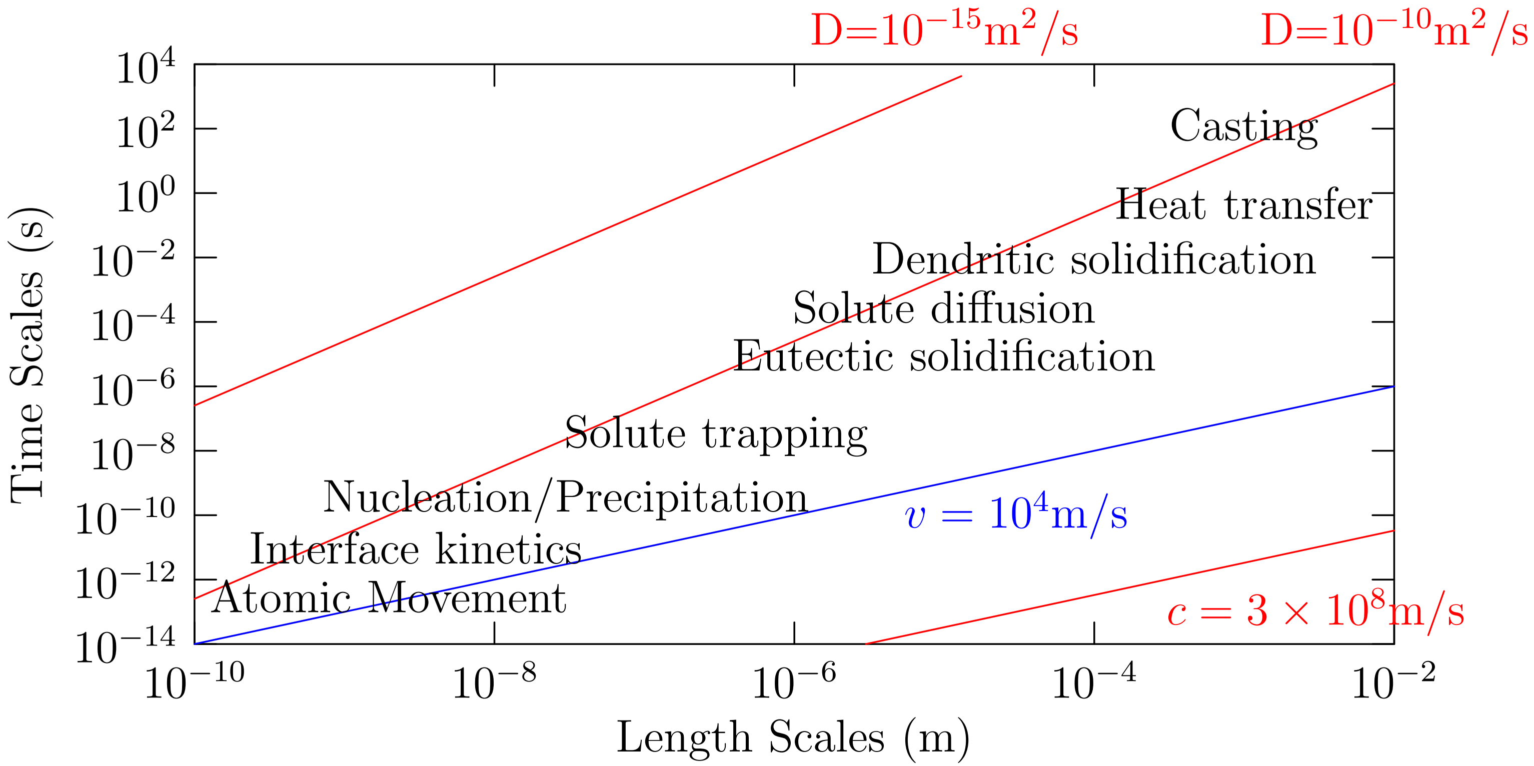
New Opportunities for XPCS

Mark Sutton
McGill University
Thanks to many collaborators.

Outline

1. Introduction (the science)
2. XPCS Basics
3. XPCS: SAXS
4. XPCS: SAXS heterodyne
5. High angle XPCS
6. The future in XPCS

Space-time diagrams



Stolen from N. Provatas, McMaster University

Length and Time Scales Again

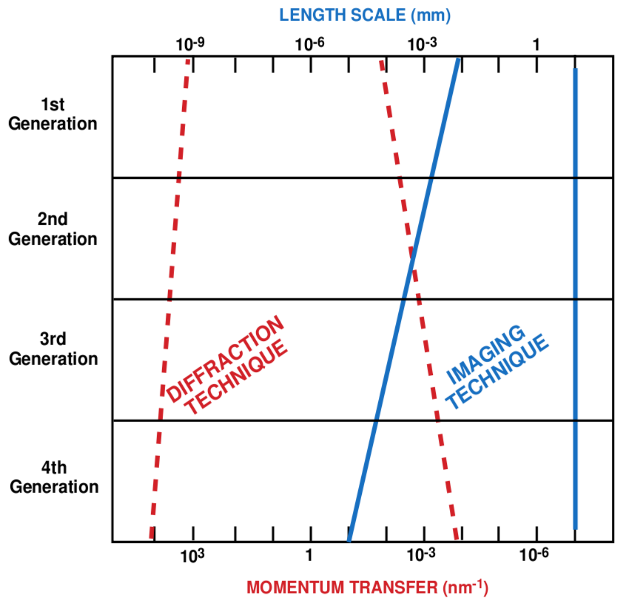


Fig. 4: Research opportunities with synchrotron radiation: spatial structure.

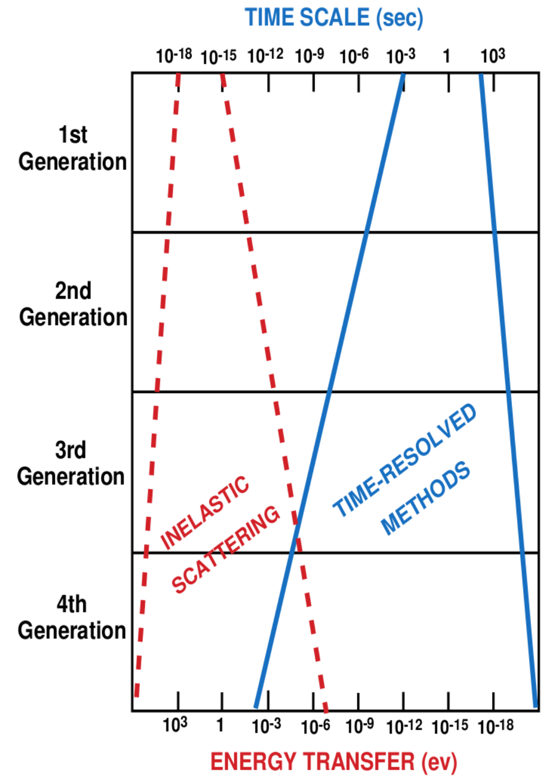
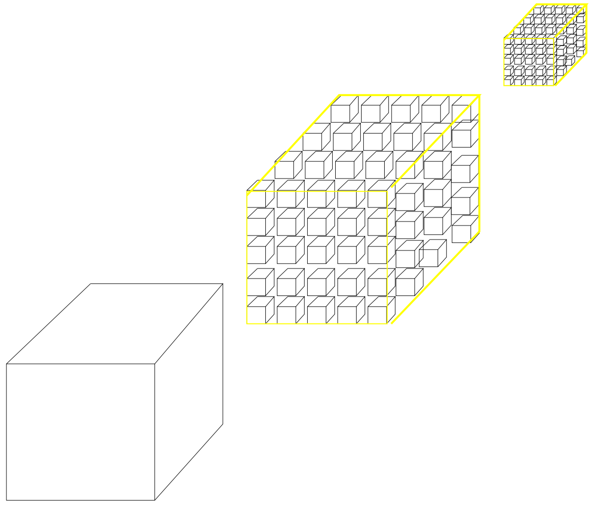


Fig. 5: Research opportunities with synchrotron radiation: temporal structure.

Ref: David E. Moncton, Toward a Fourth-Generation X-ray Source, XIX International Linear Accelerator Conference (LINAC'98) (1998).

Coarse Graining: Phase Fields

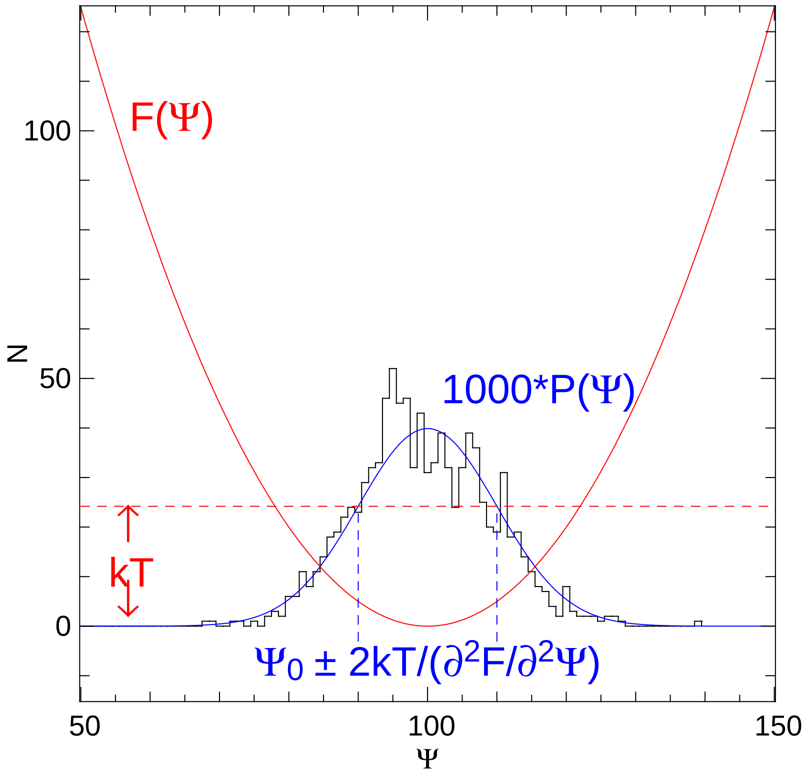


$$\widehat{\Psi}_L = \frac{1}{N}\sum \Psi_L(\vec{x}_i)$$

$$\sigma_{\Psi_L} = \frac{1}{N-1}\sqrt{\sum (\Psi_L(\vec{x}_i) - \widehat{\Psi}_L)^2}$$

$$\sigma_{\widehat{\Psi}_L} = \frac{\sigma_{\Psi_L}}{\sqrt{N}}$$

Statistical Mechanics 101



$$P(\Psi_L(\vec{x}_i)) \sim e^{-F(\Psi_L)/kT}$$

$$P(\widehat{\Psi}_L) \sim e^{-F(\widehat{\Psi}_L)/kT}$$

$$\sim e^{\frac{-F(\Psi)}{N_b kT}}$$

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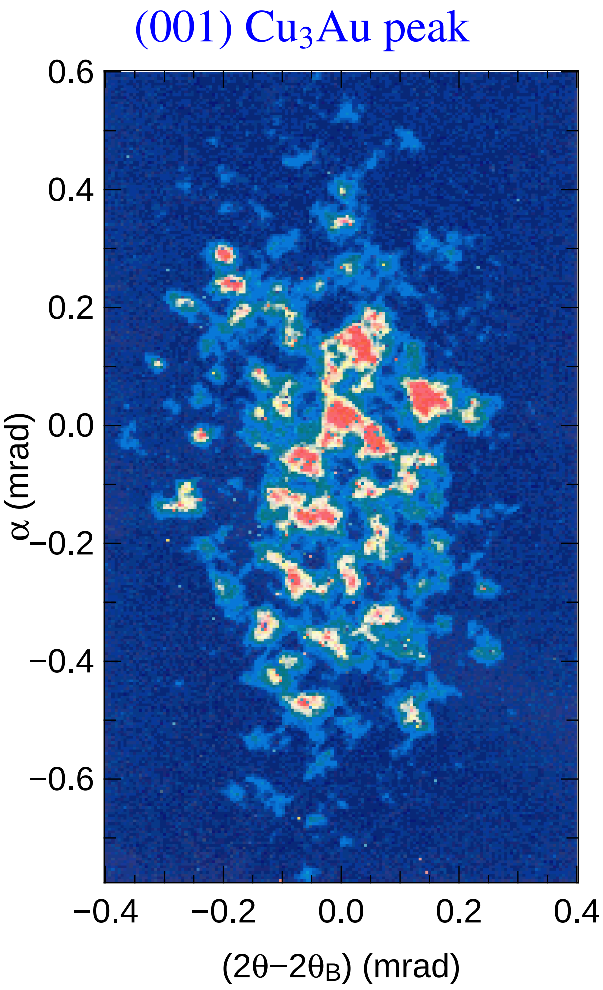
Coherent diffraction



Sutton et al., The Observation of Speckle by Diffraction with Coherent X-rays, Nature, **352**, 608-610 (1991).

Why Coherence?

Coherence allows one to measure the dynamics of a material (X-ray Photon Correlation Spectroscopy, XPCS).

$$\langle I(\vec{Q},t)I(\vec{Q}+\delta\vec{\kappa},t+\tau)\rangle = \langle I(Q)\rangle^2 + \beta(\vec{\kappa})\,\frac{r_0^4}{R^4}V^2 I_0^2 \left|S(\vec{Q},t)\right|^2$$

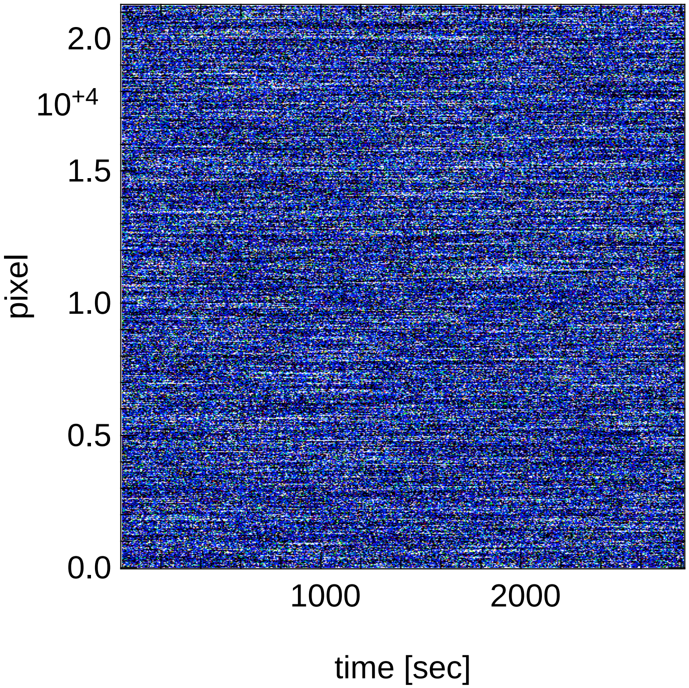
where the coherence part is:

$$\beta(\vec{\kappa}) = \frac{1}{V^2 I_0^2}\int_V\int_V e^{i\vec{\kappa}\cdot(\vec{r}_2-\vec{r}_1)}\left|\Gamma(\vec{0},\vec{r}_2^{\perp}-\vec{r}_1^{\perp},\frac{\vec{Q}\cdot(\vec{r}_2-\vec{r}_1)}{\omega_0})\right|^2 d\vec{r}_1 d\vec{r}_2$$

and $\beta(\vec{0}) \approx \frac{V_{coherence}}{V_{scattering}}$ with widths $\lambda/V^{\frac{1}{3}}$

Reference: M. Sutton, Coherent X-ray Diffraction, in **Third-Generation Hard X-ray Synchrotron Radiation Sources: Source Properties, Optics, and Experimental Techniques**, edited by. Dennis M. Mills, John Wiley and Sons, Inc, New York, (2002).

SAXS of Au particles in PS



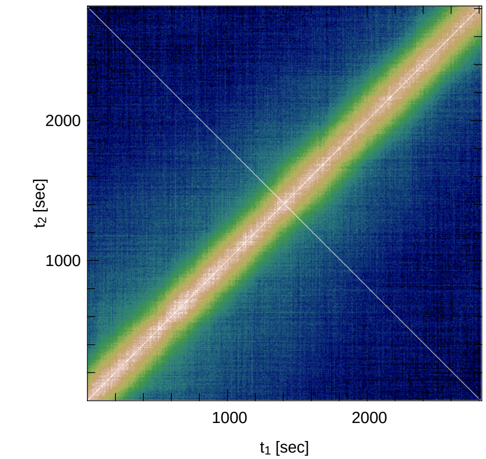
Time fluctuations in coherent scattering.

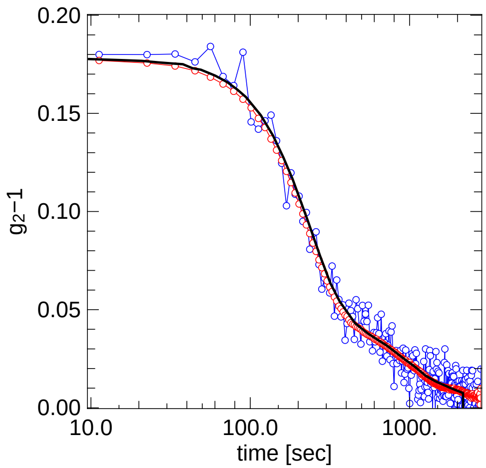
Define correlation function:

$$\begin{aligned} g^{(2)}(\vec{Q},\tau) &- 1 \\ &= \frac{\langle I(\vec{Q},t+\tau)I(\vec{Q},t)\rangle - \langle I(\vec{Q},t)\rangle^2}{\langle I(\vec{Q},t)\rangle^2} \\ &= \beta \left| g^{(1)}(\vec{Q},\tau)\right|^2 \\ &= \beta\, e^{-2\tau/\tau_Q} \end{aligned}$$

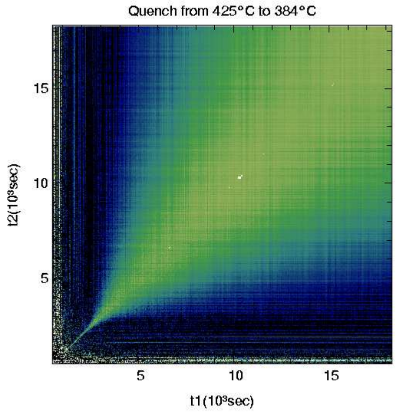
Two-time correlation functions

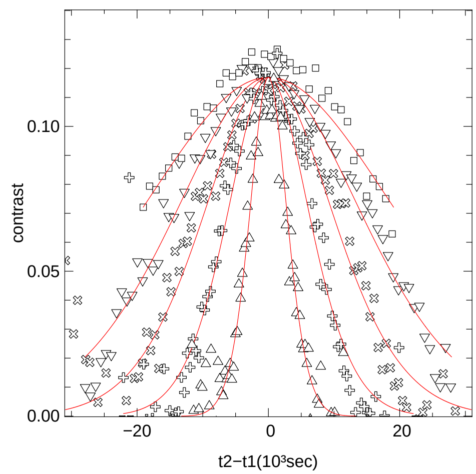
Au in polystyrene





Cu_3Au





Requirements of XIFS

1. Scattering Volume comparable to coherence volume (diffraction limited beam resolved by detector).
2. Broad scattering (i.e. disorder so there is interesting structure within beam)
3. Sufficient counts per correlation time (like about 1)
4. Sufficient number of correlations times measured (either many times at one speckle or many speckles and times with the same time constant).

Possible systems to study

1. polymers, glasses (visco-elastic effects)
2. critical scattering
3. quasi-crystals (phasons)
4. low dimensional systems
5. charge density waves
6. grain boundaries, domain walls, defect motion
7. switching in ferroelectrics, piezoelectrics
8. colloids
9. non-equilibrium systems

Signal to Noise

Signal is $g_2 - 1 = \beta$ and variance of is $var(g_2) \sim 1/(\bar{n}^2 N)$. So:

$$\begin{aligned}\frac{s}{n} &= \beta \bar{n} \sqrt{N} \\ &= \beta I \tau \sqrt{\frac{t_{total}}{\tau} N_{speckles}} \\ &= \beta I \sqrt{\tau t_{total} N_{pixels}}\end{aligned}$$

Note 1: This is linear in number of photons (as opposed to $\sqrt{\bar{n}}$).
Note 2: For fixed $s/n \sim \alpha I \sqrt{\tau/\alpha^2}$. Thus an α-fold increase in intensity is an α^2-fold increase in time resolution. Need very fast detectors.

Reference: Area detector based photon correlation in the regime of short data batches: data reduction for dynamic x-ray scattering, D. Lumma, L.B. Lurio, S.G.J. Mochrie, and M. Sutton, Rev. Sci. Instr. **71**, 3274-3289 (2000).

Signal to Noise

More explicitly:

$$
\begin{aligned}
\frac{s}{n} &\approx \beta\, B_0 dx dx' dy dy' \frac{\Delta E}{E}\ \frac{1}{V}\frac{d\sigma}{d\Omega} L\ \sqrt{N_{sp}} \\
&\approx \beta B_0 f_x f_y\, \lambda^2\, \frac{\Delta E}{E}\ \frac{1}{V}\frac{d\sigma}{d\Omega} f_z \frac{\lambda^2}{\Delta\lambda}\ \sqrt{N_{sp}} \\
&\approx \frac{1}{max(1, f_i)^3} B_0 f_x f_y f_z\, \lambda^2\, \frac{\Delta\lambda}{\lambda}\ \frac{1}{V}\frac{d\sigma}{d\Omega}\frac{\lambda^2}{\Delta\lambda}\ \sqrt{N_{sp}} \\
&\approx B_0\, \lambda^3 \frac{1}{V}\frac{d\sigma}{d\Omega}\sqrt{N_{sp}} \\
&\approx f B_0\, \lambda^3 \frac{1}{V}\frac{d\sigma}{d\Omega}\sqrt{N_{sp}} \quad (\mathrm{if\,any\,f_i} < 1).
\end{aligned}
$$

Note: should be a $\lambda^3/8$ as normally use $\lambda/2$.

Cross-sections and S(q)

$$\frac{1}{V}\frac{d\sigma}{d\Omega} = \frac{r_0^2}{V}\left|\sum_{l,k} F_l^* F_k e^{-i\vec{q}\cdot(\vec{r}_l-\vec{r}_k)}\right|^2$$

Small crystals

$$\frac{1}{V}\frac{d\sigma}{d\Omega} = r_0^2\frac{|\bar{\mathrm{F}}|^2}{N_xN_yN_zv_c}\left[\frac{\sin(N_xq_xa/2)}{\sin(q_xa/2)}\frac{\sin(N_yq_yb/2)}{\sin(q_yb/2)}\frac{\sin(N_zq_zc/2)}{\sin(q_zc/2)}\right]^2$$

$$= r_0^2\frac{|\bar{\mathrm{F}}|^2}{v_c^2}V\left[\frac{\sin(N_xq_xa/2)}{N_x\sin(q_xa/2)}\frac{\sin(N_yq_yb/2)}{N_x\sin(q_yb/2)}\frac{\sin(N_zq_zc/2)}{N_z\sin(q_zc/2)}\right]^2$$

where $v_c = abc$ and volume $N_xN_yN_zv_c = Nv_c$.

Amorphous/liquids High q limit gives:

$$\frac{1}{V}\frac{d\sigma}{d\Omega} = \frac{r_0^2}{V}\left|\sum_{l,k} F^* F e^{-i\vec{q}\cdot(\vec{r}_l-\vec{r}_k)}\right|^2$$

$$= r_0^2|F|^2\frac{N}{V} = r_0^2|F|^2\bar{n},$$

$$= r_0^2\frac{|F|^2}{v_c^2}v_c,$$

Here $v_c = 1/\bar{n}$ is the volume per atom. So for all q:

$$\frac{1}{V}\frac{d\sigma}{d\Omega} = r_0^2|F|^2\bar{n}S(q) = r_0^2\frac{|F|^2}{v_c^2}v_c S(q).$$

General S(q)

$$\frac{1}{V}\frac{d\sigma}{d\Omega} = r_0^2 V_{coh}\rho_e^2(q)$$

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Shear

Imagine that velocity varies over the diffraction volume but is in steady-state.

$$\vec{V}(\vec{r}) = \vec{V}_0 + \Gamma \cdot \vec{r}$$

Then we get:

$$\begin{aligned} G_1(\vec{q},t) &= \exp\left\{-\int_0^t [Dq'^2 + i\vec{V}_0 \cdot q'^2]dt'\right\} \int d\vec{x} I(\vec{x}) \exp\left\{-i\int_0^t dt'\vec{q}' \cdot \Gamma \cdot \vec{x}\right\} \\ &= \exp\left\{-\int_0^t [Dq'^2 + i\vec{V}_0 \cdot q'^2]dt'\right\} \bar{I}\left(\int_0^t dt'\vec{q}' \cdot \Gamma\right) \end{aligned}$$

and

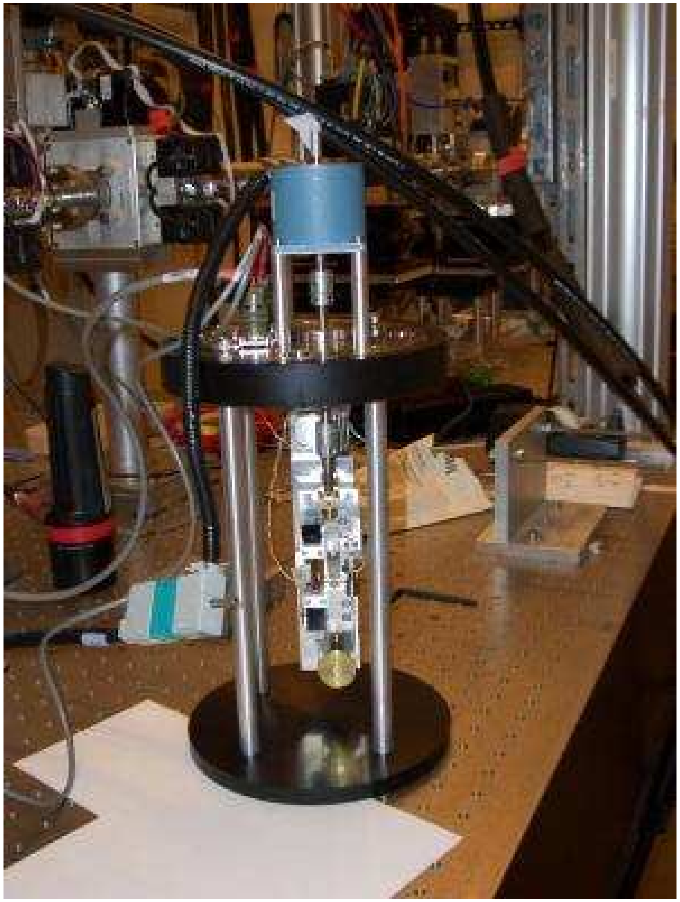
$$G_2(\vec{q},t) = \exp\left\{-2\int_0^t dt' Dq'^2\right\} \left|\bar{I}\left(\int_0^t dt'\vec{q}' \cdot \Gamma\right)\right|^2$$

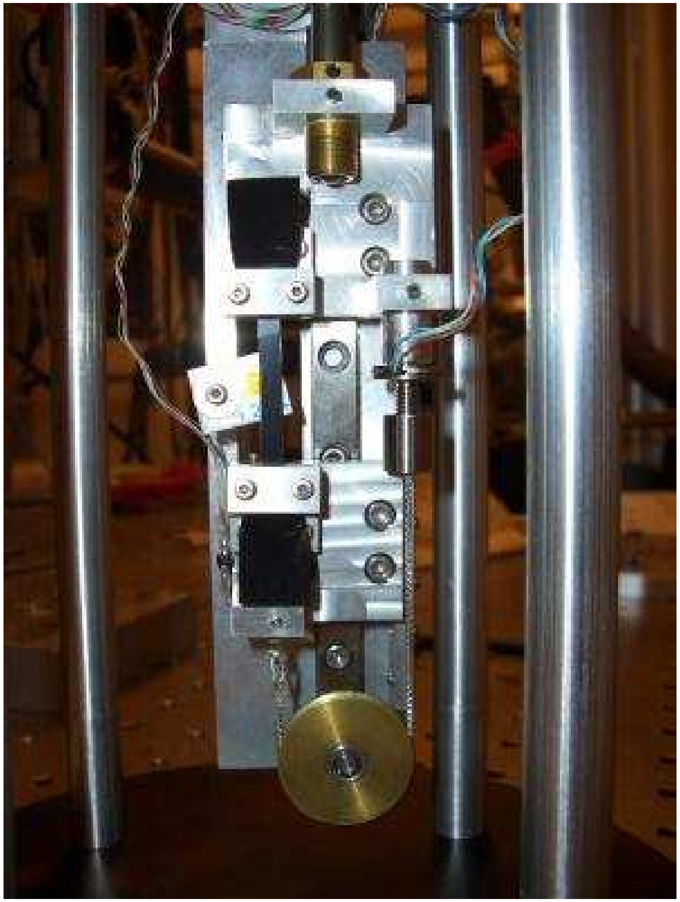
For us, $\vec{q}' = \vec{q}$, and

$$\bar{I}(\vec{q} \cdot \Gamma L t) = \mathrm{sinc}(\vec{q} \cdot \Gamma L\, t) = \frac{\sin(\vec{q} \cdot \Gamma L\, t)}{\vec{q} \cdot \Gamma L\, t}$$

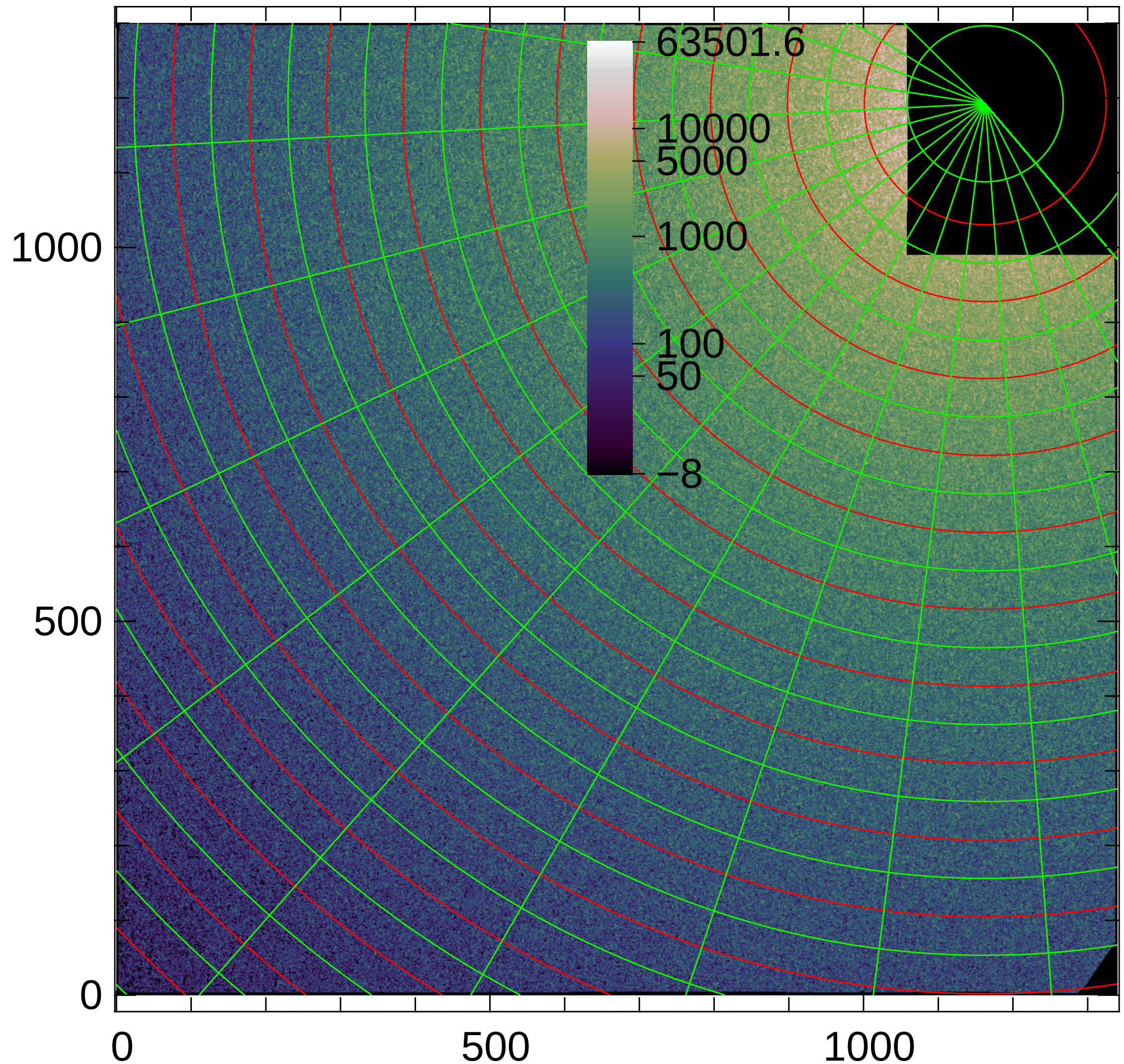
Ref: G.G. Fuller, J.M. Rallison, R.L. Schmidt and L.G. Leal, J. Fluid Mech., **100**, 555 (1980).

In-situ stress-strain cell



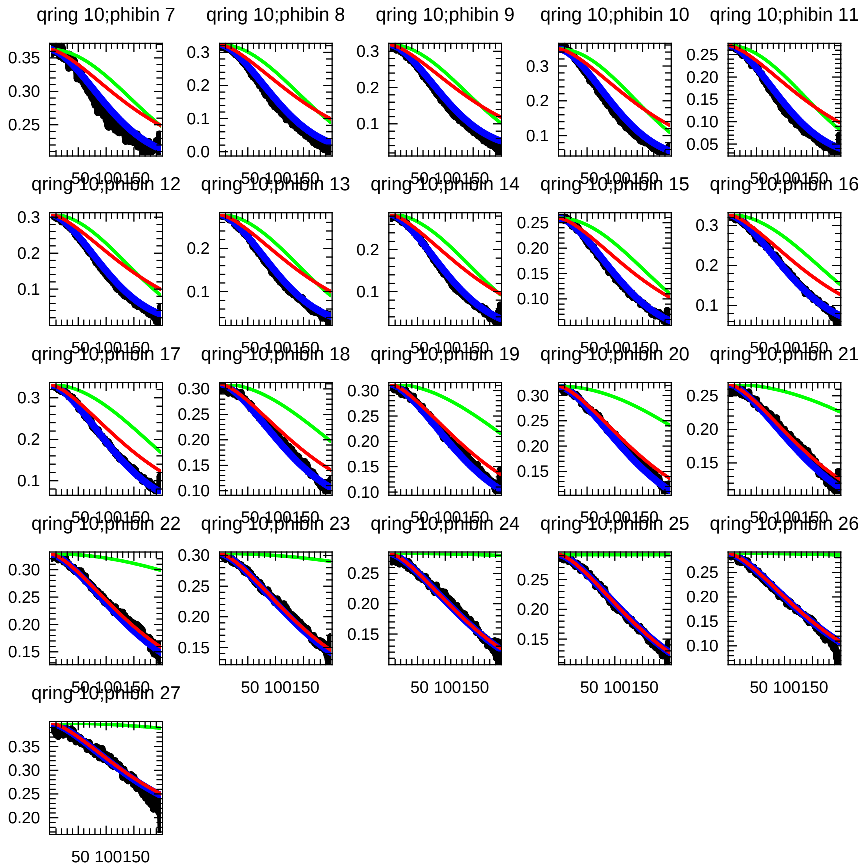


Partitioning the Scattering



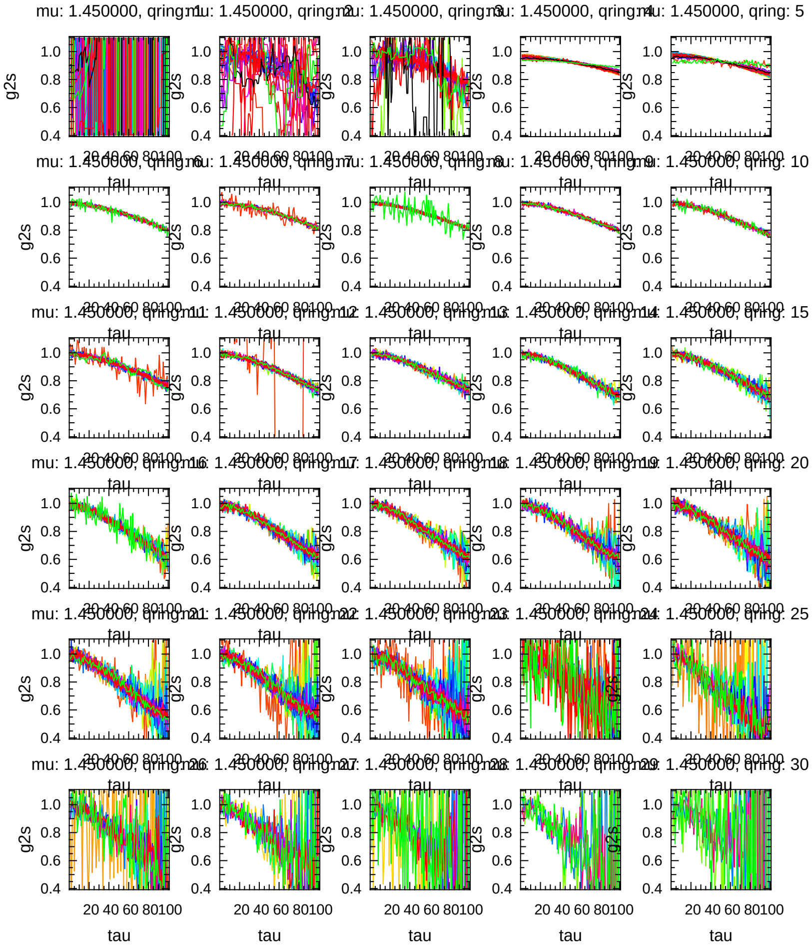
Homodyne, shear fits

green: shear; red: diffusion; blue: both multiplied



Homodyne, collapsed fits

gep6cC_8_431 g2's with shear dependence divided out (normalized)



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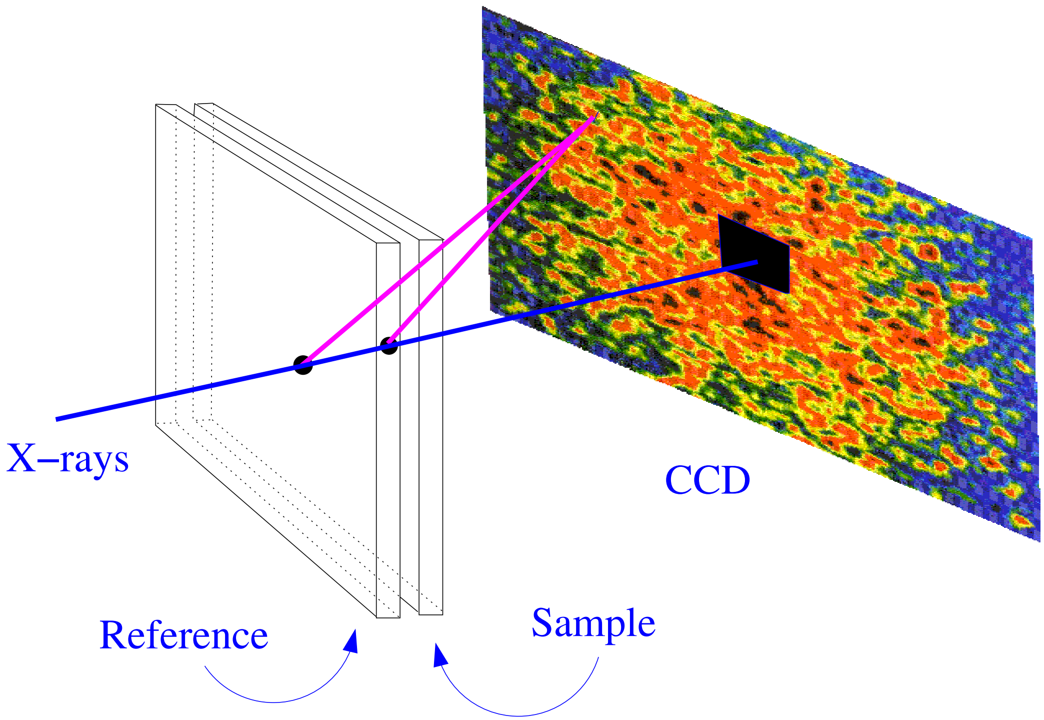
Experimental Setup



Scattering geometry

Heterodyne

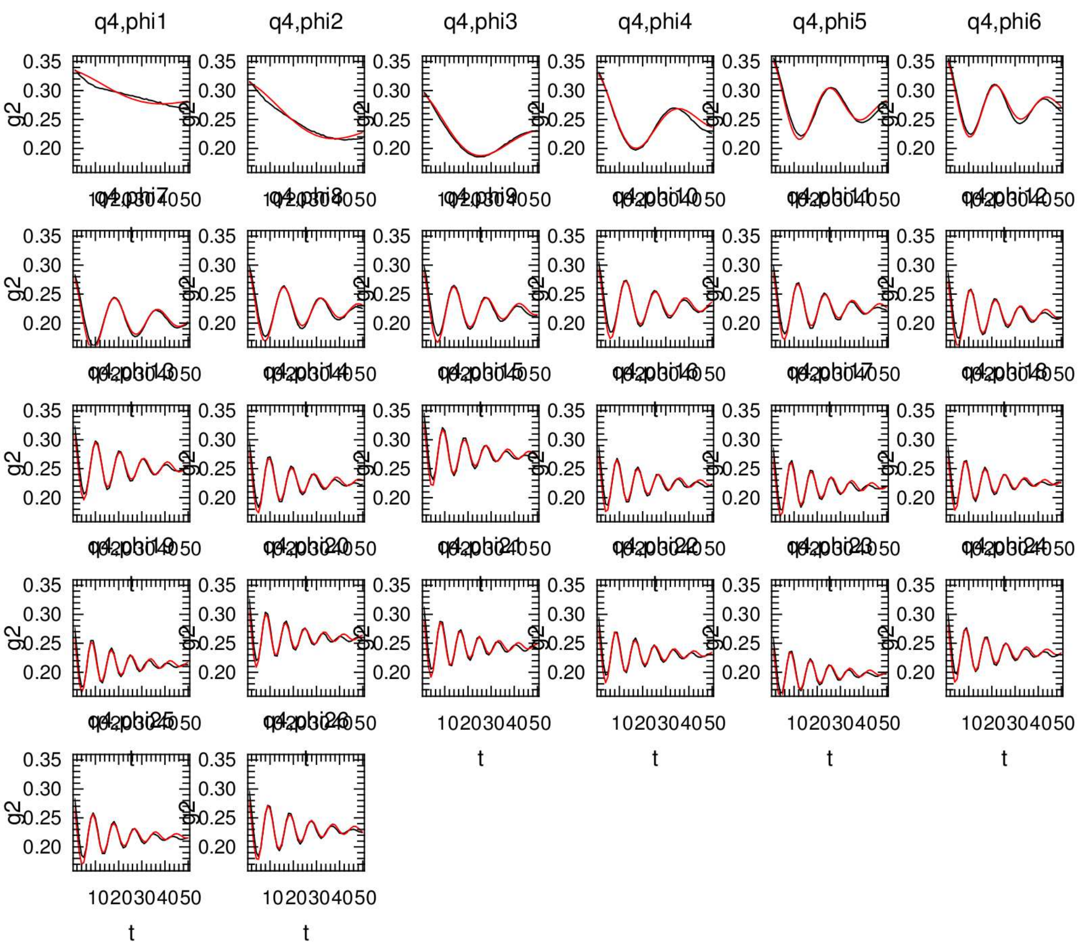
$$G_2(\vec{q},t) = I_r^2 + \langle I_s(t)\rangle_t^2(1+\beta|g_1(t)|^2) + 2I_r\langle I_s(t)\rangle_t + 2I_r\langle I_s(t)\rangle_t\beta Re(g_1(t))$$

Moving at constant velocity gives phase factor

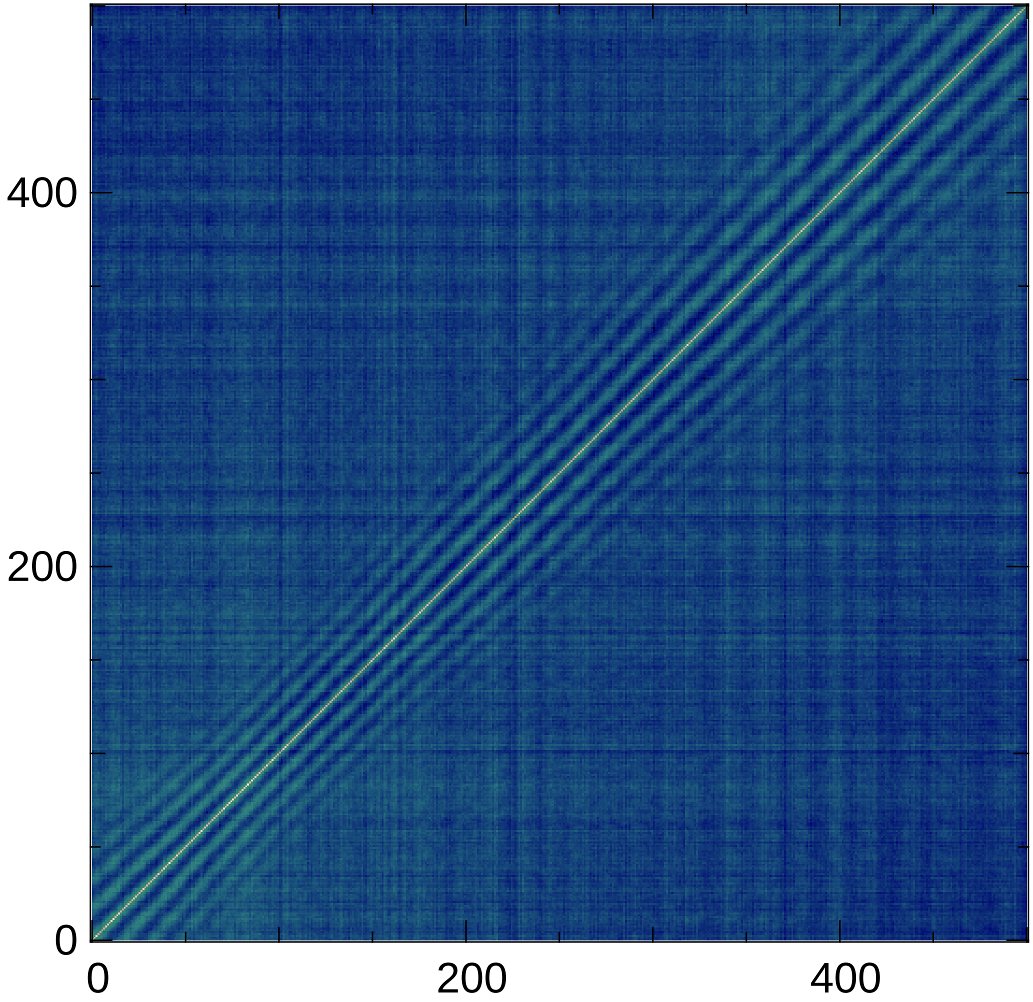
$$e^{i\vec{q}\cdot\vec{\mathrm{v}}t} = e^{i\omega t}$$

So correlation becomes ($x = I_s/(I_s+I_r)$)

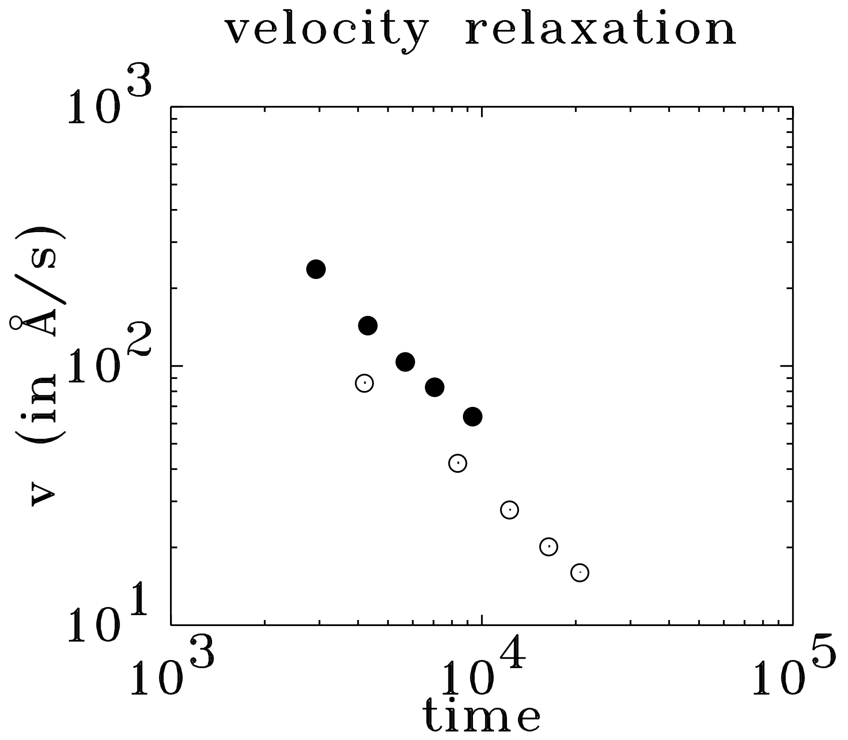
$$g_2(q,\phi,t) = 1+\beta(1-x)^2 + x^2\beta\gamma^2(t/\tau) + 2x(1-x)\beta\cos(\omega t)\gamma(t/\tau)$$


q4,phi1
q4,phi2
q4,phi3
q4,phi4
q4,phi5
q4,phi6
q4,phi7
q4,phi8
q4,phi9
q4,phi10
q4,phi11
q4,phi12
q4,phi13
q4,phi14
q4,phi15
q4,phi16
q4,phi17
q4,phi18
q4,phi19
q4,phi20
q4,phi21
q4,phi22
q4,phi23
q4,phi24
q4,phi25
q4,phi26
g2
0.35
0.30
0.25
0.20
t
10
20
30
40
50

Two-time correlations: heterodyning



Velocity



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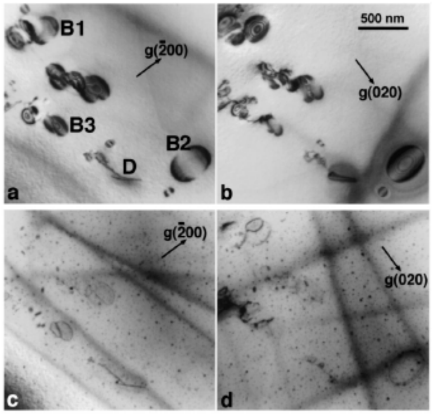
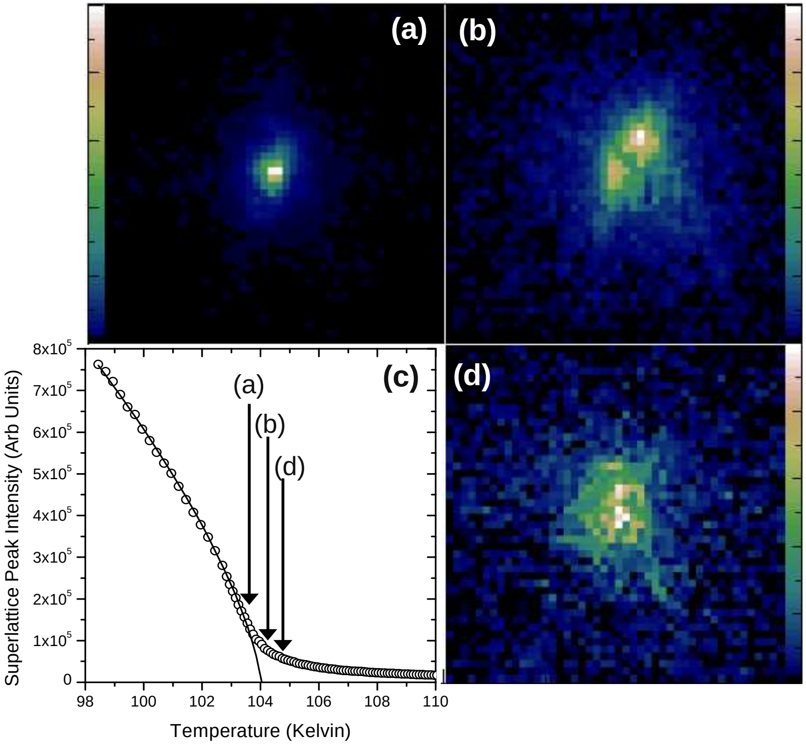
Critical X-ray scattering from $SrTiO_3$ – Coherent diffraction

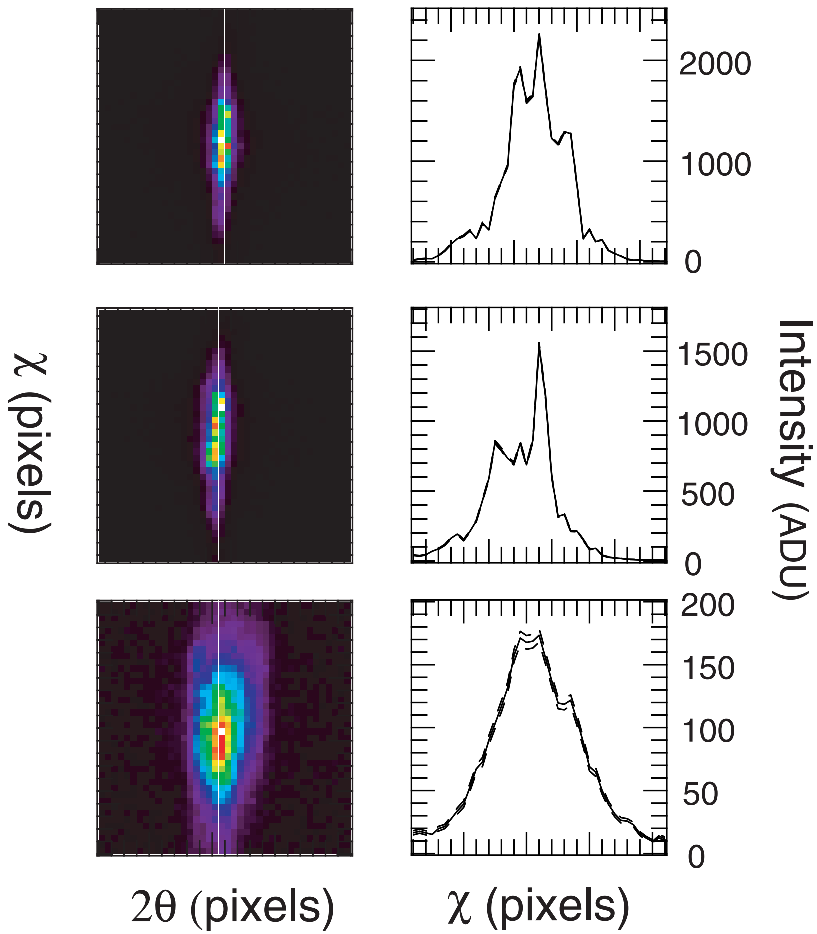
- First ever observation of static speckle pattern within central component of critical X-ray scattering

- Supports central peak origin as transition precursors – static lattice fluctuations wetting on defects

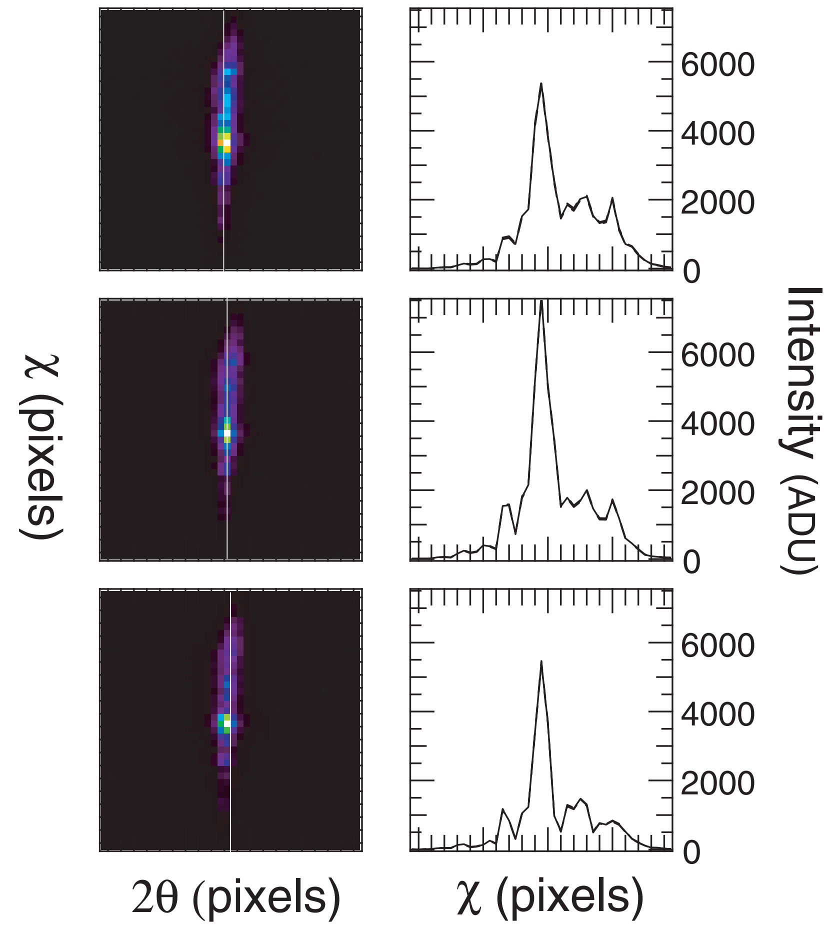




$NbSe_3$ Q_1 CDW Peak

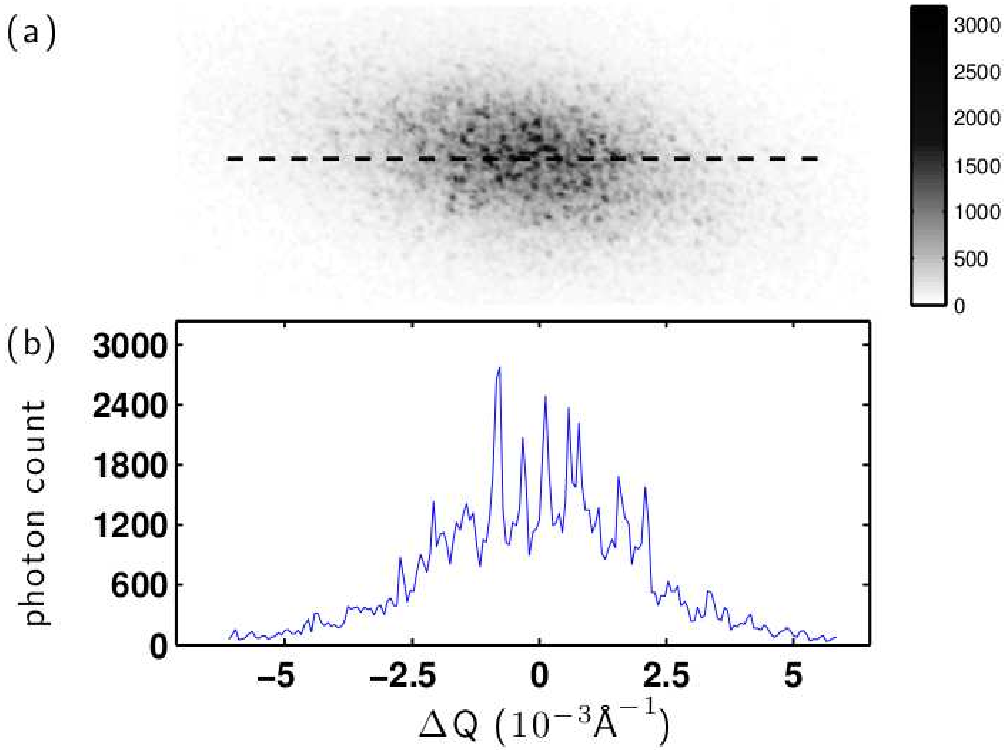


Varying field (E)

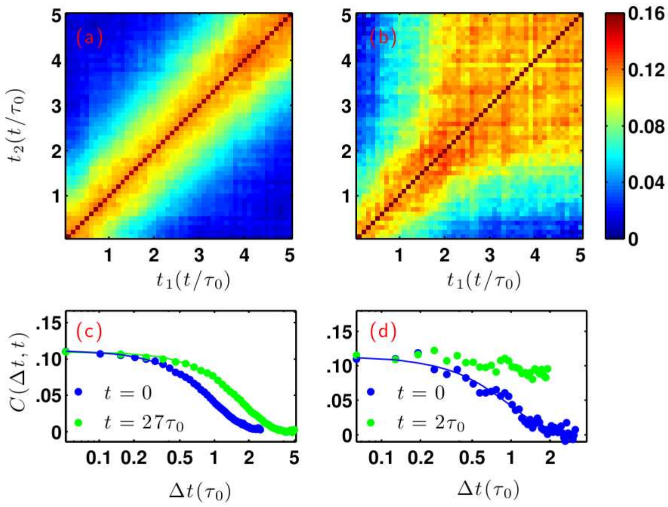


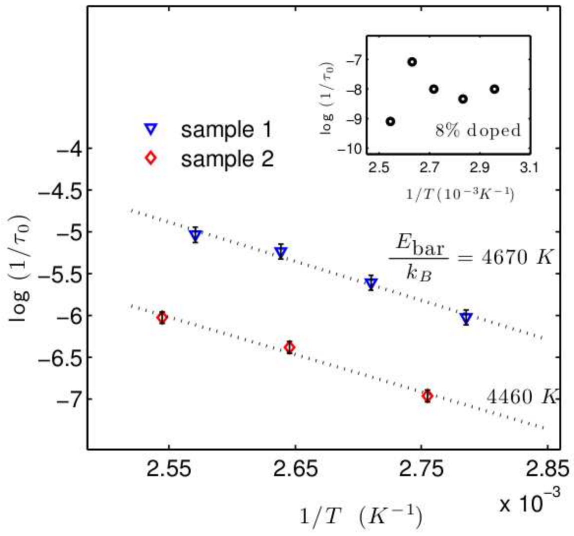
Varying slit size

CDWs in 1T-TaS_2

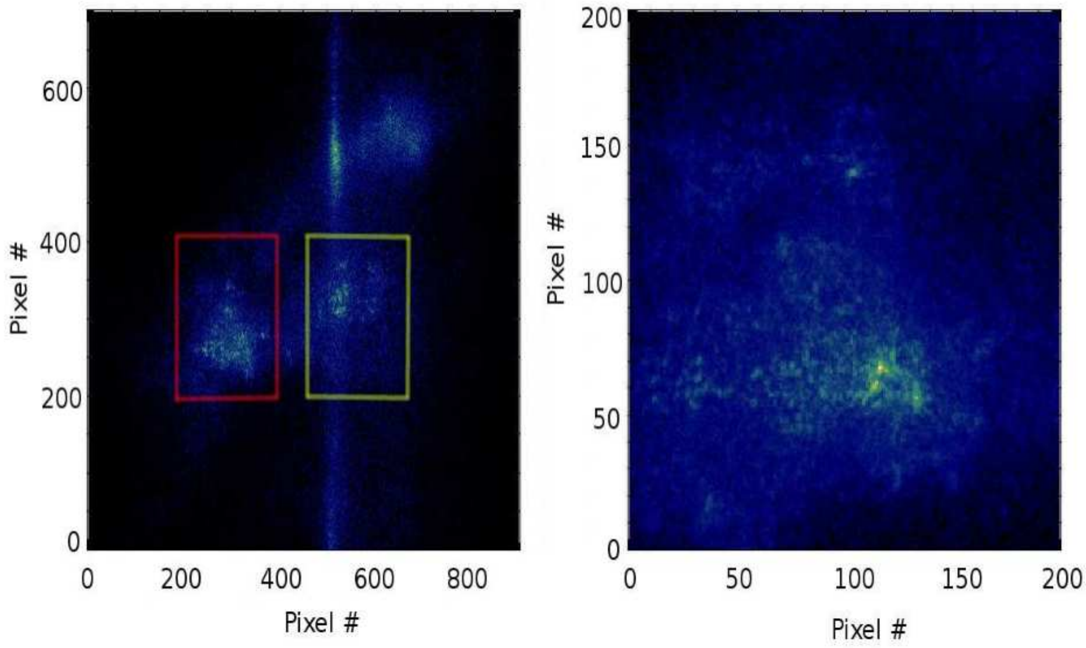


CDWs in 1T-TaS$_2$



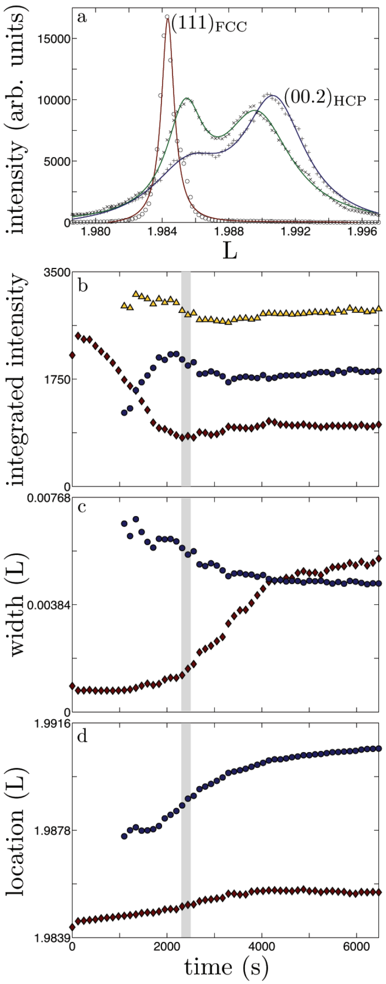


Cobalt (00ℓ) speckle



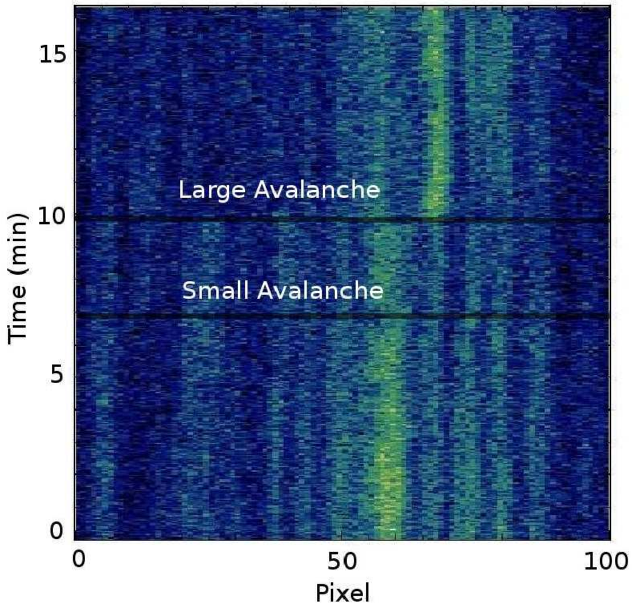
Martensitc Phase Transition in Co: FCC to HCP

K. Ludwig, C. Sanborn (B.U.) M. Rogers and M. Sutton (McGill)

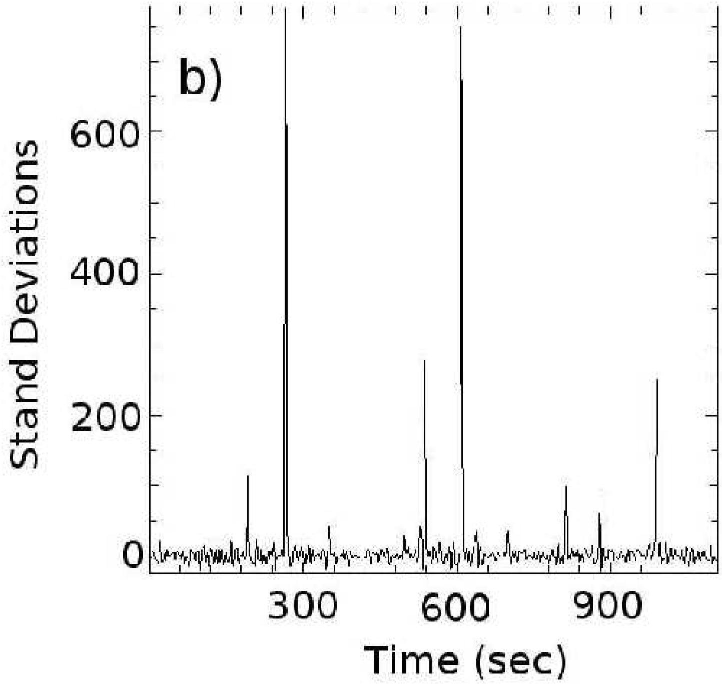


Kinetics of Co transition.

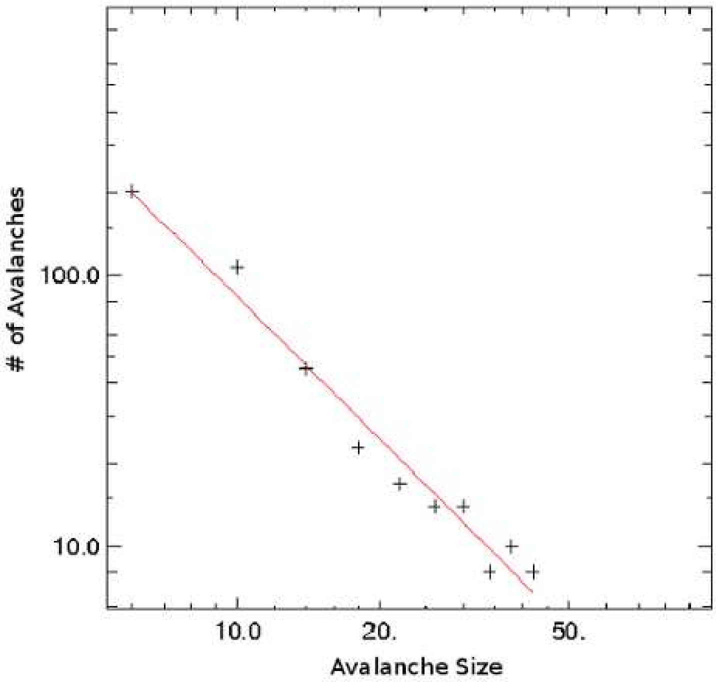
Quench from 600 C to 360 C.



Detection of avalanche in (00.2) speckle pattern.

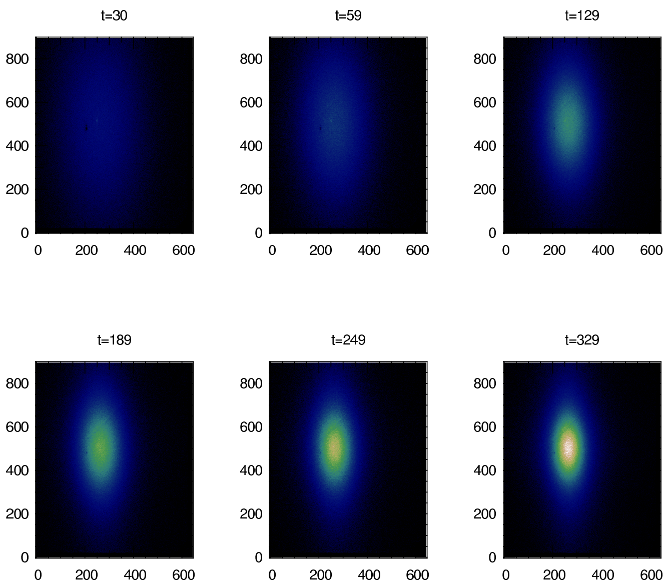


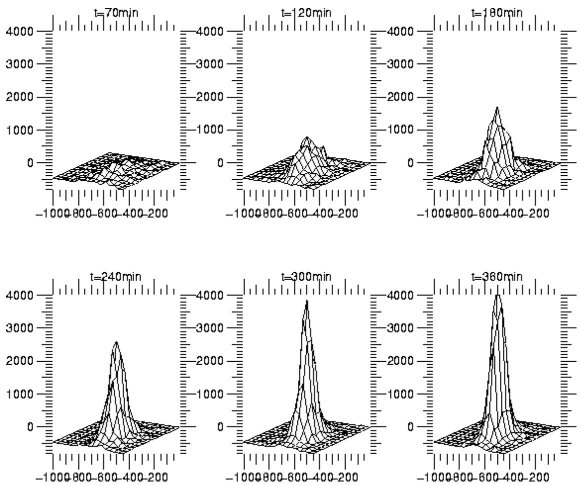
Avalanche sizes versus time after quench.

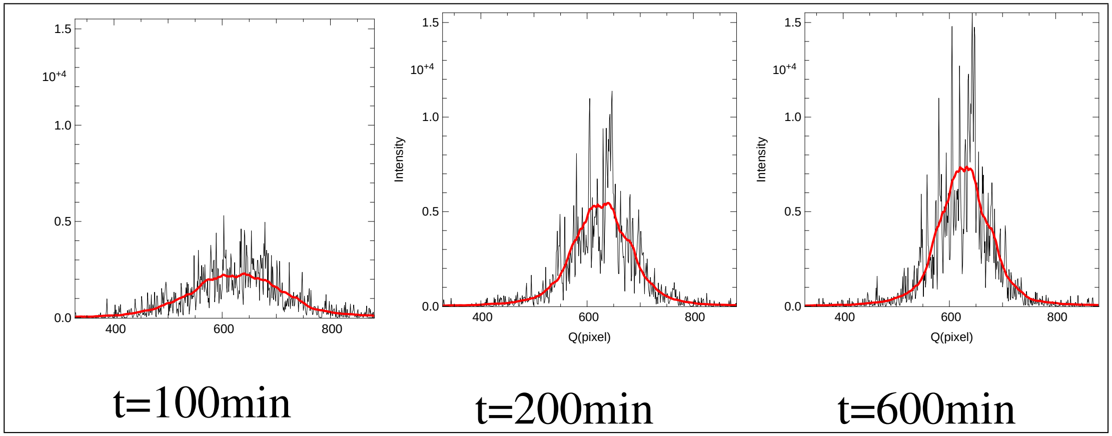


Avalanche distribution.

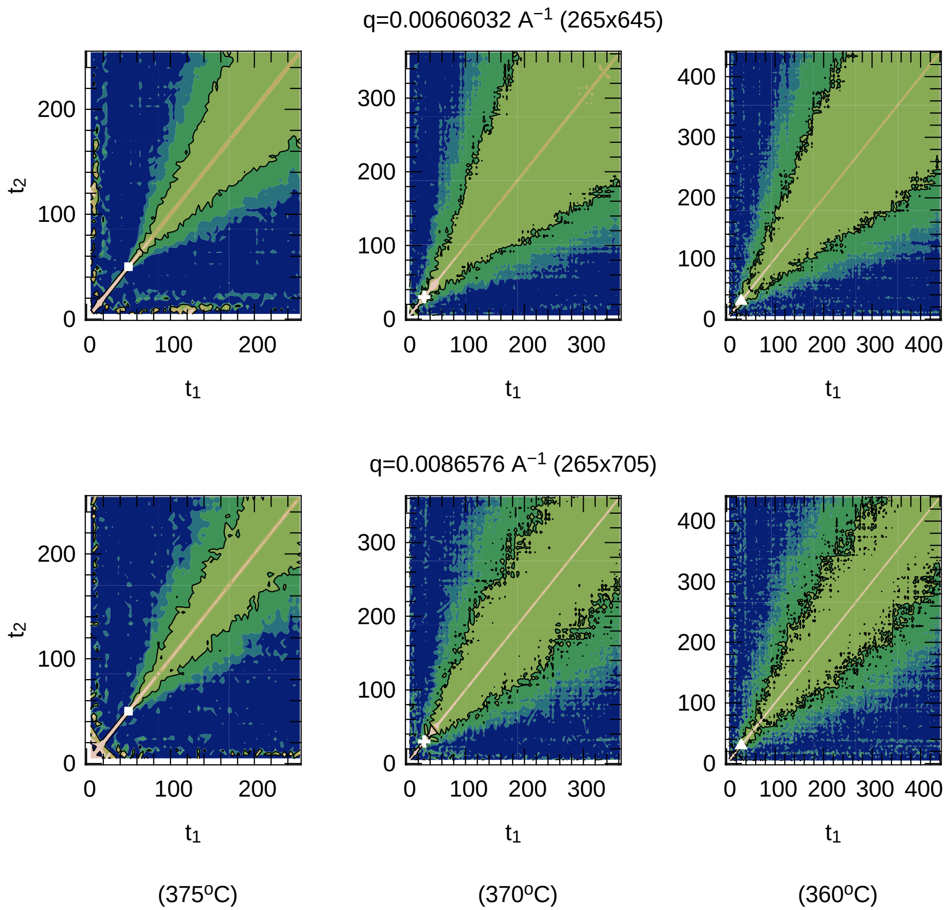
Scattering from Cu_3Au





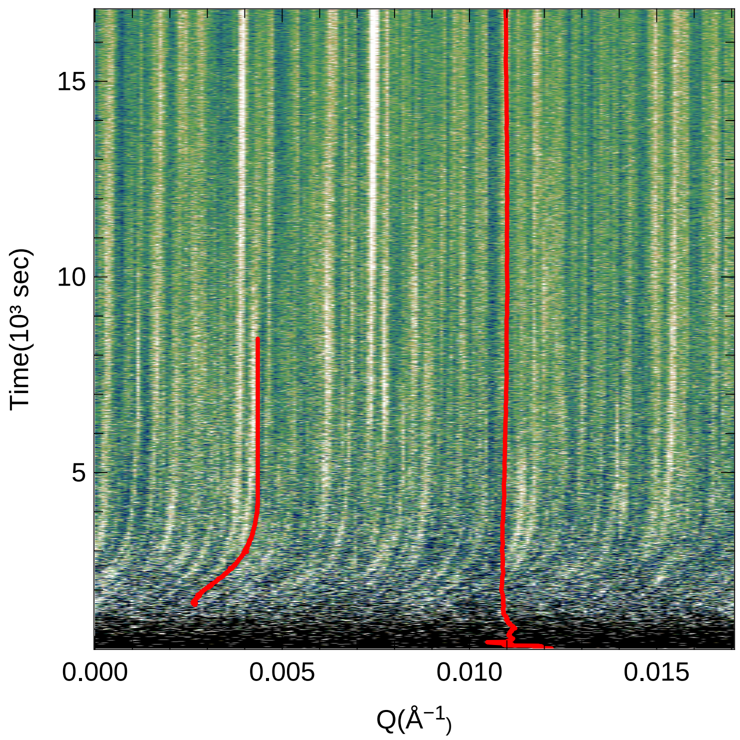


Two-Time Correlation Functions

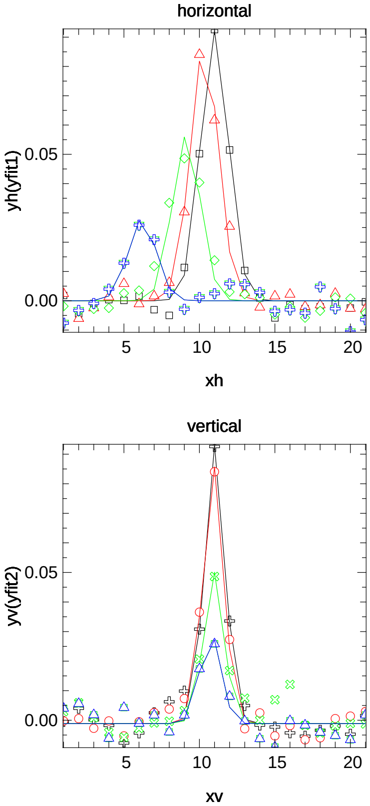


Tranverse direction

New Data

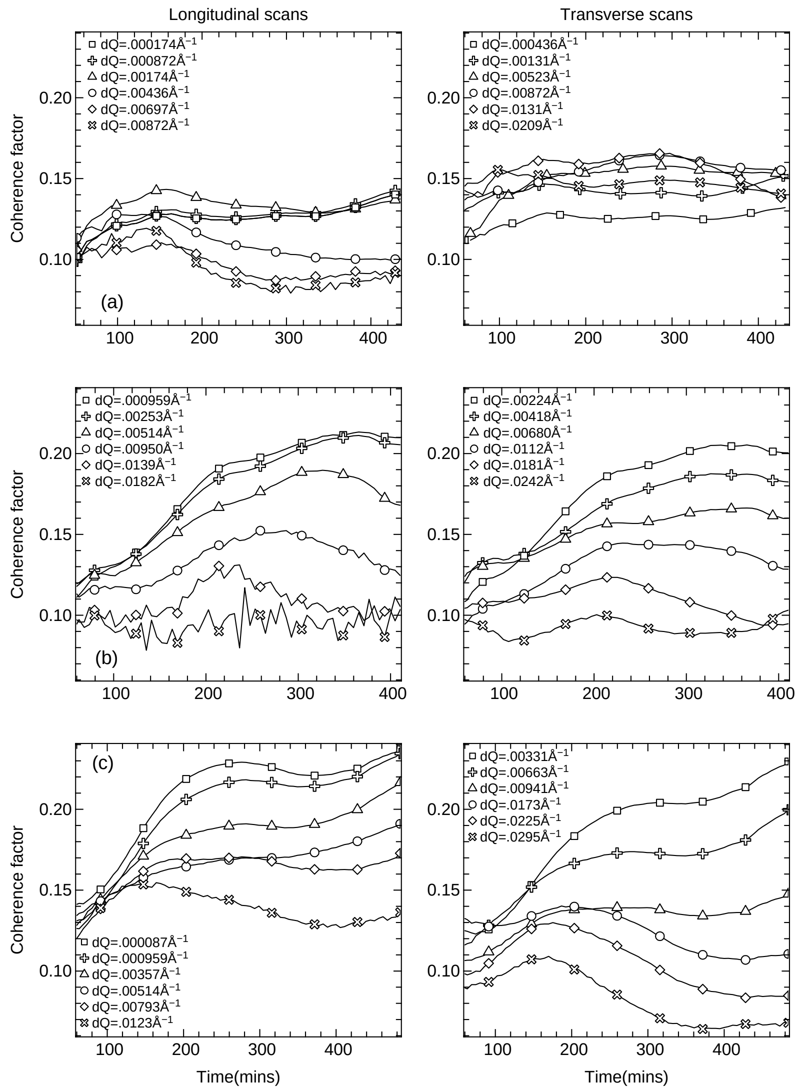


Time(10^3 sec)
15
10
5
0.000
0.005
0.010
0.015
Q(Å^{-1})

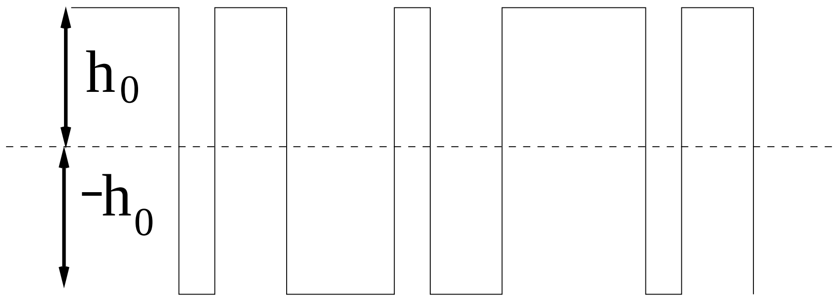


horizontal
yh(yfit1)
0.05
0.00
5
10
15
20
xh
vertical
yv(yfit2)
0.05
0.00
5
10
15
20
xv

Contrast factor



Telegraph Waves



$T(x)$ is a telegraph wave with crossings Poisson randomly distributed.
Use to model domain walls.
The trick (T(x) is ± 1):

$$e^{ih_0 T(x)} = cos(h_0) + iT(x)sin(h_0)$$

converts the phase to an amplitude.

$$S(q) = |F^*(q)F(q)| =$$
$$\int\int |f_\delta|^2 e^{2\pi i(1+\delta q)(x-x')}(cos^2(\pi/2(1+\delta q)) + \langle T(x)T(x')\rangle sin^2(\pi/2(1+\delta q))dxdx')$$

Reference: E. Jakeman, B. J. Hoenders. Optica Acta, **29**, 1587, (1982).

Outline

1. Introduction (the science)
2. XPCS Basics
3. XPCS: SAXS
4. XPCS: SAXS heterodyne
5. High angle XPCS
6. The future in XPCS

The future with XPCS

1. Coherent diffraction imaging demonstrates that coherent diffraction contains full information on structure.
2. XPCS uses only the time behaviour.
   (a) This allows us to use partial coherence.
   (b) It is a differential technique so very sensitive.
   (c) Using array detectors, can measure full correlation functions in a total times of several correlation times. IE non-equilibrium and time resolved.
3. First and foremost the future is to use current and new sources to continue to make routine XPCS measurements in ever more systems at higher time resolutions.

4. Coherent diffraction is diffraction and so use more then time evolution, such as full width at half maximum and other coarse features like number and orientational information. (Higher order moments.)
5. High angle XPCS is harder (smaller diffraction volumes), more complicated to analyze ($\vec{q}$ fluctuates in and out of diffraction) but has more information and this information is useful.
6. Ideally would like tunable focussing from .1 μm to 10 μm and scanability. Covers length scales *simultaneously* from Åto mm.
7. Take advantage of high q resolution (speckle – 10μm) in diffuse scattering. (Repeatablity, hysterisis, thermal expansion.)

Theory of Everything *Else*

Langevin dynamics (Models A through J):

$$\frac{\partial \Psi_\mu(\vec{x},t)}{\partial t} = \{F, \Psi_\mu(\vec{x},t)\}_{PB} - M_{\mu\nu}\frac{\partial F}{\partial \Psi_\nu} + \eta_\mu(\vec{x},t)$$

$$= -\int \{\Psi_\mu(\vec{x},t), \Psi_\nu(\vec{x}',t')\}_{PB}\frac{\partial F}{\partial \Psi_\nu} d\vec{x}' - M_{\mu\nu}\frac{\partial F}{\partial \Psi_\nu} + \eta_\mu(\vec{x},t)$$

$$= V_\mu(\vec{x},t) - M_{\mu\nu}\frac{\partial F}{\partial \Psi_\nu} + \eta_\mu(\vec{x},t)$$

where

$$\langle \eta_\mu(\vec{x},t)\rangle = 0$$

and (generalized Einstein-Stokes/fluctuation-dissipation)

$$\langle \eta_\mu(\vec{x},t)\eta_\nu(\vec{x}',t')\rangle = -2M_{\mu\nu}k_b T\delta(\vec{x}-\vec{x}')\delta(t-t')$$

Reference: Section 8.6.3 *Principles of condensed matter physics*, Chaikin and Lubensky(1995).