X-ray Intensity Fluctuation Spectroscopy Studies of Ordering Kinetics in a Cu-Pd Alloy

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Talk Overview:

- Background – XIFS Studies of Dynamics/Kinetics
- Background – CuPd Long-Period Superlattice Alloys
- XIFS Study of Domain Coarsening
- Final Thoughts

XIFS Studies of Equilibrium Fluctuation Dynamics

Analogous to Dynamic Light Scattering (DLS)

(Quasi-)Elastic Scattering:

$$I(q,t) = \left| \sum_i f_i e^{iq \bullet r_i(t)} \right|^2 = \rho(q,t)\rho^*(q,t)$$

2nd Order Correlation Function:

$$g_2(q,t) = \frac{\langle I(q,t')I(q,t'+t)\rangle_{t'}}{\langle I(q,t')\rangle_{t'}^2} = \frac{\langle \rho(q,t')\rho^*(q,t')\rho(q,t'+t)\rho^*(q,t'+t)\rangle_{t'}}{\langle \rho(q,t')\rho^*(q,t')\rangle_{t'}^2}$$

If fluctuations are Gaussian, this is related to the 1st Order Correlation Function (Intermediate Scattering Function):

$$g_1(q,t) = \frac{\langle \rho(q,t')\rho^*(q,t'+t)\rangle_{t'}}{\langle I(q,t')\rangle_{t'}}$$

$$g_2(q,t) = 1 + \left| g_1(q,t) \right|^2$$

The 1st Order Correlation Function is often calculated by theory/simulation and can be related to a linear response susceptibility through the fluctuation-dissipation theorem.

XIFS Studies of Non-Equilibrium Dynamics/Kinetics

How do we quantiatively understand speckle evolution in a non-equilibrium system?

$I(q,t')I(q,t'+t)$ is no longer stationary in t' !!

If the time scale for "kinetic" evolution τ_k is much longer than the time scale for "fluctuation" evolution τ_f then we could calculate a slowly changing correlation function that might be interpretable:

$$\frac{\langle I(q,t')I(q,t'+t)\rangle_{t'<<\tau_k}}{\langle I(q,t')\rangle^2_{t'<<\tau_k}}$$

BUT in general τ_k and τ_f are comparable because the kinetic evolution is closely connected to the timescales of fluctuation dynamics

XIFS Studies of Non-Equilibrium Dynamics/Kinetics

No general approach to understanding speckle fluctuations in nonequilibrium systems!

Therefore begin by looking at "well understood" case of late stage domain coarsening kinetics in metallic alloys.

<u>Stadler and coworkers</u>:
*PRB **68**, 1801001 (2003)*
*PRB **69**, 224301 (2004)*
"Fluctuation Analysis"

$$Y_j(q) = \sum_{k=1}^{j} \left(I_k - \langle I \rangle \right)$$

$$F^2(q,t) = \left\langle \left(Y_{j+t}(q) - Y_j(q) \right)^2 \right\rangle \propto t^{2\alpha}$$

Long-term correlations $\alpha > 0.5$

<u>McGill and LTPCM Groups</u>:
*Brown et al. PRE **56**, 6601 (1997); PRE **60**, 5151 (1999); Malik et al. PRL **81**, 5832 (1998); Livet et al. PRE **63**, 036108 (2001)*

Two-Time Correlation Function:

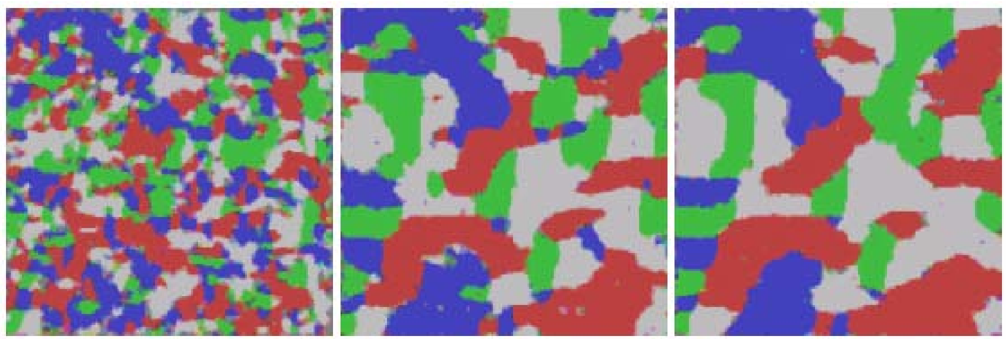
$$C(q,t_1,t_2) \propto \left(I(q,t_1) - \langle I(q,t_1) \rangle \right) \left(I(q,t_2) - \langle I(q,t_2) \rangle \right)$$

Compare with fundamental theoretical predictions and simulation

Late-Stage Coarsening Kinetics in Metallic Alloys

Average domain size grows to decrease interfacial energy associated with domain boundaries

MC simulation of coarsening kinetics in a system with 4 degenerate states



X. Flament

Dissertation Université de Cergy-Pontoise (2000)

$$\bar{d}^{\alpha} \propto (t - t_0)$$

$$\bar{d} \propto t^{1/\alpha}$$

$$q_0 \propto t^{-1/\alpha}$$

$\alpha = 2$ conserved order parameter (atomic ordering)

$\alpha = 3$ nonconserved order parameter (phase separation)

Dynamic Scaling: $I(q,t) \propto q_0^{-d} F\left(\frac{q}{q_0}\right) \propto t^{d/\alpha} F(q t^{1/\alpha})$

Theory/Simulation: Evolution of the Two-Time Correlation Function

Brown, Rikvold, Sutton & Grant: PRE ***56****, 6601 (1997); PRE* ***60****, 5151 (1999)*

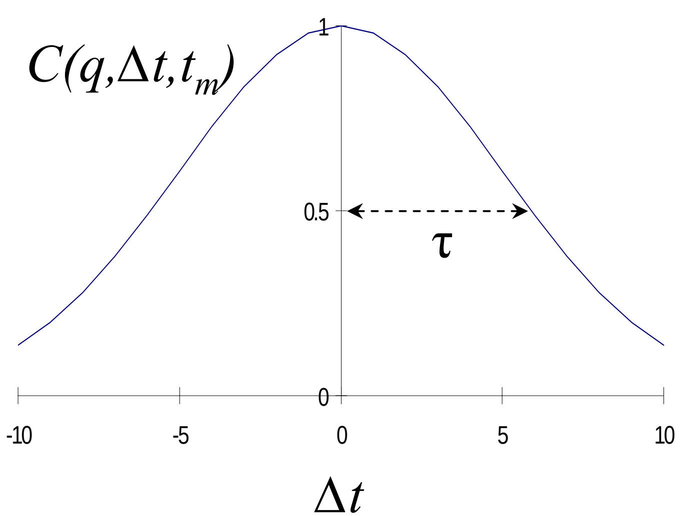
Two-time correlation function:

$$C(q,t_1,t_2) = \left[\frac{\left(I(q,t_1) - \langle I(q,t_1)\rangle\right)}{\langle I(q,t_1)\rangle}\right]\left[\frac{\left(I(q,t_2) - \langle I(q,t_2)\rangle\right)}{\langle I(q,t_2)\rangle}\right] = C(q,\Delta t,t_m)$$

$$\Delta t = t_2 - t_1$$

$$t_m = (t_1 + t_2)/2$$

Decay of $C(q,t_1,t_2)$:



Langevin calculation and simulation

→ Persistent speckles

→ New dynamic scaling

Scaling variable: $x = q^2 t$

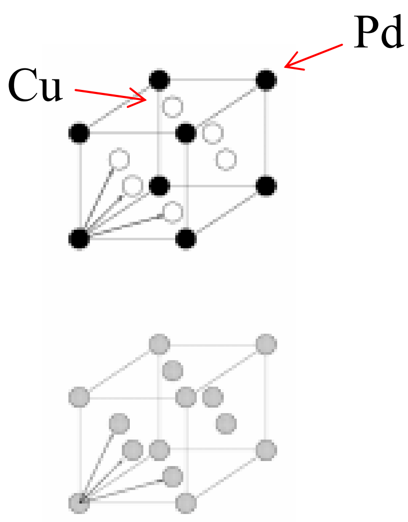
Two Regimes of Correlation Decay:

x_m small: $x_\tau \sim x_m$

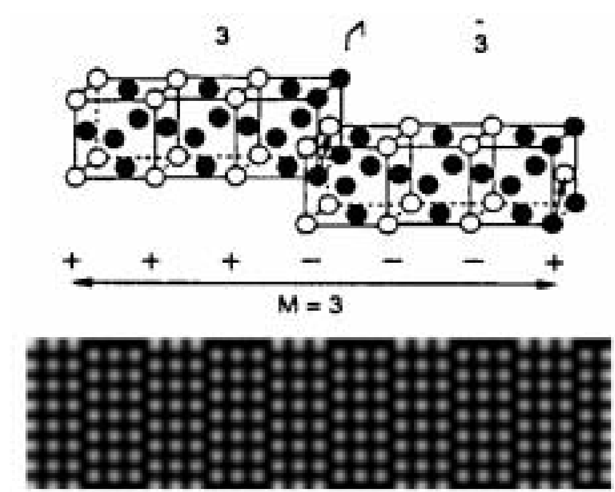
x_m large: $x_\tau \sim x_m^{1/2}$

Long-Period Superlattice (LPS) Alloy: Cu_xPd_{1-x}

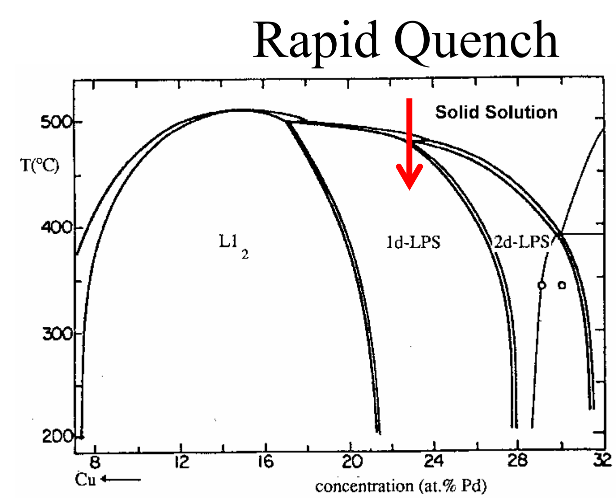
LPS Alloys: Periodic modulation between different $L1_2$ antiphase domains



$L1_2$ ordering



M cells in each antiphase domain



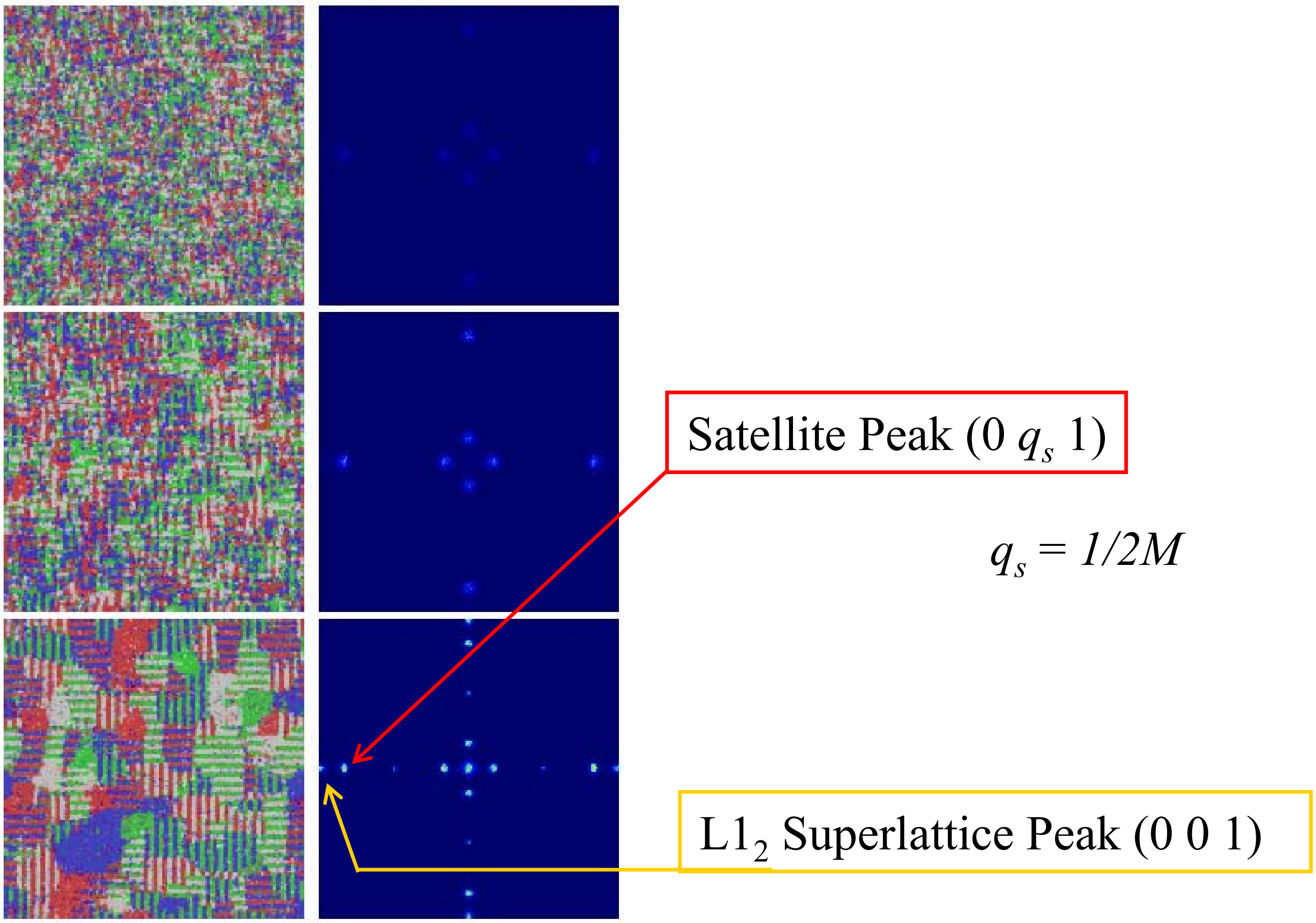
Traditional time-resolved x-ray scattering kinetics study:
Wang, Mainville, Ludwig, Flament, Finel and Caudron; PRB, in press.

Scattering from LPS Alloy

MC Simulations of LPS Ordering Kinetics

X. Flament

Dissertation Université de Cergy-Pontoise (2000)



Data Collection

ESRF Beamline ID-10A Troïka: Be lens focussing

- Si(111) monochromator – 8.07 keV, $\delta E/E \cong 1.4 \times 10^{-4}$ FWHM
  Gaussian wavepacket $\exp[-x^2/\xi_l^2]$
  → longitudinal coherence length $\xi_l \approx \lambda^2/2\Delta\lambda \approx 0.5$ μm
- Troïka source size of 900 μm horizontal by 23 μm vertical
  transverse coherence area of 6 x 220 μm (H x V FWHM)
- 12 μm pinhole located 0.23m in front of sample
- 20 μm x 20 μm guard slit, positioned halfway between pinhole and sample

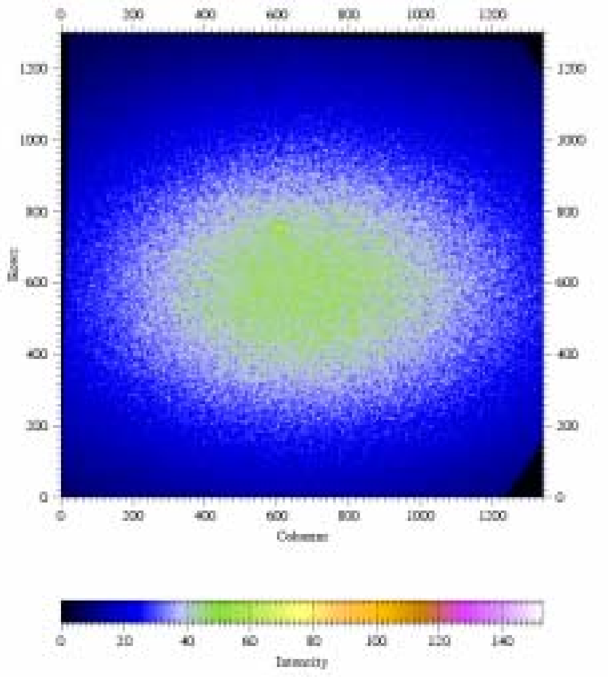
1340 x 1300 20 μm Pixel Direct-Illumination Deep-Depletion CCD (Princeton Instruments)

- Sample-detector distance of 2.3m gives speckle size of 36 μm (FWHM)
- Detector used in a photon-counting mode

[F. Livet *et al*., Nucl. Instrum. Meth. Phys. Res. A **451**, 596 (2000)].

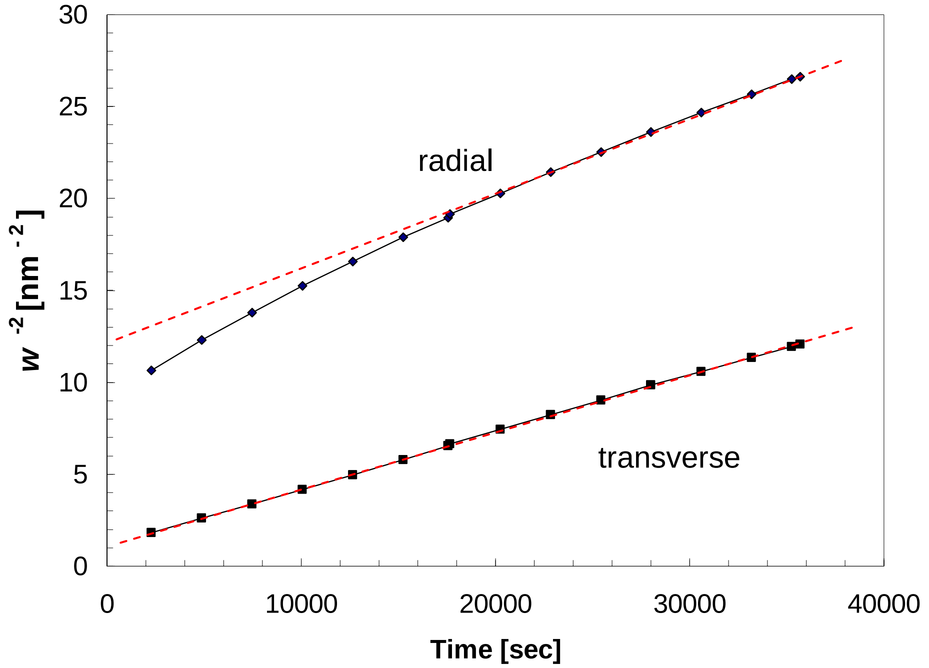
Experiment

- Disordered sample rapidly quenched into ordering region at 435 °C
- Two peaks examined to study evolution of order –
  Superlattice (001) sensitive to <u>$L1_2$ order</u>
  Satellite (0 q_0 1) sensitive to <u>modulated order</u>
- For each quench 700 frames of data collected with exposure time of 50 sec and readout time of approximately 1.6 sec (36120 sec total time)
- Region of peak examined limited by size of CCD chip



Onset of Coarsening – Evolution of Superlattice Peak Widths

Coarsening: $w^2 = a(t-t_0)$

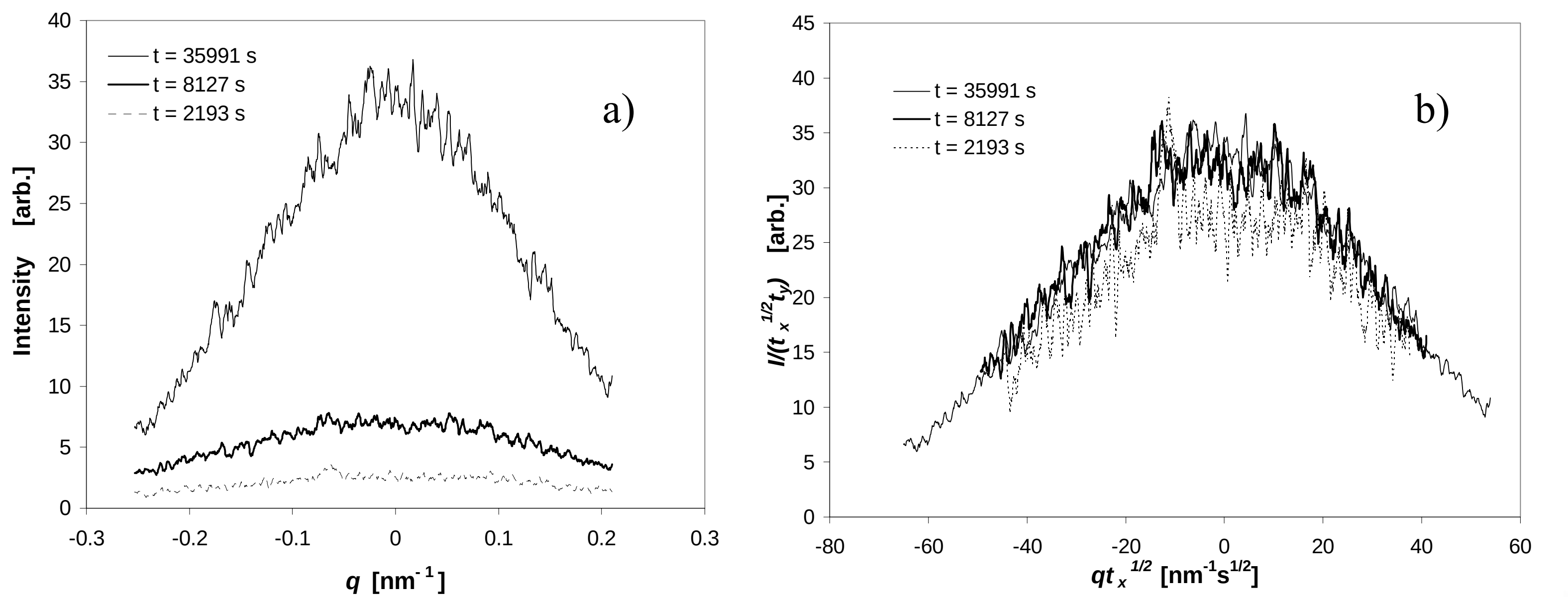


Simple 2-d Gaussian Fits: Difficult to evaluate precisely the onset of coarsening behavior

Onset of Coarsening – Dynamic Scaling

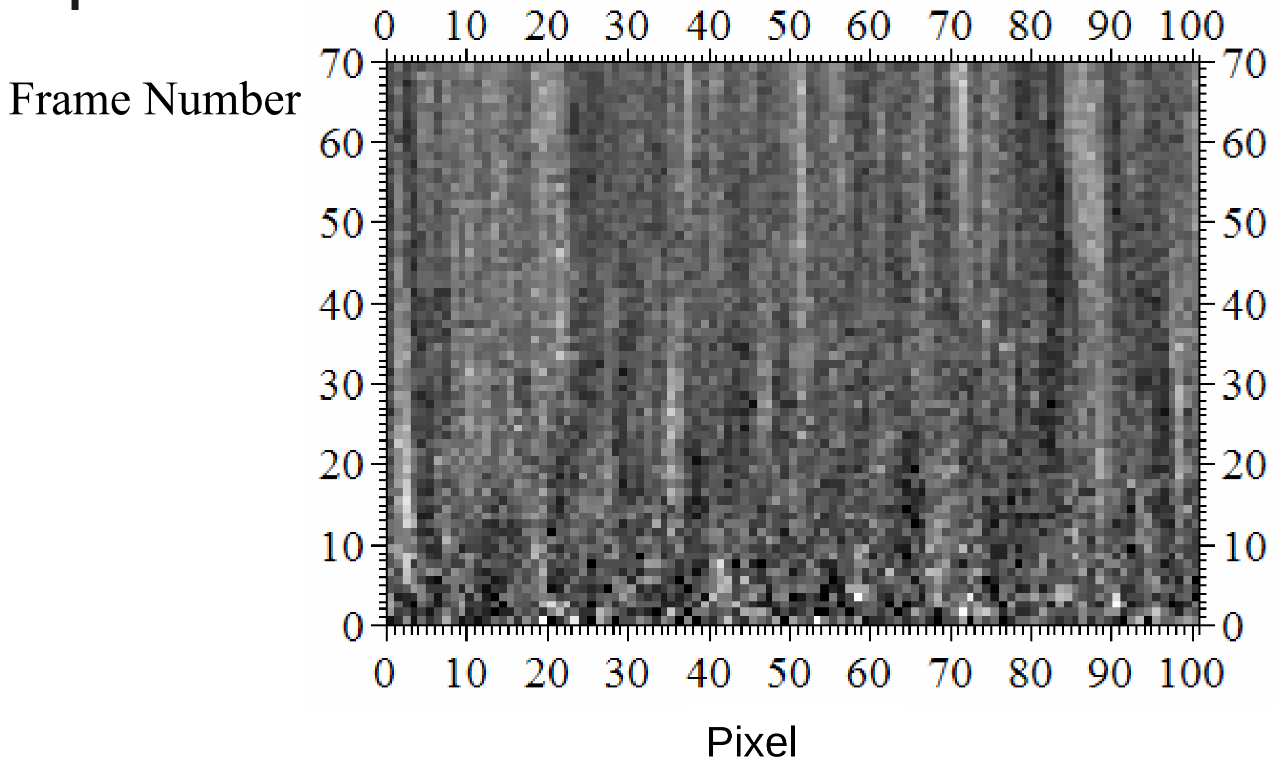
Stronger requirement – Dynamic Scaling of *I(q,t)*

Anisotropic peakshapes: Scaling function $t_x^{-1/2} t_y^{-1} I(q t_x^{1/2})$



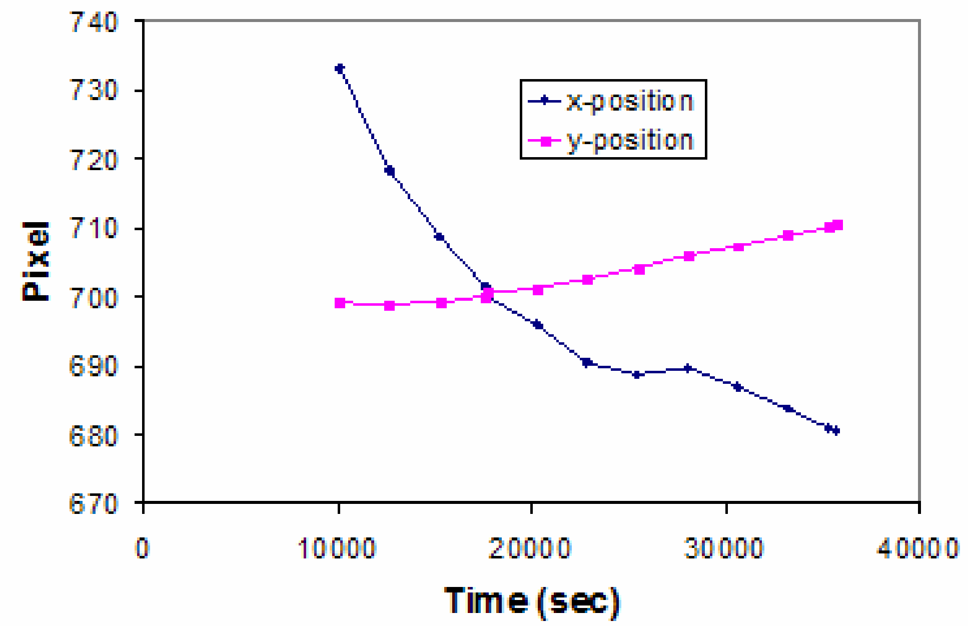
Good *I(q,t)* scaling is observed after 5000-8000 sec

Qualitative View of Speckle Evolution



Persistent speckles develop as predicted by theory

Peak Shifts



Peak positions shift during experiment by up to 0.003 reciprocal lattice units

Peaks shift – Speckles don’t !

A. Fluerasu, M. Sutton, E.M. Dufresne, PRL **94**, 055501 (2005): Lattice Distortions at Antiphase Domain Boundaries?

Transverse Coherence

ID10A Source Size: 900 μm horizontal by 23 μm vertical

$\xi_t \sim \lambda R/(2s)$ → coherence area 6 x 220 μm (*H* x *V* FWHM)

12 μm x 12 μm pinhole

IMMY/XOR-CAT Coherence calculator: http://8id.xor.aps.anl.gov/UserInfo/Analysis/

→ coherence factor $\beta_{theory} \approx 0.3$

SAXS from aerosyl to check this result:

$$\beta = \frac{< I^2(q,t) > - < I(q,t) >}{< I(q,t) >^2} - 1$$

$$\beta \cong 0.2$$

Longitudinal Coherence – Calculated

Monochromator 8.07 keV, $\delta E/E \cong 1.4 \times 10\text{-}4$ FWHM
Gaussian wavepacket $\exp[-x^2/\xi_l^2]$
$\rightarrow$ longitudinal coherence length $\xi_l \approx \lambda^2/2\Delta\lambda \approx 0.5\ \mu m$

Absorption Length: $\mu^{-1} \approx 10\ \mu m$

Bragg case geometry: $\theta \approx 12°$

Typical path length difference $\delta r = 2\mu^{-1}\sin^2\theta \approx 0.86\ \mu m$

Try to calculate effect of finite longitudinal coherence in symmetric Bragg case geometry:

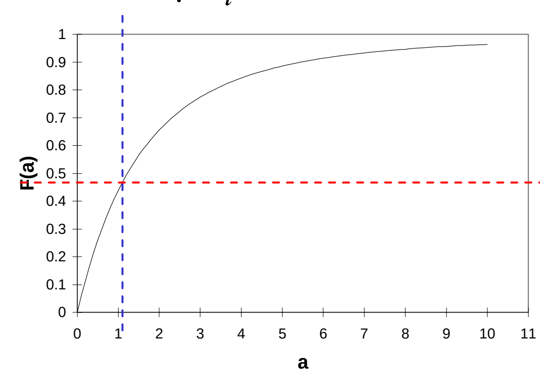
Gaussian wavepacket: $E^0_{inc}(r) = \frac{E_0}{\sqrt{2\pi\xi}} e^{-r^2/\xi^2}$

Scattered field: $dE^{\det}_{scatt}(r',z) = \beta \frac{E_0}{\sqrt{2\pi\xi}} e^{-(r'+2z\sin\theta)^2/\xi^2} e^{-\mu z/\sin\theta} \frac{dz}{\sin\theta}$

Normalized intensity function:

$$F(a) = \frac{I_{\det}(a)}{\beta^2 E_0^2/\sqrt{8\pi}\mu^2} = \frac{\sqrt{2\pi}}{16} a^2 e^{a^2/8} \int_{-\infty}^{\infty} e^{ax} Erfc^2\left(x + \frac{a}{4}\right) dx \approx 0.46$$

$a = \mu\xi_l \sin^{-2}\theta \approx 1.1$



So we might expect $\beta_{scatt} \approx 0.46 {*} \beta_{trans} \approx 0.09$

Longitudinal Coherence – Measured

Two ways to calculate β_{scatt}:

1) Examine variance over equivalent pixels: $$\beta = \frac{<I^2(q,t)> - <I(q,t)>}{<I(q,t)>^2} - 1$$

2) Examine limiting behavior of $C(q,t_1,t_2)$: $$\beta = \lim_{t_1 \to t_2} C(q,t_1,t_2)$$

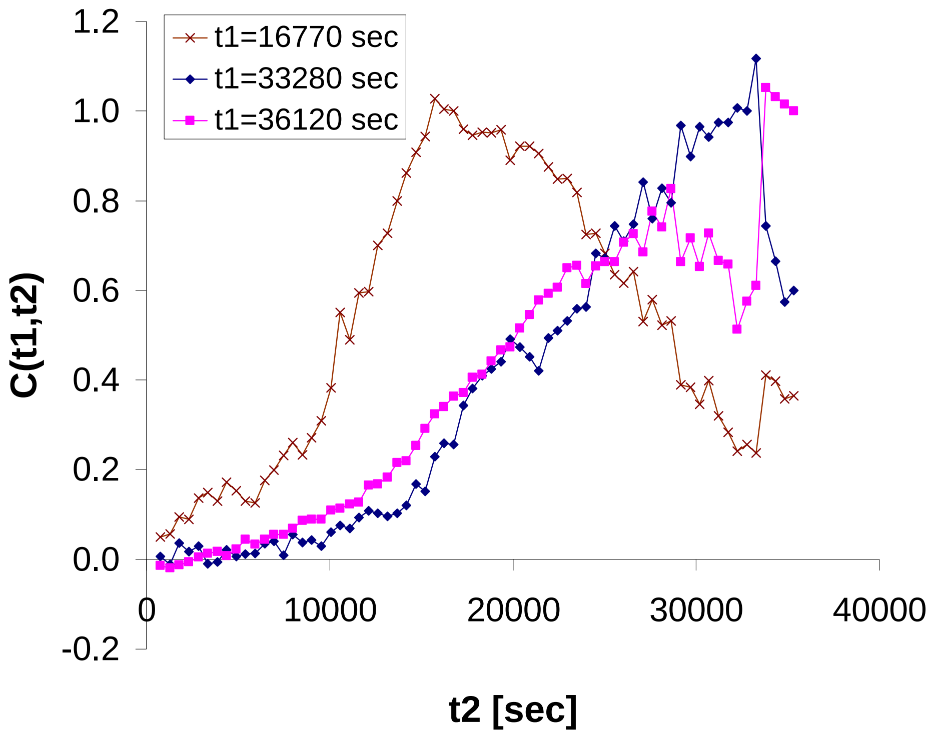
Both give $\beta_{scatt} \approx 0.03\text{-}0.04$.

Smaller than expected by factor of 2

Normalize $C(q,t_1,t_2)$ to remove effect of imperfect coherence:

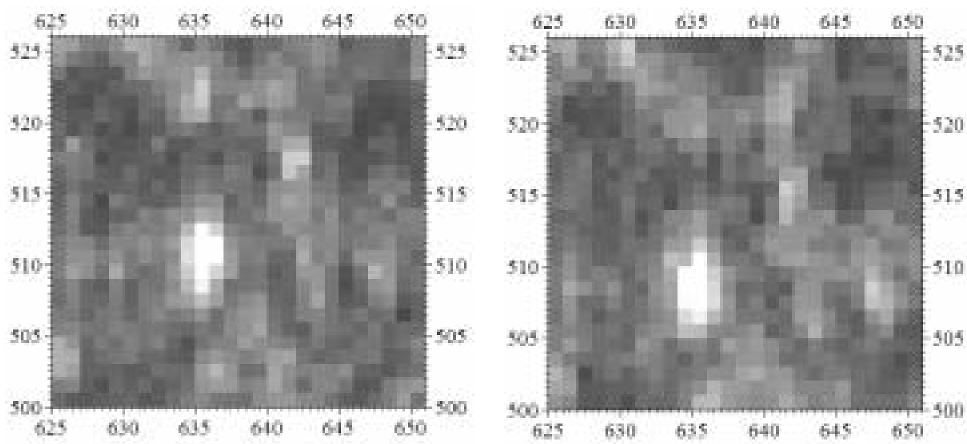
$$C_{norm}(q,t_1,t_2) = \frac{2C(q,t_1,t_2)}{\left[C(q,t_1,t_1-\delta t)+C(q,t_1,t_1+\delta t)\right]^{1/2}\left[C(q,t_2,t_2-\delta t)+C(q,t_2,t_2+\delta t)\right]^{1/2}}$$

Normalized Two-Time Correlation Function



Sudden Change in Correlation

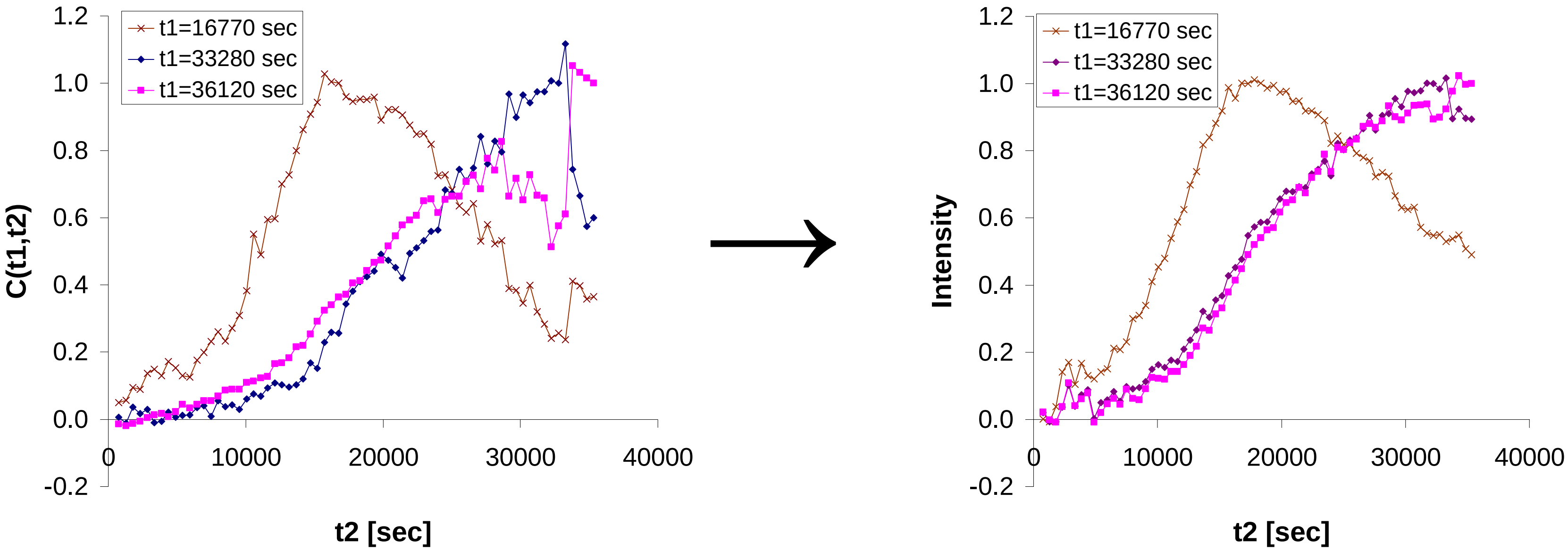
Sudden Shifts in Speckle Pattern on the Detector



To first approximation, small changes in incident beam angle shift the entire speckle pattern on the detector if the change in the angle is perpendicular to the scattering plane. If the change in angle is not perpendicular to the scattering plane, then it is still true that beam motion causes a shift if the speckles are significantly longer in the radial direction than in the transverse direction. Here the penetration depth into the sample $(\mu^{-1}\sin\theta)/2 \sim 1\ \mu\text{m} \ll$ beam footprint on the sample $12\ \mu\text{m}/\sin\theta \sim 58\ \mu\text{m}$.

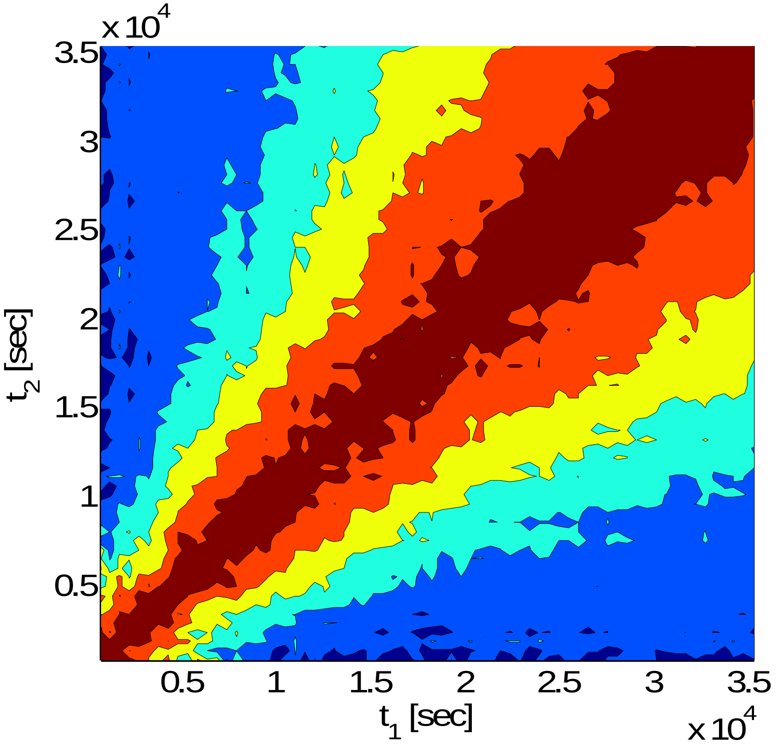
We shifted each pattern slightly to maximize overlap with an arbitrary pattern in the middle of the data set.

“Corrected” Normalized Two-Time Correlation Function



Effect of shifting speckle pattern

Normalized Two-Time Correlation Function



Contours:

> 0.8

> 0.6

> 0.4

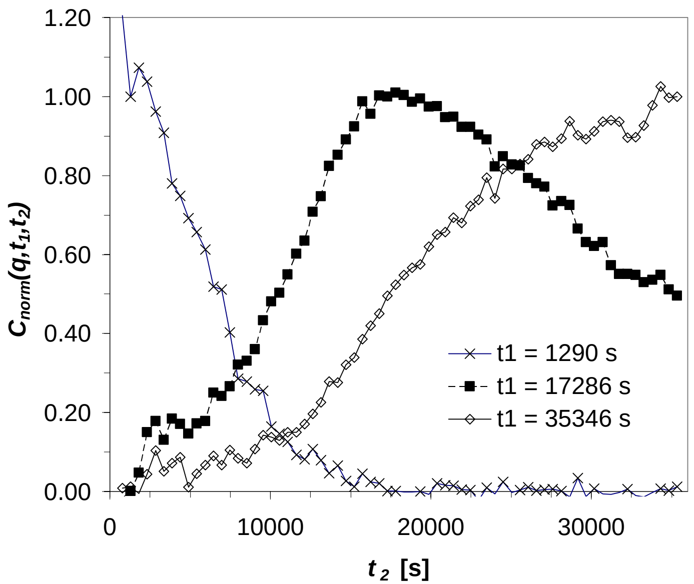
> 0.2

> 0.0

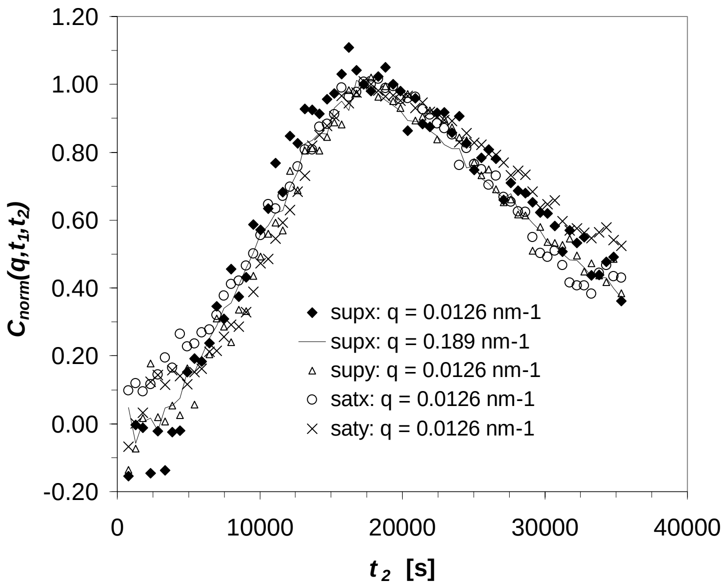
$C_{norm}(q=0.0126\ nm^{-1}, t_1, t_2)$ for the superlattice peak

Evolution of Normalized 2-time Correlation Function

$C_{norm}(q=0.0126\ nm^{-1},t_1,t_2)$ for the satellite peak in the detector x-direction at three times t_1 near the beginning, middle and end of the experiment.

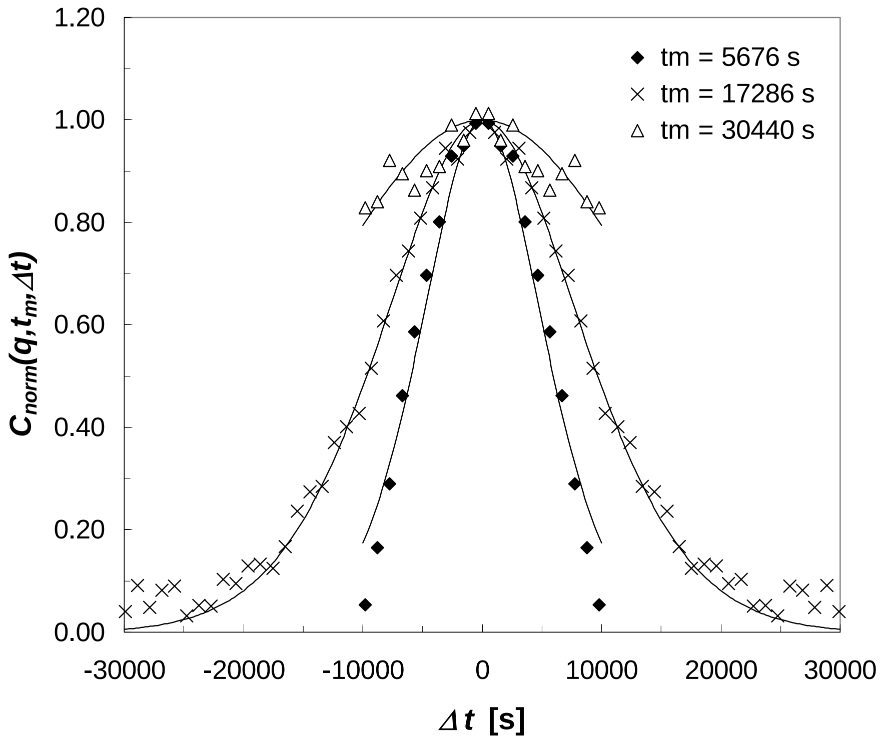


$C_{norm}(q,t_1,t_2)$ at t_1 = 17286 s for the superlattice (sup) and satellite (sat) peaks in the detector x- and y-directions.



No dependence on peak (satellite vs. $L1_2$ superlattice) or direction is observed

Normalized Two-Time Correlation Function as a Function of Δt

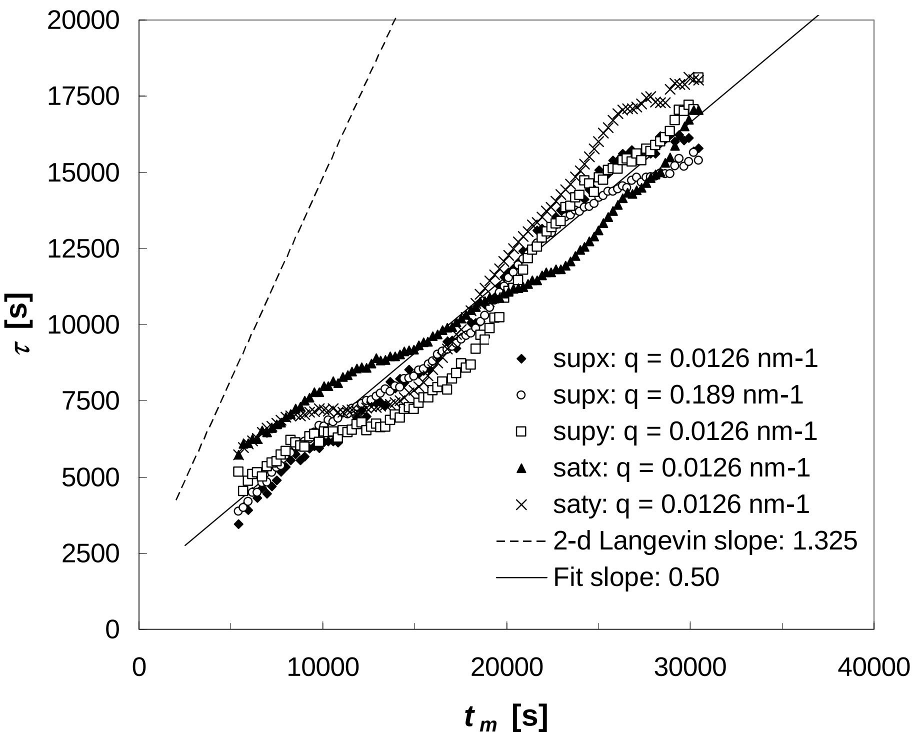


Fits to theoretical form:

$$C(z) = (z^2 K_2(z)/2)^2$$

$$z = A\Delta t/t_m^{1/2}$$

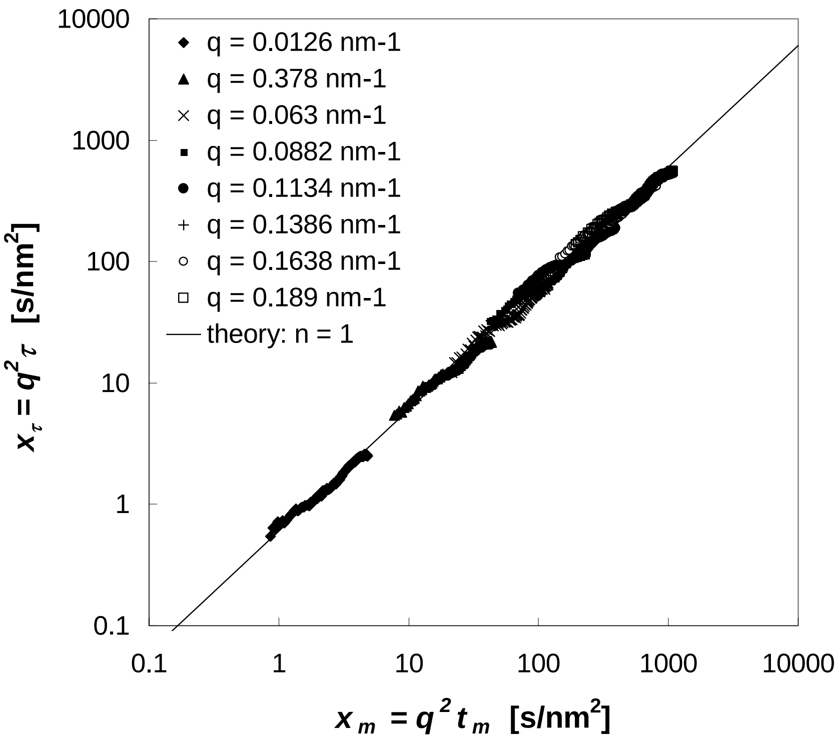
Decay Time τ of Normalized Two-Time Correlation Function



τ is linear in t_m

τ is independent of direction and peak (satellite vs. $L1_2$ superlattice)

Scaling of Normalized Two-Time Correlation Function Decay



As predicted by the Langevin theory and simulations of Brown *et al.* for small $x = q^2 t$:

$$x_\tau \sim x_m$$

i.e. the speckles' persistence increases linearly with mean coarsening time.

Conclusions – Things We May Understand…

Despite complexity of LPS phase, $C(q,t_1,t_2)$ appears to follow expectations from theory/simulation of a Langevin equation with a nonconserved order parameter:

- Decay of $C(q,t_1,t_2)$ can be fit well with theoretical lineshape
- $C(q,t_1,t_2)$ independent of direction, peak ($L1_2$ vs. modulated)
- Speckle is Persistent with $x_\tau \sim x_m$

Conclusions – Things We May Not [Yet] Understand…

1) Although $x_\tau \sim x_m$ in agreement with theory/simulation, the dimensionless slope (ratio) between them is much smaller than expected –

0.5 (experiment) vs. ~ 1.4 (theory)

Similar situation seen in Cu_3Au: A. Fluerasu, *et al*., PRL **94**, 055501 (2005)

Our own MC Ising model simulations using spin-exchange agree well with Langevin theory.

Why the difference between experiment and theory?

2) Significant peak motion without speckle motion observed –

Inhomogeneous strain release at antiphase boundaries?

Normalized Two-Time Correlation Function