Northern Illinois University

Introduction to X-ray Photon Correlation Spectroscopy

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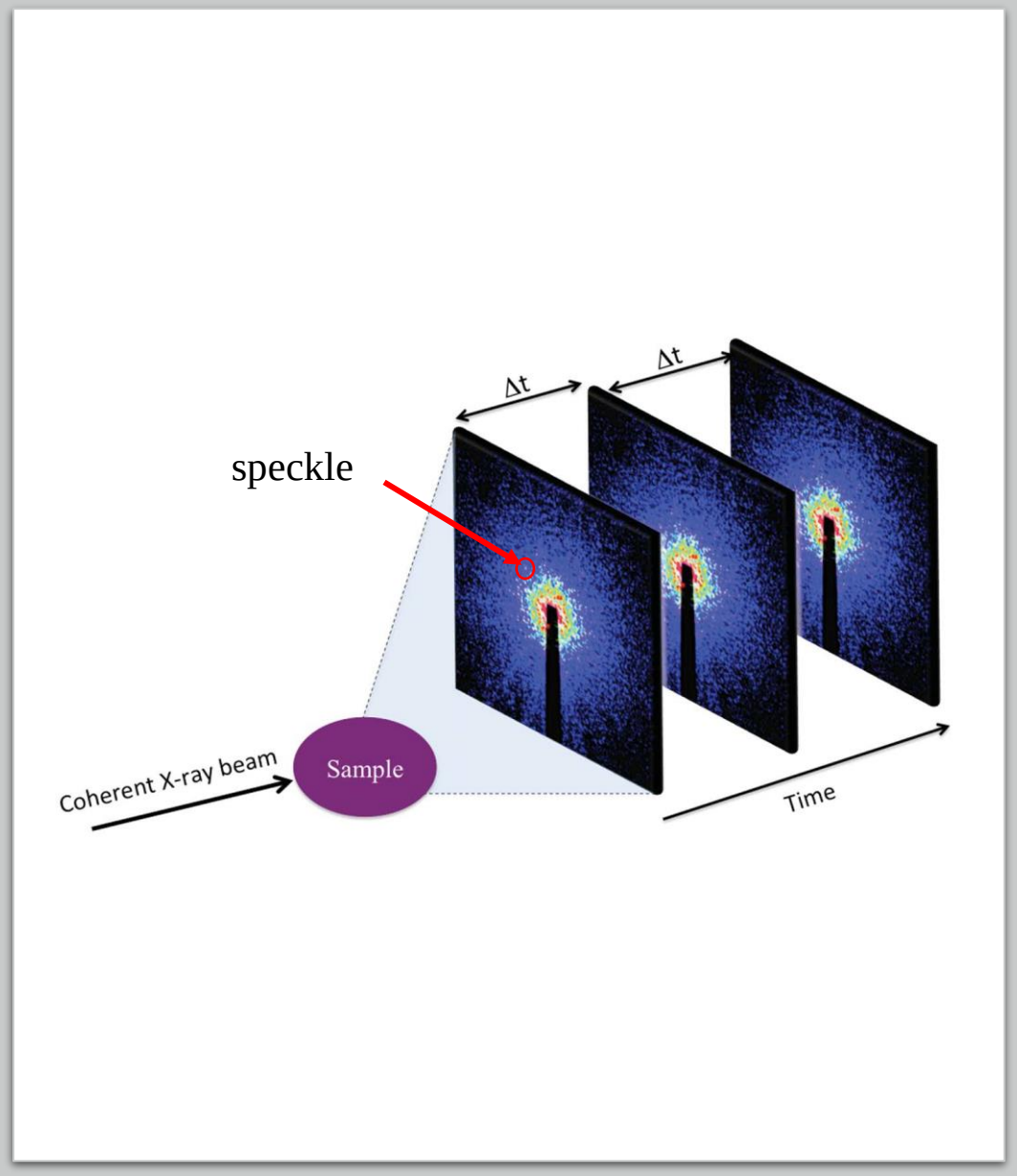
Outline

1. Overview of XPCS
2. Introduction to the 8-ID beamline and the NX school XPCS experiment
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.
- $g_2(q,\tau) = \langle I(q,t)I(q,t+\tau)\rangle / \langle I(q)\rangle^2$

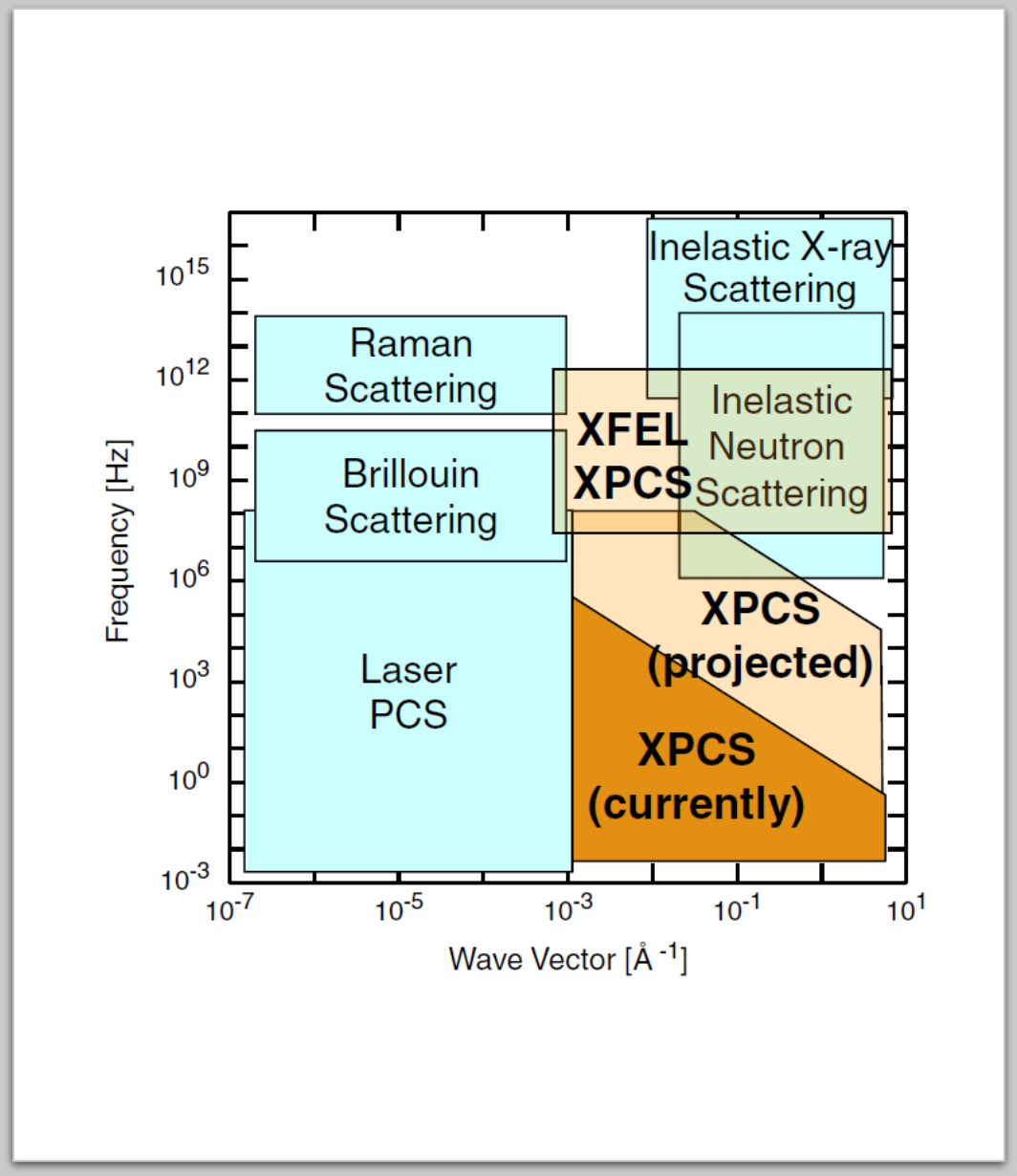
- This measured quantity is directly related to the dynamic structure factor of the material:
- $g_2(\vec{q},\tau) = 1 + \beta|f(\vec{q},\tau)|^2$
- $f(\vec{q},\tau) = S(\vec{q},\tau)/S(\vec{q},0)$
- $S(\vec{q},t) = \int e^{i\vec{q}\cdot\vec{r}} S(\vec{r},\tau)$
- $S(\vec{r},\tau) = \langle \rho(r,\tau),\rho(0,0)\rangle_{eq}$



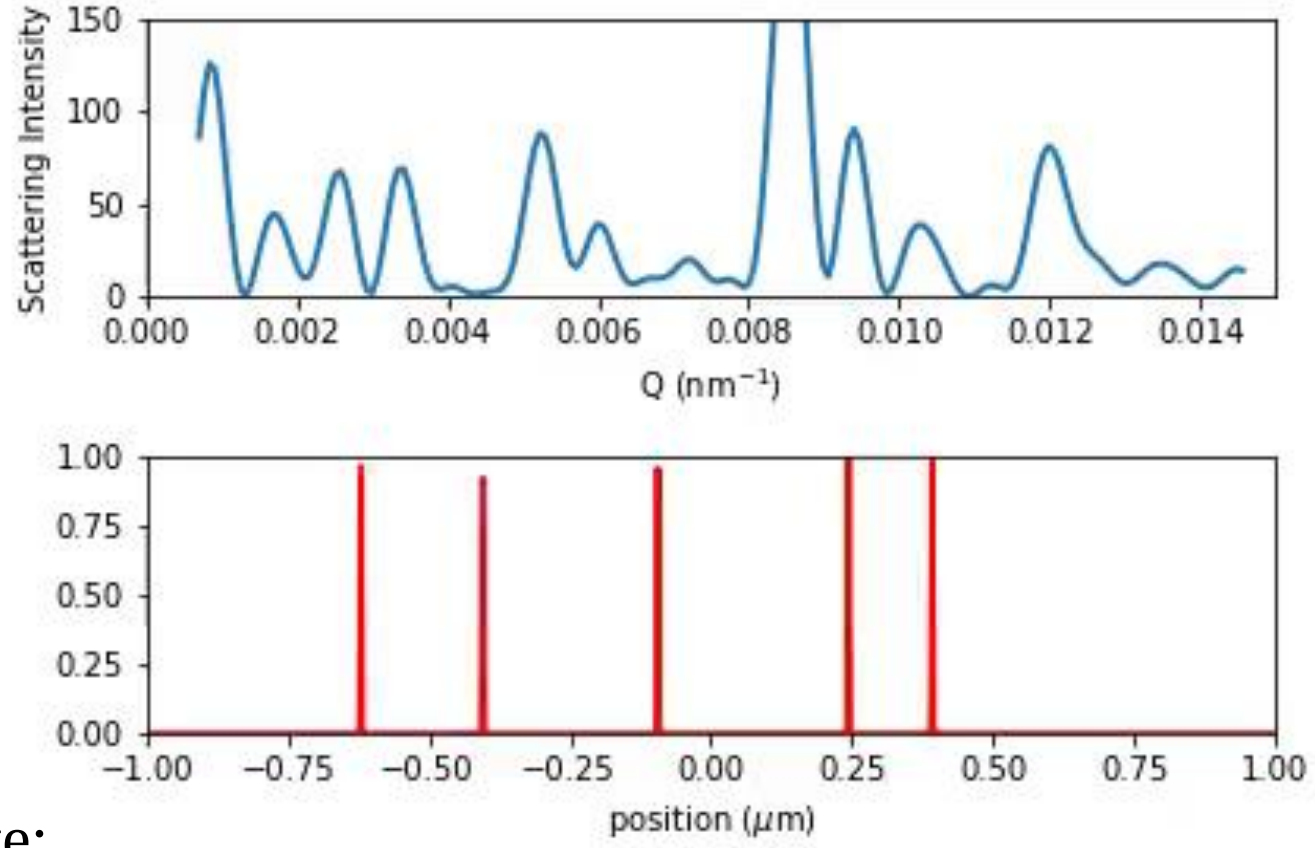
Uses of $f(q,\tau)$

- 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.



1-D simulated XPCS



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:

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

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

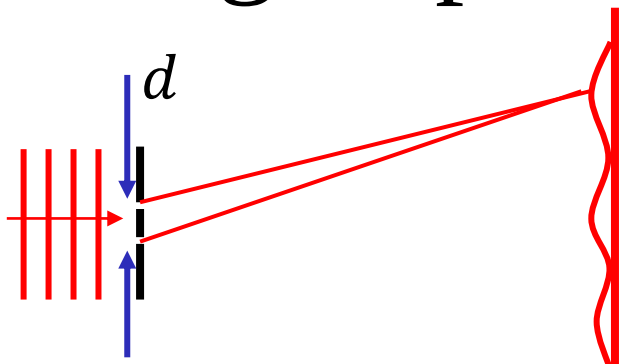
$$\vec{E} = \hat{\epsilon} E_0 e^{i\vec{k}\cdot\vec{r} - \omega t}.$$

- 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 in the near future, coherent x-ray scattering will become the norm rather than the exception.

Transverse coherence and angle spread

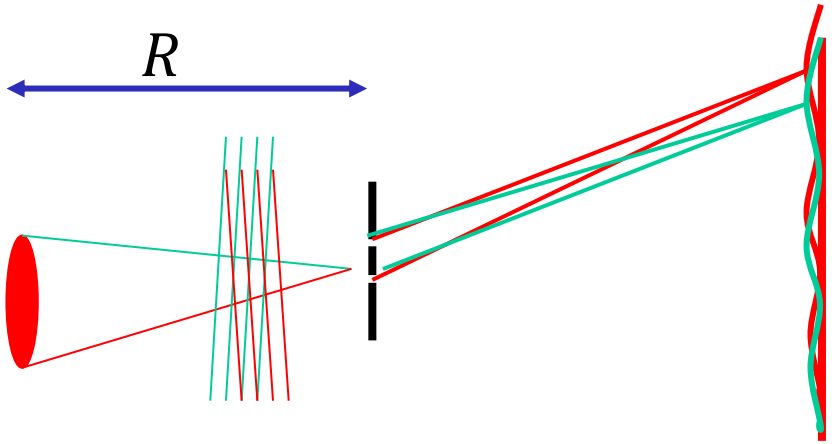
Ideal Young's double slit experiment

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



Real Young's double slit experiment

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

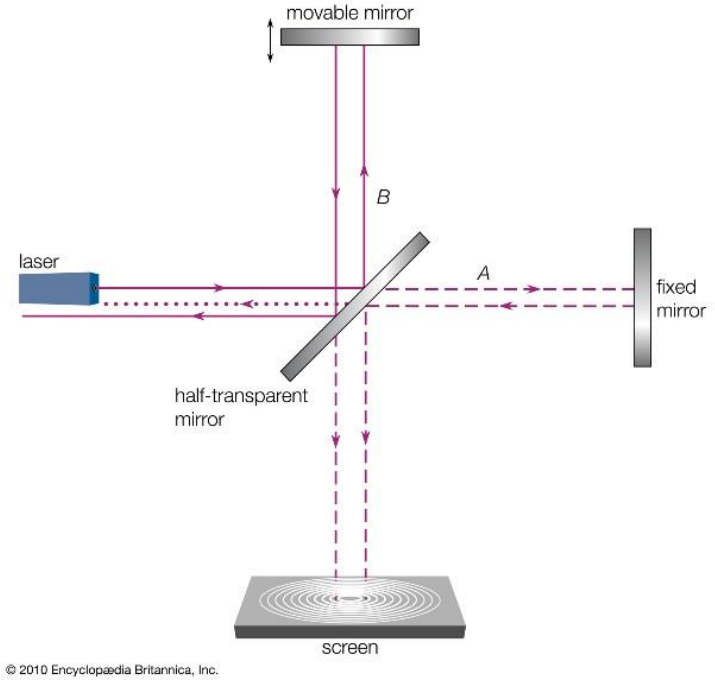


Longitudinal coherence length ξ, largest distance between slits which still yields interference pattern. For gaussian source distribution of width σ:

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

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?



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

Coherence at the APS (8-ID-I)

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

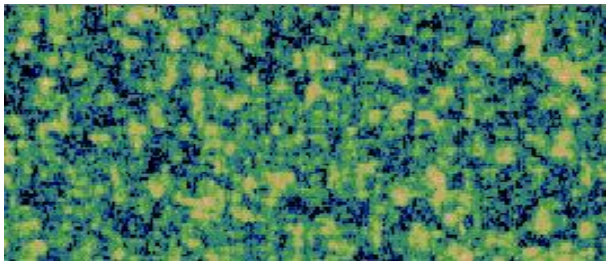
Horizontal coherence length $\xi_x = 14\mu m$

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

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

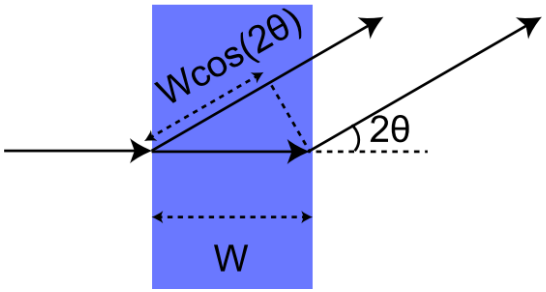
Typical APS SAXS beamline has 10^{12} photons/s on sample

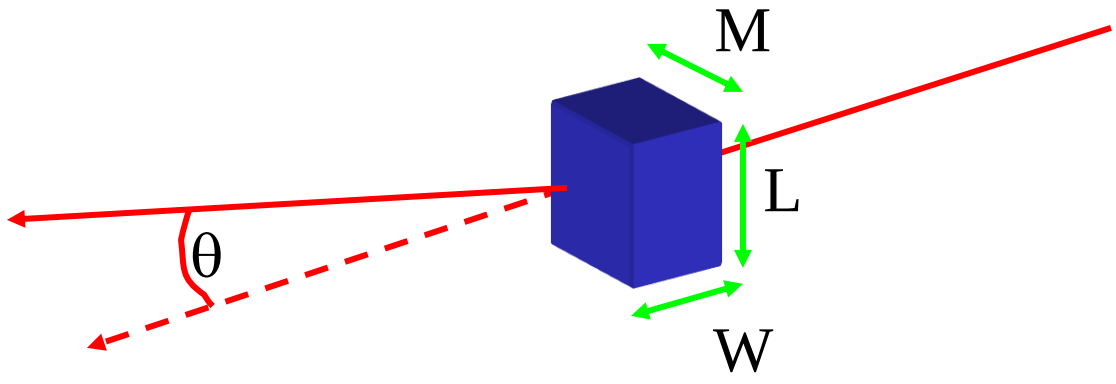
Speckle Contrast



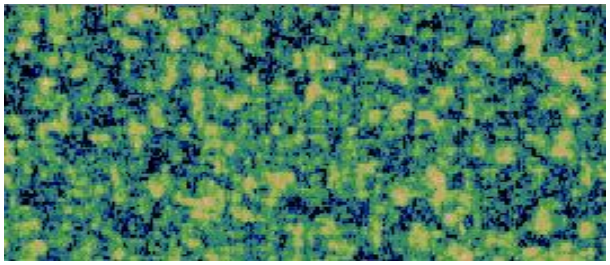
The contrast can have a maximum value of 1 (speckle intensity varies from 0, to 2x average), or a minimum of 0 (no speckle)

It is given by the ratio of the scattering volume to the coherence volume $\left(\frac{\Lambda\xi_x\xi_y}{MLW}\right)\frac{1}{2\sin^2\theta}$





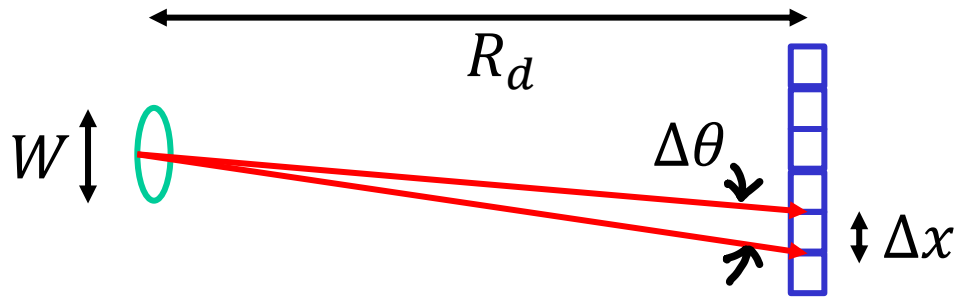
Speckle Size



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

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

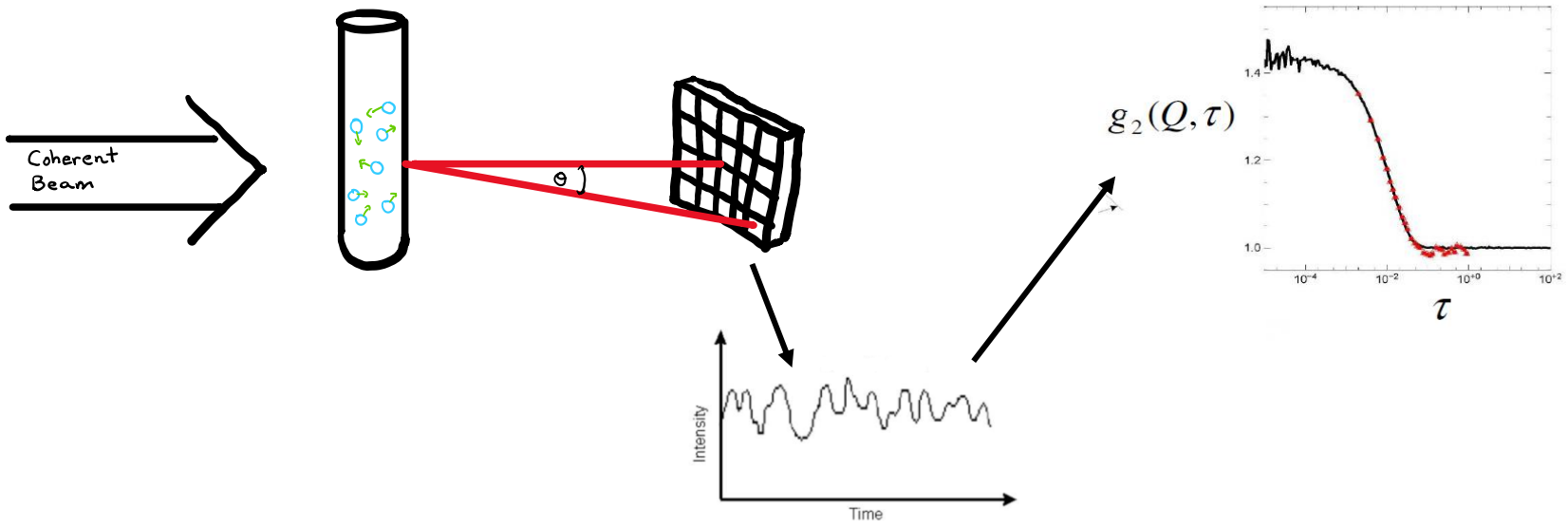
Typically, a few tens of microns



If detector cannot resolve speckles, contrast is reduced.

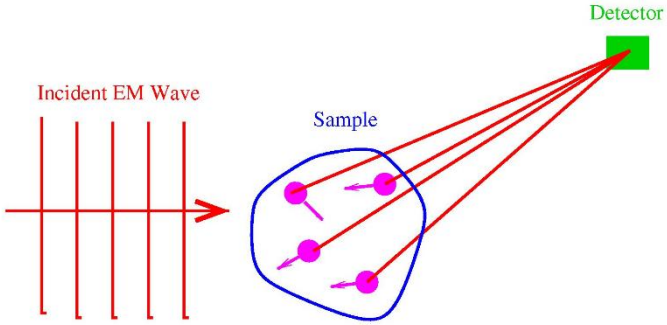
Sometimes the incident x-ray beam is focused onto the sample to reduce the spot size, leading to bigger speckles which better match the camera

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: $D = k_B T / 6\pi\eta r$

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

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.

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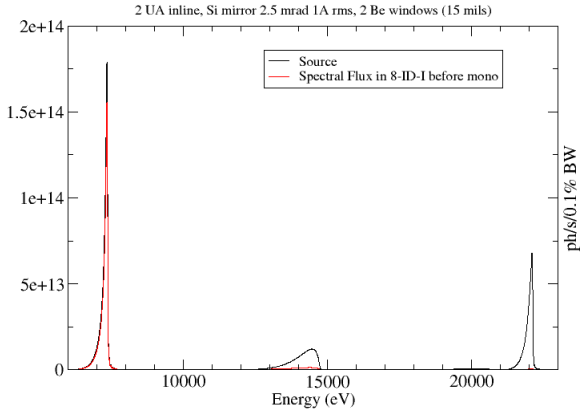
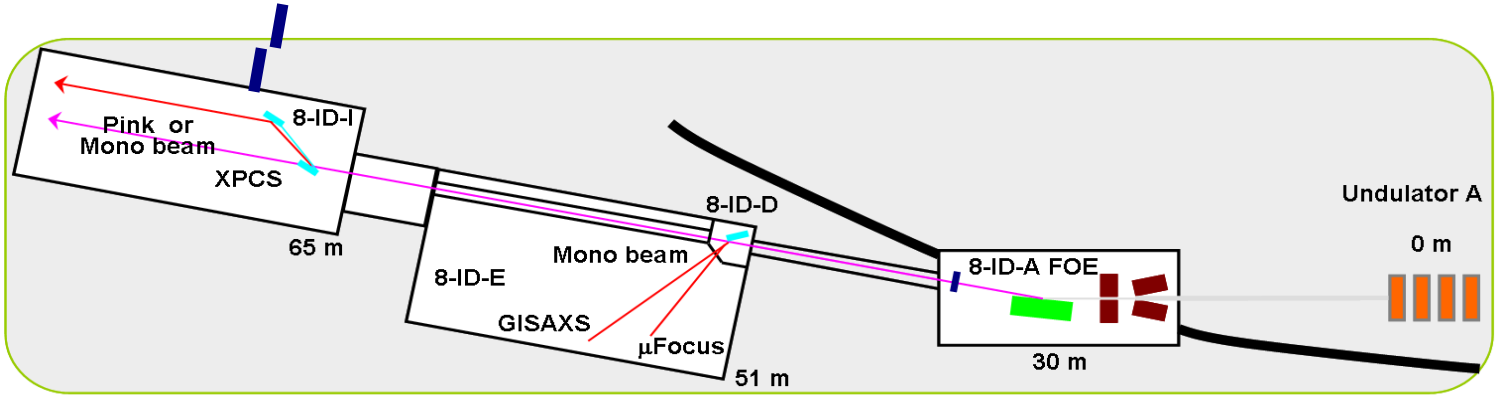
2. (*) Introduction to the 8-ID beamline and the NX school XPCS experiment
3. XPCS applications

Part II: Introduction to 8-ID and the NX-School Experiment

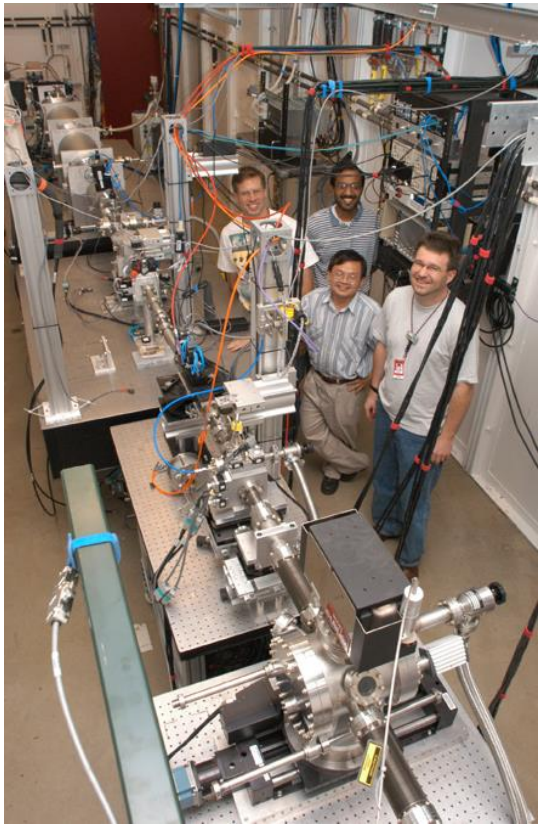


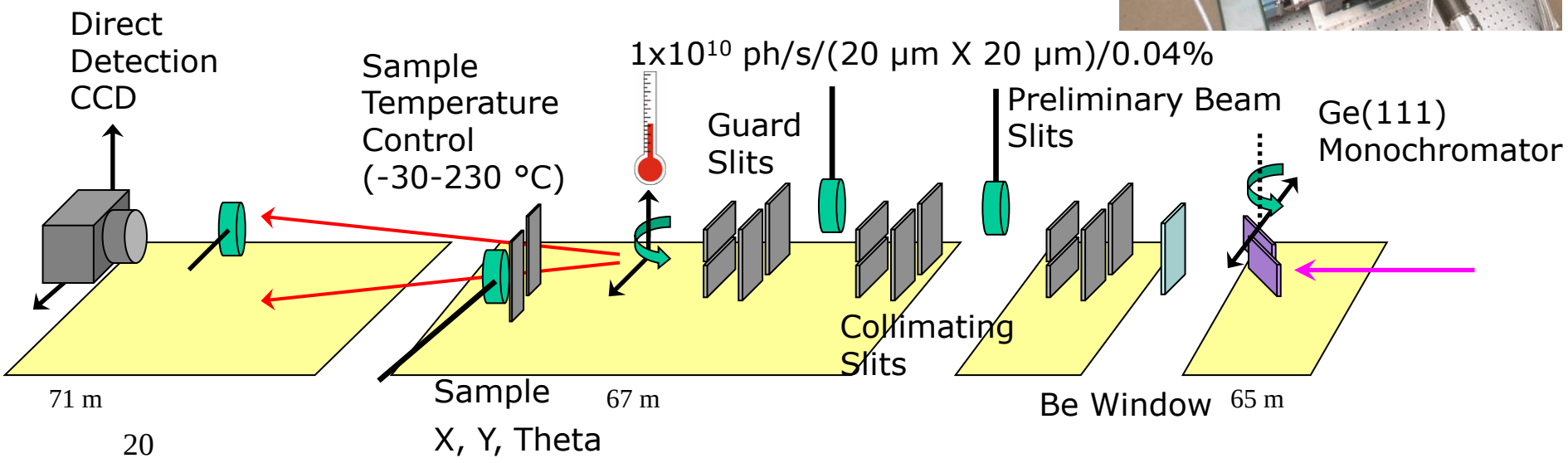
- How is XPCS realized at 8-ID?
  - Simple undulator beamline → improved stability
  - Minimal beam size – only central cone into optics enclosure
  - 2 phased undulator A using the full straight section



8-ID-I Coherent SAXS

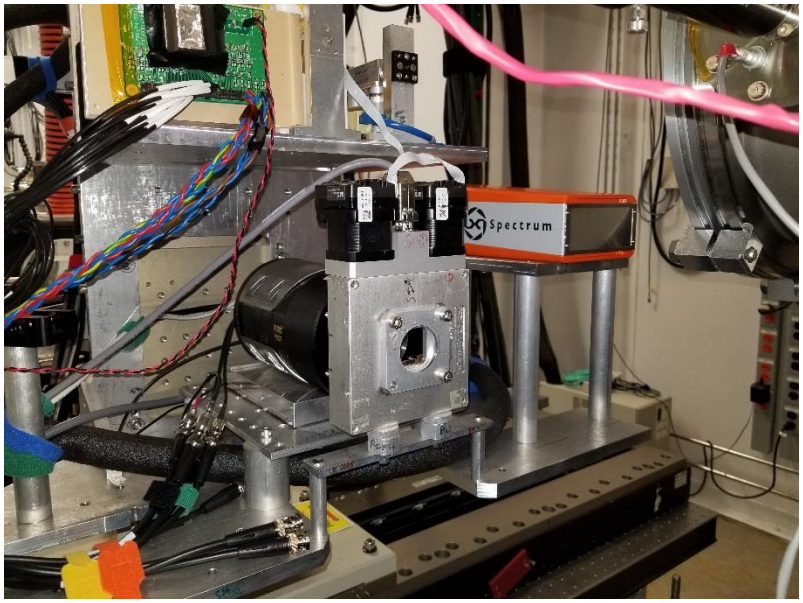
- 8-ID-I Station Features
  - Ge(111) monochromator
  - Polished Be window
  - In-vacuum slits- preliminary, collimating and guard slits (X2)
  - In-vacuum sample “oven”
  - In-vacuum alignment detectors and beam stops
  - Direct-detection CCD, and Pixel-Array Detectors





XPCS Area Detectors Requirements

- High resolution to resolve speckle.
- Large area.
- Single photon counting.
- Fast frame rate.
- High efficiency.



Rigaku pixel array detector

500k 75 $\mu m \times 75\ \mu m$ pixels

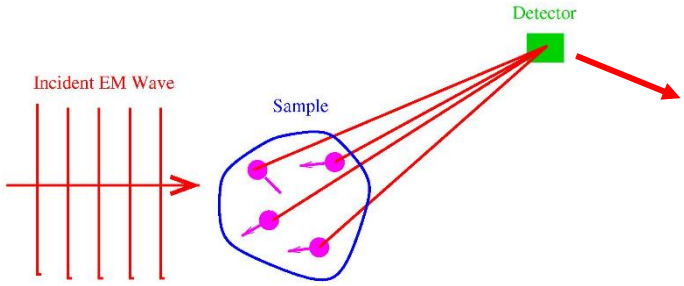
50 kHz readout

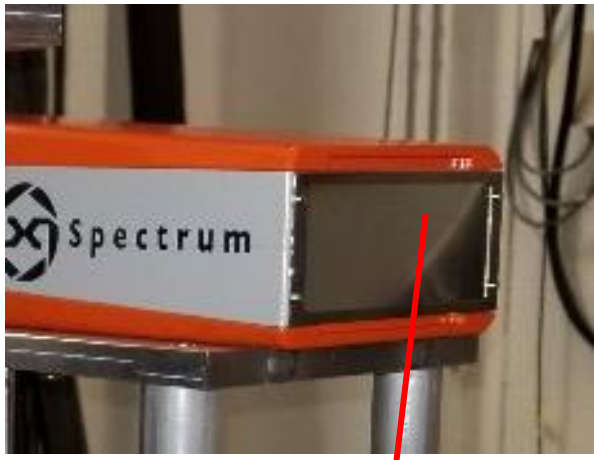
single photon counting

close to 100% efficiency at 11 keV

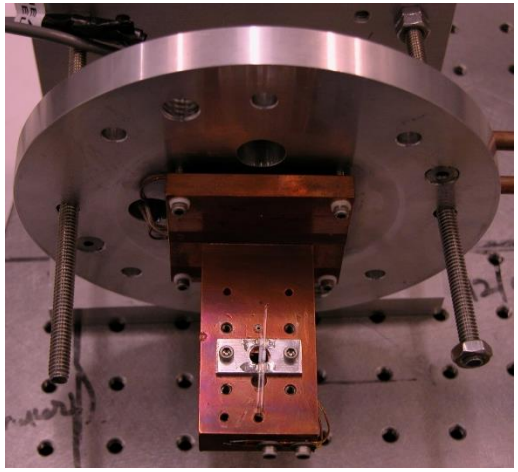
Other detectors with smaller pixels but slower readout

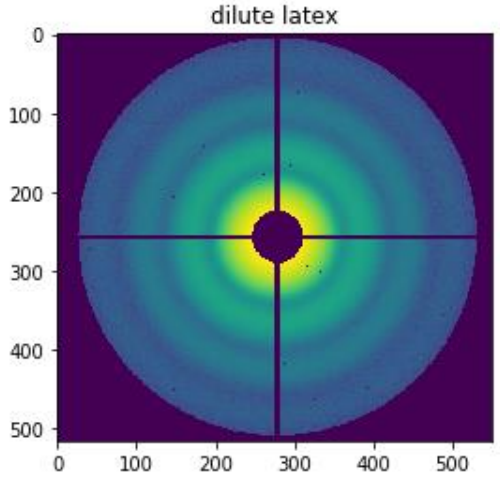
The NX School Experiment



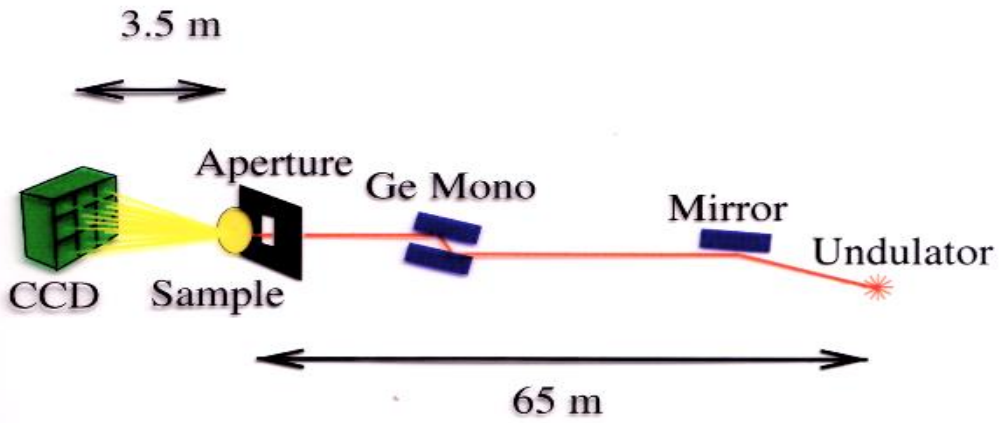


- Look at XPCS from colloidal suspensions of 67 nm radius latex beads in glycerol
- Compare XPCS for dilute and concentrated colloids.
- 2 concentrations in glycerol (to slow dynamics) in 2 glass capillaries on separate mounting plates
- ≈ 2% vol. frac.
- ≈ 40% vol. frac.
- PRL Lurio, 2000





Static Scattering



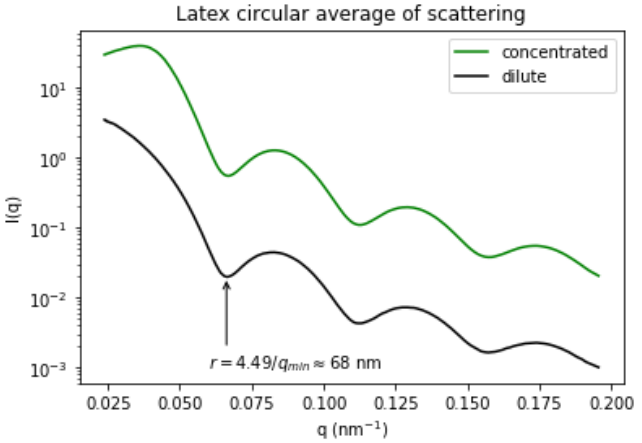
- Sphere form factor $x = qr$

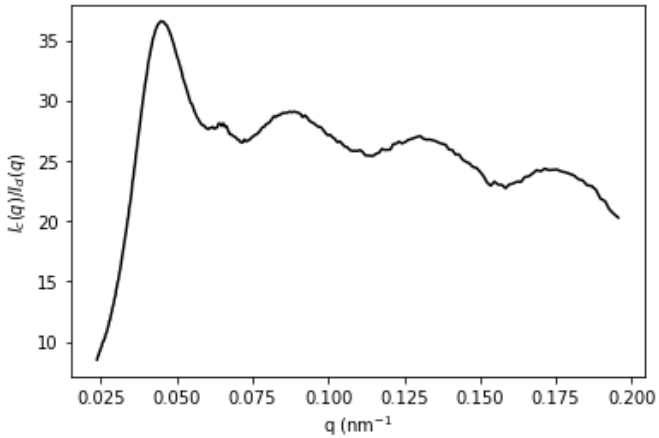
$$F(Q) = \left[3\frac{\sin x - x\cos x}{x^3}\right]^2$$

- At high concentration, scattering modified by interparticle correlations:

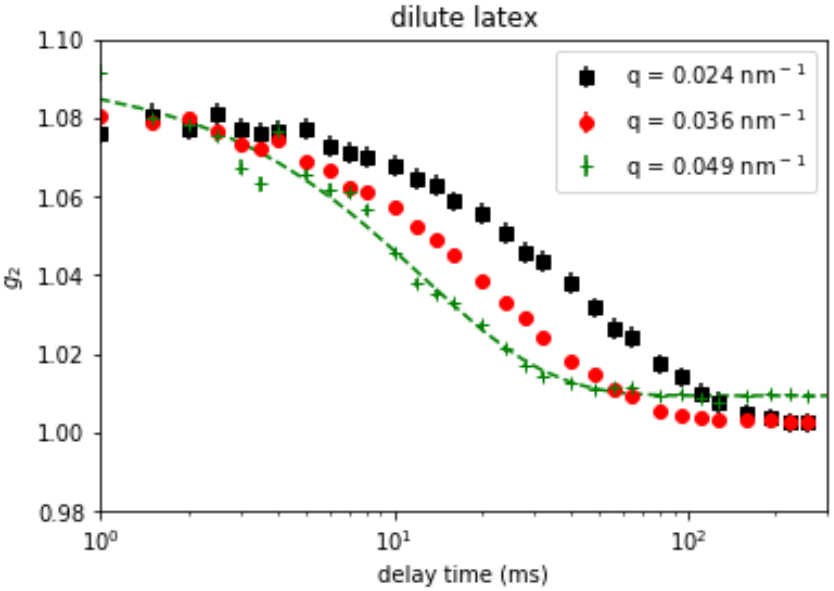
$$I(Q) \propto F(Q)S\,(Q)$$

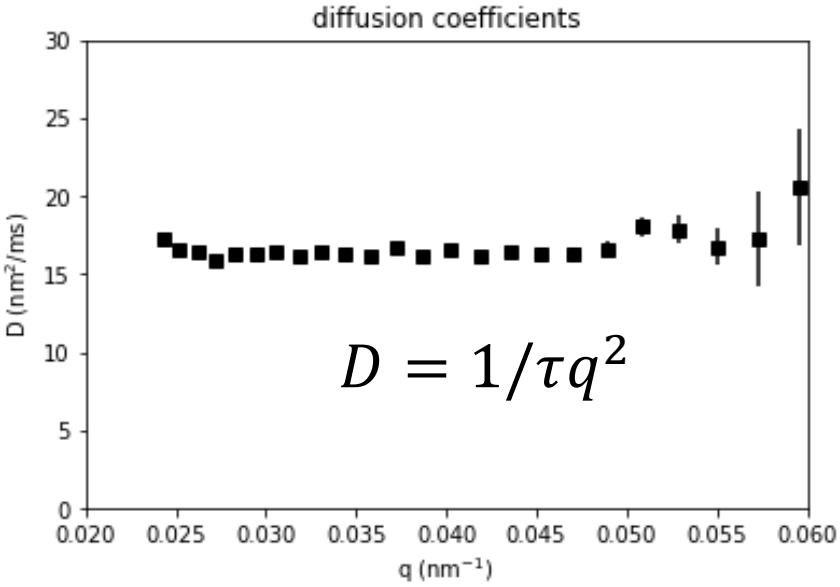
$$S(Q) \approx \left(\frac{\phi_{dil}}{\phi_{conc}}\right) \times I_{conc}/I_{dil}$$

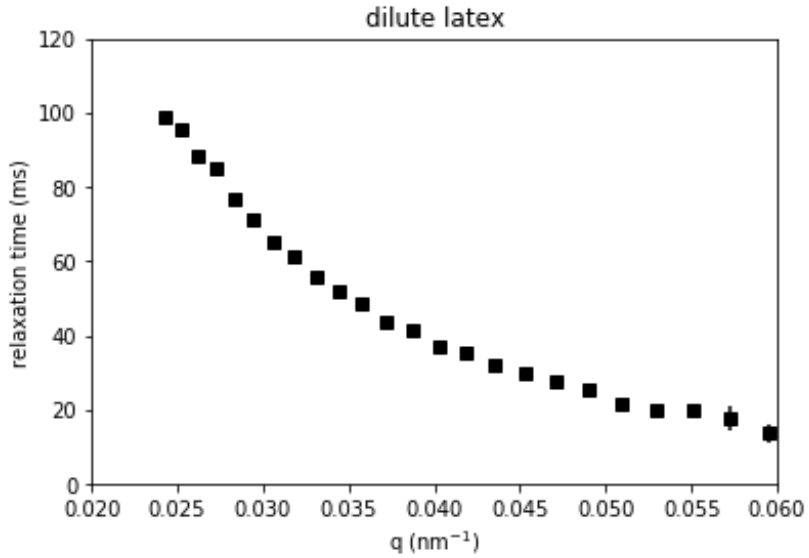




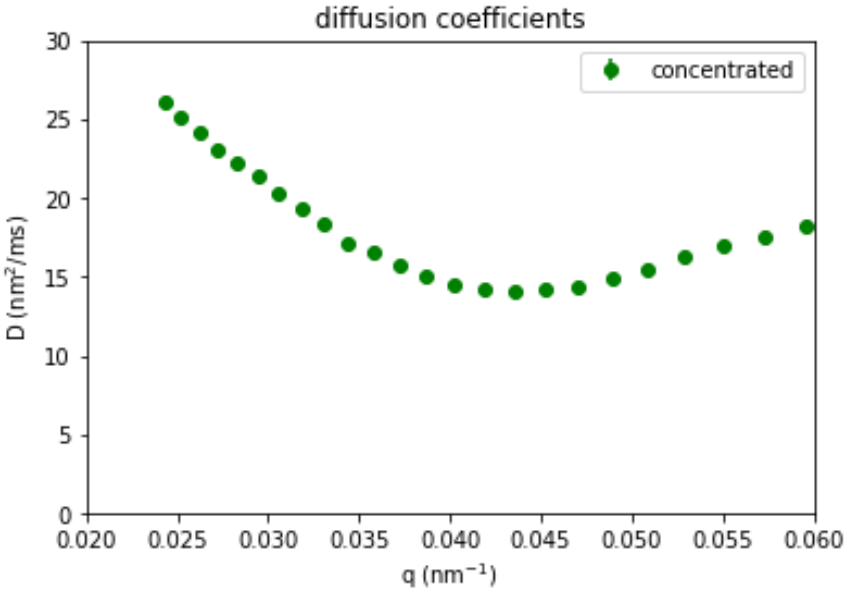
Dynamics Results: Dilute

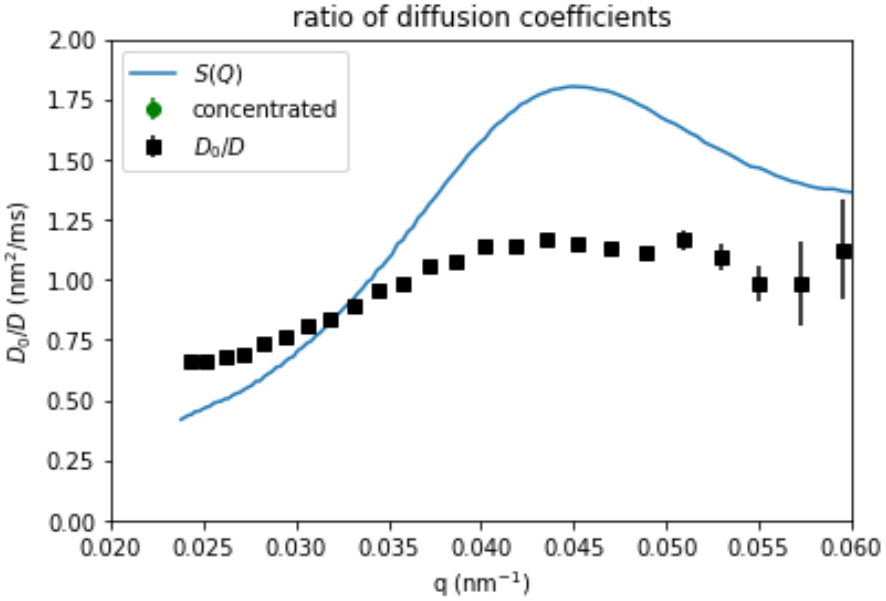






Dynamics Results: Concentrated





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

de Gennes narrowing assumes particle velocities are uncorrelated. In fact, hydrodynamic flow create significant velocity correlations. This reduces the size of the effect

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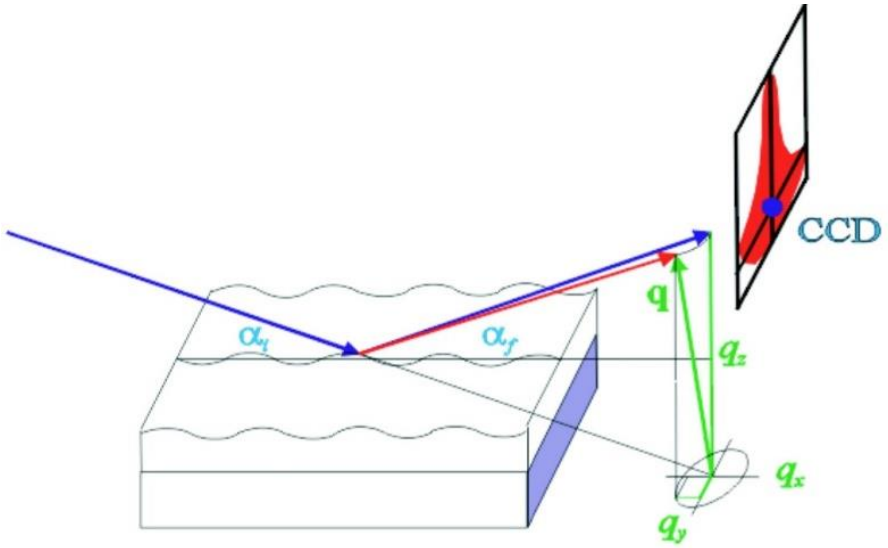
Dynamics of Polymer Surfaces

PRL Kim 2003, PRE Jiang 2006, PRL Jiang 2007, PRL Jiang 2008



- Polystyrene films on Si wafers are highly viscous and their g_2's show exponential decay
- Dynamics due to overdamped surface capillary wave modes.

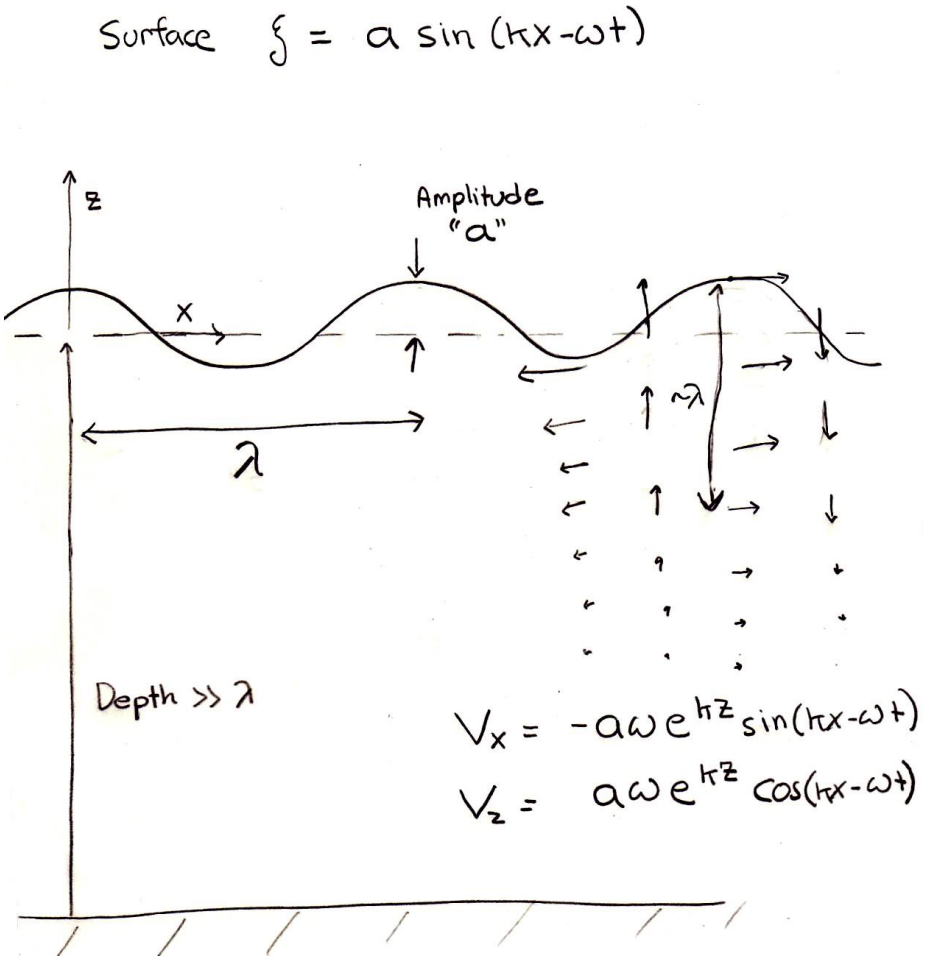
Dynamics at a Simple Liquid Interface: Thermally Driven Capillary Waves

Static Structure from Interfacial Energy

$$H = \int d^2\vec{r}\left(\frac{\gamma\Delta h^2}{2} + g\rho h^2/2\right)$$

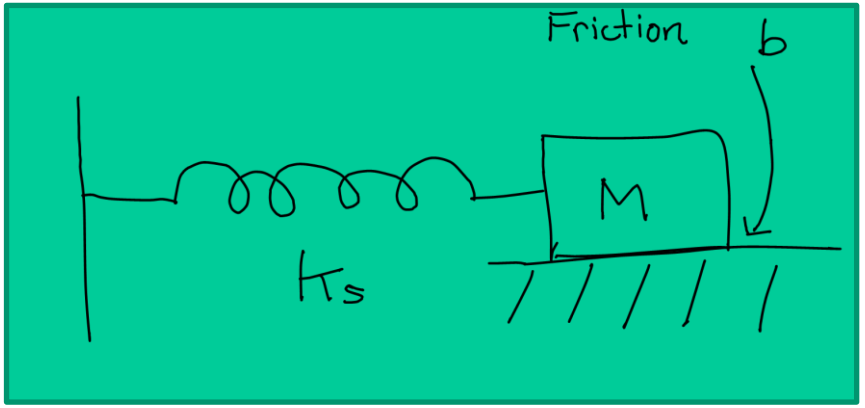
Dynamics from Linearized Navier-Stokes Equation

$$\rho\frac{d\vec{v}}{dt} = -\vec{\nabla}P + \eta\nabla^2\vec{v}$$



Calculation of Time Constants

J. Jäckle, J. Phys.: Condens. Matter 10 (1998) 7121.



For a film of thickness h

$$\tau = \frac{k\gamma[-2kh + \sinh(2kh)]}{2\eta[1 + 2h^2k^2 + \cosh(2hk)]}$$

$$\tau \to \frac{2\eta}{\gamma k}\left[\frac{3}{2(kh)^3}\right] \sim \frac{1}{k^4} \text{ for } kh \to 0$$

$$\tau \to \frac{2\eta}{\gamma k} \sim \frac{1}{k} \text{ for kh} \to \infty$$

Overdamped $\tau \to b/k_s$

For deep waves, use dimensional analysis

only dimension is wavevector, k

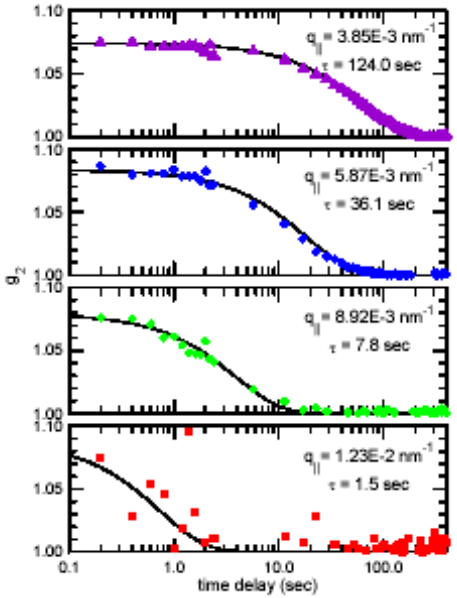
$= 2\pi/\lambda$

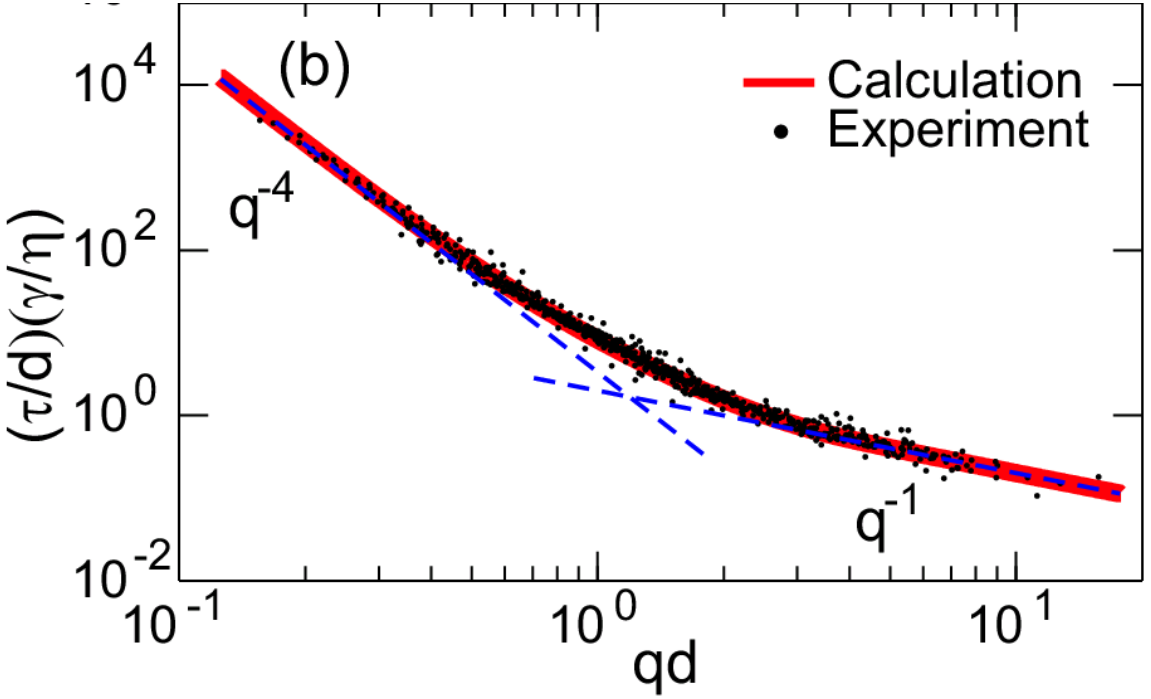
$k_s \to \gamma k^2$

$b \to \eta k$

Expect $\tau \sim \eta/k\gamma$

$$\tau = \frac{k\gamma\left[-2kh + \sinh\left(2kh\right)\right]}{2\eta\left[1 + 2h^2k^2 + \cosh\left(2hk\right)\right]}$$





From Jiang et. al. PRL, 246104, 2008

Atomic jumps in a binary alloy

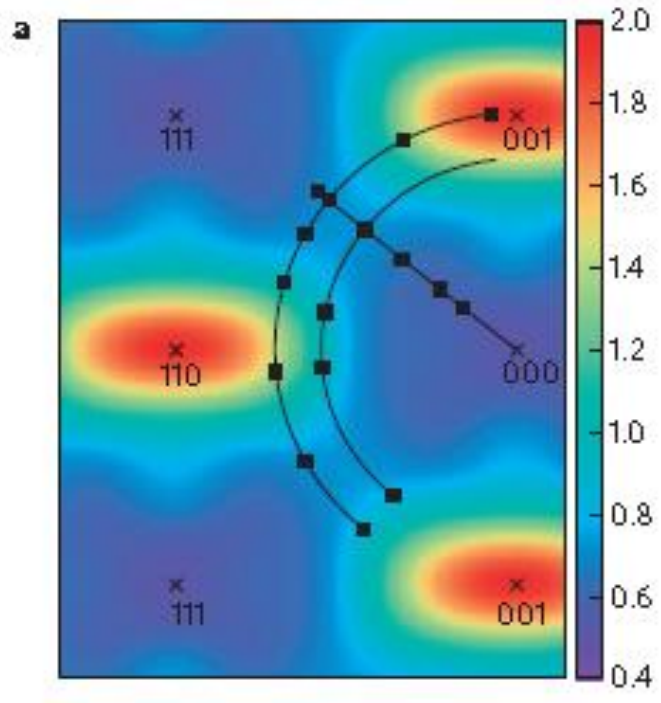
M. Leitner, B. Sepiol, L.-M. Stadler, B. Pfau, and G. Vogl, Nature Materials **8, 717-20 (2009).**

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

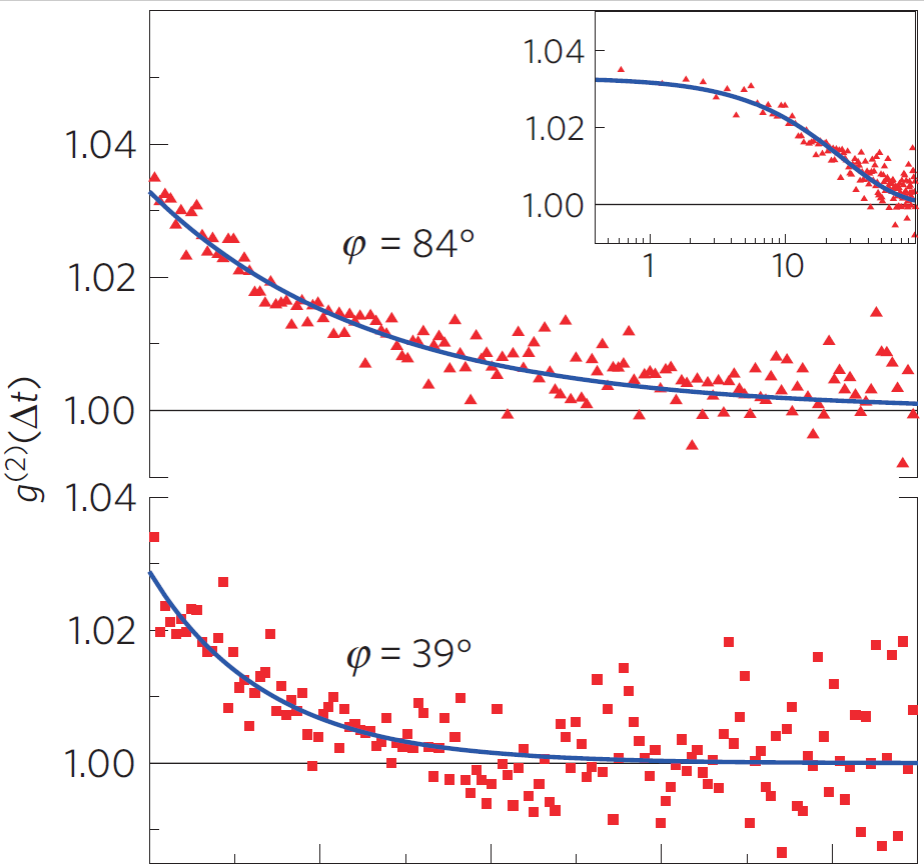
Measure XPCS from thermal diffuse scattering between Bragg peaks.

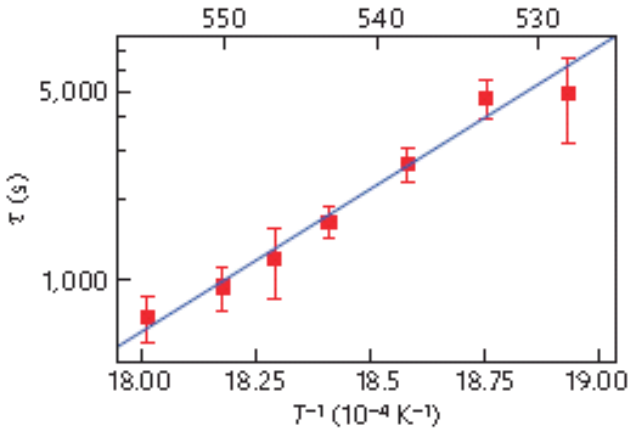
Dynamics corresponds to Cu-Au place exchange.

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.

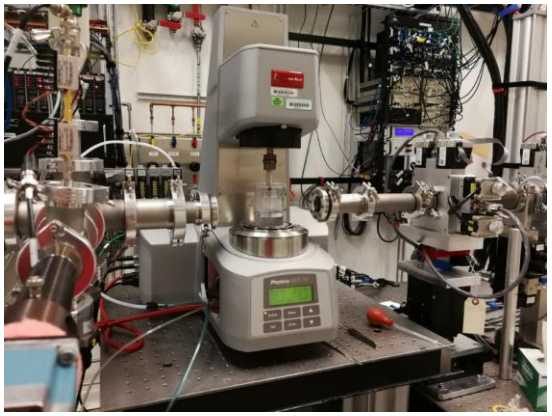
Significance

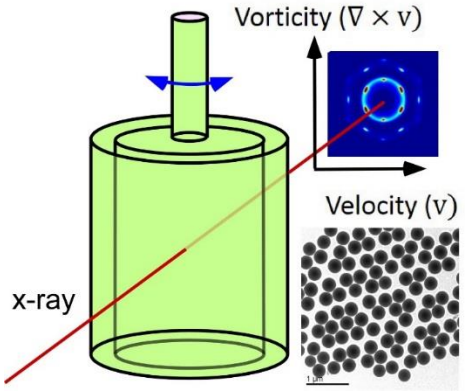
- XPCS doesn’t only apply to large molecules or colloidal particles, but can be used for individual atoms.
- Dynamics also occurs in crystals due to place exchange.
- This is cutting edge XPCS, need strong scatterer (gold) and very slow dynamics. With the APSU these sorts of experiments could become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

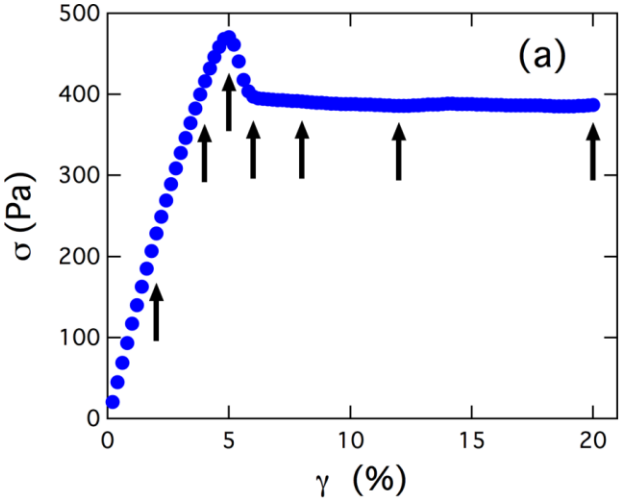
Stress relaxation in colloidal glasses

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 return to a solid after force removed.

What are the dynamics of this transition?

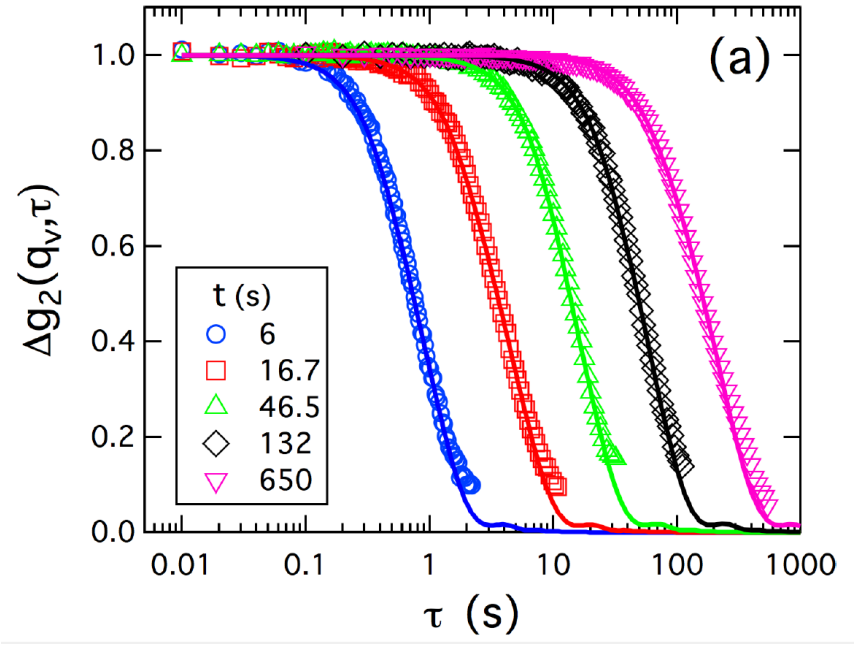
Relaxation along flow direction

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

$$\Delta g_2(\vec{q},\tau) = \mathrm{sinc}\left(\frac{q_v v_0 \tau}{2}\right)$$

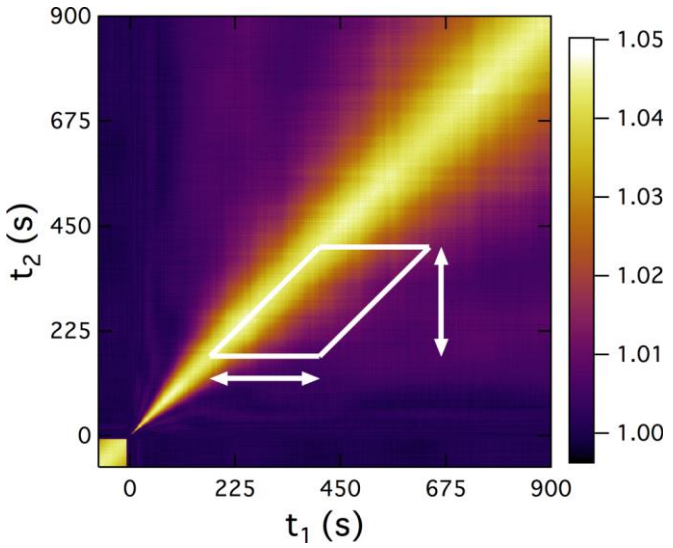
Here Δg_2 has the constant subtracted and is normalized by contrast.



What about dynamics along vorticity direction?

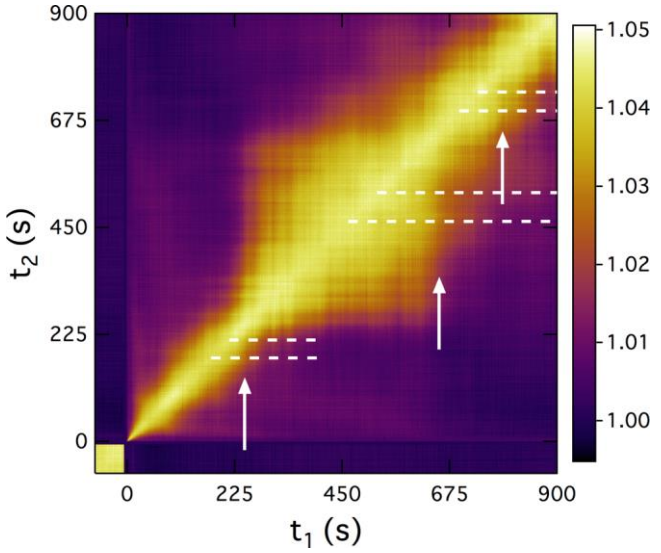
- Dynamics are complex and depend on both waiting time and time delay.
- Can't analyze with a simple g_2 function.
- Instead define a two-time correlation function
- $C(\vec{q}, t_1, t_2) = \frac{\langle I(\vec{q},t_1) I(\vec{q},t_2)\rangle}{\langle I(\vec{q},t_1)\rangle\langle I(\vec{q},t_2)\rangle}$

Two-time correlation functions



Velocity direction

Dynamics are regular and slow down with overall time.



Vorticity direction

Correlations punctuated by decorrelation events. Indicates avalanche type dynamics.

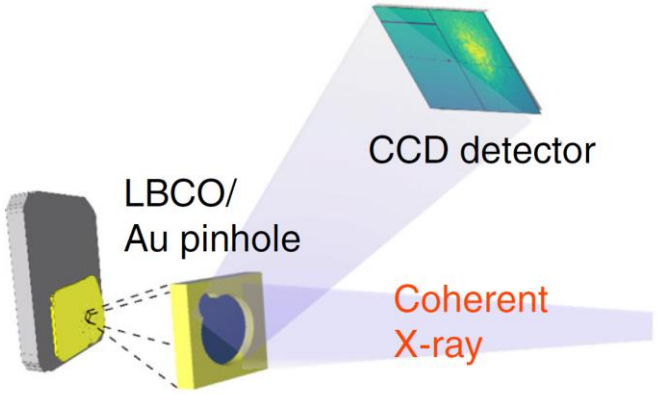
Some observations

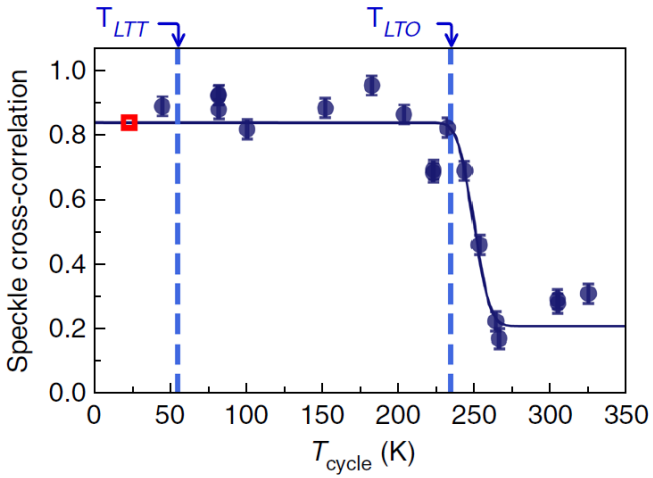
- XPCS used to study a non-equilibrium system.
- In flow direction, observe quasi-equilibrium behavior around evolving dynamics
- Directional dependence of $\vec{q}$ used to distinguish very different dynamics in two directions.
- Two-time correlation functions can be used to identify avalanche like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

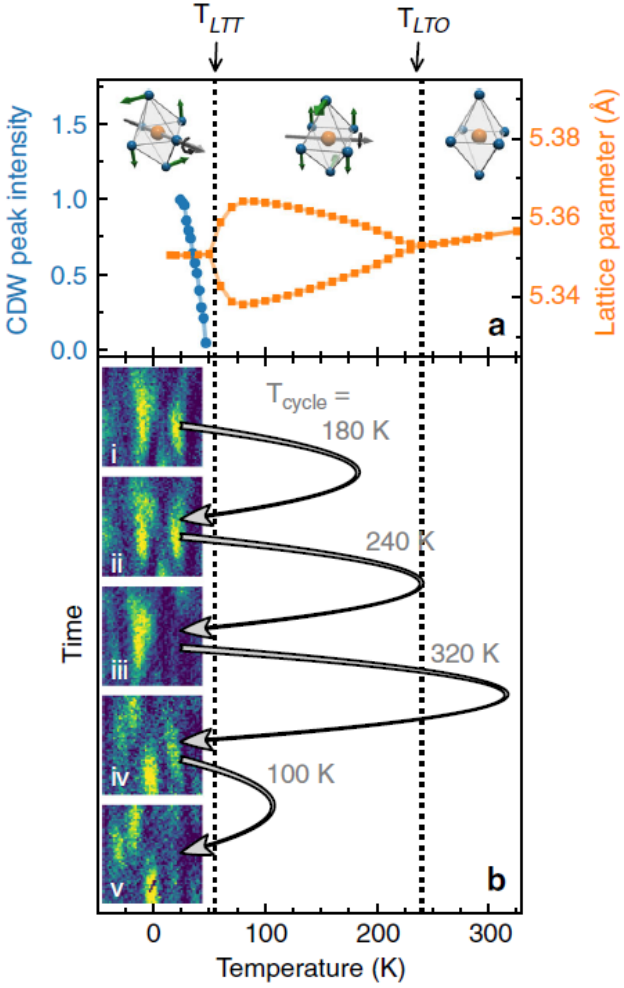
Speckle in Charge Density Waves

(Nature Comm: Chen et. al. 2019)

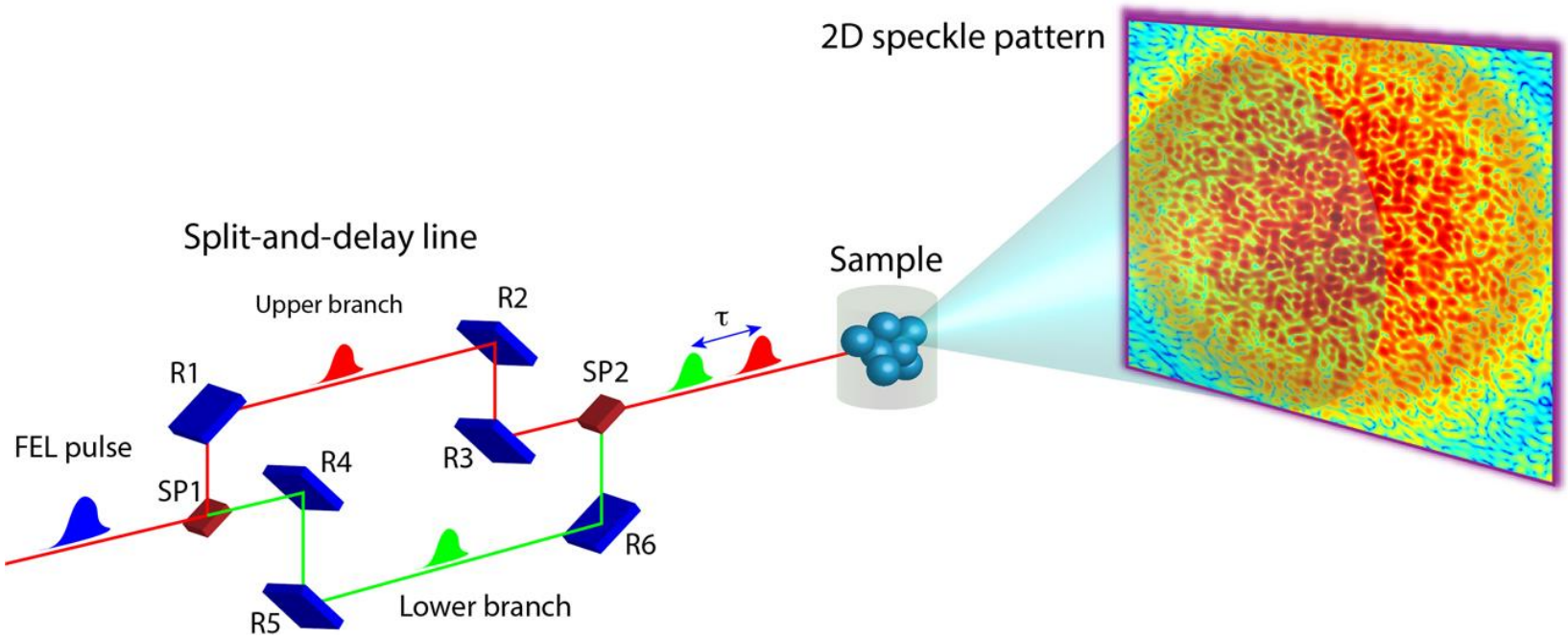
- Unique use of speckle to measure persistence of structure, rather than dynamics
- Superconductivity in LBCO 1/8 is suppressed relative to similar compounds due to the formation of charge density waves.
- Measure low energy diffraction at Cu L edge (931 eV) to enhance contrast.
- Speckles disappear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







XPCS with free electron lasers

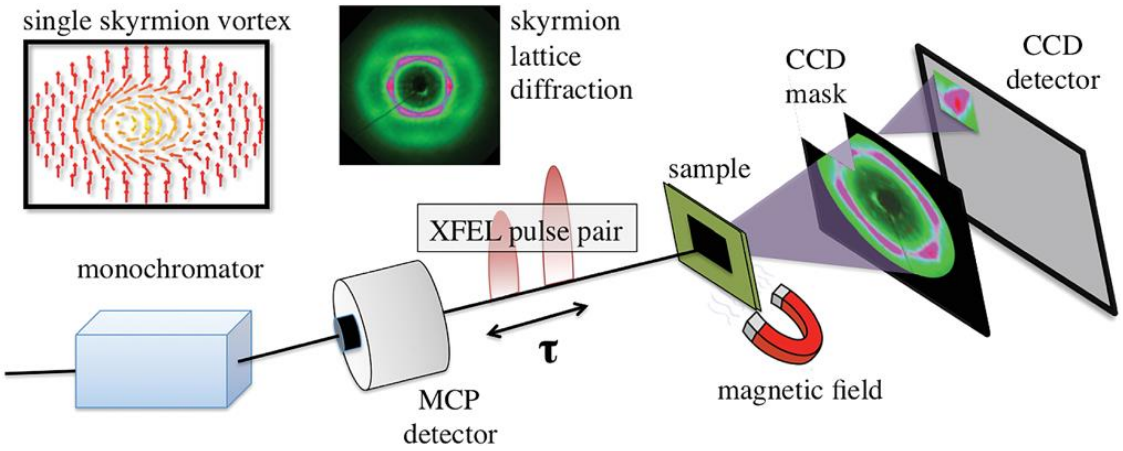


Alternately, a double pulse can be generated in the accelerator rather than splitting a single pulse.

Magnetic Skyrmion Dynamics

PRL Seaberg, et. al. 2017

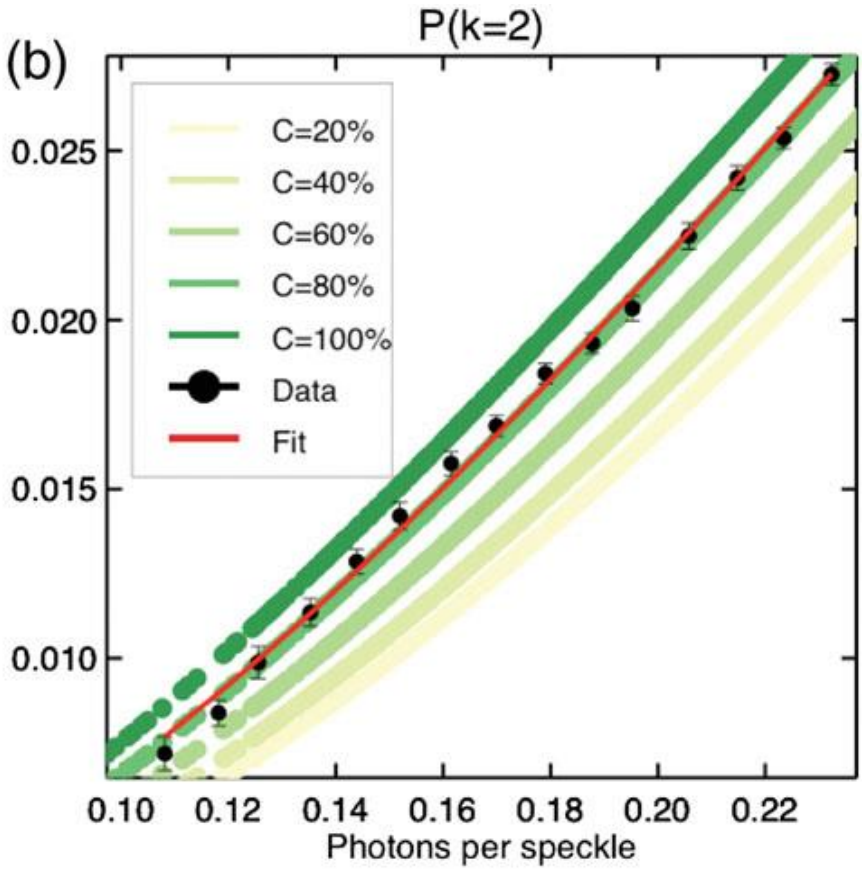
- Use resonant L-edge energy to gain sensitivity to magnetic structure.
- Use free electron laser pulses to measure with nanosecond time resolution
- Rather than split pulse, use pulse pair created by hitting electron source with two closely spaced laser pulses.



Use photon statistics to extract contrast

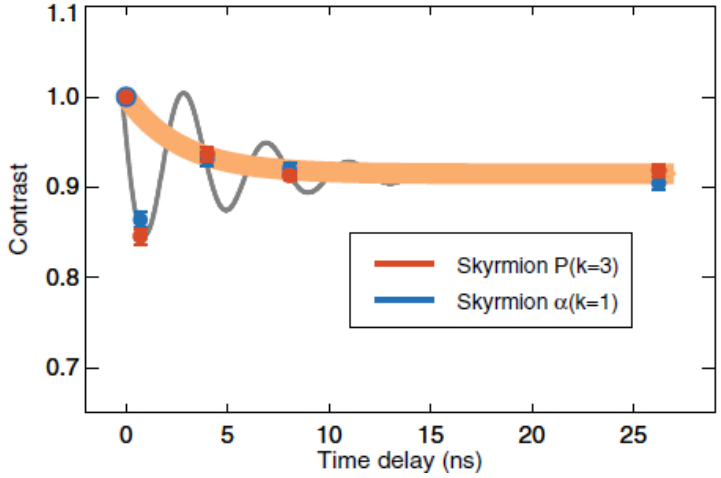
$$P_M(I) = \frac{M^M I \langle I \rangle^{M-1} \exp\left(-\frac{MI}{\langle I \rangle}\right)}{\Gamma(M)\langle I \rangle}$$

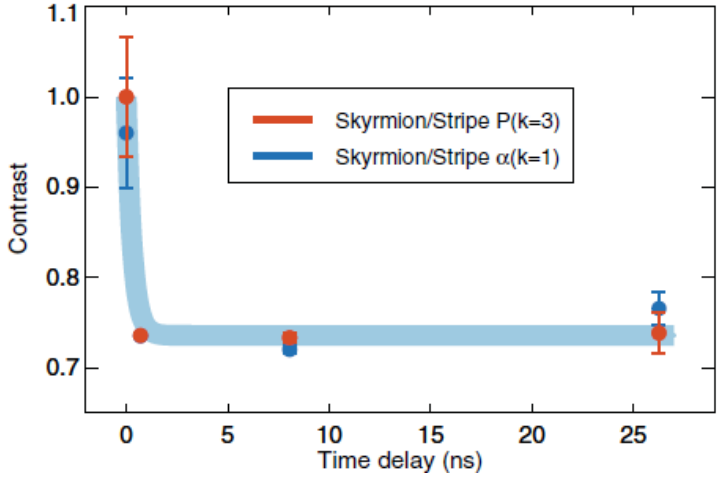
Probability to scatter 2 photons into one pixel as a function of the average counts/pixel and the contrast, C



Dynamics

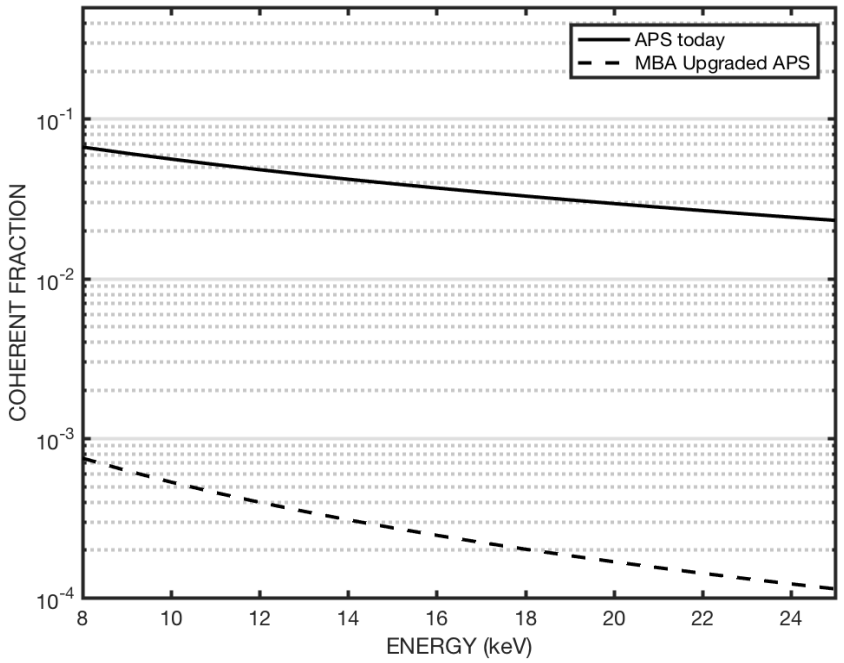
- Skyrmion phase dynamics speed up near the skyrmion/stripe phase boundary.
- Still unexplained dip at short times





APS MBA Upgrade

- Installation begins 2022
- Will provide sub microsecond XPCS
- Shorter times limited by detector technology rather than flux
- fs to ns dynamics will be done at FELs, μs and up at MBA.
- ns to µs ?



References

- XPCS Reviews
  - Sutton, M. (2008). A review of X-ray intensity fluctuation spectroscopy. *Comptes Rendus Physics*, *9*, 657–667
  - Grübel, G., Madsen, A., & Robert, A. (2008). X-Ray Photon Correlation Spectroscopy (XPCS). In R. Pecora (Ed.), *Soft-Matter Characterization*. Heidelberg: Springer.
  - Shpyrko, O. G. (2014). X-ray photon correlation spectroscopy. *JSR*, *21*, 1057–1064.
  - Leheny, R. L. (2012). XPCS: Nanoscale motion and rheology. *Current Opinion in Colloid and Interface Science*. Sinha, S. K., Jiang, Z., & Lurio, L. B. (2014). X-ray photon correlation spectroscopy studies of surfaces and thin films. *Advanced Mat.*, *26*(46). Sandy, A. R., Zhang, Q., & Lurio, L. B. (2018). Hard X-Ray Photon Correlation Spectroscopy Methods for Materials Studies. In *Annual Rev. Mat. Res.h* (Vol. 48).
  - Zhang, Q., Dufresne, E. M., & Sandy, A. R. (2018). Dynamics in hard condensed matter probed by X-ray photon correlation spectroscopy: Present and beyond. *Curr. Opin. Solid State and Materials Science*.
- Representative Experiments
  - NX School experiment
    - Lurio, L. B., Lumma, D., Sandy, A. R., Borthwick, M. A., Falus, P., Mochrie, S. G. J., Stephenson, G. B. (2000). Absence of scaling for the intermediate scattering function of a hard-sphere suspension: Static and dynamic x-ray scattering from concentrated polystyrene latex spheres. *Physical Review Letters*, *84*(4).
  - Charge Density Waves
    - Chen1, X. M., Mazzoli, C., Cao, Y., Thampy, V., Barbour, A. M., Hu, W., … Robinson, I. K. (2019). Charge density wave memory in a cuprate superconductor. *Nature Comm*, *10*, 1435.
  - Polymer dynamics
    - Jiang, Z., Mukhopadhyay, M. K., Song, S., Narayanan, S., Lurio, L. B., Kim, H., & Sinha, S. K. (2008). Entanglement effects in capillary waves on liquid polymer films. *PRL*, *101*(24).
    - Jiang, Z., Kim, H., Mochrie, S. G. J., Lurio, L. B., & Sinha, S. K. (2006). Surface and interfacial dynamics of polymeric bilayer films. *PRE*, *74*(1).
    - Jiang, Z., Kim, H., Jiao, X., Lee, H., Lee, Y.-J., Byun, Y., … Sinha, S. K. (2007). Evidence for viscoelastic effects in surface capillary waves of molten polymer films. *PRL*, *98*(22).
  - Sheer flow
    - Chen, Y., Roger, S. A., Narayanan, S., Harden, J. L., & Leheny, R. L. (2020). Microscopic dynamics of stress relaxation in a nanocolloidal soft glass. *Phys. Rev. Mat.*, *4*, 035602.
  - Atomic diffusion
    - Leitner, M., Sepiol, B., Stadler, L.-M., Pfau, B., & Vogl, G. (2009). Atomic diffusion studied with coherent X-rays. *Nature Mat.*, *8*, 717–720.
  - Magnetic Skyrmions
    - Seaberg, M. H., Holladay, B., Lee, J. C. T., Sikorski, M., Reid, A. H., Montoya, S. A., Turner, J. J. (2017). Nanosecond X-Ray Photon Correlation Spectroscopy on Magnetic Skyrmions. *PRL*, *119*(6)

Feedback
Lecture – 1:00 – 2:00
X-ray Photon Correlation - Larry Lurio
https://forms.office.com/g/n3dUuS01sv