Using coherent x-rays to study disordered materials

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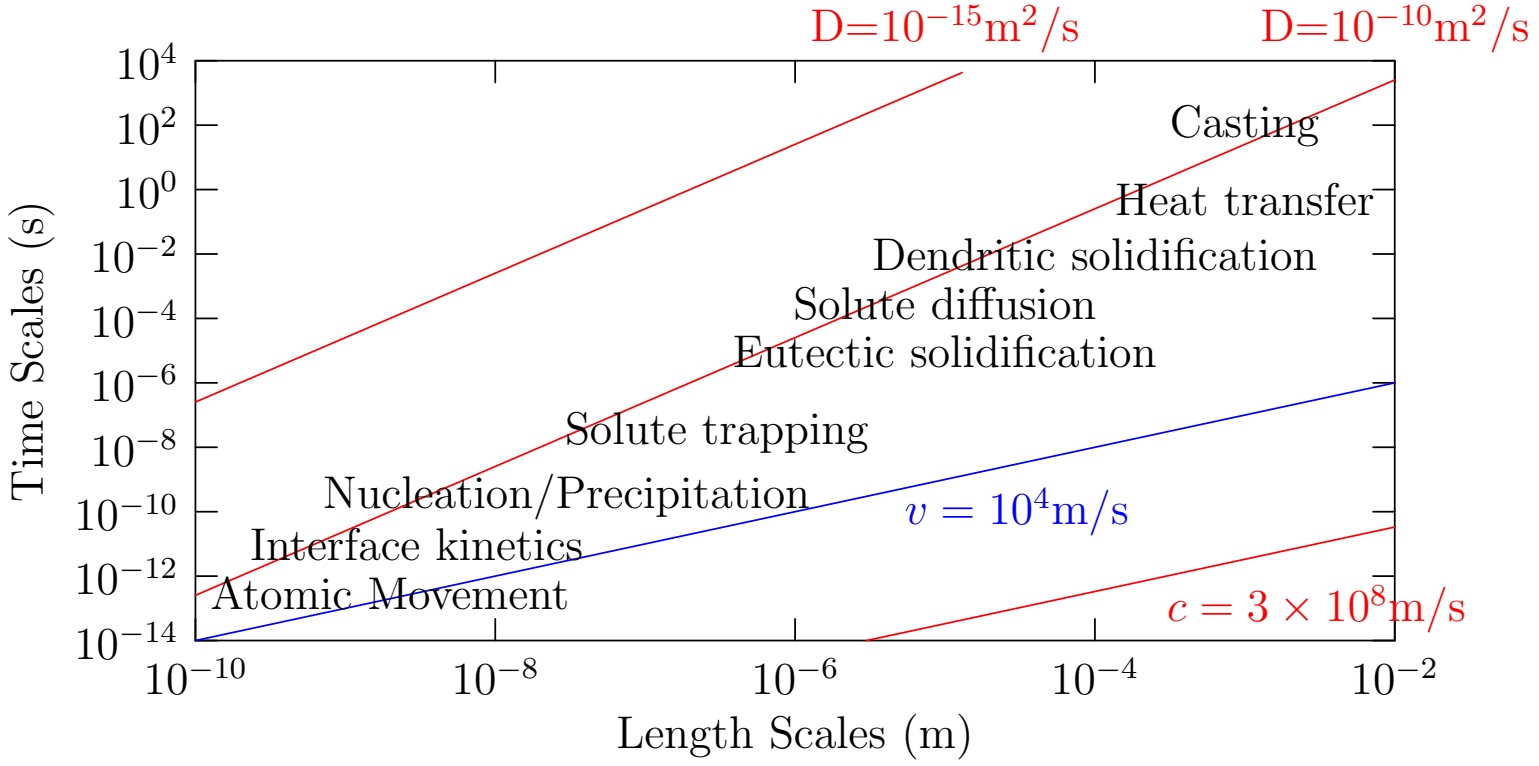
Outline

1. Introduction
2. Speckle
3. Velocity profiles
4. Wide Angle XPCS
5. Conclusions

Suggested Themes

1. Strongly correlated materials
2. Energy storage materials
3. Self assembly of mesoscale functional materials
4. complexity in glass and fluids
5. Magnetism (combined with strongly correlated materials?)
6. Biophysics of protein, membrane, and cells.
7. Extreme conditions
8. Ferroelectric films and devices
9. Nanoparticles, bio-nano and photovoltaic devices
10. Earth science: minerals under pressure

Space-time diagrams



Stolen from N. Provatas, Mcgill University

Langevin dynamics (Models A through J)

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

where

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

and (generalized Einstein-Stokes/fluctuation-dissipation)

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

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

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Why Coherence?

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

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

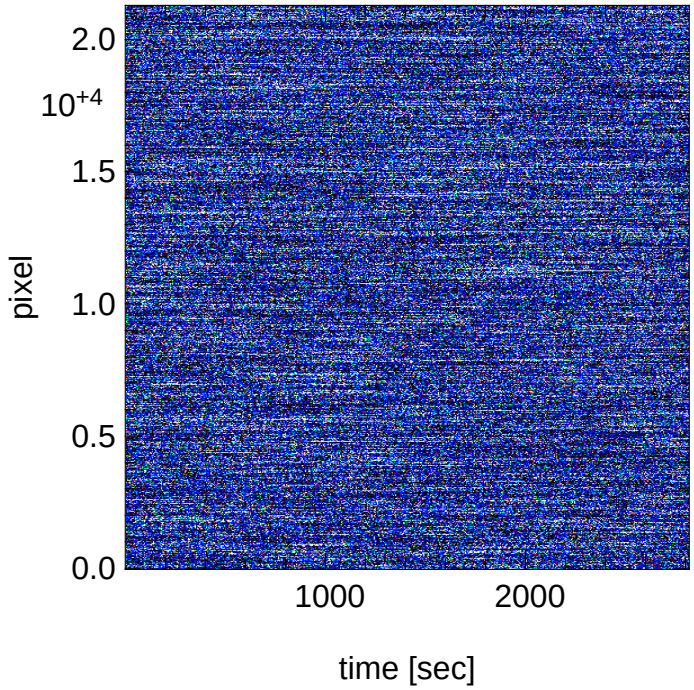
where the coherence part is:

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

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:

$$g^{(2)}(\vec{Q},\tau) - 1 = \frac{\langle I^2(\vec{Q},t)\rangle - \langle I(\vec{Q},t)\rangle^2}{\langle I(\vec{Q},t)\rangle^2}$$

$$= \beta(\vec{0}) \left| g^{(1)}(\vec{Q},\tau) \right|^2$$

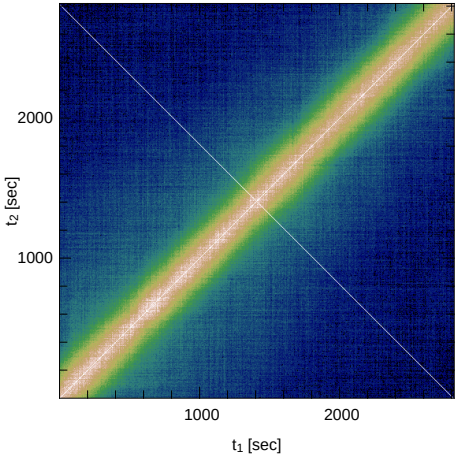
$$= \beta(\vec{0})\, e^{-2\tau/\tau_Q}$$

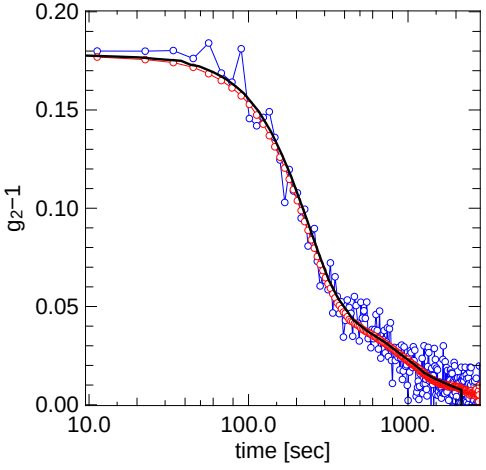
Often $g^{(1)}$ is a stretched exponential:

$$g^{(1)}(\vec{Q},\tau) = e^{-\left(\tau/\tau_Q\right)^{\alpha}}$$

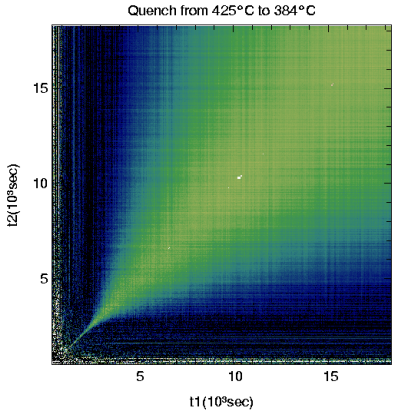
Two-time correlation functions

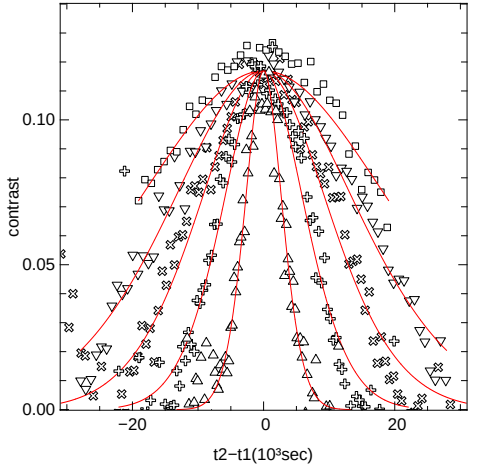
Au in polystyrene





Cu_3Au





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:

$$
\begin{aligned}
\frac{s}{n} &\approx \beta\, B_0 dx dx' dy dy' \frac{\Delta E}{E}\ \frac{1}{V}\frac{d\sigma}{d\Omega} L\ \sqrt{N_{sp}} \\
&\approx \beta B_0 f_x f_y\ \frac{\lambda^2}{4}\ \frac{\Delta E}{E}\ \frac{1}{V}\frac{d\sigma}{d\Omega} f_z \frac{\lambda^2}{2\Delta\lambda}\ \sqrt{N_{sp}} \\
&\approx \frac{1}{max(1, f_i)^3} B_0 f_x f_y f_z\ \frac{\lambda^2}{8}\ \frac{\Delta\lambda}{\lambda}\ \frac{1}{V}\frac{d\sigma}{d\Omega}\frac{\lambda^2}{\Delta\lambda}\ \sqrt{N_{sp}} \\
&\approx B_0\ \frac{\lambda^3}{8}\frac{1}{V}\frac{d\sigma}{d\Omega}\sqrt{N_{sp}} \\
&\approx f B_0\ \lambda^3 \frac{1}{V}\frac{d\sigma}{d\Omega}\sqrt{N_{sp}} \quad (if any f_i < 1).
\end{aligned}
$$

Detector Resolution

Speckle size (width of $\beta(\vec{\kappa})$) is given by diffraction limit of beam. So need to match:

$$\Delta\theta \approx \frac{\lambda}{d_{coh}} \approx \frac{d_{coh}}{R_{det}}$$

to resolve on detector. Thus

$$R_{det} = \frac{d_{coh}^2}{\lambda}$$

Don't want too large a mismatch between speckle size and the "diffraction width" of sample peak.
Probably should focus for a virtual source, IE for 1.5Å , a 100μm source at 10m gives $d_{coh} = 15\mu$m.
Ideally optics could tune coherence lengths.

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Dispersion in velocity

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

$$G_2(\vec{q},t) = 1 + \beta \exp\left\{-2\int_0^t dt' Dq'^2\right\} \left|\bar{I}\left(\int_0^t dt' \vec{q}' \cdot \Gamma\right)\right|^2$$

where, $\frac{d\vec{q}'}{dt} = -\Gamma^T \cdot \vec{q}'$, $\vec{q}'(0) = \vec{q}$.

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

Homodyne anisotropic line shapes

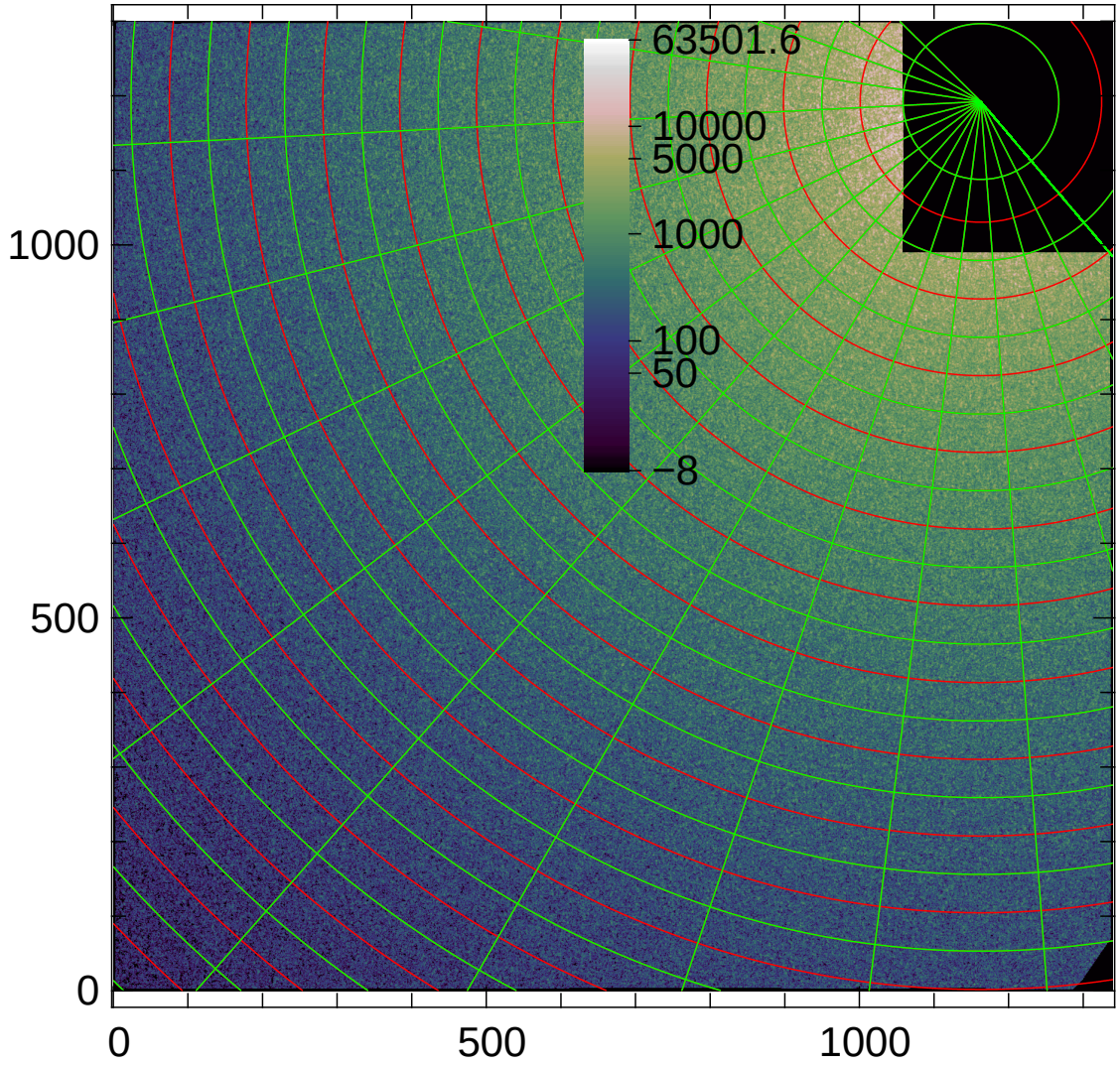
For simple linear shear and constant intensity over a rectangular beam we get:

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

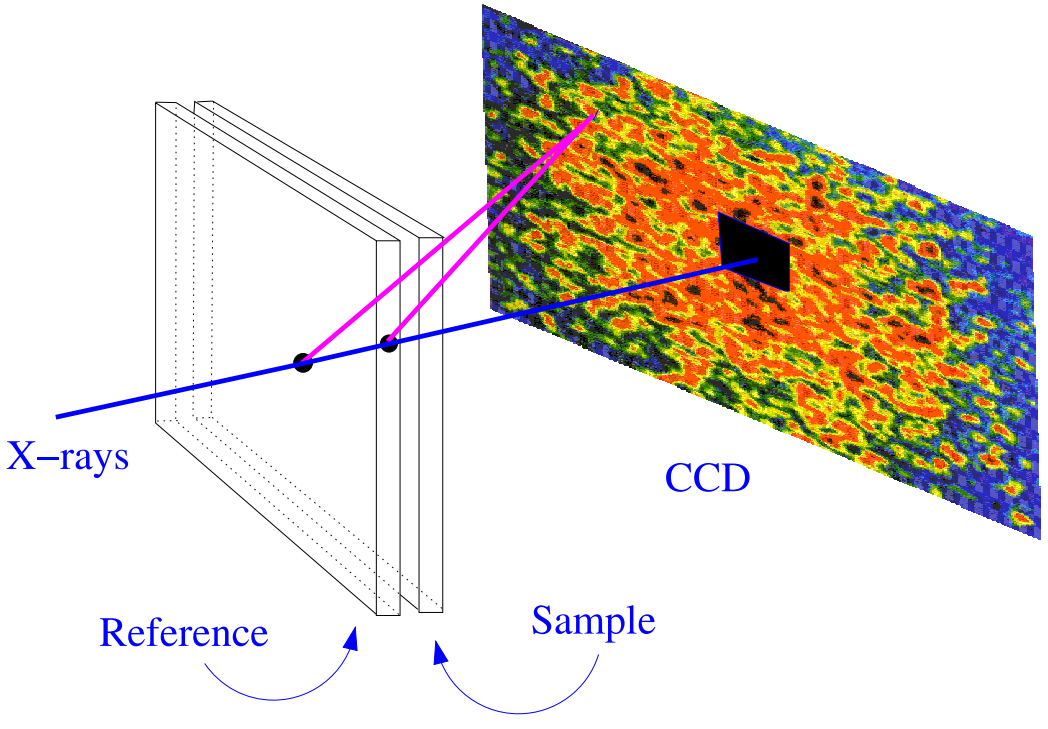
For Poiseuille flow $\vec{V}(r) = V_0\hat{z}\left(1-(r/R)^2\right)$ can do the integrals in terms of Fresnel Integrals (or complex erf).

$$|g_1(\tau)|^2 = \frac{\pi^2}{16 q_z \tau V_0}\left|\mathrm{erf}\left(\sqrt{\frac{4 i q_z \tau V_0}{\pi}}\right)\right|^2.$$

Partitioning the Scattering



Experimental Setup



Scattering geometry

Heterodyne

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

Moving at constant velocity gives phase factor

$$e^{i\vec{q}\cdot\vec{r}(t)} = e^{i\vec{q}\cdot\vec{v}t} = e^{i\omega t}$$

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

$$g_2(q,\phi,\tau) = 1+\beta(1-x)^2+x^2\beta g_2^2(t/\tau)+2x(1-x)\beta\cos(\omega t)g_1(t/\tau)$$

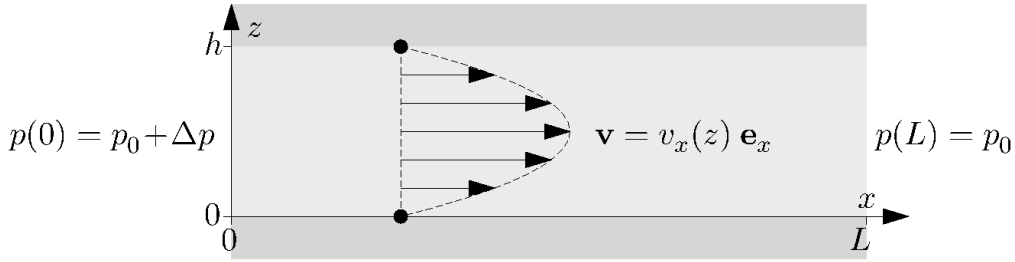
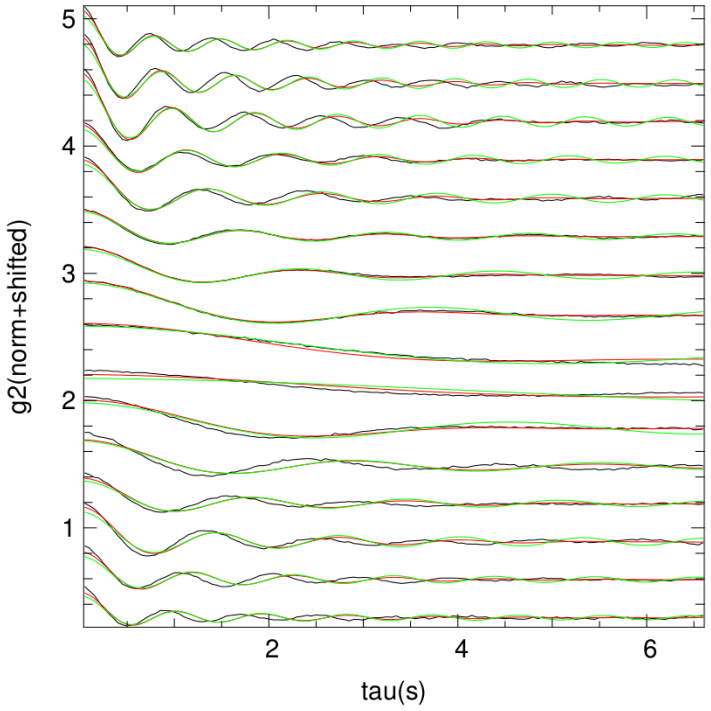
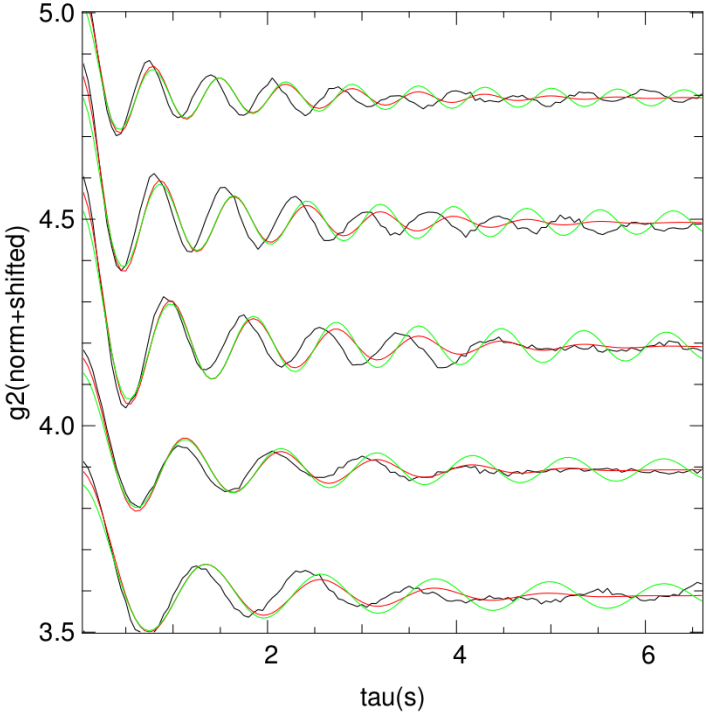


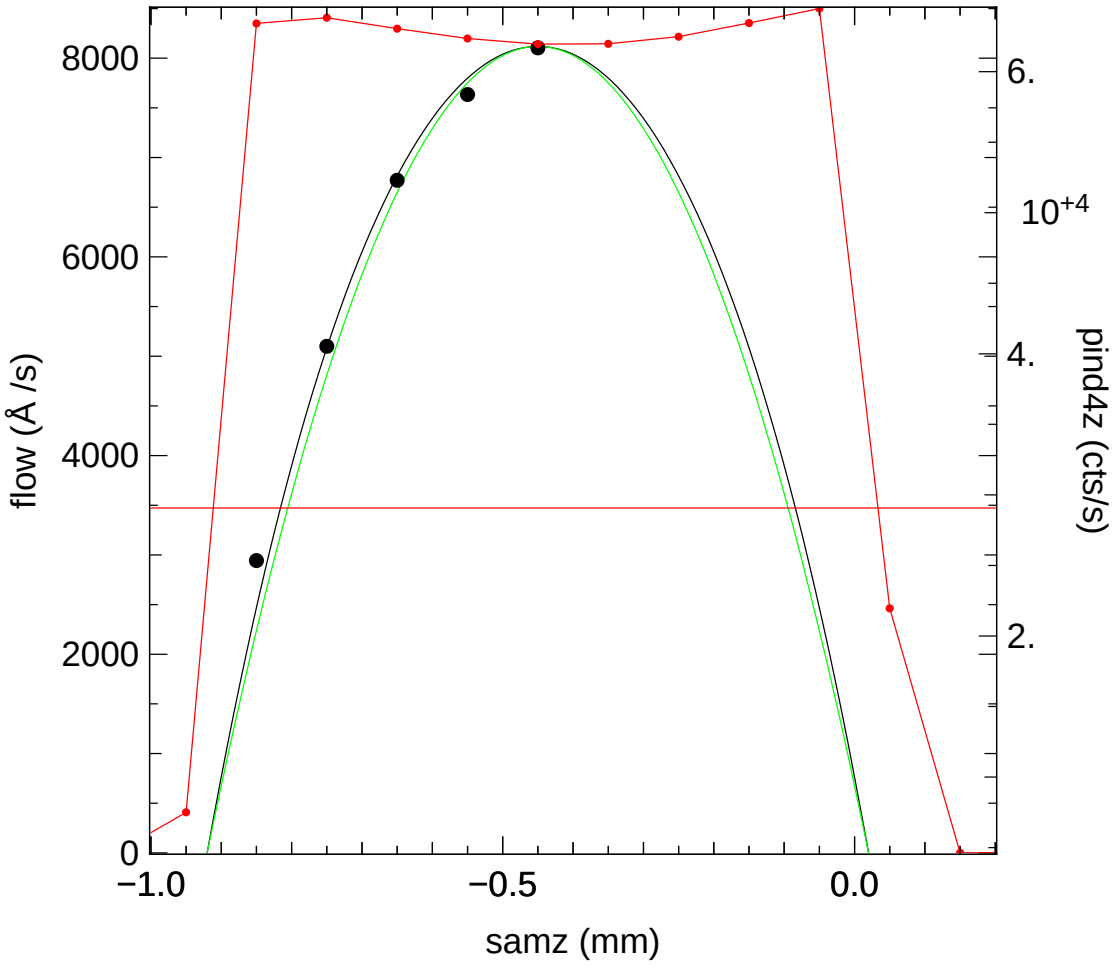
Figure 2.9: A sketch in the xz plane of an infinite, parallel-plate channel of height h. The system is translation invariant in the y direction and fluid is flowing in the x direction due to a pressure drop Δp over the section of length L.

Flow correlations





Velocity profile



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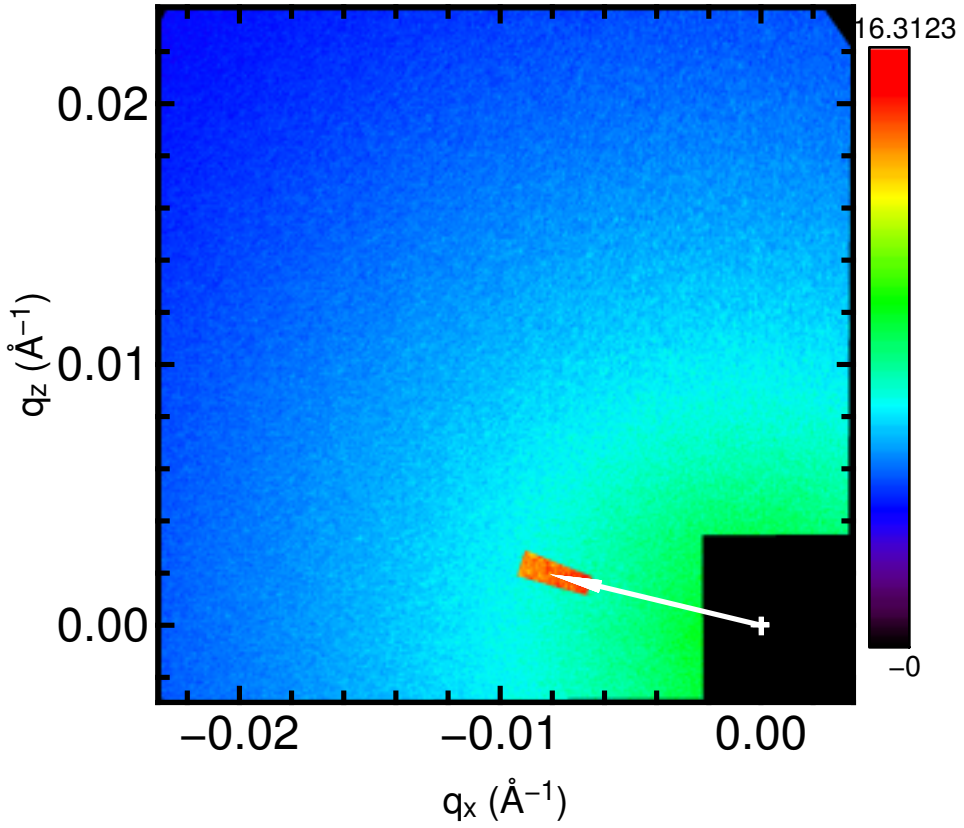
Speckle $\vec{Q}$ correlations.



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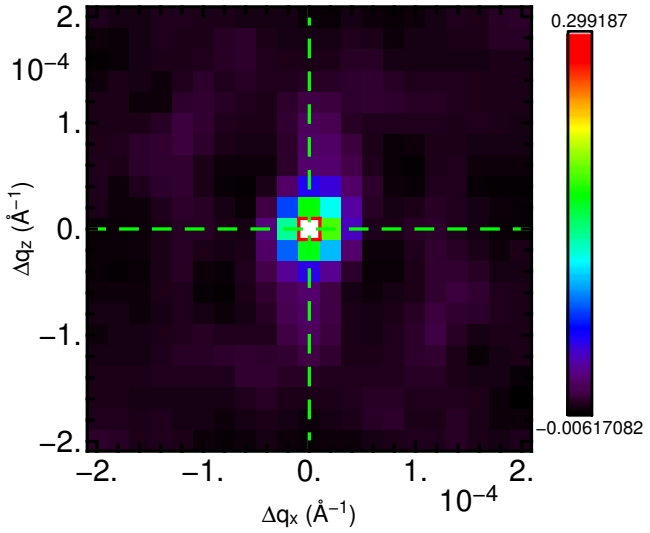
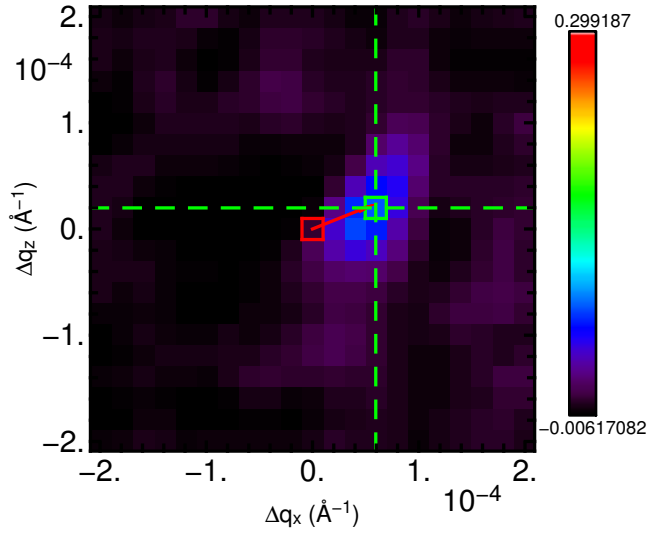
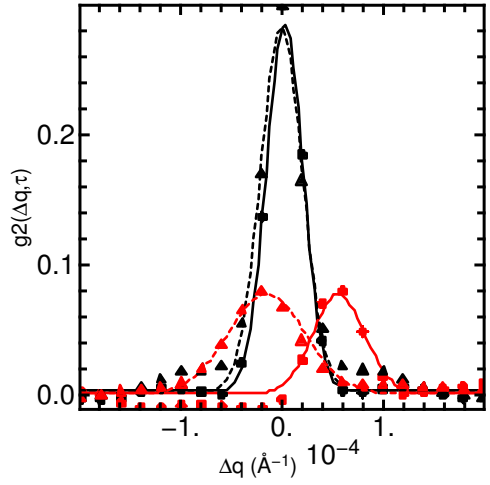
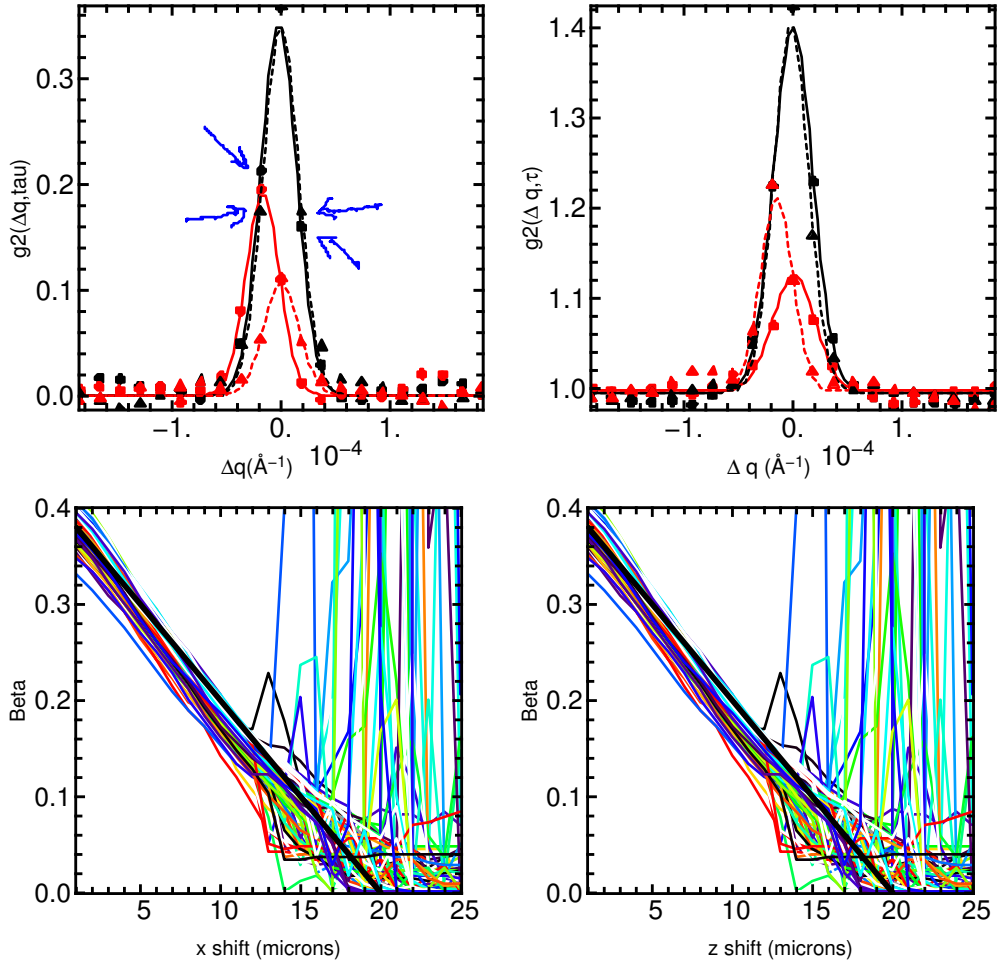






Horizontal Shift
for typical bin
11 μ,1 μm

Vertical Shift
for typical bin
11 μ,1 μm



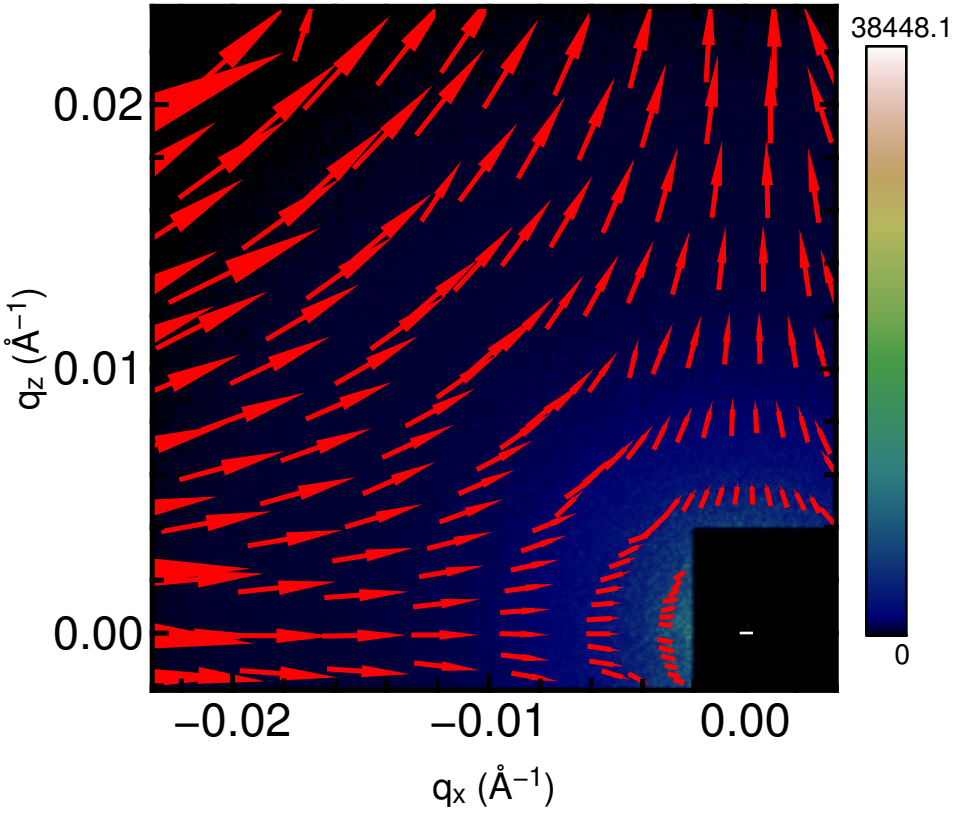
$g_2 - 1 \approx f^2 \beta$

$f = 1 - \frac{\text{shift}}{w}$

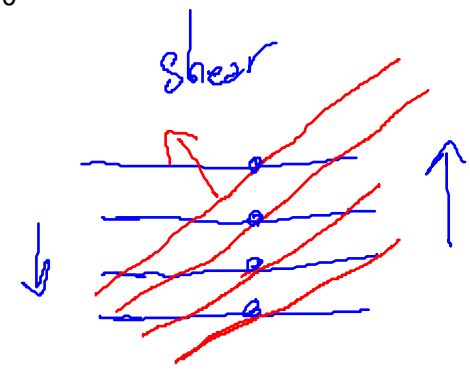
Loss of contrast

Loss of contrast

Flow in rubber under stress



Length of arrows are 200 times shift.



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3. Martensitic transtions: Co
4. Charge Density Waves: TaS_2
5. Heterodyne
6. Translations
7. Rotations
8. Shear
9. Conclusions

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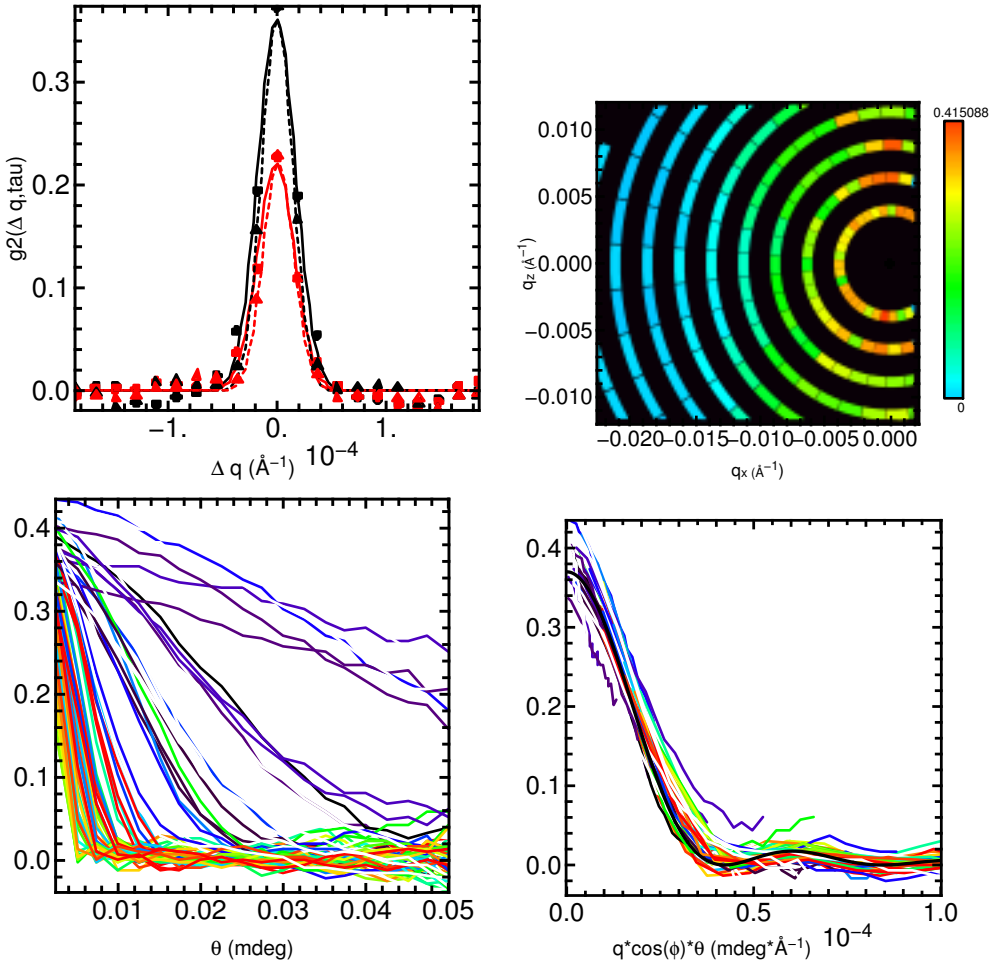
Rotations



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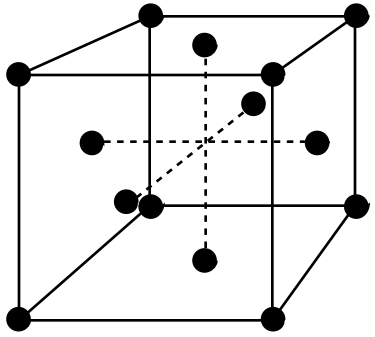
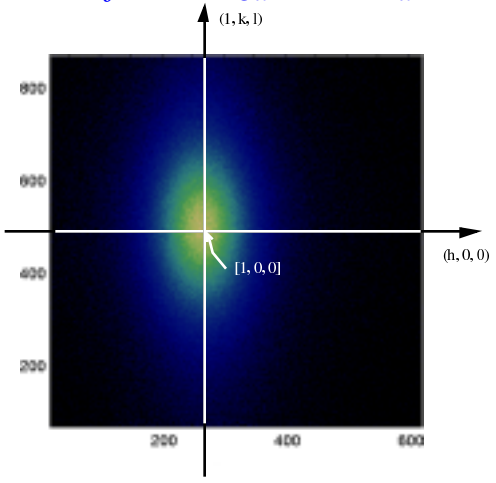
Order-disorder phase transitions in Cu_3Au

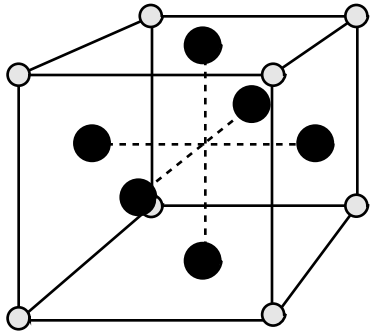
Disorder:



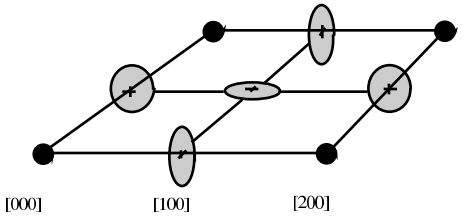
f=0.75 f_{Cu}+0.25 f_{Au}



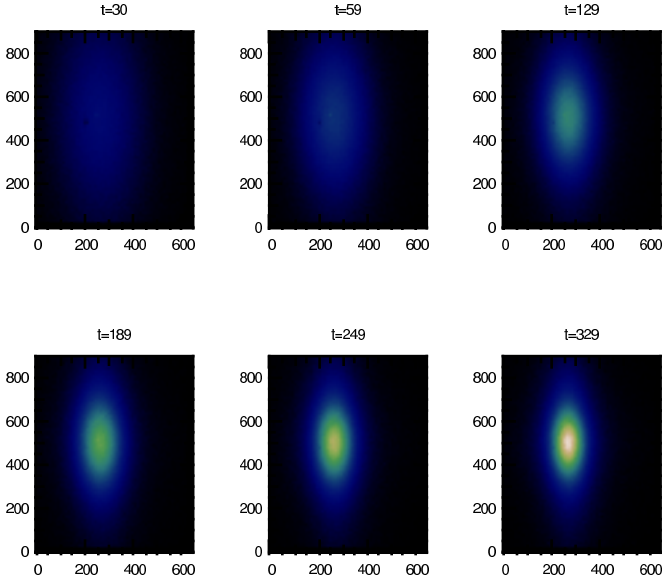
Order:

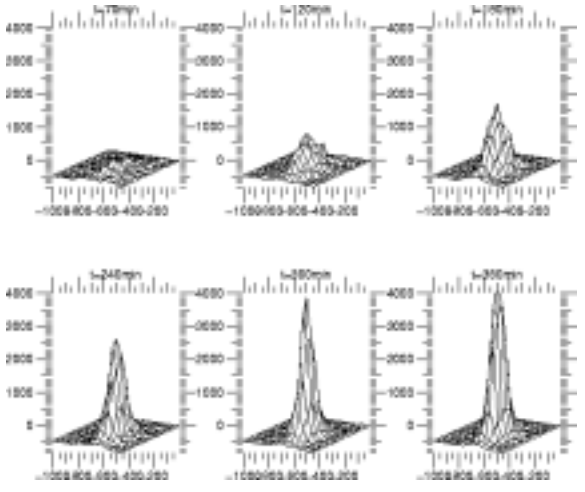


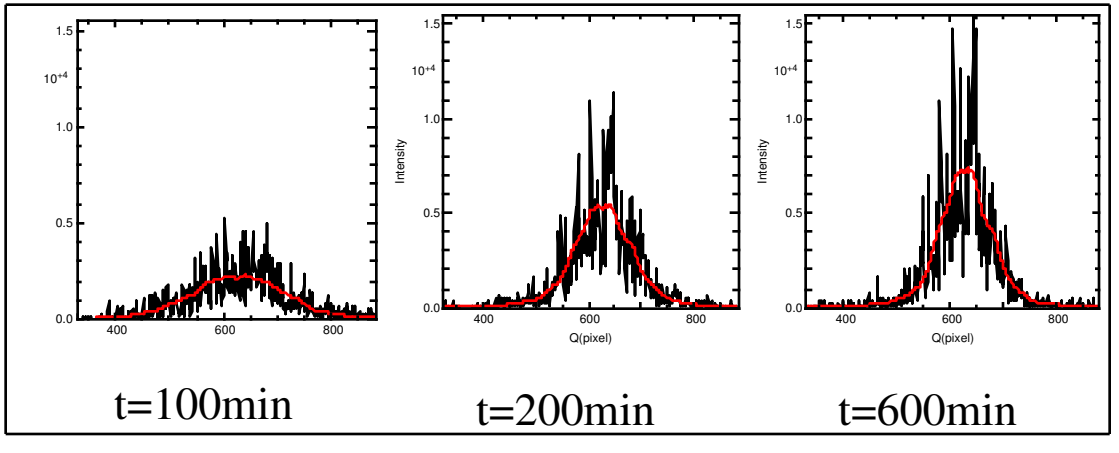
f_{Cu}, f_{Au}



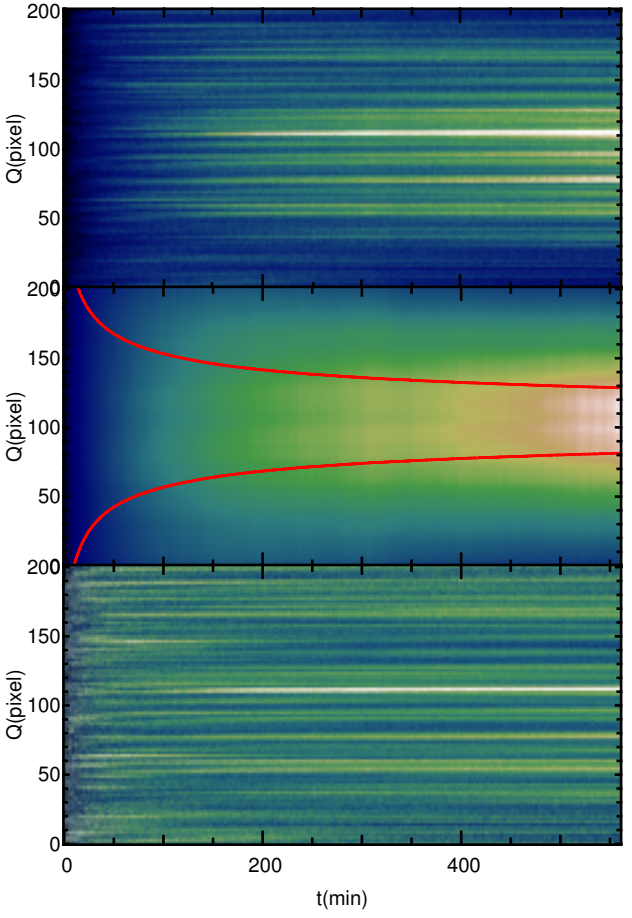
Scattering from Cu_3Au



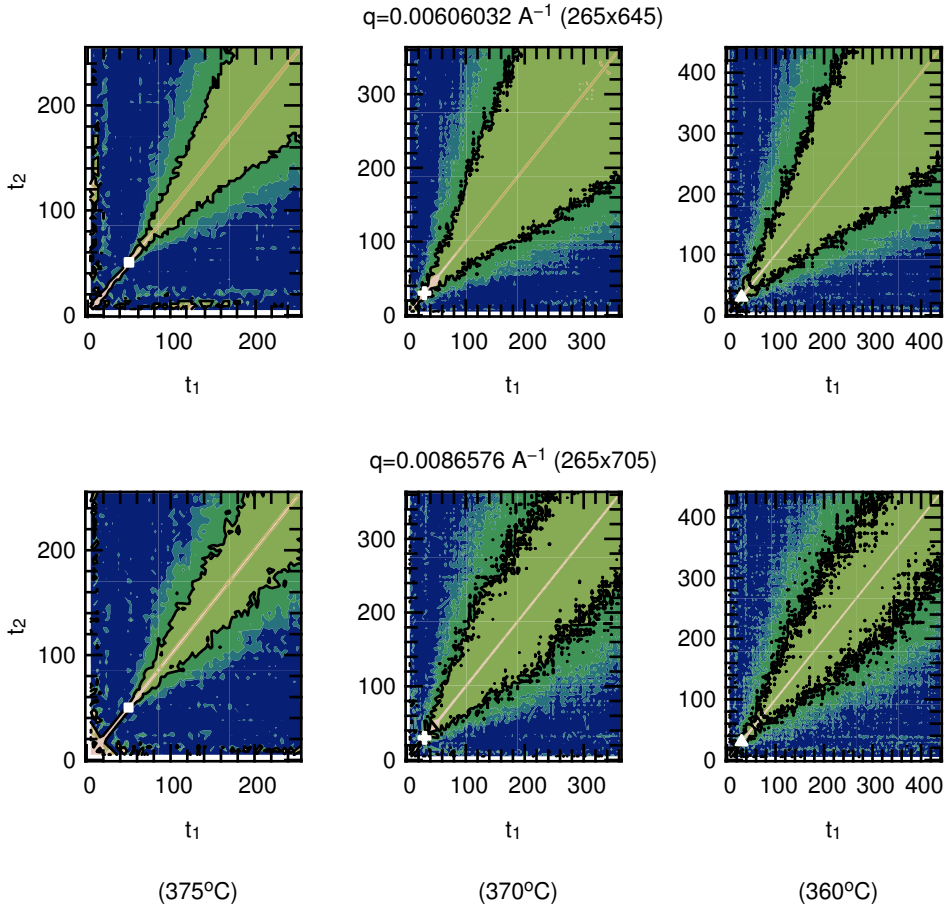




Cu_3Au Evolution

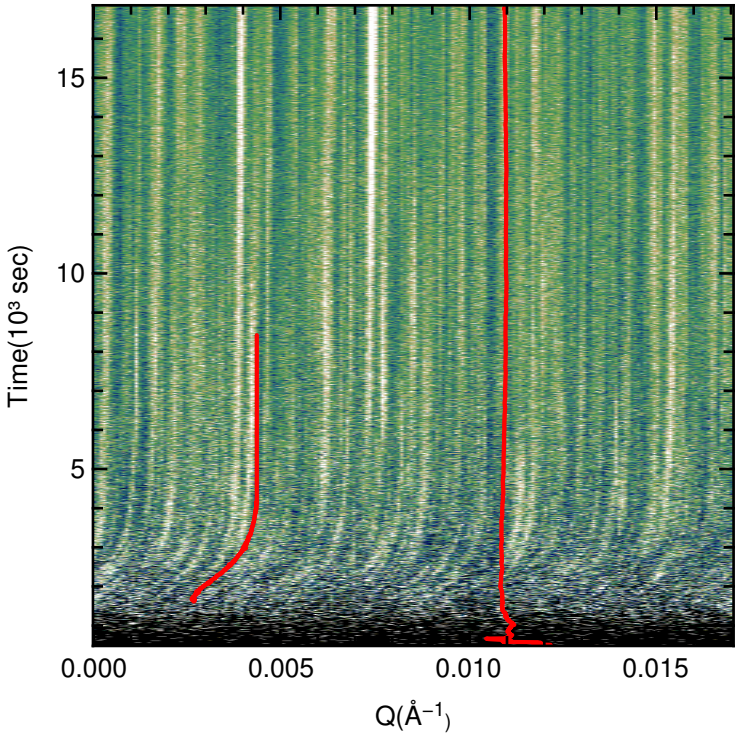


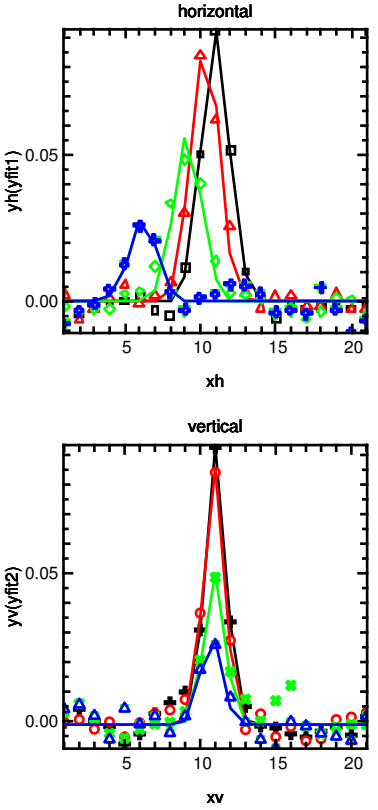
Two-Time Correlation Functions



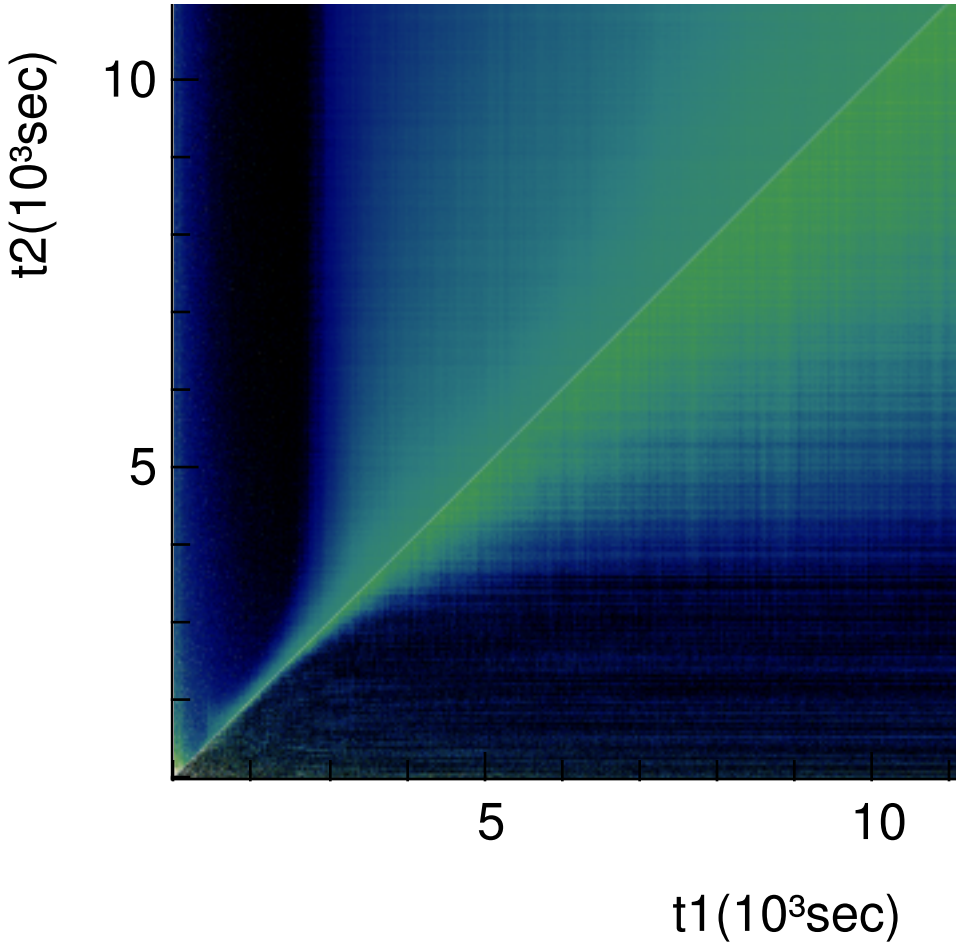
Tranverse direction

New Data

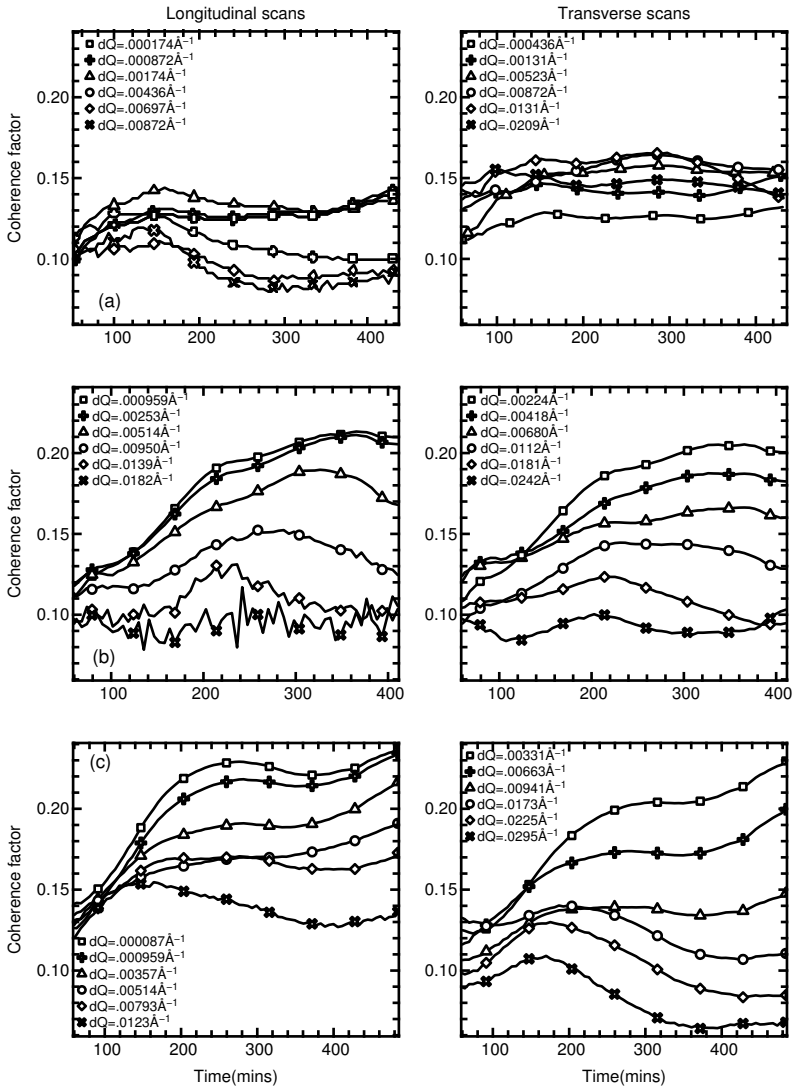

Time(10^3 sec)
15
10
5
0.000
0.005
0.010
0.015
Q(Å^{-1})


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

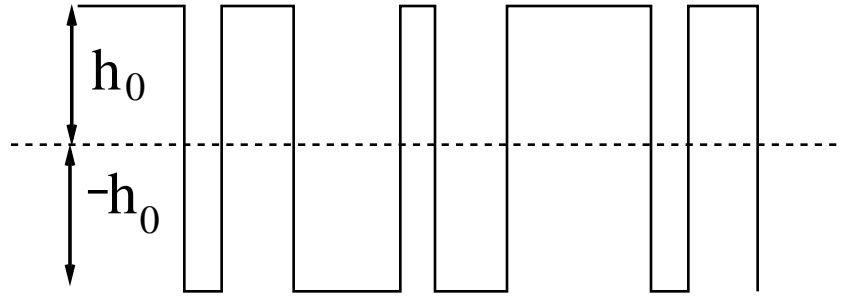
Two-$\vec{Q}$ two-time correlations



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):

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

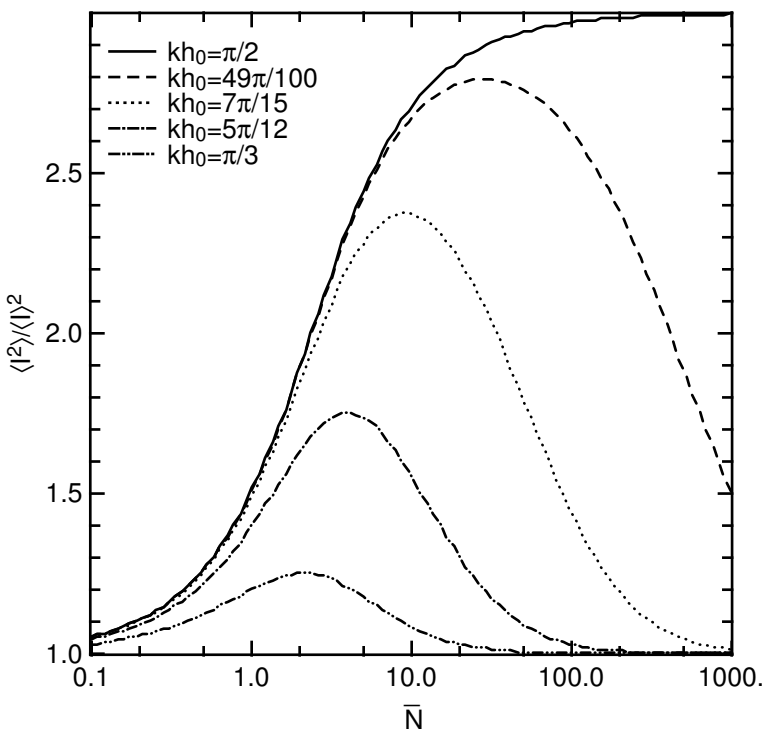
converts the phase to an amplitude.

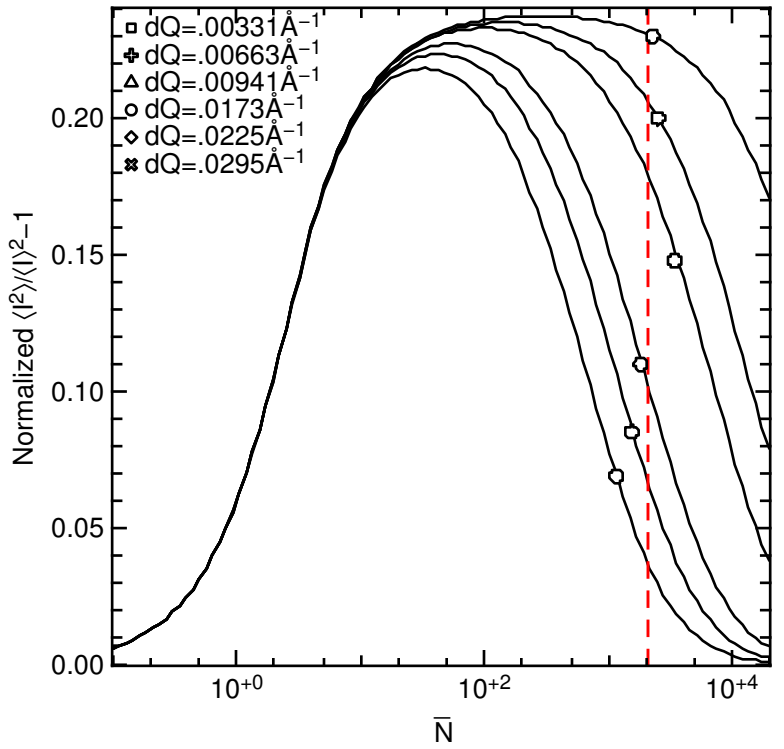
$$S(q) = |F^*(q)F(q)| =$$

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

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

Telegraph Waves



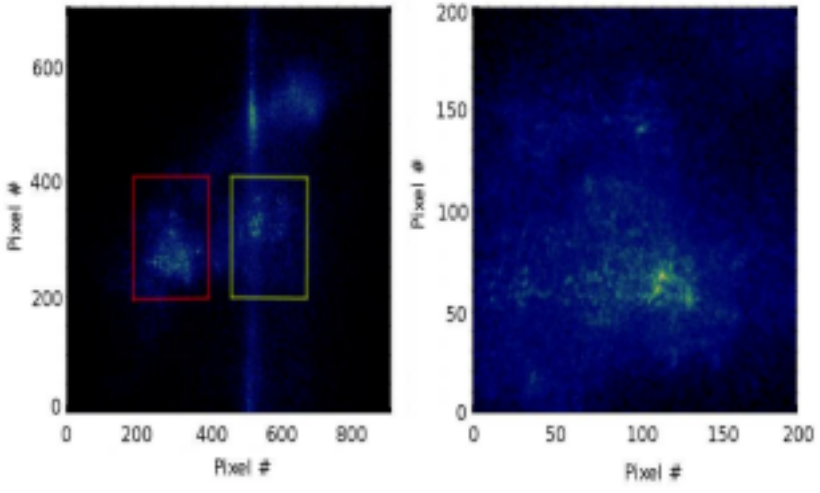


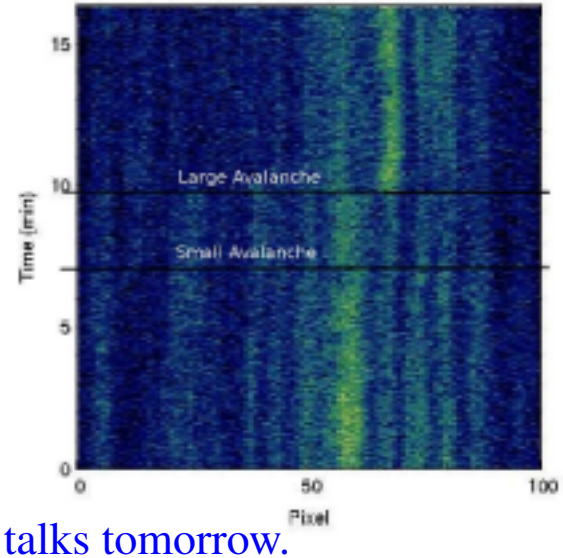
If phase shift of domain wall is 180° ($kh_0 = \pi/2$), crossing two domain walls correlates again and $cos(kh_0) = 0$.

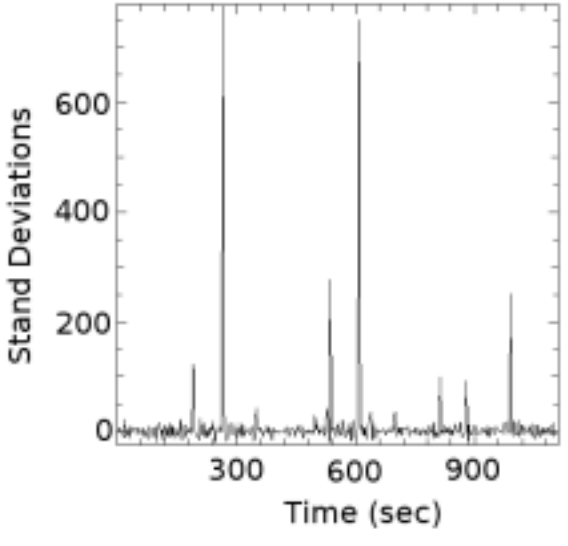
Outline

1. Introduction
2. Order-Disorder transtions: Cu_3Au
3. Martensitic transtions: Co
4. Charge Density Waves: TaS_2
5. Heterodyne
6. Translations
7. Rotations
8. Shear
9. Conclusions

Co: FCC to HCP transition

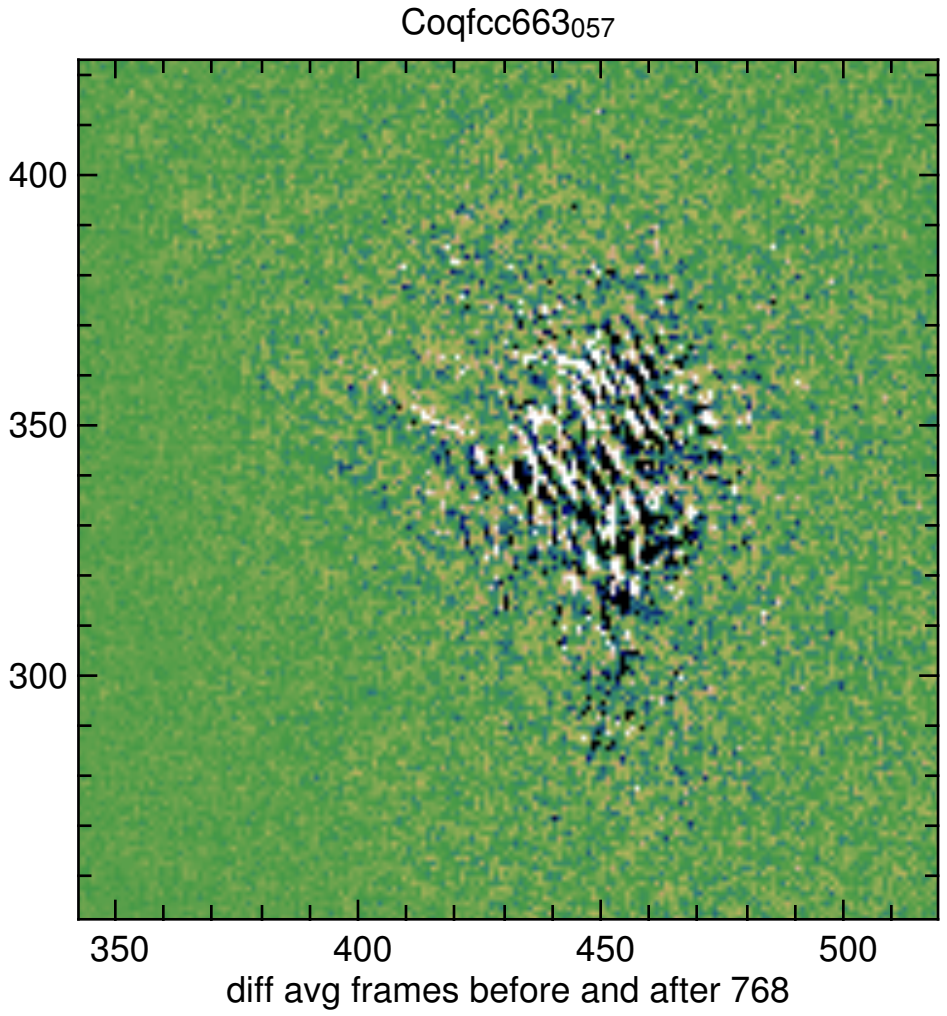






M. Rogers talks tomorrow.

Co: FCC to HCP transition



$\Delta S(q)$ ~~at~~ near (103) at 1 avalanche.

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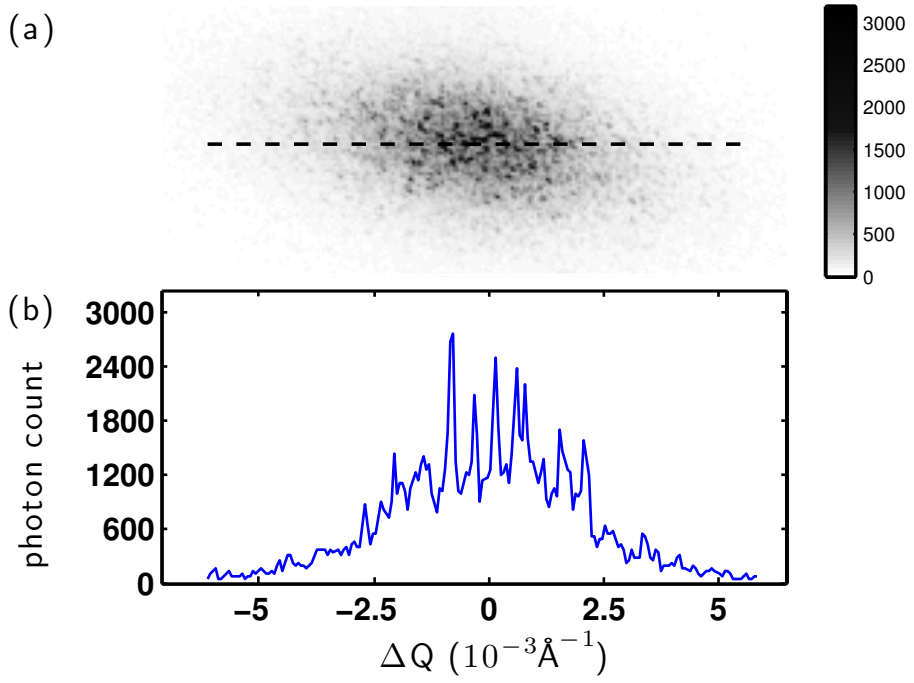
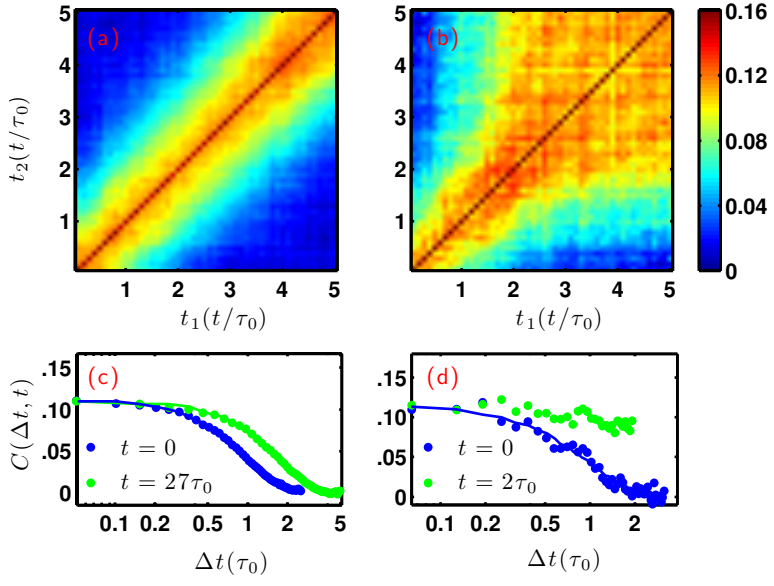
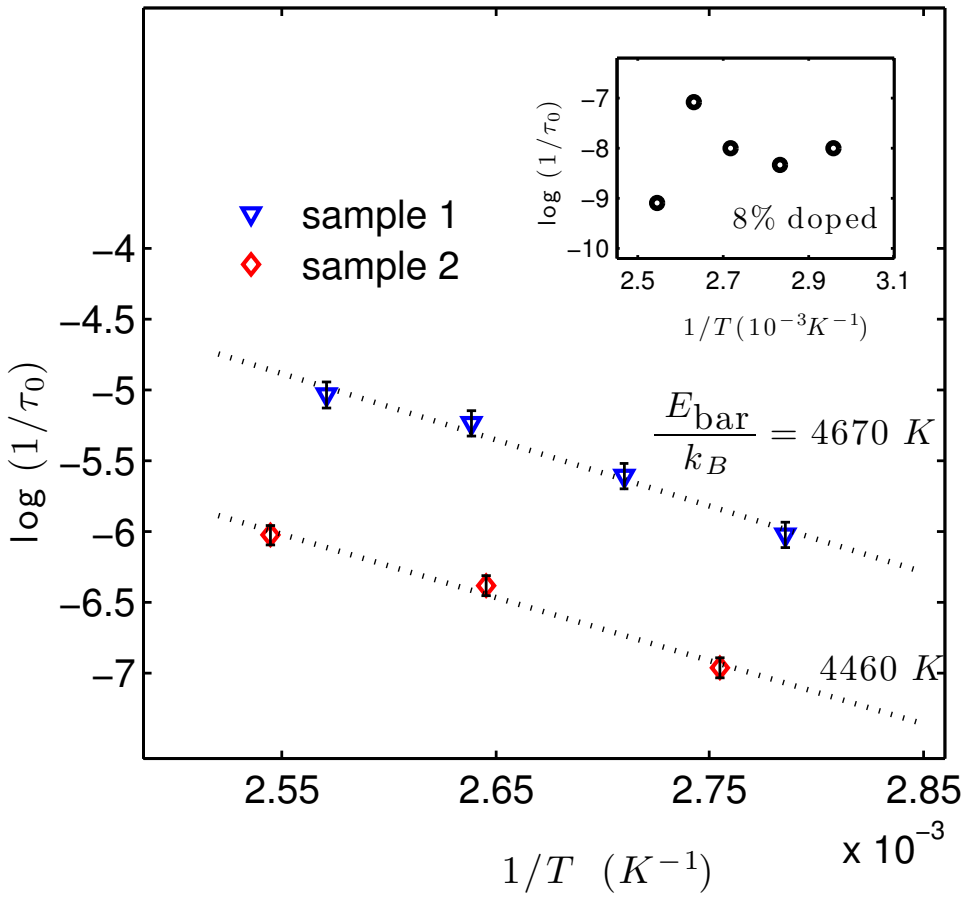
CDWs in TaS_2


(a)
3000
2500
2000
1500
1000
500
0
(b)
photon count
3000
2400
1800
1200
600
0
−5
−2.5
0
2.5
5
ΔQ (10⁻³Å⁻¹)


(a)
(b)
(c)
(d)
$t_2(t/\tau_0)$
$t_1(t/\tau_0)$
$C(\Delta t, t)$
$\Delta t(\tau_0)$
$t = 0$
$t = 27\tau_0$
$t = 2\tau_0$
0.16
0.12
0.08
0.04
0
.15
.10
.05
0.1
0.2
0.5
1
2
5

CDWs in TaS_2


sample 1
sample 2
$\frac{E_{\rm bar}}{k_B} = 4670\ K$
4460 K
log (1/τ0)
1/T (K^-1)
x 10^-3
−4
−4.5
−5
−5.5
−6
−6.5
−7
2.55
2.65
2.75
2.85
8% doped
log (1/τ0)
1/T (10^-3 K^-1)
−7
−8
−9
−10
2.5
2.7
2.9
3.1

Outline

1. Introduction
2. Speckle
3. Velocity profiles
4. Wide Angle XPCS
5. Conclusions

Conclusions

- Large angle XPCS is more powerful than small angle XPCS. Demonstrated with three examples. More powerful, but more tricky to interpret.
- In Cu3Au, see speckles shift (but not lattice constant) and measure a contrast twice measured instrumental contrast.
- In Co, see intermittent dynamics and get structural information on the avalanches.
- in TaS2, measure activation energy by small temperature jumps.
- Note these can be consider as high diffraction resolution mea- surements in low resolution
- Co-ordinated speckle shifts give further detailled information. Can meaure diverenges, rotations and shear.
- We should use cross pixel correlations.