How can x-ray intensity fluctuation spectroscopy push the frontiers of Materials Science

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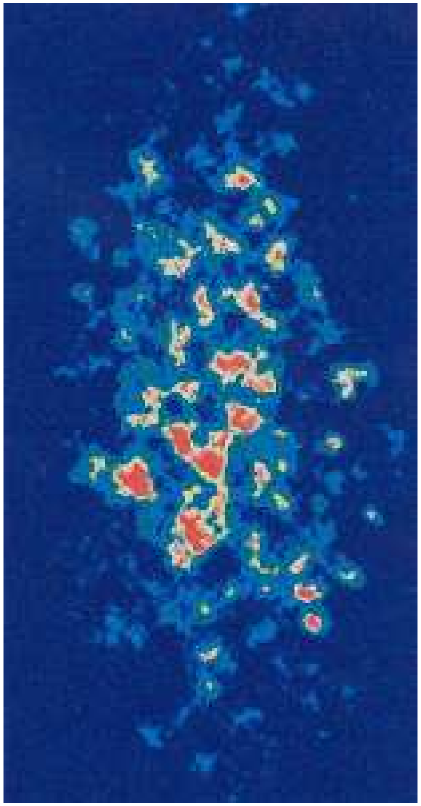
Coherent diffraction

(001) Cu_3Au peak



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 Intensity Fluctuation Spectroscopy, XIFS).

$$\langle I(\vec{Q},t)I(\vec{Q}+\delta\vec{\kappa},t+\tau)\rangle = \langle I(Q)\rangle^2 + \beta(\vec{\kappa})\,\frac{k^8}{(4\pi R)^4}V^2 I_0^2\left|S(\vec{Q},t)\right|^2$$

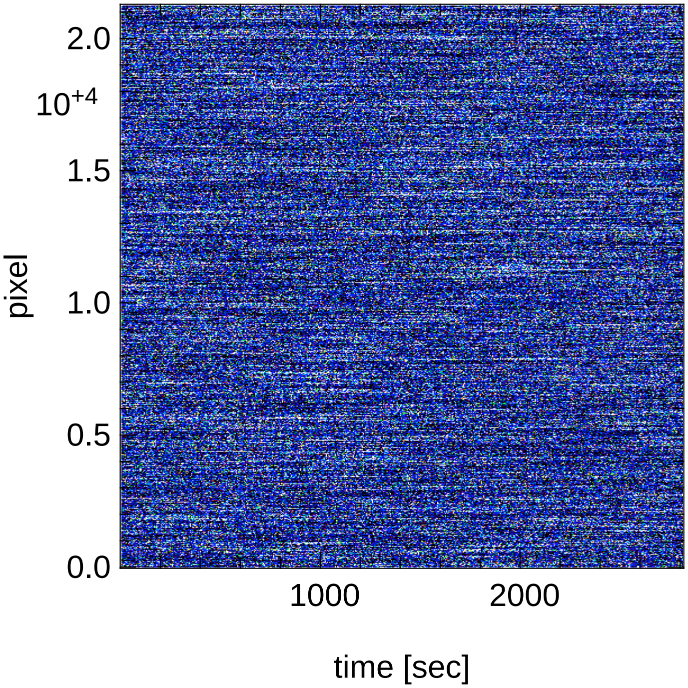
where the coherence part is:

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

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



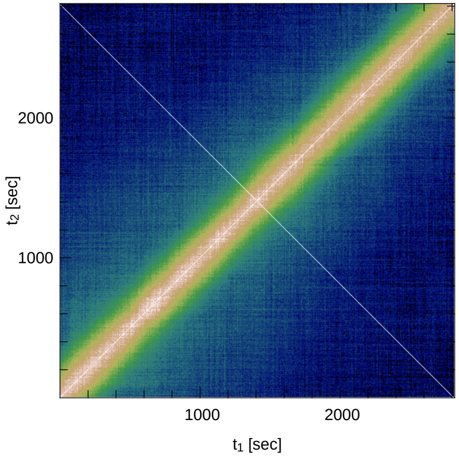
Time fluctuations in coherent scattering.

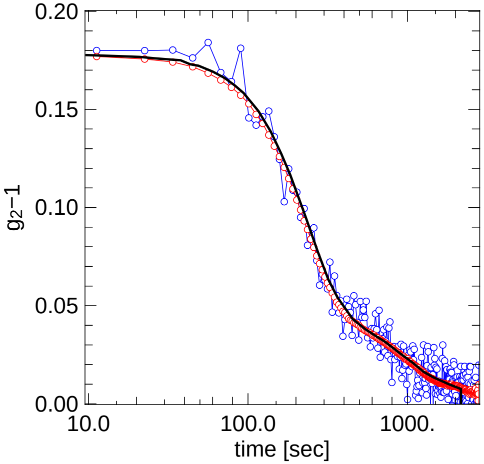
Define correlation function:

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

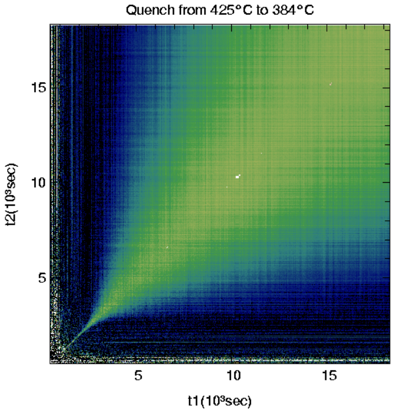
Two-time correlation functions

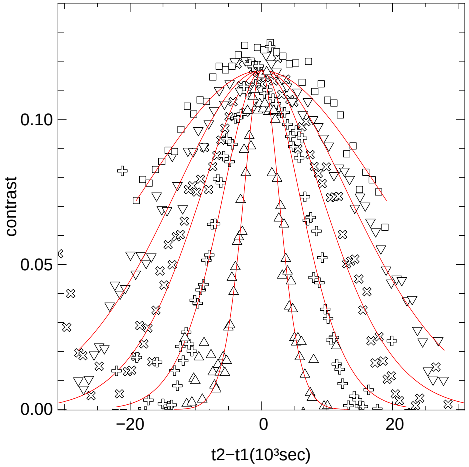
Au in polystyrene





Cu$_3$Au





Scientific Case for an Energy-Recovery Linac at Cornell University

X-Ray Photon Correlation Spectroscopy

Detlef-M. Smilgies, CHESS

Scientific Applications

Frontiers of the technique are compiled in the following subsections:

- Phase Transitions and Domain Wall Dynamics
- Dynamics of Complex Fluids
- Dynamics at Surfaces
- Dynamics of Lattice Defects and Disordered Systems
- Ultrasoft Modes in Soft Condensed Matter and Biological Systems

“Real” Equation of Everything

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).

Equilibrium Time Dependence

In equilibrium F has no linear term in Ψ so equation of motion becomes:

$$\frac{\partial\Psi(\vec{x},t)}{\partial t} = -M\left(\frac{\partial^2 F}{\partial\Psi^2}\right)_{eq}\Psi + \eta(\vec{x},t)$$

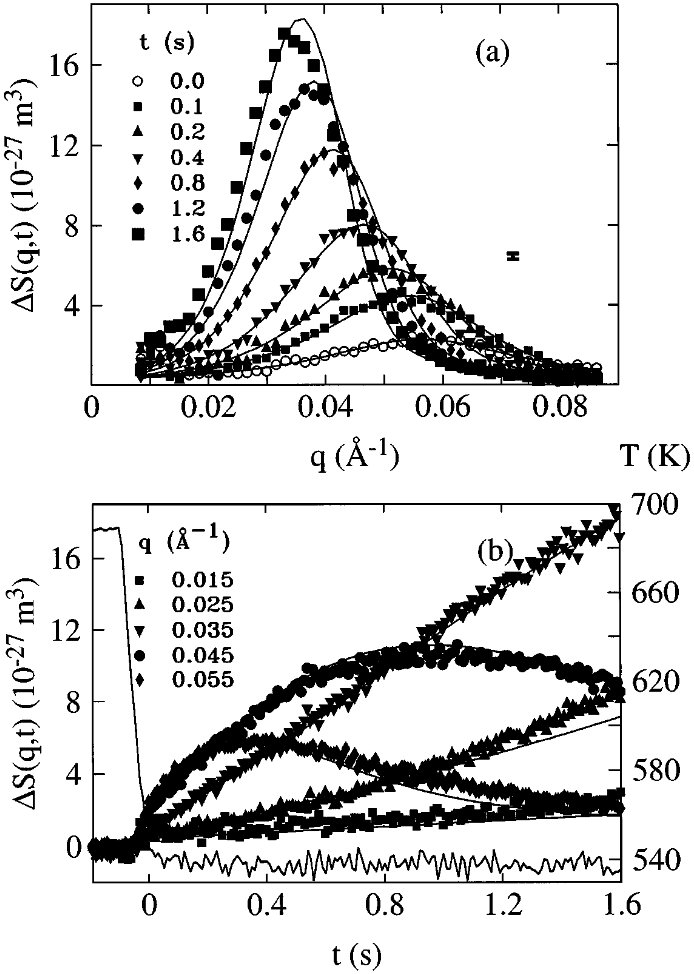
or

$$\frac{\partial\Psi(\vec{Q},t)}{\partial t} = -\frac{Mk_bT}{S(\vec{Q})}\Psi + \eta(\vec{Q},t)$$

Where the structure factor is:

$$\begin{aligned} S(\vec{Q},t) &= \langle\Psi^\dagger(\vec{Q},t)\Psi(\vec{Q},t)\rangle \\ &= k_bT\Big/\left(\frac{\partial^2 F}{\partial\Psi^2}\right)_{eq} \end{aligned}$$

Phase Separation of AlZn



$$\frac{1}{2Mq^2}\frac{\partial S(q,t)}{\partial t} = -\left(\kappa q^2 + \frac{\partial^2 f}{\partial c^2}\right)_{c_0} S(q,t) + \frac{1}{6}\left(\frac{\partial^4 f}{\partial c^4}\right)_{c_0} S_4(q,t) + k_b T$$

1) Equation of motion from J. S. Langer, M. Bar-on, and H. D. Miller, Phys. Rev. A, **11**, 1417 (1975).

2) Data from: Mainville et al, Phys. Rev. Lett., **78**, 2787 (1997).

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:

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

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

Detector Resolution

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

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

to resolve on detector. Thus

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

Problem if horizontal and vertical lengths are too different or if any coherence length is too long.

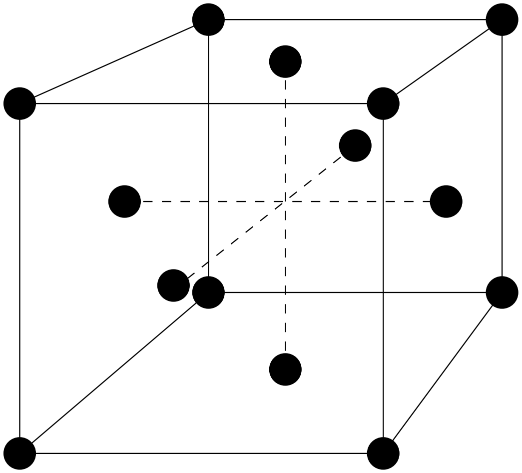
Similarly, don't want too large a mismatch between speckle size and the "diffraction width" of sample peak.

Focus for a virtual source, for 1.5Å , a 100μm source at 10m gives $d_{coh} = 15\mu$m.

Ideally optics could tune coherence lengths.

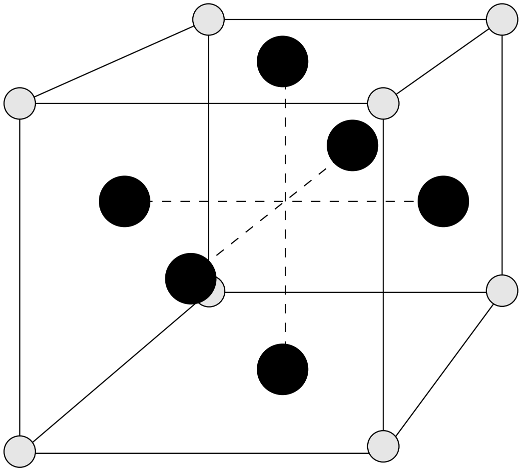
Order-disorder phase transitions in Cu_3Au

Disorder:



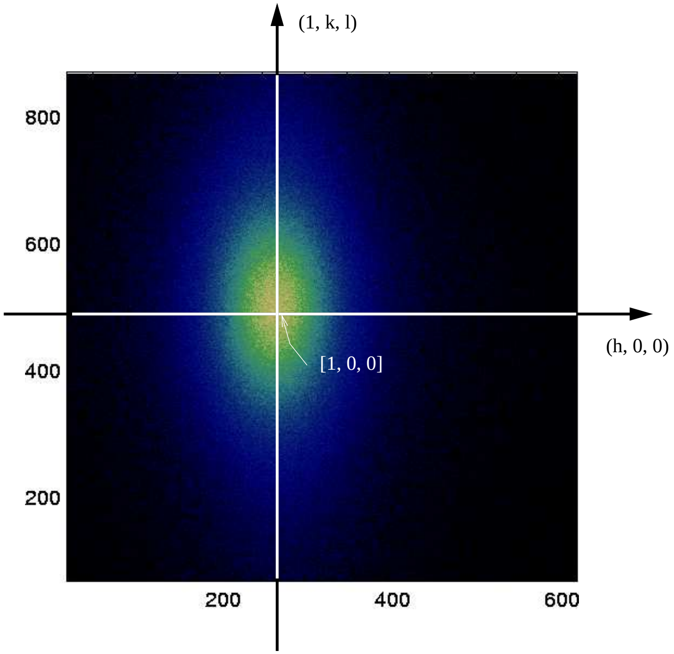
$f = 0.75\ f_{Cu} + 0.25\ f_{Au}$

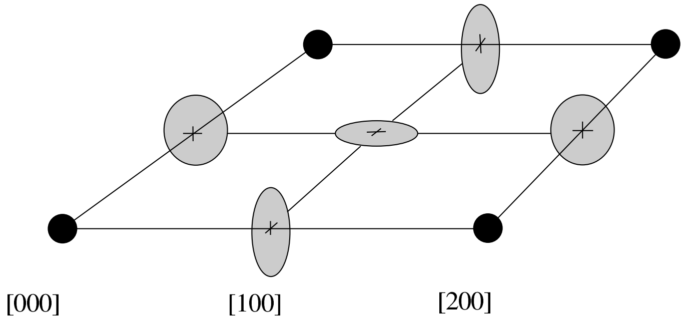
Order:



$f_{Cu},\ f_{Au}$

Scattering from Cu_3Au

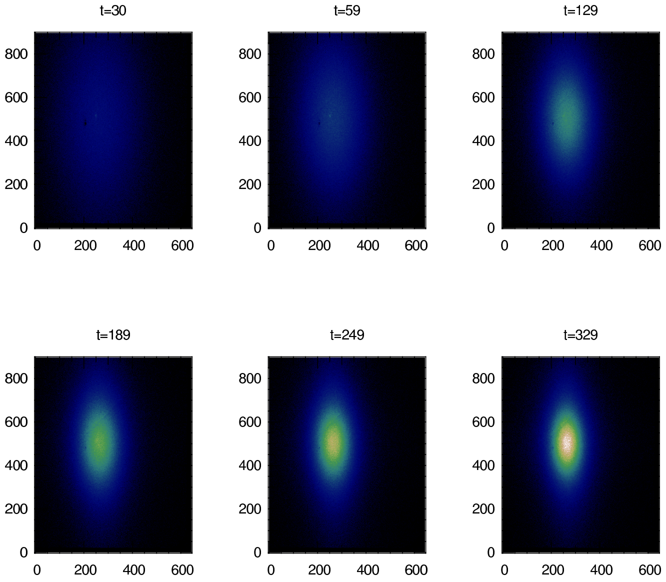


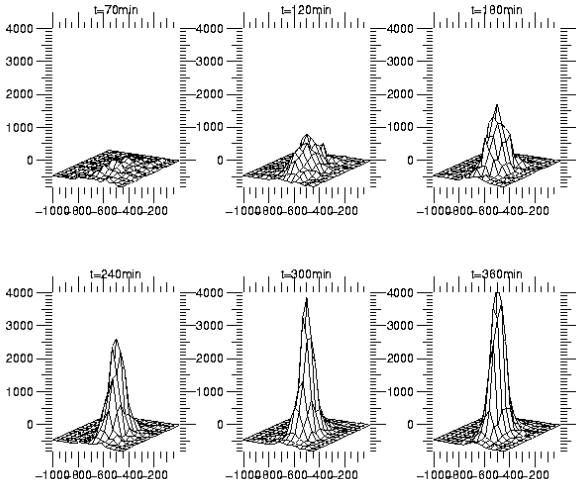


S(q,t) Movie

B.E.Warren, *X-ray Diffraction*, Dover, NY, 1969,1990

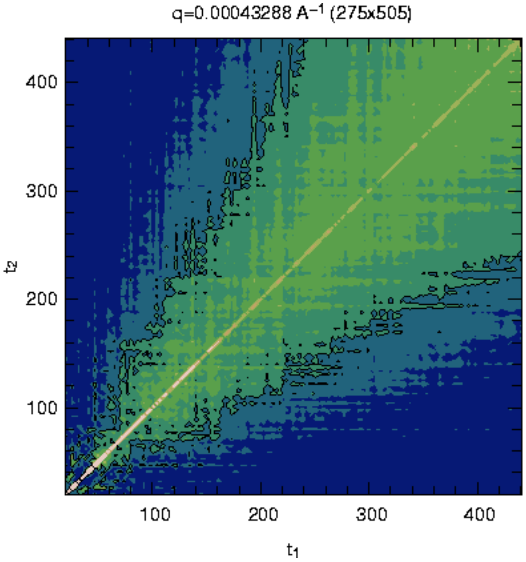
Scattering from Cu_3Au

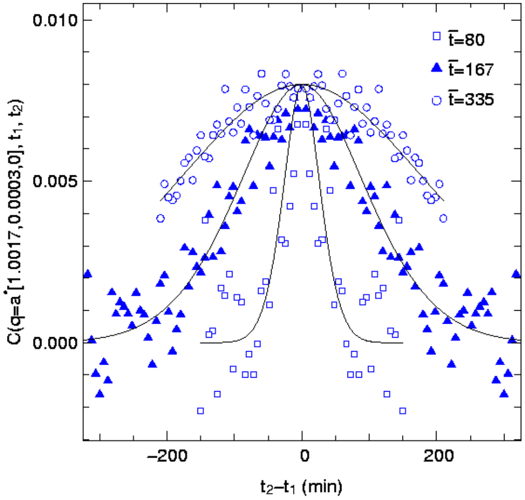




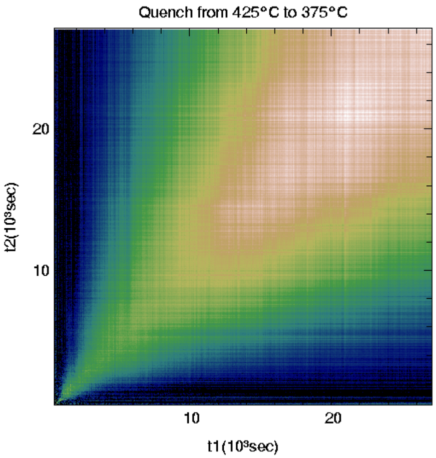
Two-Time Correlation Functions

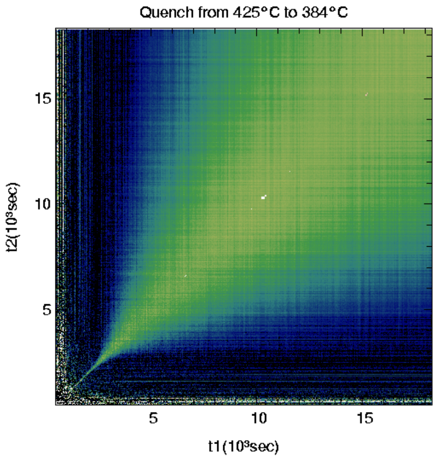
Non-stationary so autocorrelate $\frac{I(q,t_1)-\langle I(q,t_1)\rangle}{\langle I(q,t_1)\rangle}$

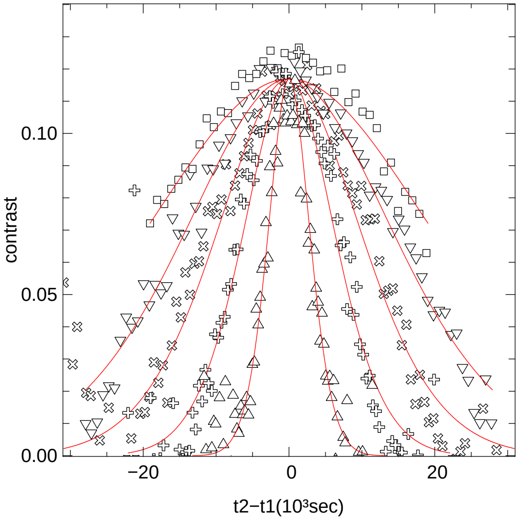




Upgrades to the beamline allow us to obtain better data, especially important for the early time region.

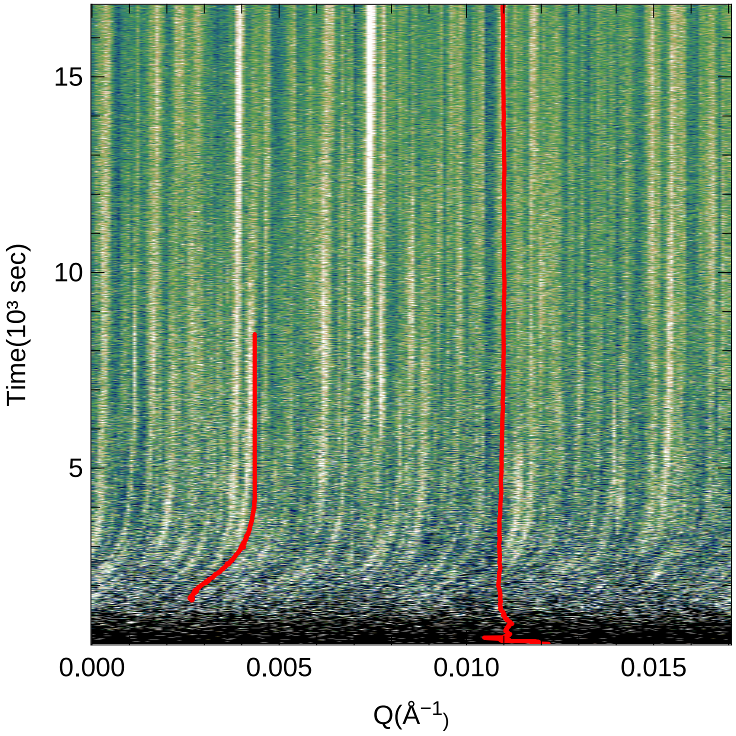


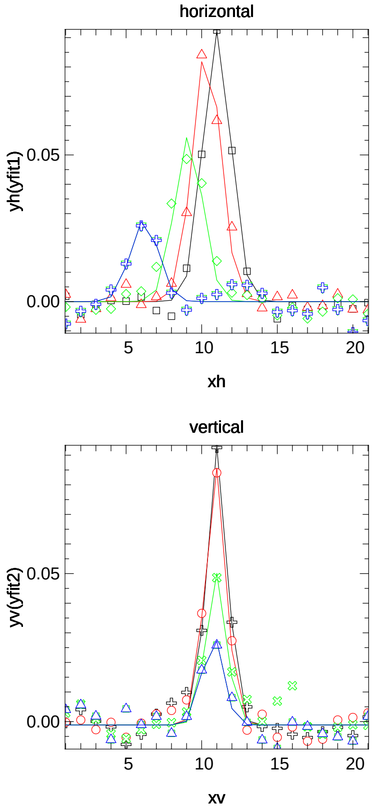




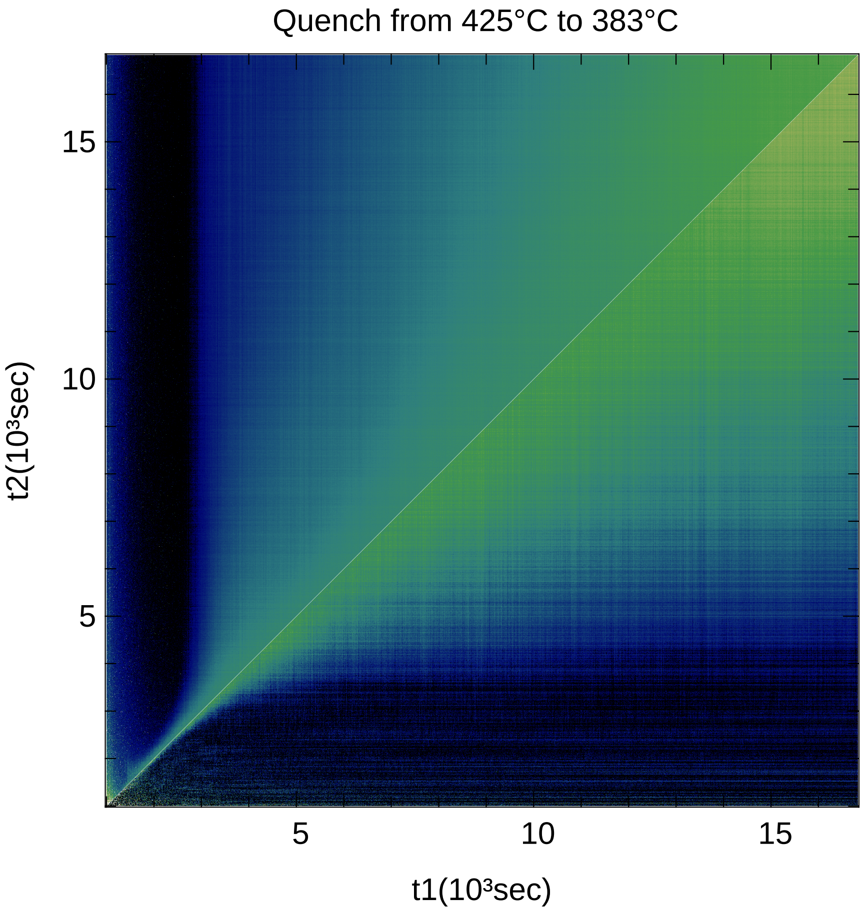
Cross-section of several slices

New Data

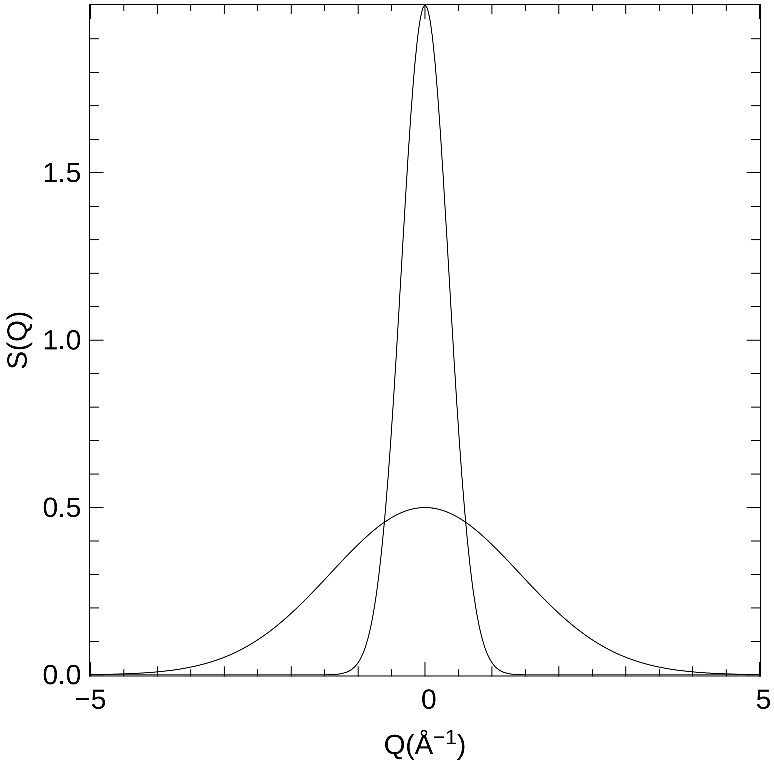

Time(10³ sec)
15
10
5
0.000
0.005
0.010
0.015
Q(Å⁻¹)


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



Particle Size Effects



Q and ϕ dependence

Non-Gaussian Nature

Intensity related to Fourier transform of density-density correlation function. For non-zero correlations, must have pair of points within a correlation length ξ.

$$\begin{aligned}\langle\delta\rho(\vec{r}_1,0)\delta\rho(\vec{r}_2,0)\delta\rho(\vec{r}_3,\tau)\delta\rho(\vec{r}_4,\tau)\rangle &\sim \langle\delta\rho(\vec{r}_1,0)\delta\rho(\vec{r}_2,0)\rangle\langle\delta\rho(\vec{r}_3,\tau)\delta\rho(\vec{r}_4,\tau)\rangle\\ &+ \langle\delta\rho(\vec{r}_1,0)\delta\rho(\vec{r}_3,0)\rangle\langle\delta\rho(\vec{r}_2,\tau)\delta\rho(\vec{r}_4,\tau)\rangle\\ &+ \langle\delta\rho(\vec{r}_1,0)\delta\rho(\vec{r}_4,0)\rangle\langle\delta\rho(\vec{r}_3,\tau)\delta\rho(\vec{r}_2,\tau)\rangle\end{aligned}$$

This overcounts the volume when all four $\vec{r}_i$ are within the same correlation length. When Fourier transformed, this correction is of order $(\xi^3/V)^2$.

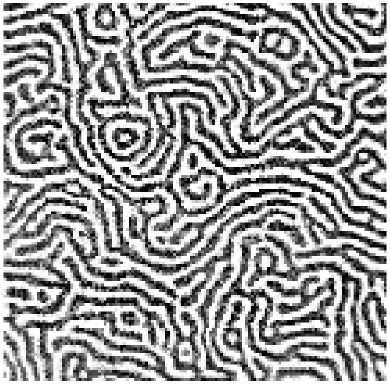
Gaussian Decoupling

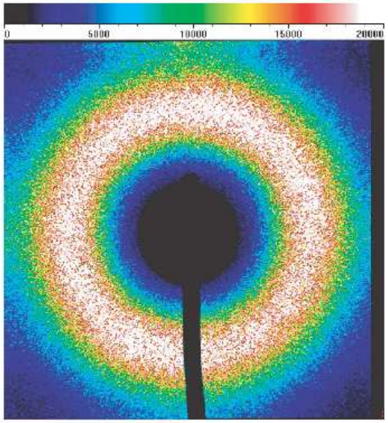
$$\begin{aligned}
\langle I(\vec{q},t_1)I(\vec{q},t_2)\rangle_T &= \langle\Psi^*(\vec{q},t_1)\Psi(\vec{q},t_1)\Psi^*(\vec{q},t_2)\Psi(\vec{q},t_2)\rangle_T \\
&= \langle\Psi^*(\vec{q},t_1)\Psi(\vec{q},t_1)\rangle_T\langle\Psi^*(\vec{q},t_2)\Psi(\vec{q},t_2)\rangle_T \\
&\quad +\langle\Psi^*(\vec{q},t_1)\Psi(\vec{q},t_2)\rangle_T\langle\Psi^*(\vec{q},t_2)\Psi(\vec{q},t_1)\rangle_T \\
&\quad +\langle\Psi^*(\vec{q},t_1)\Psi^*(\vec{q},t_2)\rangle_T\langle\Psi(\vec{q},t_1)\Psi(\vec{q},t_2)\rangle_T \\
&= [1+\delta(\vec{q})]S^2(\vec{q},t_1,t_2)+\langle I(\vec{q},t_1)\rangle_T\langle I(\vec{q},t_2)\rangle_T
\end{aligned}$$

Where: $S(\vec{q},t_1,t_2) = \langle\Psi^*(\vec{q},t_1)\Psi(\vec{q},t_2)\rangle_T$ and $I(\vec{q},t) = S(\vec{q},t,t)$

Metrology (high resolution from broad scattering)

Quasistatic X-Ray Speckle Metrology of Microscopic Magnetic Return-Point Memory, M.S. Pierce, R.G. Moore, L.B. Sorensen, S.D. Kevan, O. Hellwig, E.E. Fullerton, and J.B. Kortright, Phys. Rev. Lett., **90**, 175502, (2003).





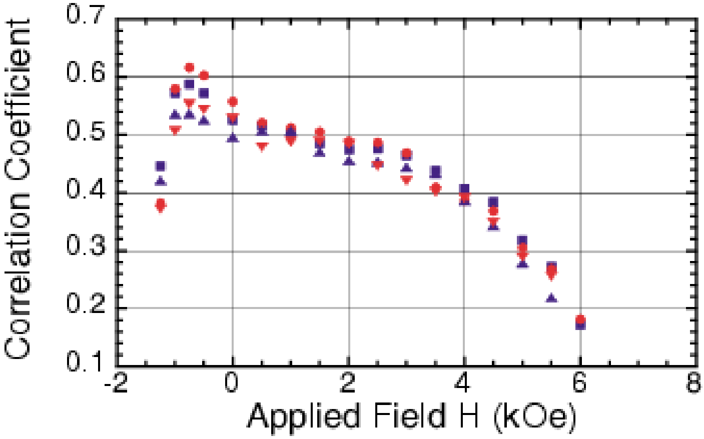
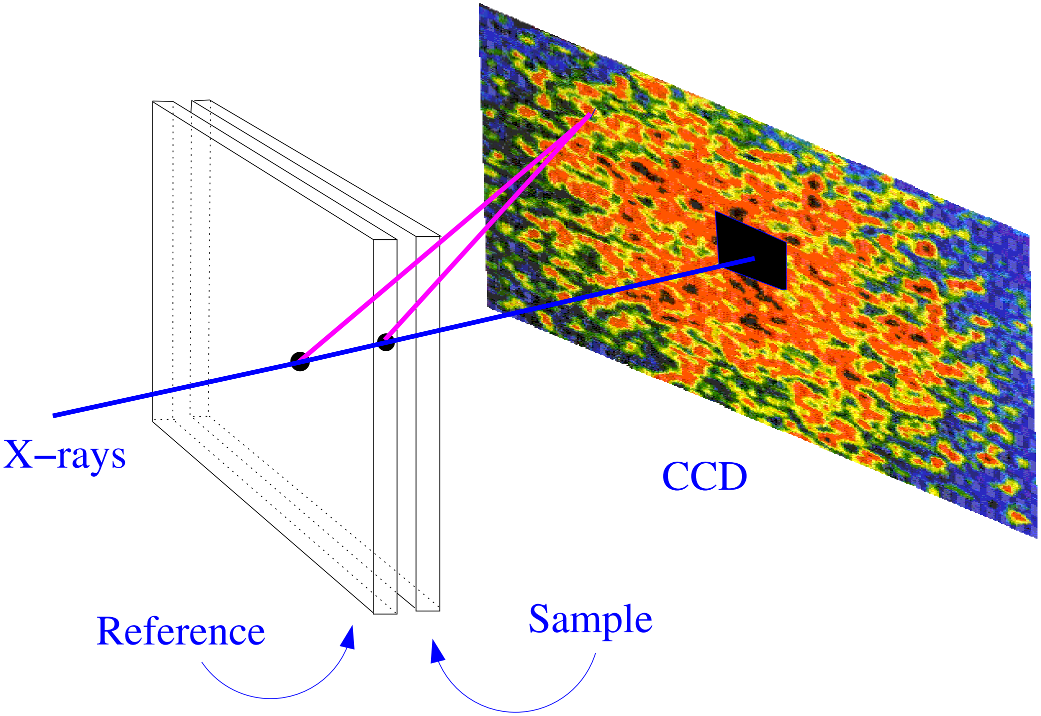


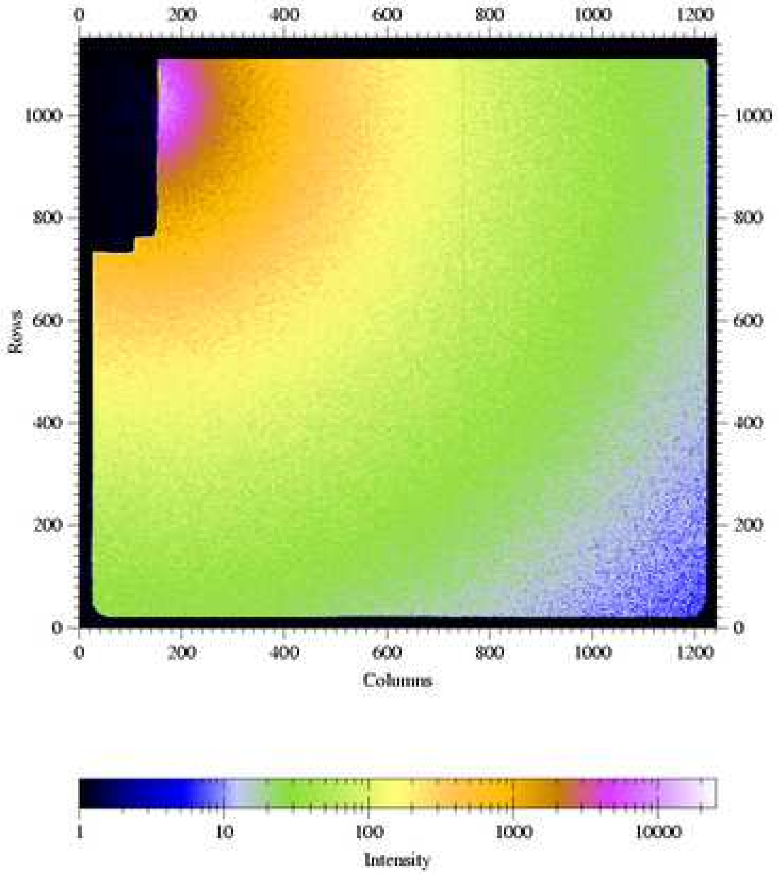
FIG. 4 (color online). The measured major loop microscopic correlation coefficients for the 12 mT sample. The circles and squares (the triangles) represent the correlations between the first and the second (eleventh) loop.

Experimental Setup



Scattering geometry

Rubber



Scattering of model rubber
(EPR with carbon black)

Heterodyne

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

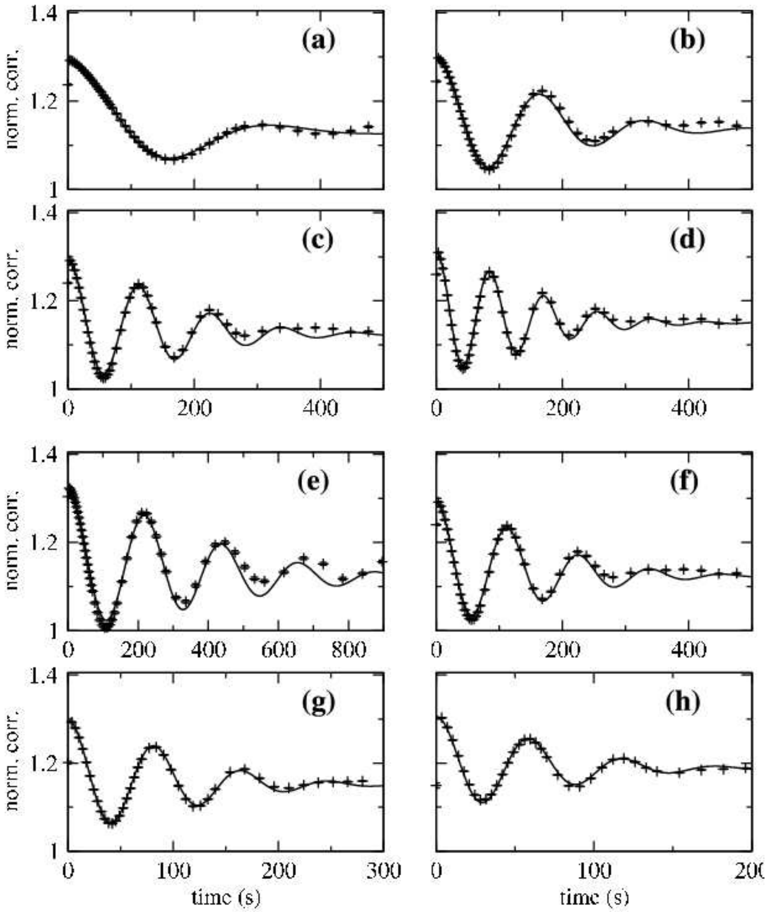
Moving at constant velocity gives phase factor

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

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

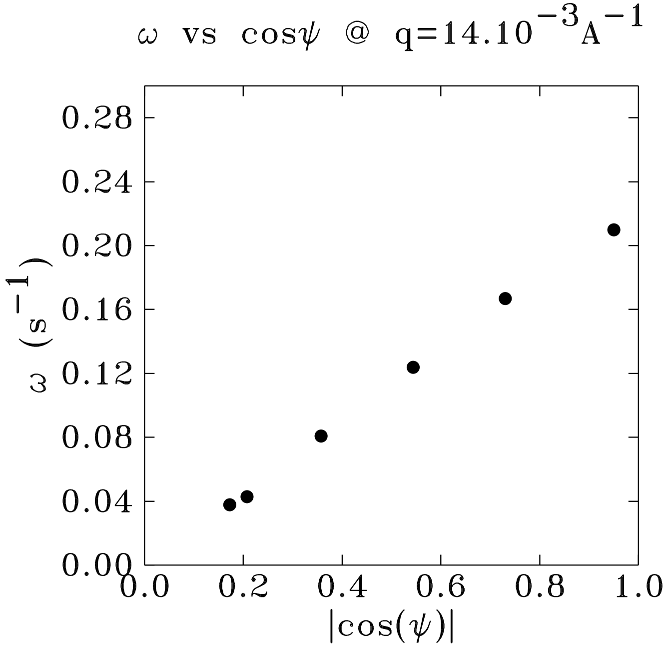
$$g_2(q,\phi,t) = 1+\beta(1-x)^2 + x^2\beta\gamma^2(t/\tau) + 2x(1-x)\beta\cos(\omega t)\gamma(t/\tau)$$

Rubber

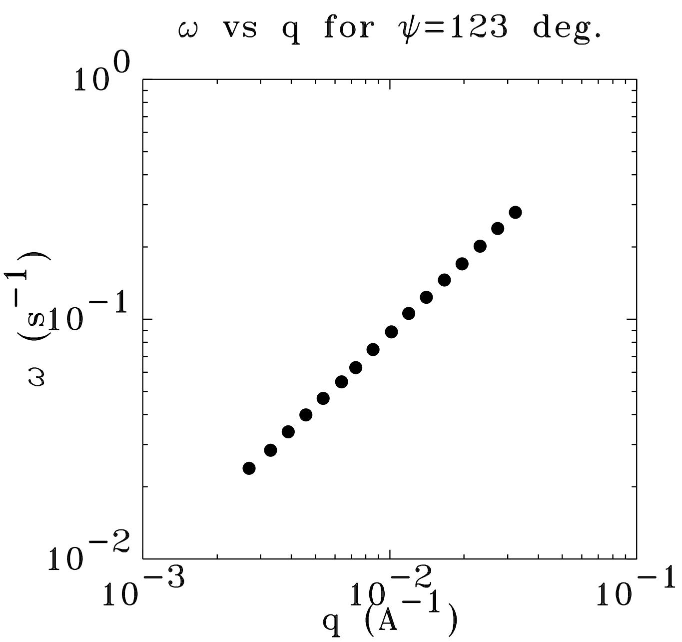


Q and ϕ dependence

qvcos(ω)

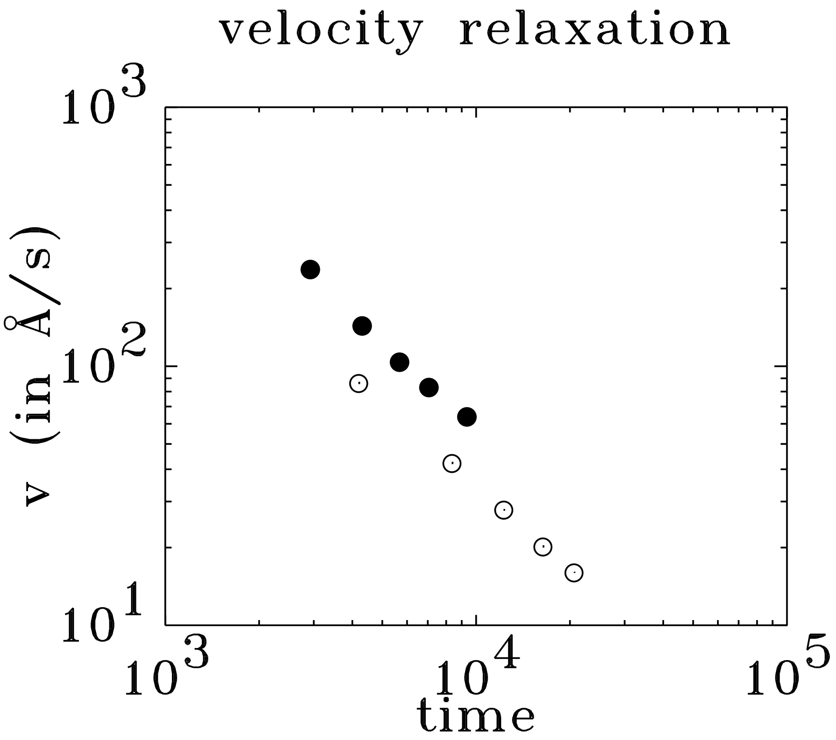


Azimuth dependence

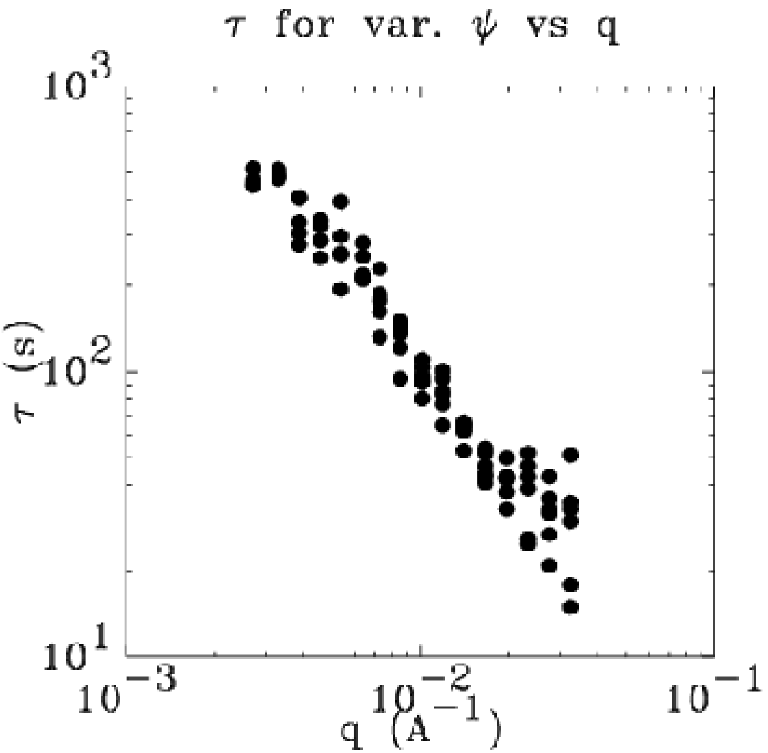


Wavevector dependence

Velocity



Wave vector dependence



Hydrodynamics

For instance given density $\rho(\vec{x},t)$ and momentum density $\rho(\vec{x},t)\vec{v}(\vec{x},t)$:

$$\{\rho(\vec{x},t),\rho(\vec{x}',t')v_i(\vec{x}',t')\}_{PB} = \nabla_i(\rho(\vec{x},t)\delta(\vec{x}-\vec{x}')).$$

Thus

$$\frac{\partial\rho}{\partial t} = -\vec{\nabla}\cdot(\rho\vec{v})$$

and (linearizing for simplicity)

$$\frac{\partial(\rho\vec{v})}{\partial t} = \vec{\nabla}\left[\left(\frac{\partial p}{\partial\rho}\right)_S \delta\rho(\vec{x})\right] + \vec{\eta},$$

(p is pressure and S is entropy).

These are the linearized hydrodynamic equations.

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

Conclusions

1. Understanding the time evolution of the microstructure is key to understanding Materials Science.
2. XIFS is a powerful and direct way to measure this dynamics, both in and out of equilibrium.
3. This dynamics is controlled by the thermodynamic fluctuations of the system and XIFS directly measures these.
4. Did not show many examples, but has been done in SAXS, Diffuse Reflectivity, Short-range quasi-Bragg peaks. Essentially all forms of diffuse scattering
5. Can heterodyne. This will give access to understanding how microscoptic structure controls visco-elastic properties (rubber). Can separate advection from disspation effects in the equation of motion.

6. Can use speckle to obtain high resolution structural information from “very disordered” materials. (Thermal expansion of a glass, reversible and irreversible hysterisis effects in magnetic domains).
7. Two-Q Two-time correlations give unique information about microstructure. non-Guassian fluctuations.