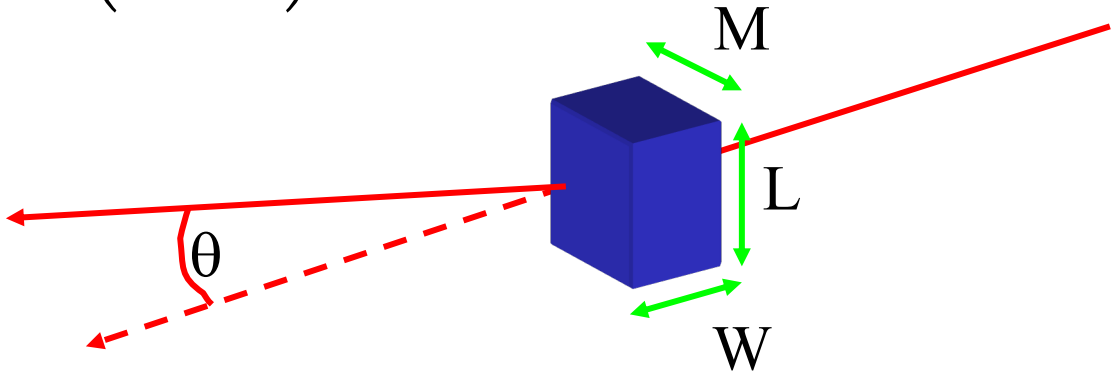
Speckle Contrast



The contrast can have a maximum value of 1 (speckle intensity varies from 0, to 2x average), or a minimum of 0 (no speckle). It is given by the ratio of the scattering volume to the coherence volume

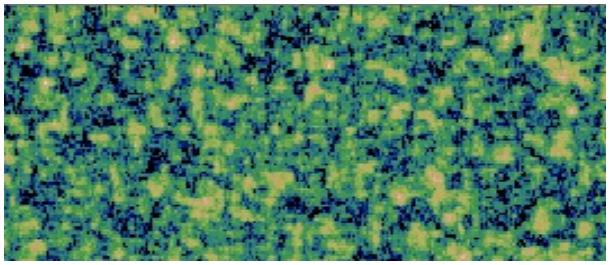
$$\beta = \left(\frac{\Lambda \xi_x \xi_y}{MLW}\right) \frac{1}{2\sin^2\theta}$$





Note that the contrast is what allows you to "see" the intermediate scattering function $g_2(\vec{q},\tau) = 1 + \beta|f(\vec{q},\tau)|^2$

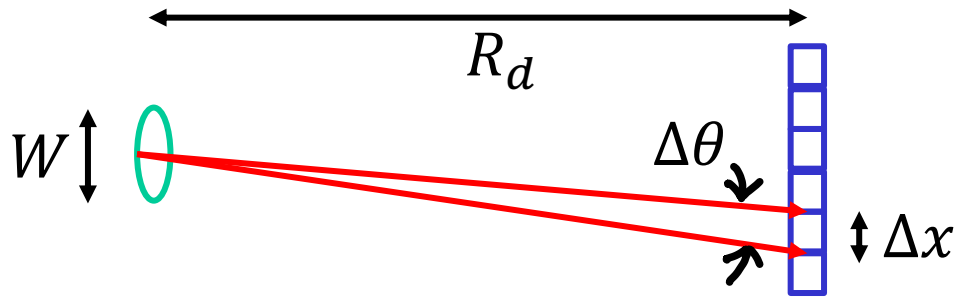
Speckle Size



The speckle widths are approximately the size of the diffraction pattern from a slit the size of the sample:

Typically, a few tens of microns

$$\Delta x = \frac{R_d \lambda}{W}$$



If detector cannot resolve speckles, contrast is reduced.

Sometimes the incident x-ray beam is focused onto the sample to reduce the spot size, leading to bigger speckles which better match the camera

Coherence at the (Old) APS (8-ID-I)

$\sim 10^{10}$ Photons/Coherence Area/s

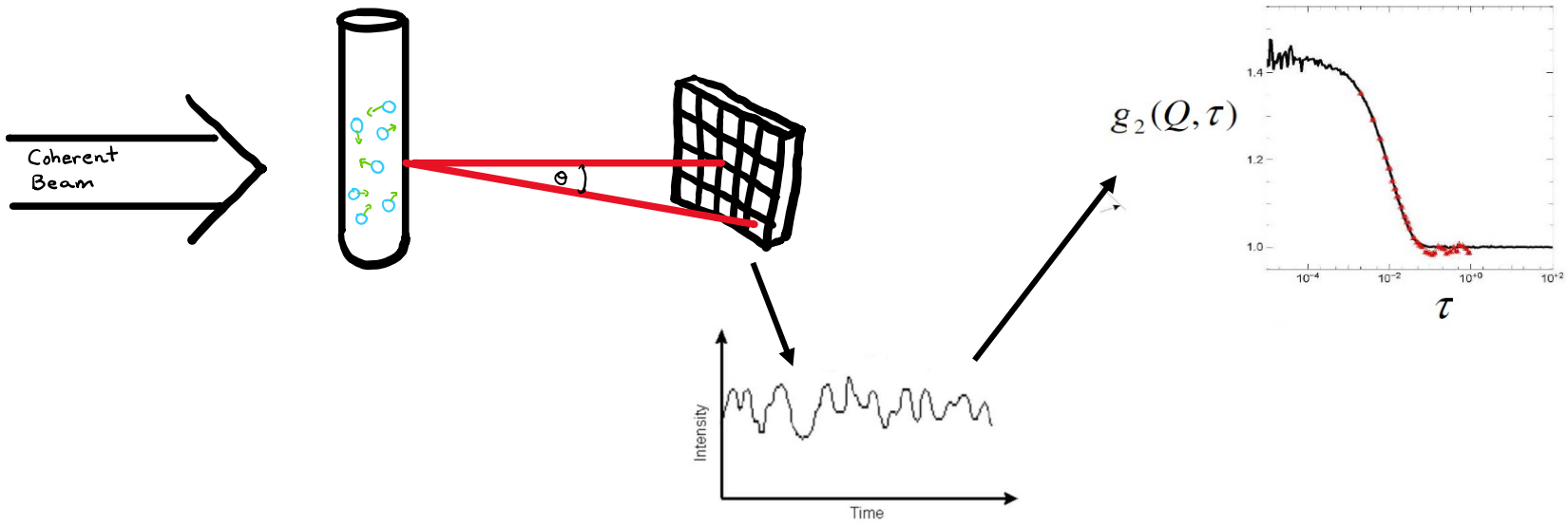
Horizontal coherence length (with slits) $\xi_x = 14\mu m$

Vertical coherence length $\xi_y = 306\mu m$

Longitudinal coherence length $\Lambda = 0.66\mu m$

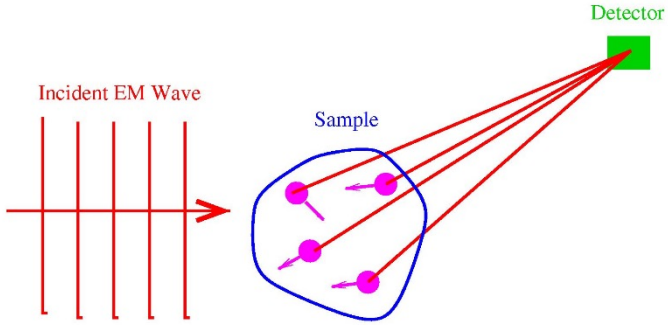
Typical APS SAXS beamline has 10^{12} photons/s on sample

Prototypical system: diffusion of spheres in a fluid (Brownian Motion)



$$g_2(Q,\tau) = \frac{\langle I(Q,t)I(Q,t+\tau)\rangle}{\langle I\rangle^2} = 1 + \beta|f(Q,\tau)|^2$$

Point Particles



$$f(\mathbf{Q},\tau) = \frac{1}{N}\sum_{i,j} e^{i\mathbf{Q}\cdot\left(\mathbf{r}_i(0)-\mathbf{r_j}(\tau)\right)} \approx \frac{1}{N}\sum_{i} e^{i\mathbf{Q}\cdot\left(\mathbf{r}_i(0)-\mathbf{r}_i(\tau)\right)}$$

Take equilibrium average assuming a gaussian random distribution of phases*:

$$\left\langle \sum_i e^{i\mathbf{Q}\cdot\boldsymbol{\Delta}\mathbf{r}} \right\rangle = e^{-\frac{1}{2}\left\langle(\mathbf{Q}\cdot\boldsymbol{\Delta}\mathbf{r})^2\right\rangle} = e^{-\frac{1}{6}Q^2\langle\Delta r(\tau)\rangle^2}$$

*Baker-Hausdorff theorem, see Jens Als-Nielson appendix D

Particle Diffusion

One dimensional diffusion: $\langle \Delta x \rangle^2 = 2\mathrm{D}\tau$

$$\langle \Delta r^2 \rangle = \sqrt{\Delta x^2 + \Delta y^2 + \Delta z^2} = 6\mathrm{D}\tau$$

Stokes-Einstein Relation: $D = k_B T / 6\pi\eta r$

$$f(Q,\tau) = \exp(-DQ^2\tau)$$

$$g_2(Q,\tau) = 1 + \beta e^{-2\Gamma\tau}$$

$$\Gamma = DQ^2$$

r radius, η viscosity, D diffusion coefficient, T temperature

- XPCS gives you the particle radius or the viscosity.
- For more complicated systems you can extract a distribution of particle sizes or the variation of the viscosity with length scale (caging).

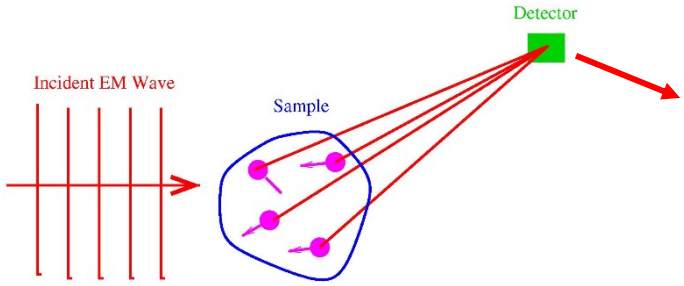
But: not all systems are simple diffusion …

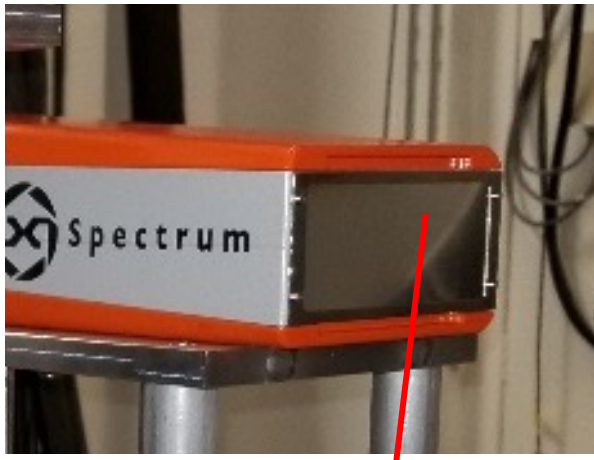
More general significance of $f(q,\tau)$

How do you analyze random processes?

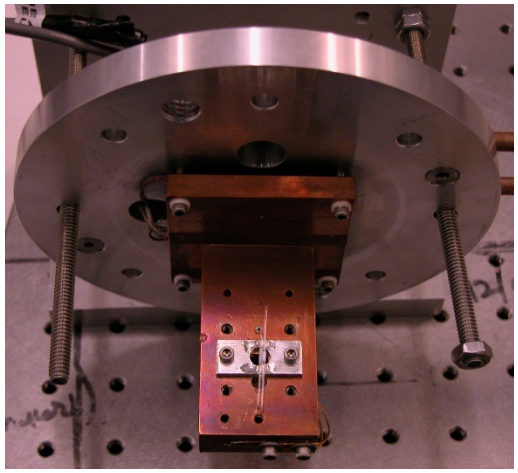
- Consider the Langevin equation: $m\dot{v} + \alpha v = \zeta(t)$
- $\zeta(t)$ is a random force with zero average, so at first glance, this equation appears useless.
- But useful information can be obtained from the time correlation function of ζ. The time correlation function of a random force is not zero even if the average force is zero.
- This correlation function, $< \zeta(t)\zeta(t+\tau) >$, is related to the time correlation function of position $< x(t)x(t+\tau) > \sim f(\tau)$.
- Thus, from a study of correlation functions we can learn how fluctuating thermal forces lead to molecular rearrangement in materials.

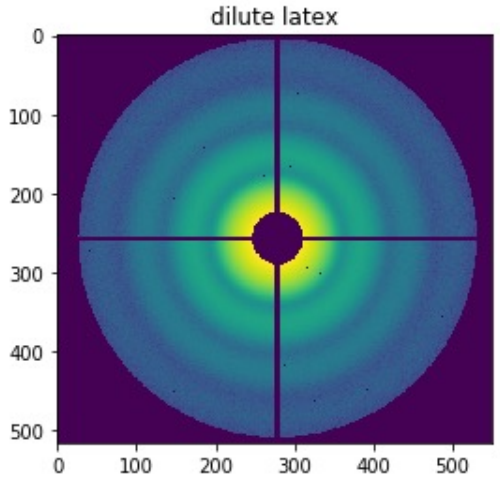
The NX School Experiment



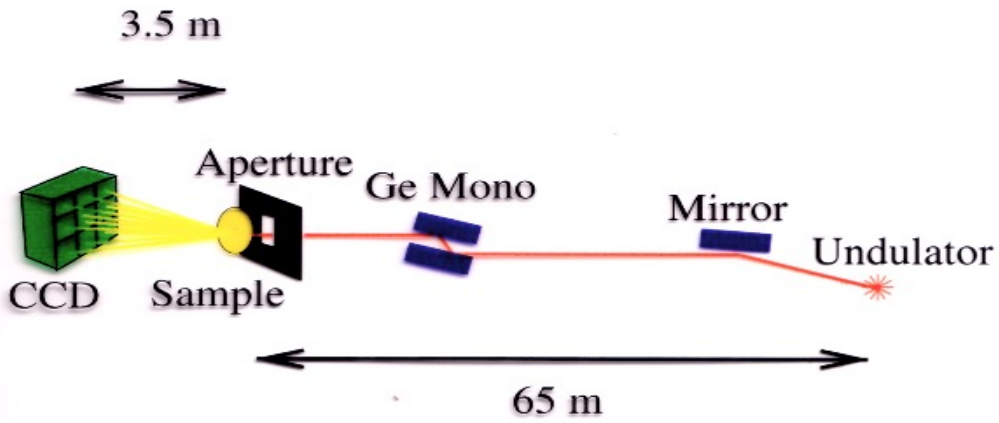


- Look at XPCS from colloidal suspensions of 67 nm radius latex beads in glycerol
- Compare XPCS for dilute and concentrated colloids.
- 2 concentrations in glycerol (to slow dynamics) in 2 glass capillaries on separate mounting plates
- ≈ 2% vol. frac.
- ≈ 40% vol. frac.
- PRL Lurio, 2000





Static Scattering



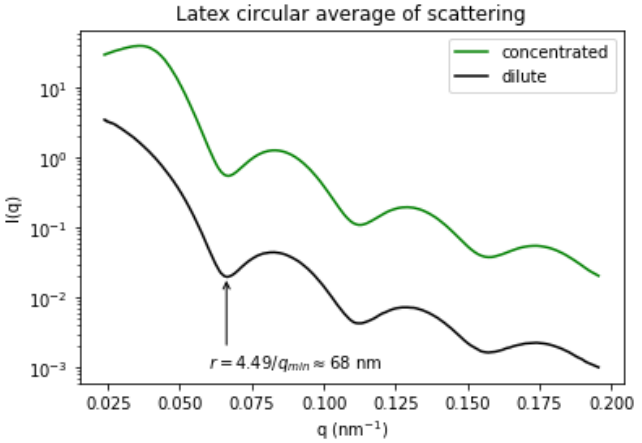
- Sphere form factor $x = qr$

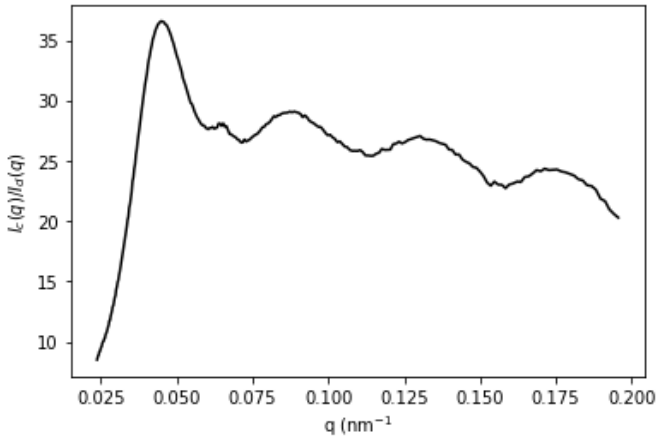
$$F(Q) = \left[3\frac{\sin x - x\cos x}{x^3}\right]^2$$

- At high concentration, scattering modified by interparticle correlations:

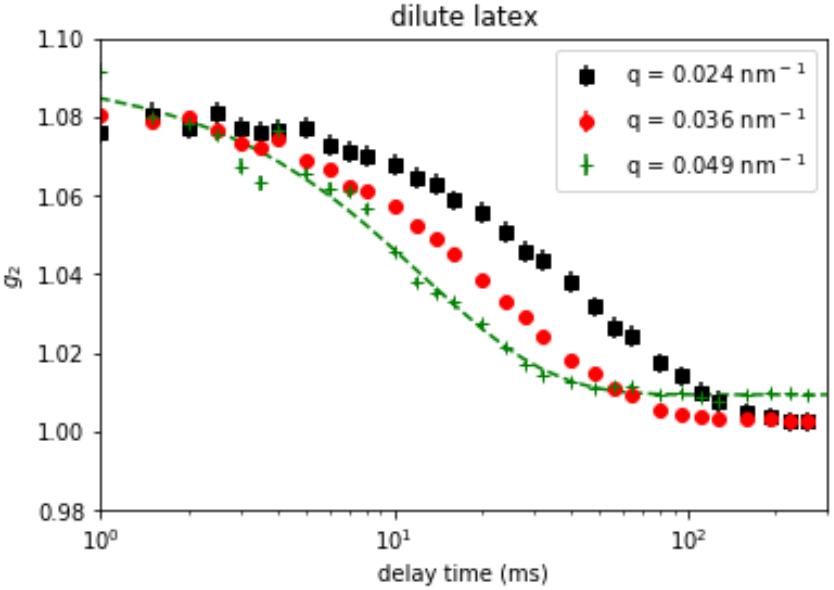
$$I(Q) \propto F(Q)S\,(Q)$$

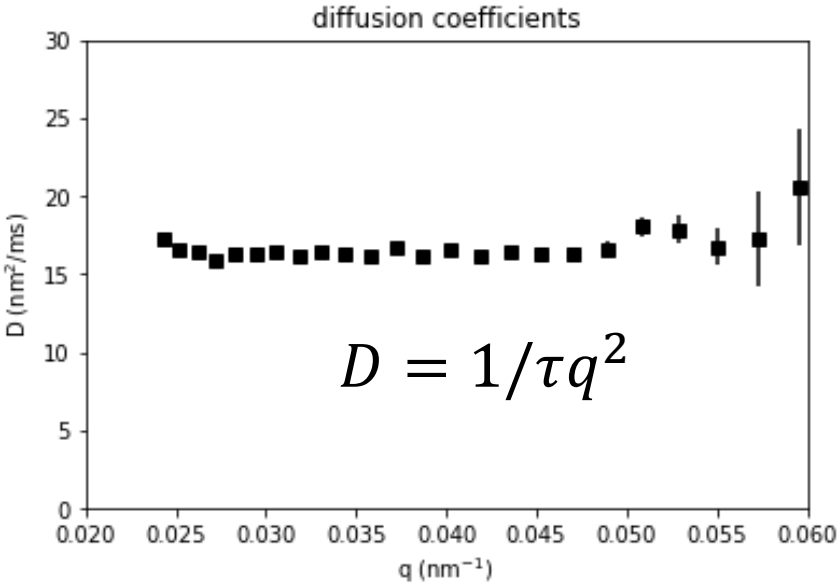
$$S(Q) \approx \left(\frac{\phi_{dil}}{\phi_{conc}}\right) \times I_{conc}/I_{dil}$$

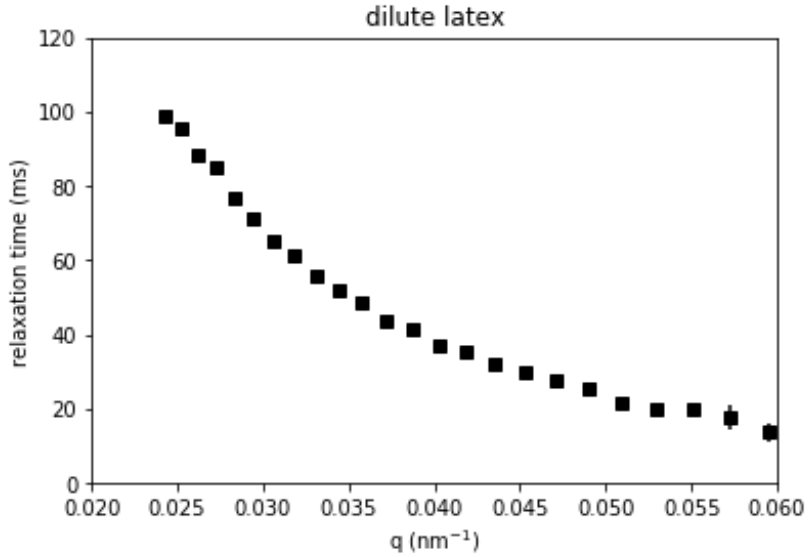




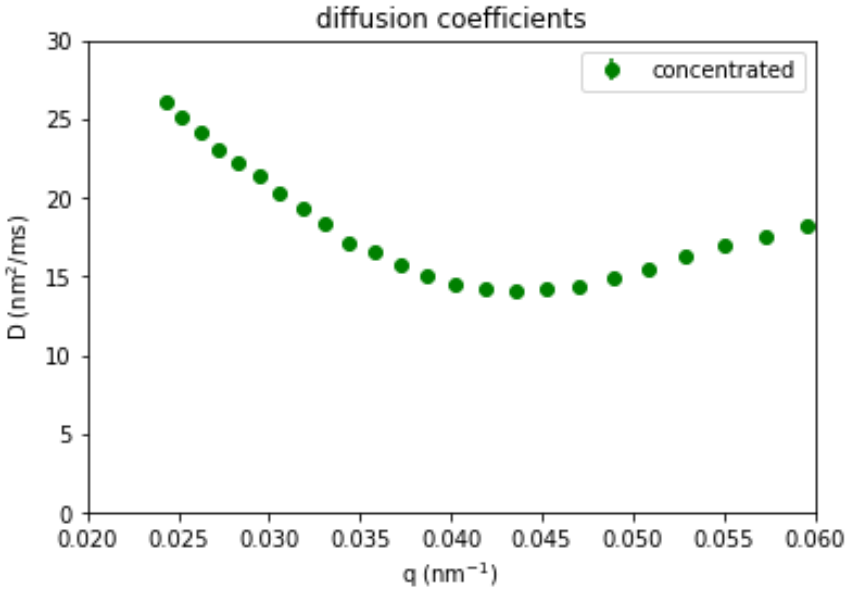
Dynamics Results: Dilute

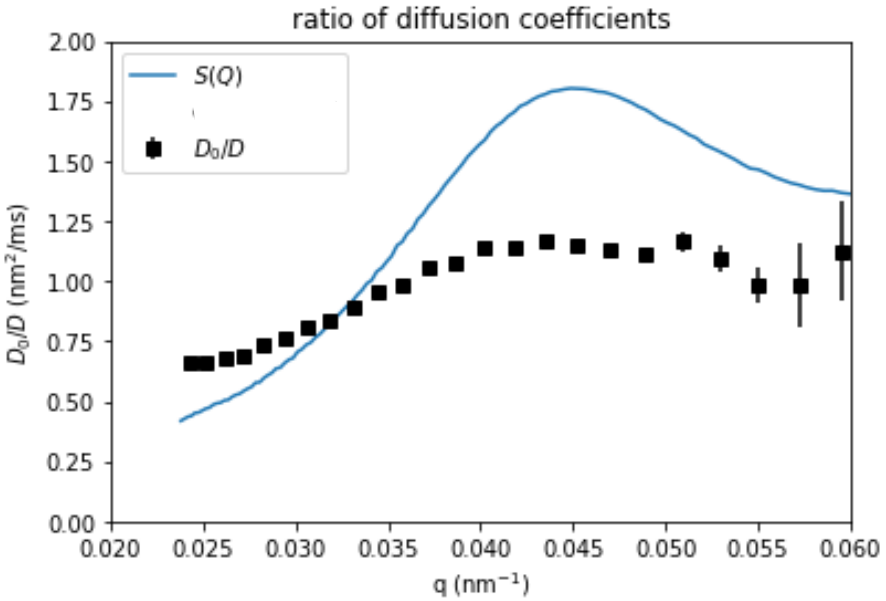






Dynamics Results: Concentrated





$$\frac{D_0}{D(Q)} = S(Q) \ldots \text{de Gennes Narrowing}$$

Assume velocities are uncorrelated but hydrodynamic flow creates correlations.

Length scale dependent deviations from diffusion tell you something new about correlated motion!

Atomic jumps in a binary alloy

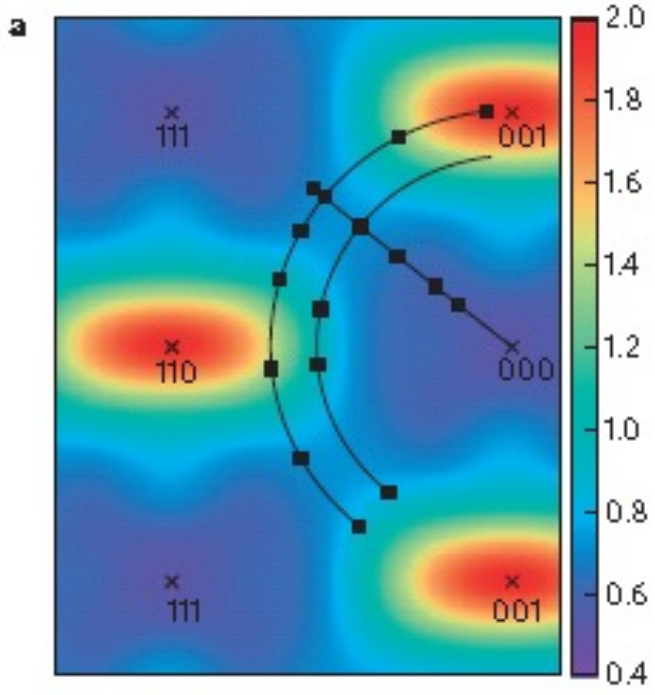
M. Leitner, B. Sepiol, L.-M. Stadler, B. Pfau, and G. Vogl, Nature Materials **8, 717-20 (2009).**

Study $Cu_{90}Au_{10}$ alloy.

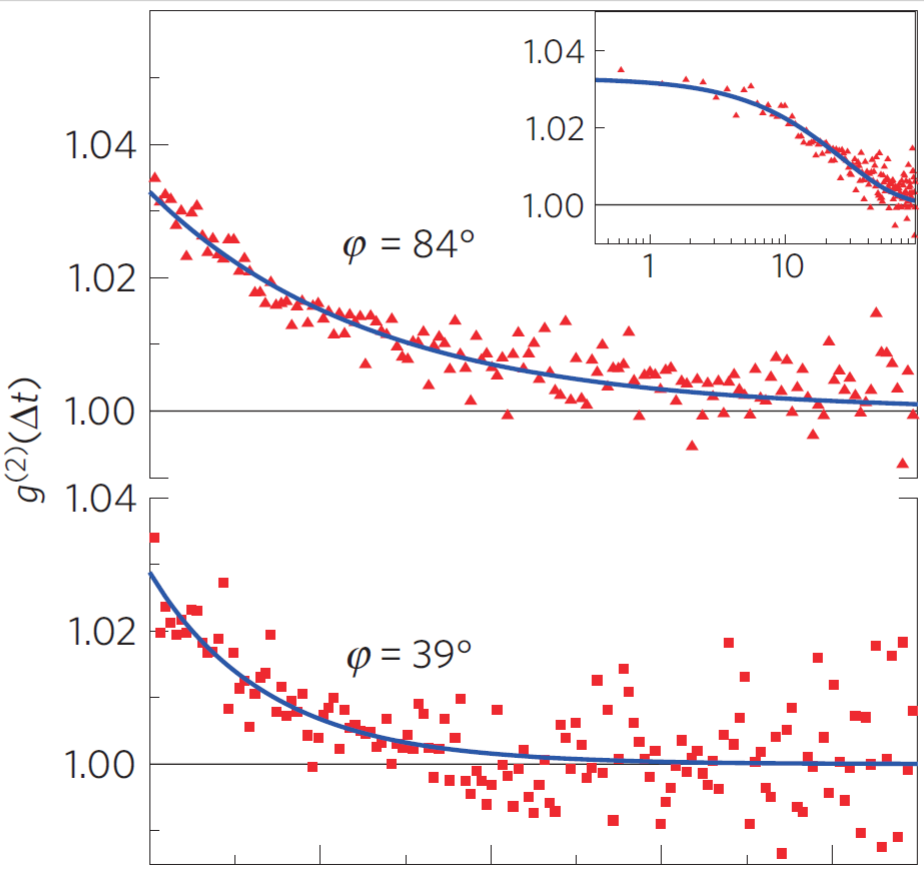
Measure XPCS from thermal diffuse scattering between Bragg peaks.

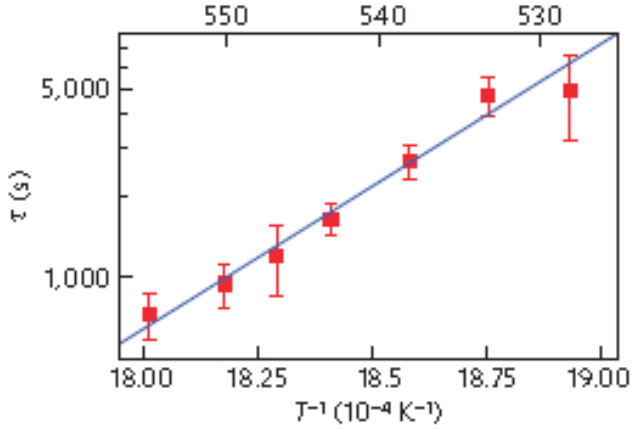
Dynamics corresponds to Cu-Au place exchange.

For this system: $f(q,t)$ is the F.T. of the place exchange probability



Atomic Dynamics





See simple exponential decay with dynamics varying as a function of azimuthal angle and temperature.

Significance

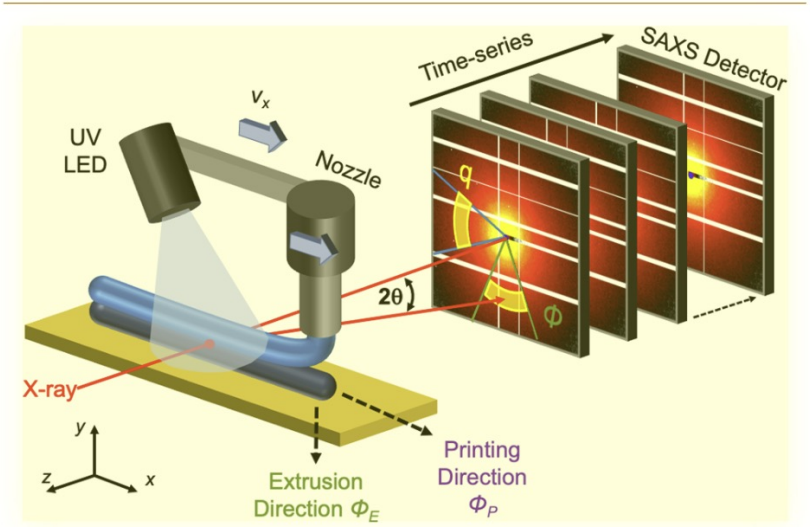
- XPCS doesn't only apply to large molecules or colloidal particles, but can be used for individual atoms.
- Dynamics also occurs in crystals due to place exchange.
- Need strong scatterer (gold) and very slow dynamics. With the APSU these sorts of experiments could become routine!

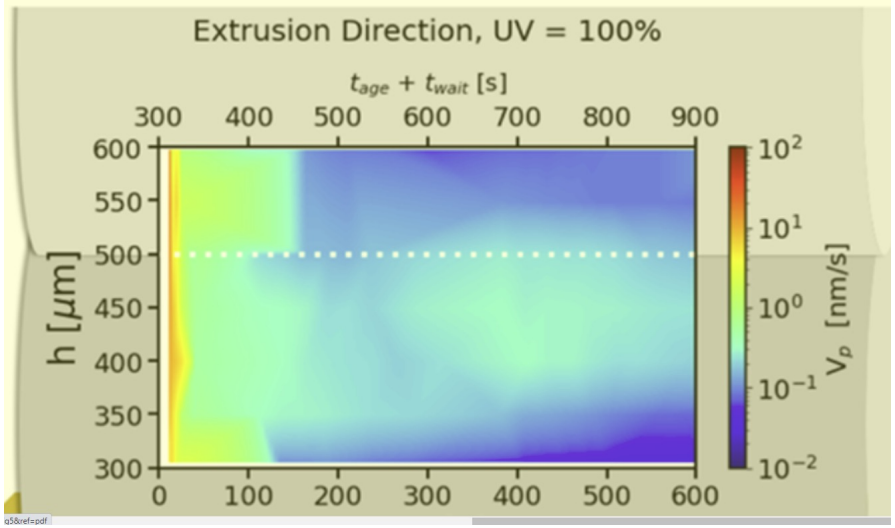
Imaging Dynamics in Additive Manufacturing

Spatial-Temporal Dynamics at the Interface of 3D-Printed Photocurable Thermoset Resin Layers

Benjamin M. Yavitt, Lutz Wiegart, Daniel Salatto, Zhixing Huang, Leonidas Tsapatsaris, Maya K. Endoh, Sascha Poeller, Manuel Schiel, Stanislas Petrash*, and Tadanori Koga*

ACS Appl. Eng. Mater. 2023, 1, 2, 868–876



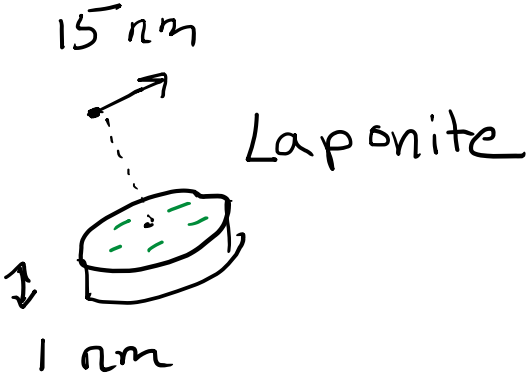


Beyond simple diffusion

- For simple diffusion we expect $f(q,\tau) = e^{-\frac{\tau}{Dq^2}}$.
- We saw for dense colloids $D \rightarrow \frac{D}{S(q)}$
- Dynamics of laponite clay undergoing a gelation transition shows different $q-$ dependence and τ dependence.
- PRL Bandyopadhyay, 2004

Gelation of Laponite

- Dilute clay suspension $\phi > .007$ slowly gel with time over around 1000 s
- Correlation functions non exponential:
- $g_2 = 1 + b\left[Ae^{-\left(\frac{t}{\tau}\right)^{\beta}}\right]^2$
- b represents the contrast.
- A represents unseen fast relaxation mode
- β is stretching exponent



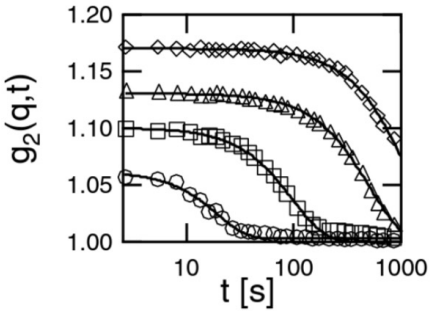
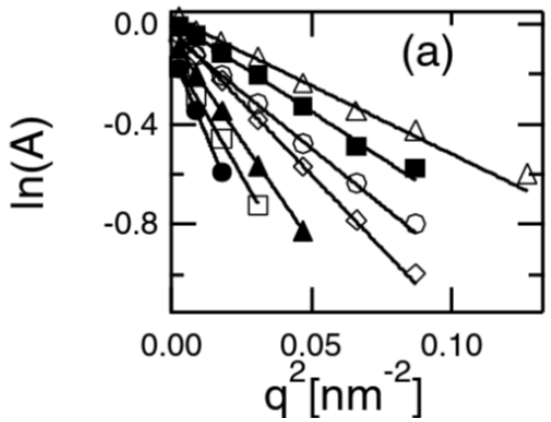
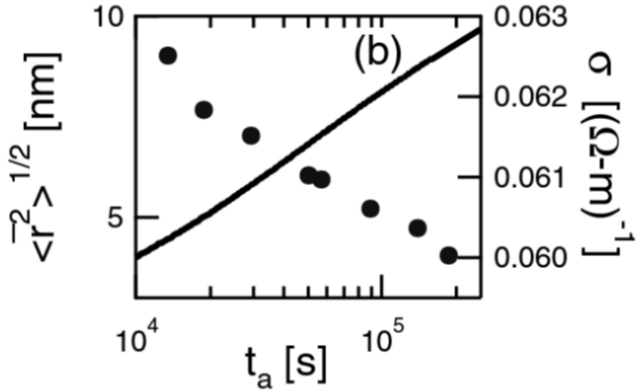


FIG. 1. Intensity autocorrelation function $g_2(q, t)$ at $q = 0.14\ \text{nm}^{-1}$ for a laponite suspension of volume fraction $\phi = 0.012$ at four ages: $t_a = 1.3 \times 10^4$ s (circles), 3×10^4 s (squares), 9×10^4 s (triangles), and 2×10^5 s (diamonds). Solid lines are the results of fits to Eq. (1).

What can we learn from this?

- Fast relaxation time gives a mean square displacement, represents a Debye-Waller like term $A = e^{-\frac{q^2\langle u^2\rangle}{3}}$





Ballistic Flow

- Stretching exponent $\beta = 1.5$
- $\tau \sim 1/q$
- Both indicate driven ballistic flow in response to stress rather than diffusion.

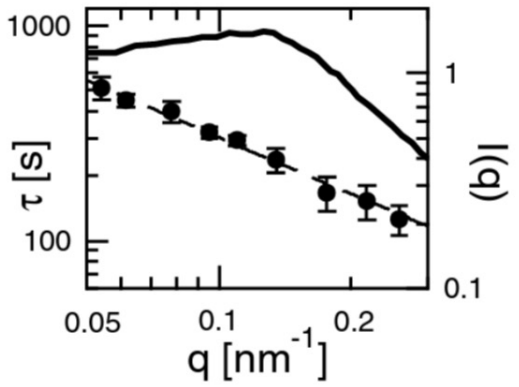


FIG. 3. Characteristic relaxation time τ (solid circles) at $t_a = 4 \times 10^4$ s and scattering intensity $I(q)$ (solid line) from SANS for a laponite suspension with $\phi = 0.012$ as a function of wave vector q. The dashed line displays the fit result $\tau \sim q^{-0.9\pm0.1}$.

Dynamics of Aging

- By watching how exponents change with overall time you can see how the aging process occurs during gelation.

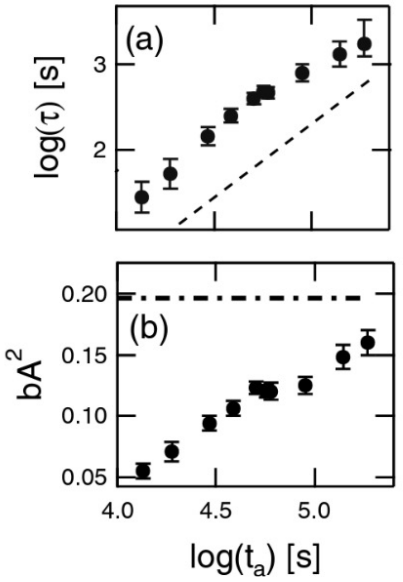


FIG. 2. (a) Characteristic relaxation time and (b) amplitude of $g_2(q, t)$ at short times for a laponite suspension of $\phi = 0.012$ at $q = 0.14\ \mathrm{nm}^{-1}$ as a function of age. The dashed line in (a) has a slope of 1.8. The dashed-dotted line in (b) shows the value of the contrast measured using a static aerogel sample.

Two Time Correlation Functions

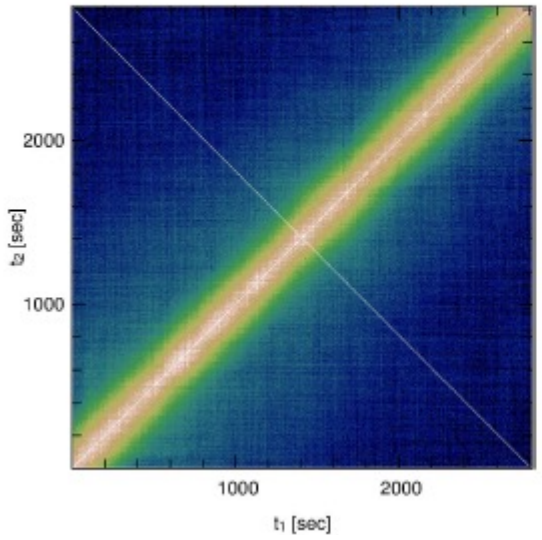
- For processing showing aging, you can approximately measure $g_2(\tau)$ at different absolute times from your starting point.
- More generally, you can define a new correlation function that depends on two times, t_1 the start time of your correlation and t_2 the time you are correlating with t_1

Two-time correlation function

- $C(t_1, t_2) = \frac{\langle I(t_1) I(t_2) \rangle}{\langle I(t_1) \rangle \langle I(t_2) \rangle}$

Equilibrium dynamics

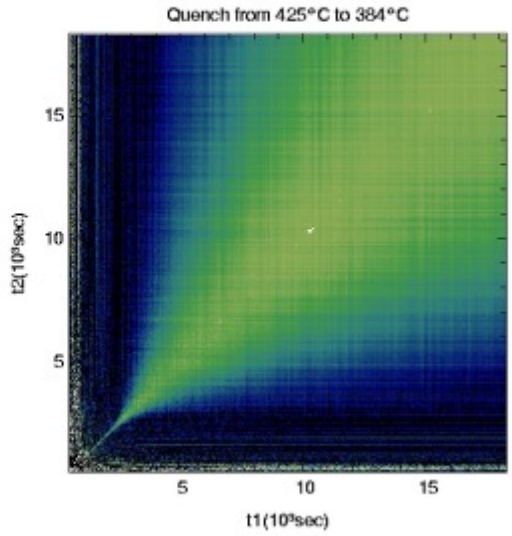
Au in polystyrene



Steady state diffusion

Nucleation and growth

Cu_3Au

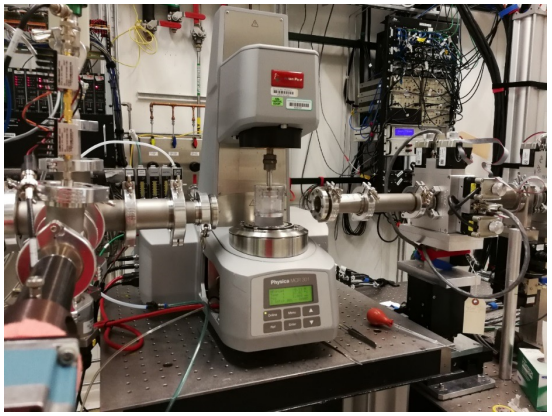


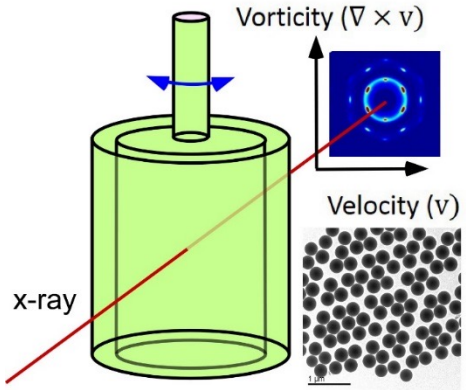
Mark Sutton

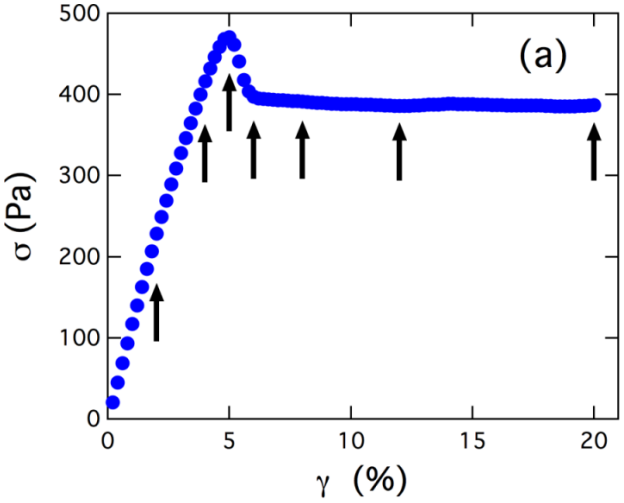
Stress relaxation in colloidal glasses

PRM Chen et. al. 2020

Measure dynamics of colloidal glass under sheer using in-situ sheer cell. σ is stress, γ is strain.







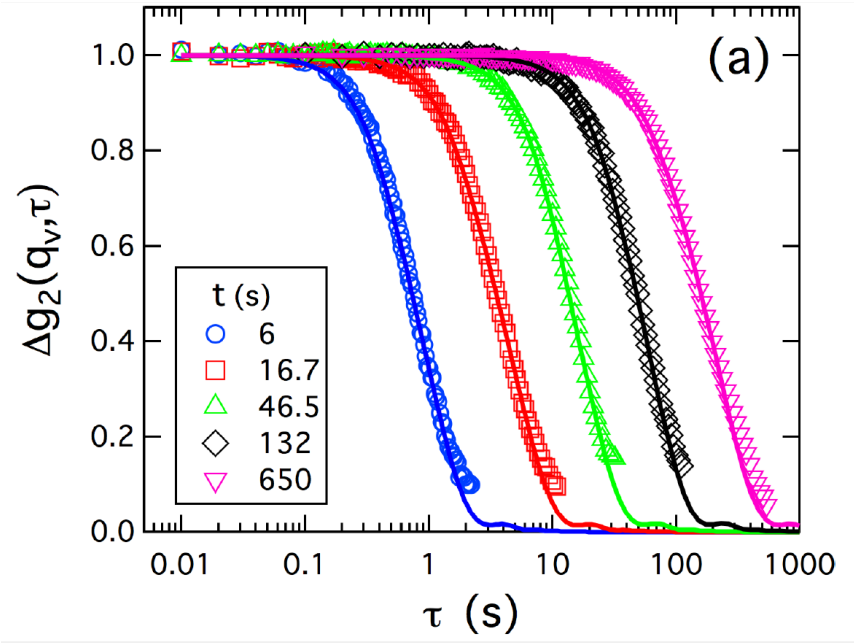
- Yield-stress material: acts like a fluid with sufficient force, but returns to a solid after force removed.
- What are the dynamics of this transition?

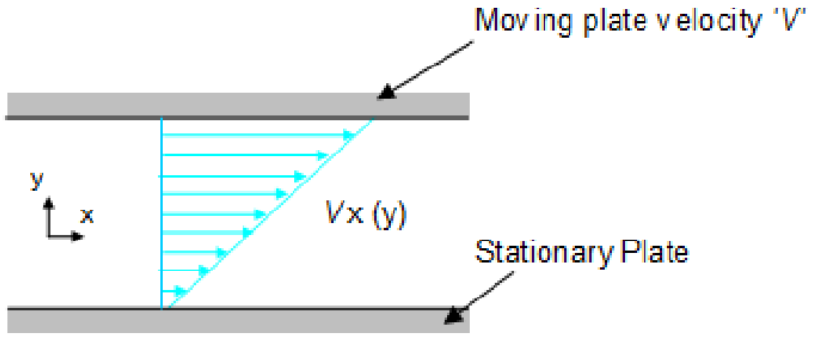
Relaxation along flow direction

- Relaxation times change with overall wait time since step flow.
- Dynamics is not diffusive, but shows flow with a range of velocities. Measuring relaxation of flow induced by residual stress

$$\Delta g_2(\vec{q},\tau) = \frac{\sin^2(qv_0\tau/2)}{\left(\frac{qv_0\tau}{2}\right)^2}$$

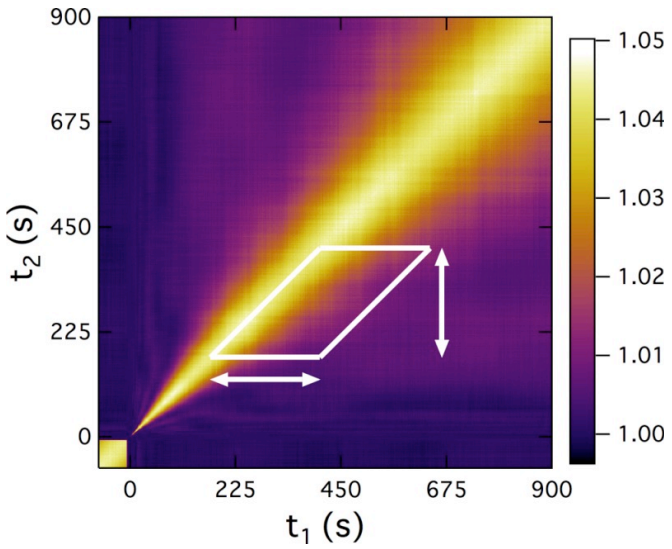
- Here Δg_2 has the constant subtracted and is normalized by contrast.
- v_0 is the peak velocity between the two walls.
- XPCS only sees velocity gradient, not absolute velocity.



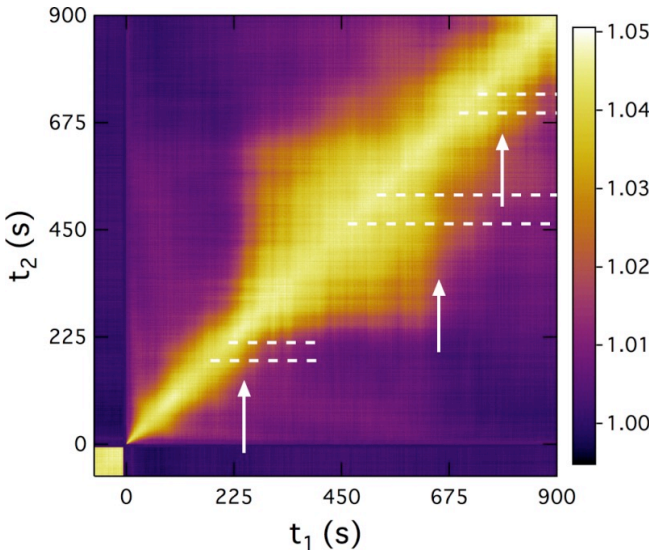


What about dynamics along vorticity direction?

- Dynamics are complex and depend on both waiting time and time delay.
- New feature, “avalanches”, discontinuous events that destroy correlations.



Velocity direction



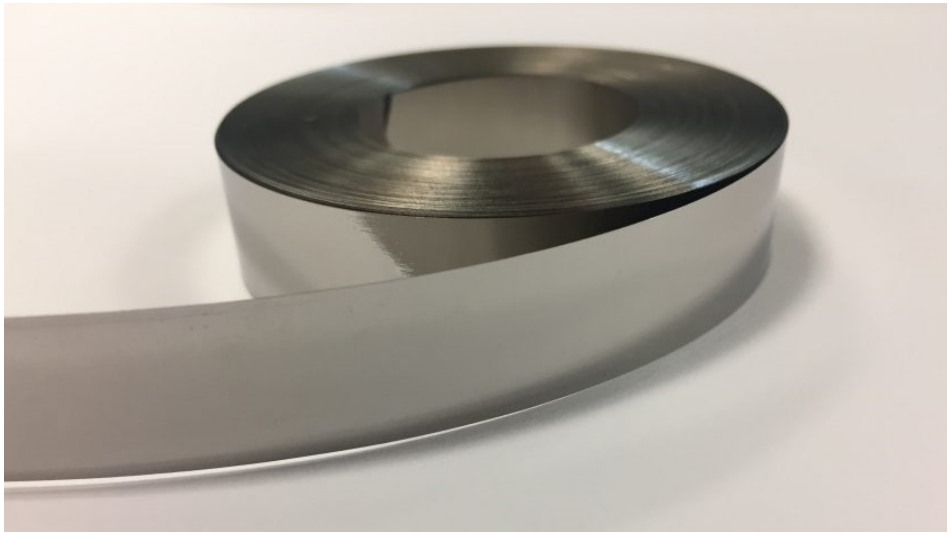
Vorticity direction

Some observations

- XPCS used to study a non-equilibrium system.
- In flow direction, observe quasi-equilibrium behavior around evolving dynamics
- Directional dependence of $\vec{q}$ used to distinguish very different dynamics in two directions.
- Two-time correlation functions can be used to identify avalanche like events which cause decorrelation.

Relaxation in Metallic Glasses

- Metallic glasses are formed by rapid quenching of metal alloys.
- They have high strength, large elastic elongation and high corrosion resistance.
- Downside is they are only metastable, so they slowly transform with time.
- Understanding the dynamics of aging and how to counteract aging effects is crucial for this technology



Antoine Cornet and Beatrice Ruta

Comptes Rendus

Physique

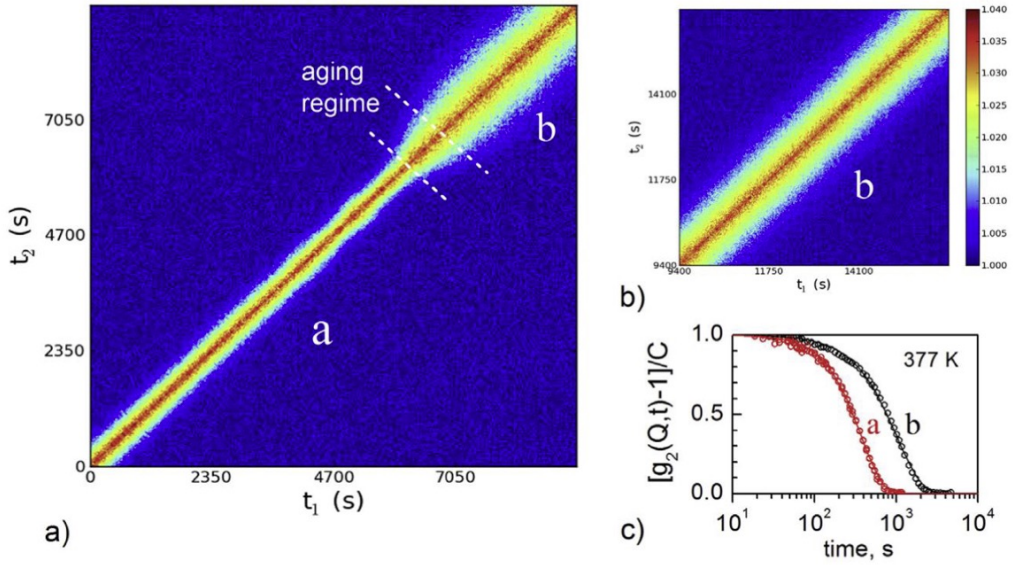
New pathways to control the evolution of the atomic motion in metallic glasses

Published online: 20 April 2023

https://doi.org/10.5802/crphys.149

Aging in metallic glasses occurs in short bursts with long quasi-static regimes interspersed.

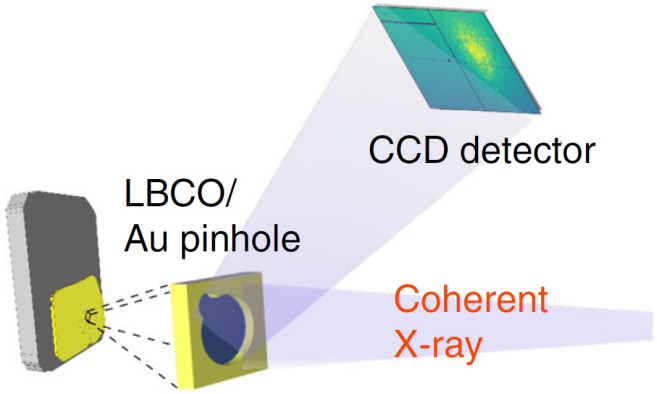
$Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$

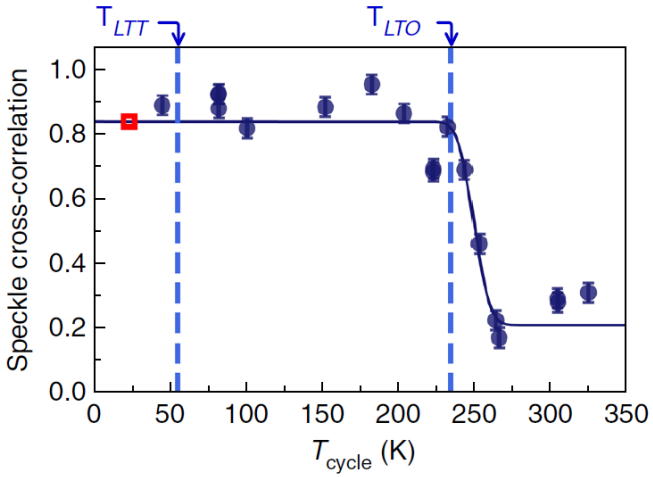


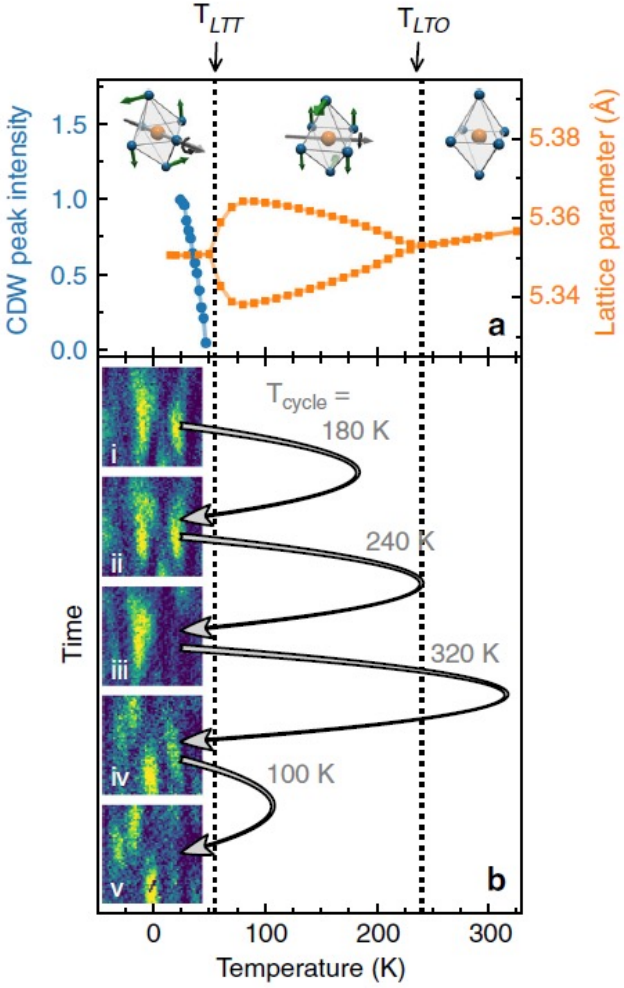
Speckle in Charge Density Waves

(Nature Comm: Chen et. al. 2019)

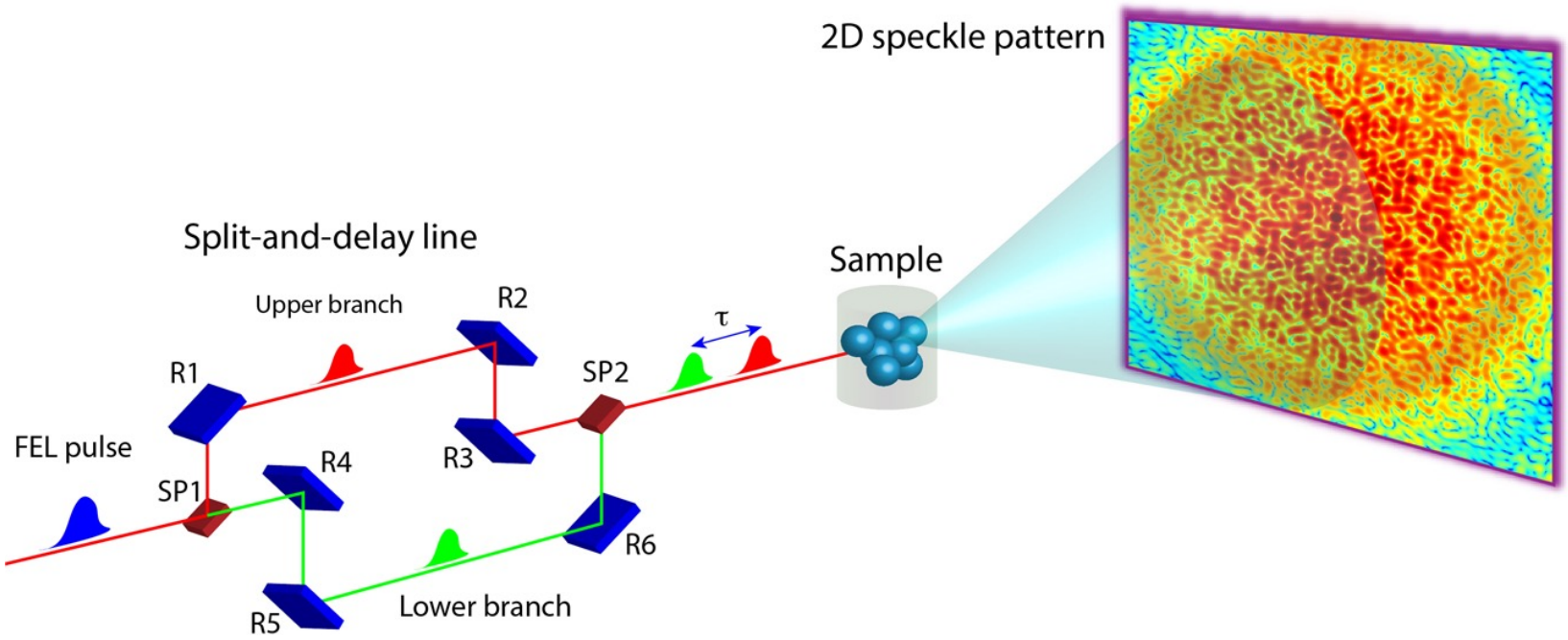
- Unique use of speckle to measure persistence of structure, rather than dynamics
- Superconductivity in LBCO 1/8 is suppressed relative to similar compounds due to the formation of charge density waves.
- Measure low energy diffraction at Cu L edge (931 eV) to enhance contrast.
- Speckles disappear after annealing, but then re-emerge with correlations upon cooling.
- Only heating above a second phase transition removes correlations.







XPCS with free electron lasers

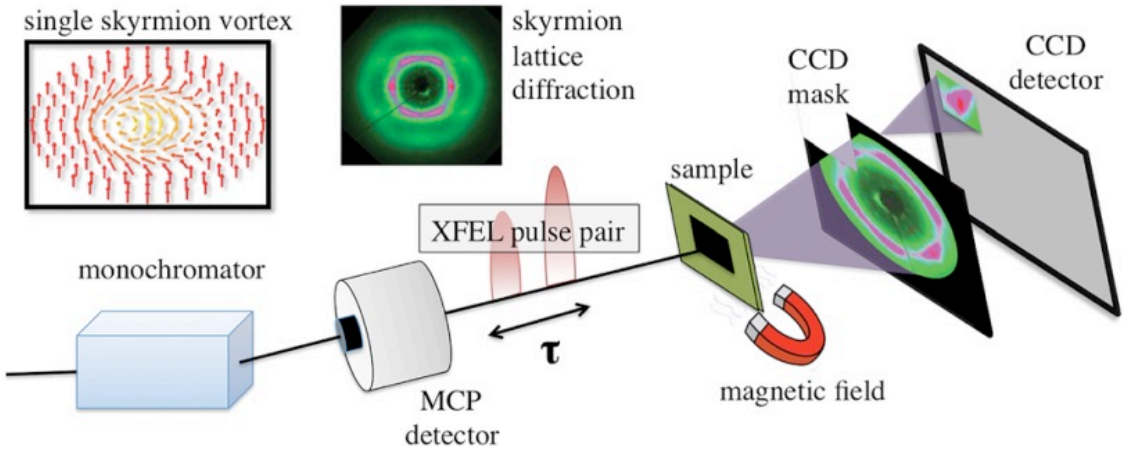


Alternately, a double pulse can be generated in the accelerator rather than splitting a single pulse.

Magnetic Skyrmion Dynamics

PRL Seaberg, et. al. 2017

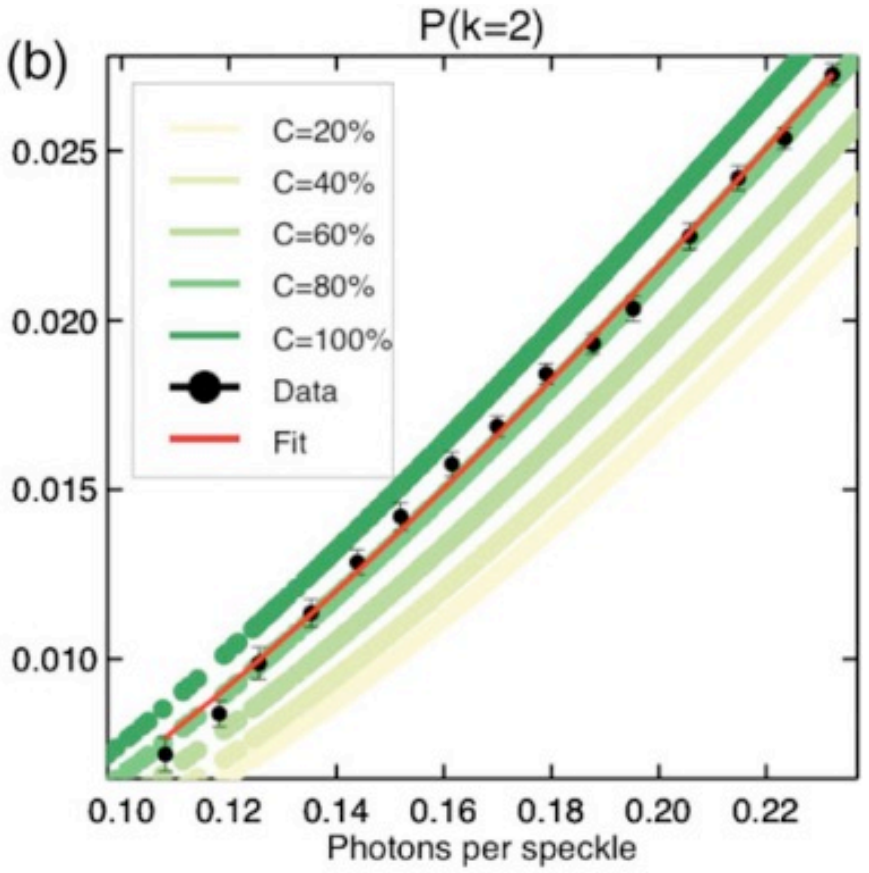
- Use resonant L-edge energy to gain sensitivity to magnetic structure.
- Use free electron laser pulses to measure with nanosecond time resolution
- Rather than split pulse, use pulse pair created by hitting electron source with two closely spaced laser pulses.



Use photon statistics to extract contrast

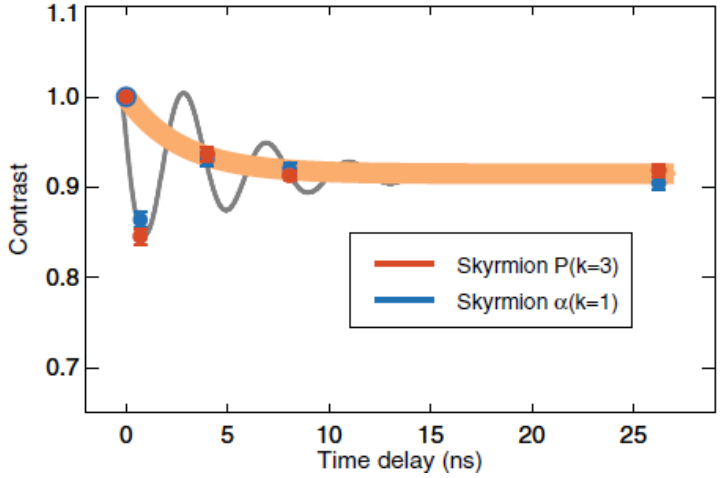
$$P_M(I) = \frac{M^M I \langle I \rangle^{M-1} \exp\left(-\frac{MI}{\langle I \rangle}\right)}{\Gamma(M)\langle I \rangle}$$

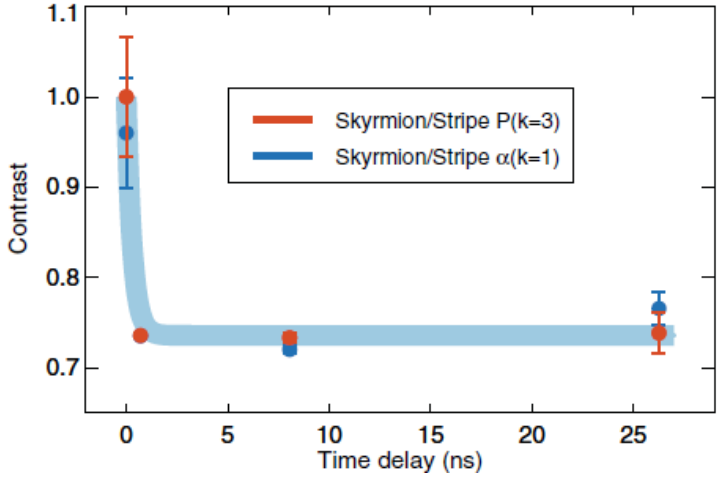
Probability to scatter 2 photons into one pixel as a function of the average counts/pixel and the contrast, C



Dynamics

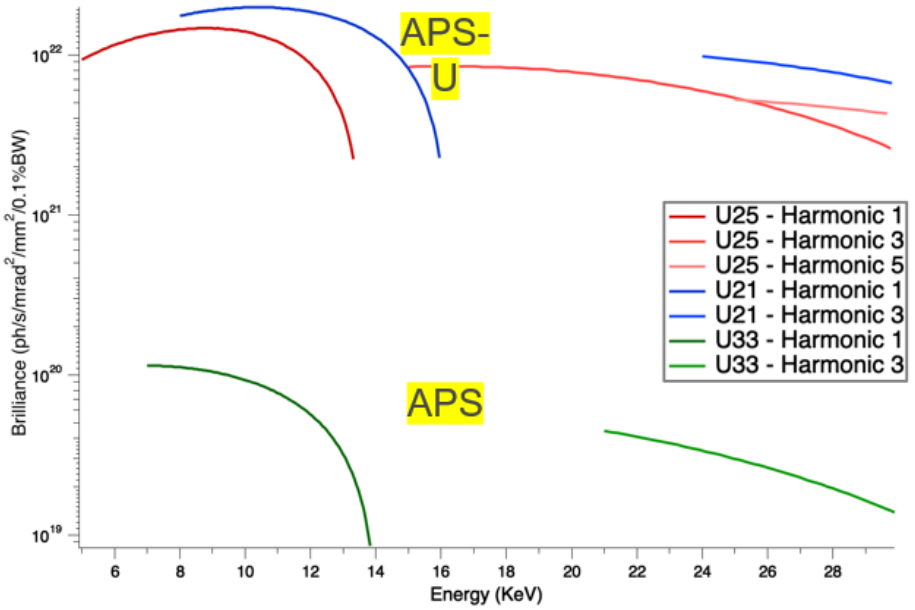
- Skyrmion phase dynamics speed up near the skyrmion/stripe phase boundary.
- Still unexplained dip at short times



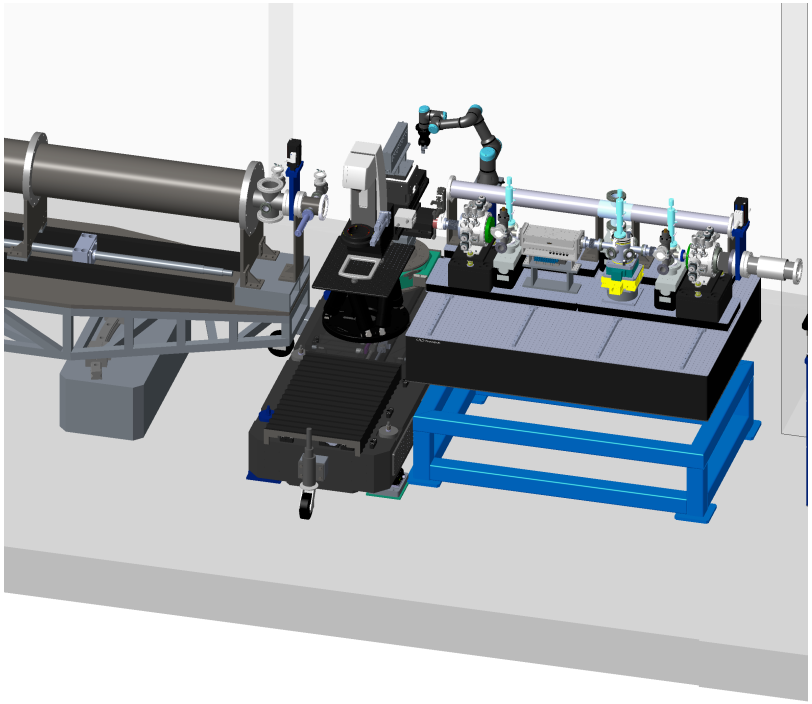


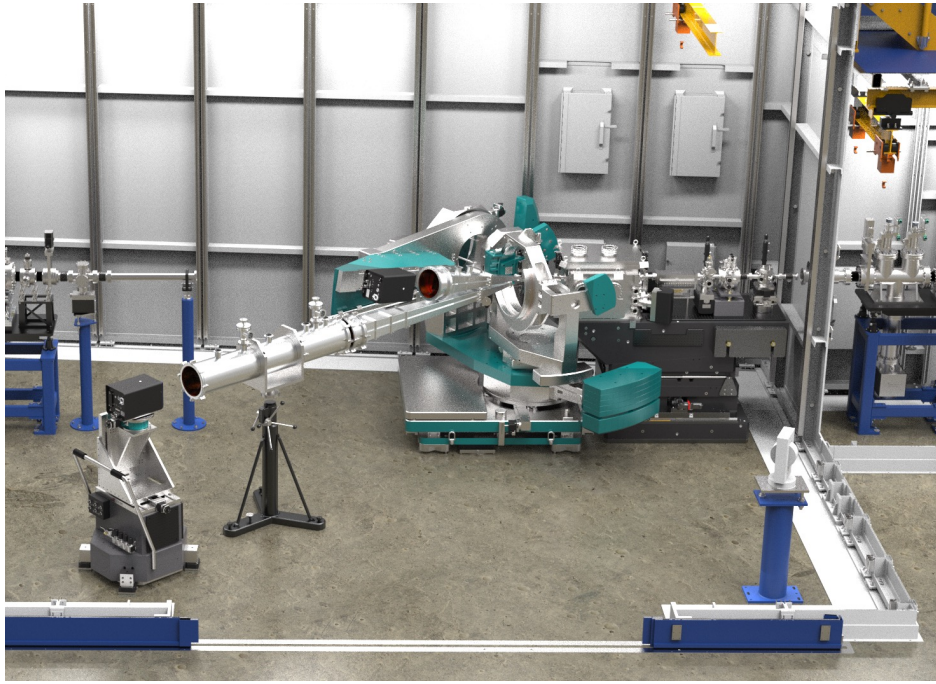
Upgraded APS

- 8-ID XPCS Beamlines : Suresh Narayanan, Eric Dufresne, Qingteng Zhang
- ~100x more brightness
- Or ~20x more flux but 100% coherent instead of 20%
- Or 500x less x-ray damage for the same SNR




10-ID





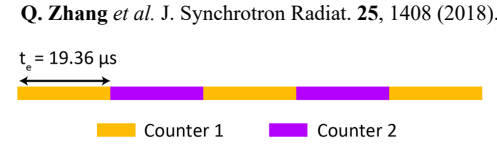
Single-Photon-Counting Detectors

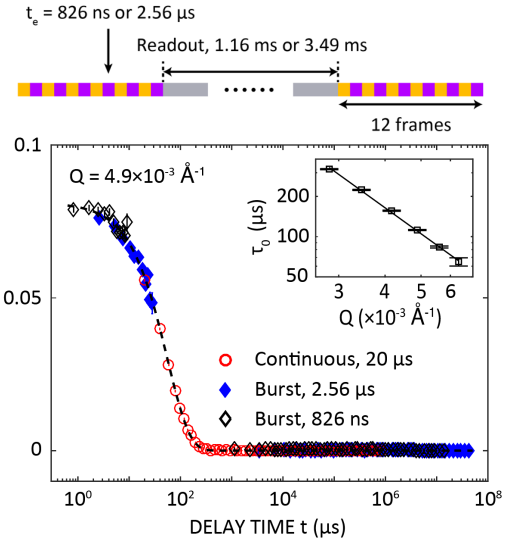
2048 (H) x 2048 (V) pixels, Pixel size = 75 μm

- Eiger 4M CdTe sensor for XPCS with max photon energy of 25 keV at 8-ID-I.
- Max frame rate = 4 kHz (250 μs).

2048 (H) x 1536 (V) pixels, Pixel size = 76 μm

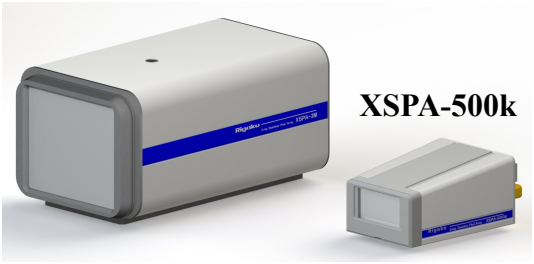
Q. Zhang *et al.* J. Synchrotron Radiat. **25**, 1408 (2018).





XSPA-3M

XSPA-500k



- Rigaku XSPA 3M (6x larger than 500k) Si sensor for XPCS with photon energy < 12 keV.
- Gapless coverage from 1 μs to 10^3 s by stitching different modes.

How to Calculate a Correlation Function

- We want to find $g_2(\tau) = \frac{\langle I(t+\tau)I(t)\rangle}{\langle I\rangle^2}$
- Each pixel is a sequence of N intensity measurements I_j
- $g_2(\tau = \mathrm{m}\Delta t) = \frac{1}{N-k}\frac{1}{\langle I\rangle^2}\sum_{j=1}^{N-k} I_j I_{j+k}$
- Interesting feature: The signal to noise ratio scales as I, rather than $\sqrt{I}$ since g_2 is second order in I
- Shortest accessible times scales as $\frac{1}{B^2}$, where B is the synchrotron brilliance.
- APS-U should see 10^4 faster times!

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