Coherent X-ray Scattering Opportunities in Non-Equilibrium Physics

Workshop on Frontier Science with X-ray Correlation Spectroscopies – June 29-30, 2011

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Overview

What can we learn from an XPCS study of a non-equilibrium system that we can't learn from a conventional time-resolved experiment?

Answer:
We can probe fluctuations about ensemble-averaged behavior.

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Overview

- XPCS studies of equilbrium vs. non-equilibrium systems
- Non-equilibrium processes – XPCS examples
  - *Nonlinear scaling process:*
    Late-stage coarsening kinetics in long-period superlattice alloy
  - *Heterogeneous process:*
    Martensitic transformation of Co
- Prospects for future studies of non-equilibrium processes
  - *Driven steady-state processes on surfaces*

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Most XPCS studies to date – Equilibrium Fluctuation Dynamics

Analyze correlation functions within framework of linear response theory

e.g. concentration fluctuations (diffusion)

$$\frac{\partial c(\vec{r},t)}{\partial t} = -D\nabla^2 c + \eta(\vec{r},t)$$

$$I(\vec{q},t) \approx c^*(\vec{q},t)c(\vec{q},t)$$

intensity autocorrelation function

$$g_2(\tau) \equiv \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2} = 1 + e^{-2Dq^2\tau}$$

A KEY Problem for XPCS studies of non-equilibrium systems:

There is no general framework within which to analyze the data !

Instead, experiments have had to rely on approaches specific to a given problem

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XPCS studies of non-equilibrium systems: Domain Coarsening Dynamics

Langevin equation describing kinetics is highly nonlinear

Material	Reference
Borosilicate Glass (phase separating)	Malik *et al.* PRL **81**, 5832 (1998)
AlLi Alloy (phase separating)	Livet *et al.* PRE **63**, 036108 (2001)
Cu_3Au Alloy (phase ordering)	Fluerasu *et al.* PRL **94**, 055501 (2005)
Cu_3Pd Alloy (phase ordering)	Ludwig *et al.* PRB **72**, 144201 (2005)
Al-Zn/Al-Ag (phase separating)	Stadler *et al.* PRB **68**, 180101 (2003)
$Co_{60}Ga_{40}$ (phase ordering)	Stadler *et al.* PRB **69**, 224301 (2004)
Ni-Al-Mo (phase separating)	Pfau *et al.* PRB **73**, 180101 (2006)
Al-Zn/Al-Ag (phase separating)	Stadler *et al.* PRE **74**, 041107 (2006)

Detrending analysis – compare w/simulations

Comparison with specially-developed scaling theory

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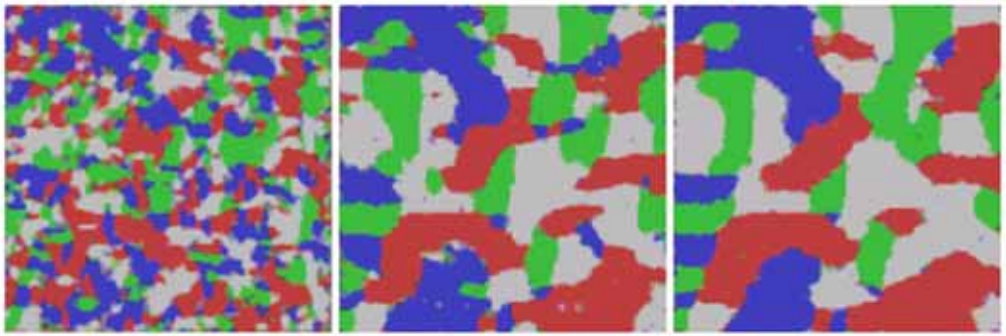
Late-Stage Coarsening Kinetics

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)

average domain size $\bar{d}$ $\qquad q_0 \approx 2\pi / \bar{d}$ *characteristic wavenumber*

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

- $\alpha = 2$ nonconserved OP (phase ordering)
- $\alpha = 3$ conserved OP (phase separating)

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

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

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

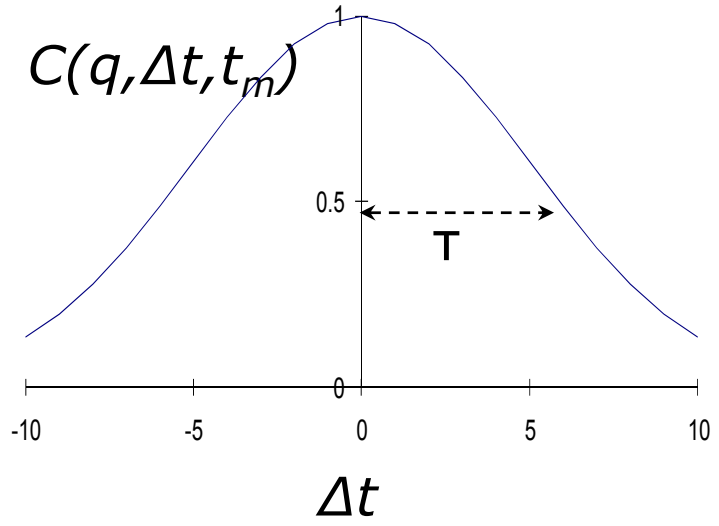
Two-time correlation function:

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

$$\Delta t = t_2 - t_1$$

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

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



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

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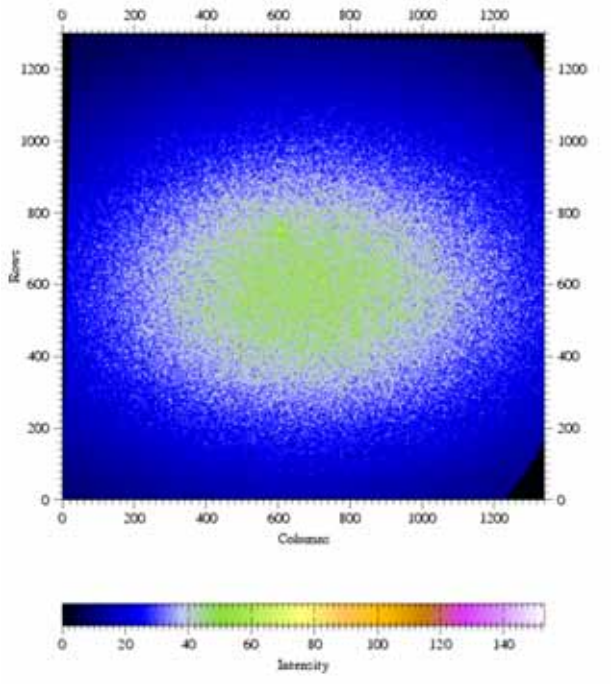
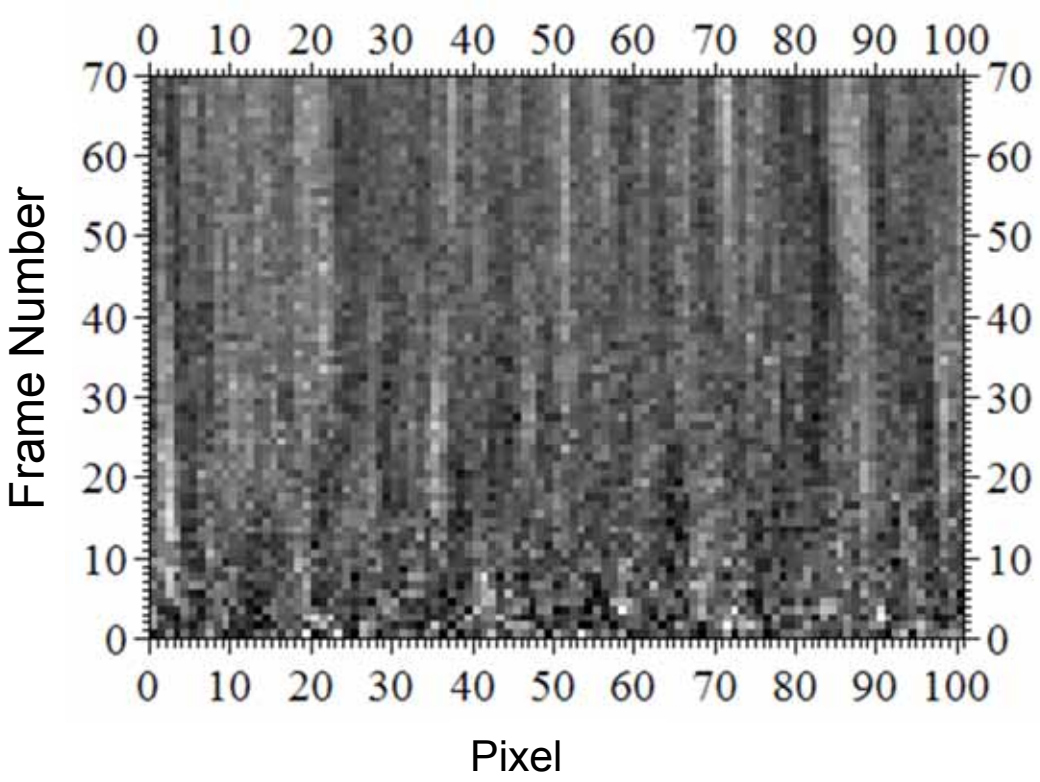
Speckle Evolution





Persistent speckles develop as predicted by theory

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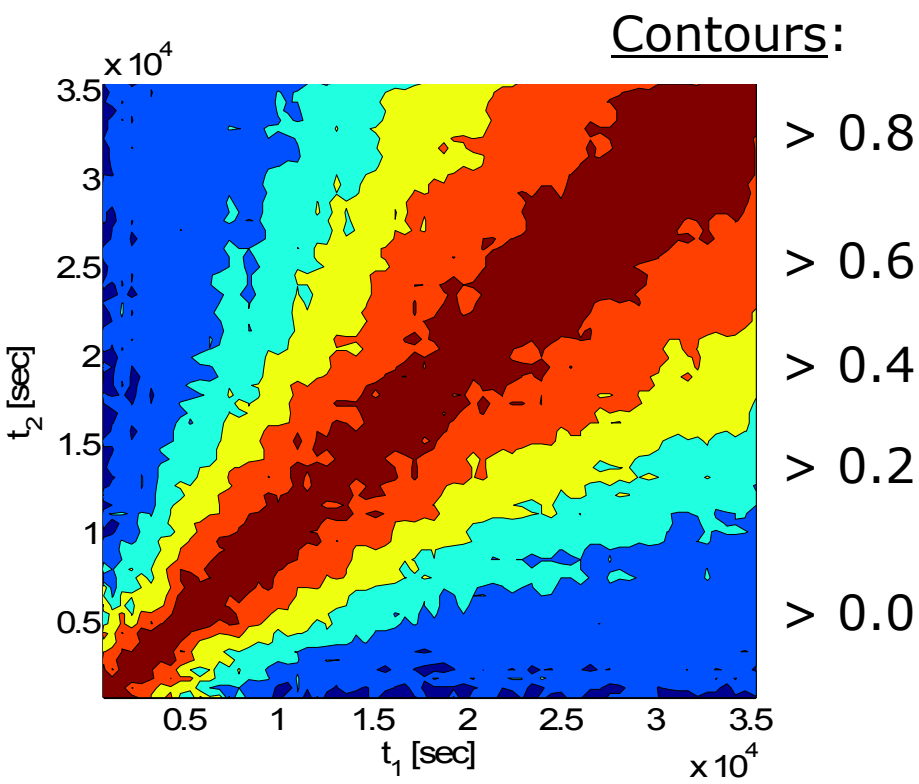
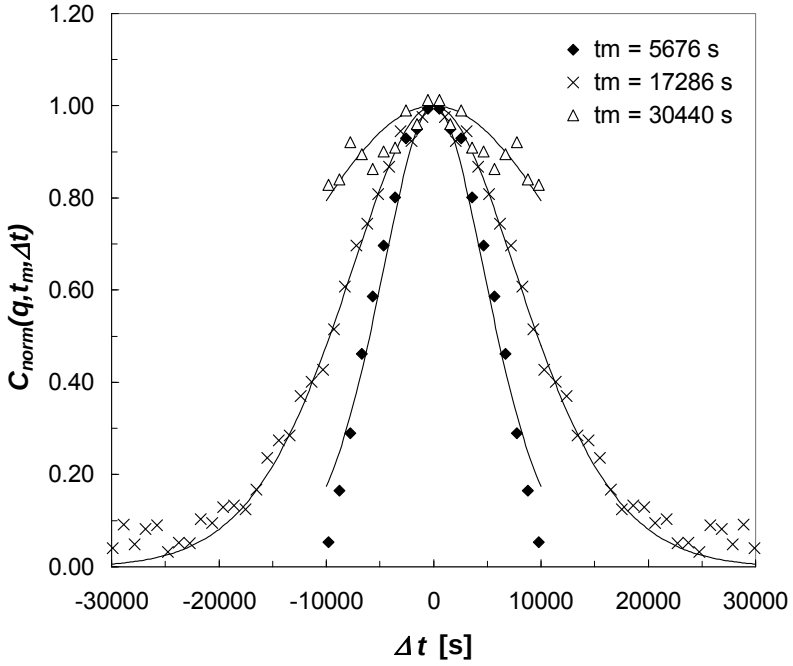
Normalized Two-Time Correlation Function





Fits to theoretical form:

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

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

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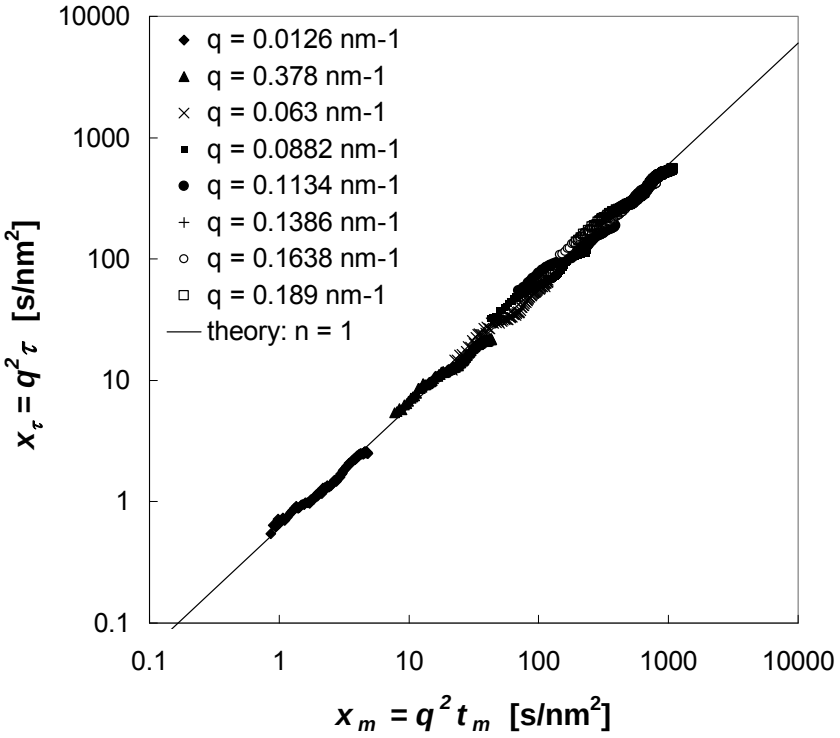
Comparison with Scaling Predictions



• As predicted by the theory and simulations:

$$x_\tau \sim x_m$$

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

• Although $x_\tau \sim x_m$, the dimensionless slope (ratio) between them is much smaller than expected –

0.5 (experiment) vs. ~ 1.4 (theory)

Importance (or not) still unclear….

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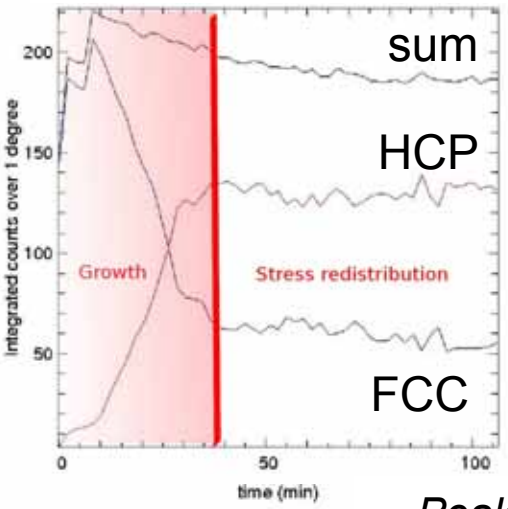
Martensitic Phase Transition in Co

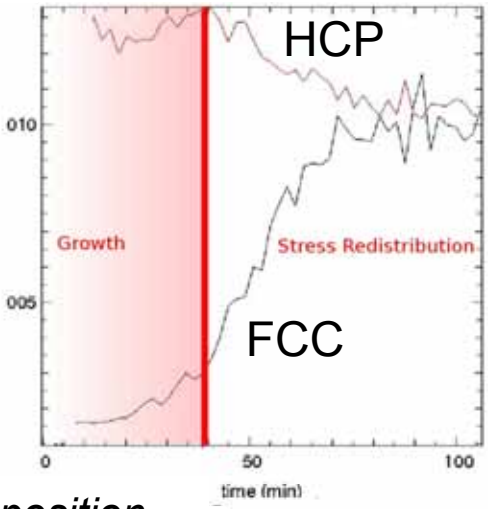
Cobalt: Martensitic phase transition from FCC to HCP at $T_{tr} \approx 720$ K

APS 8-ID: Sanborn, Ludwig, Rogers, and Sutton; PRL in press.

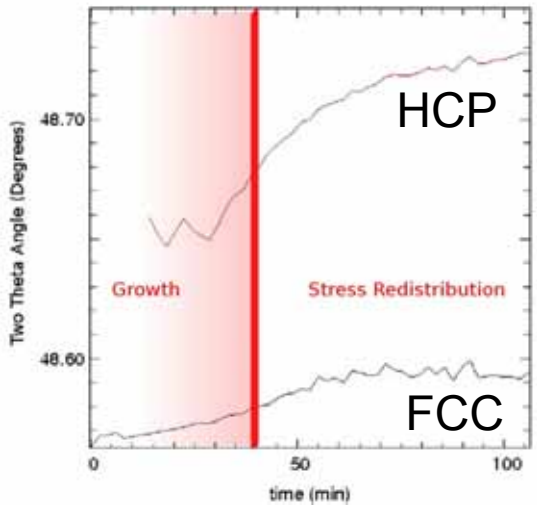
Integrated Peak Intensity



Peak Widths



Peak position



Results from conventional real-time x-ray scattering study of FCC → HCP transformation following rapid quench from anneal temperature to 10 K below T_{tr}.

Two regimes in FCC → HCP transformation:

- Growth of strained HCP regions form with stacking faults
- Strain redistribution accompanying local stacking changes

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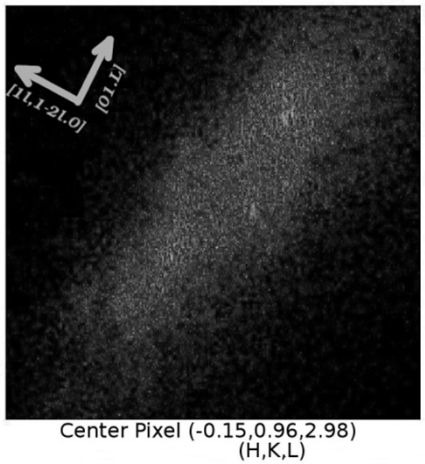
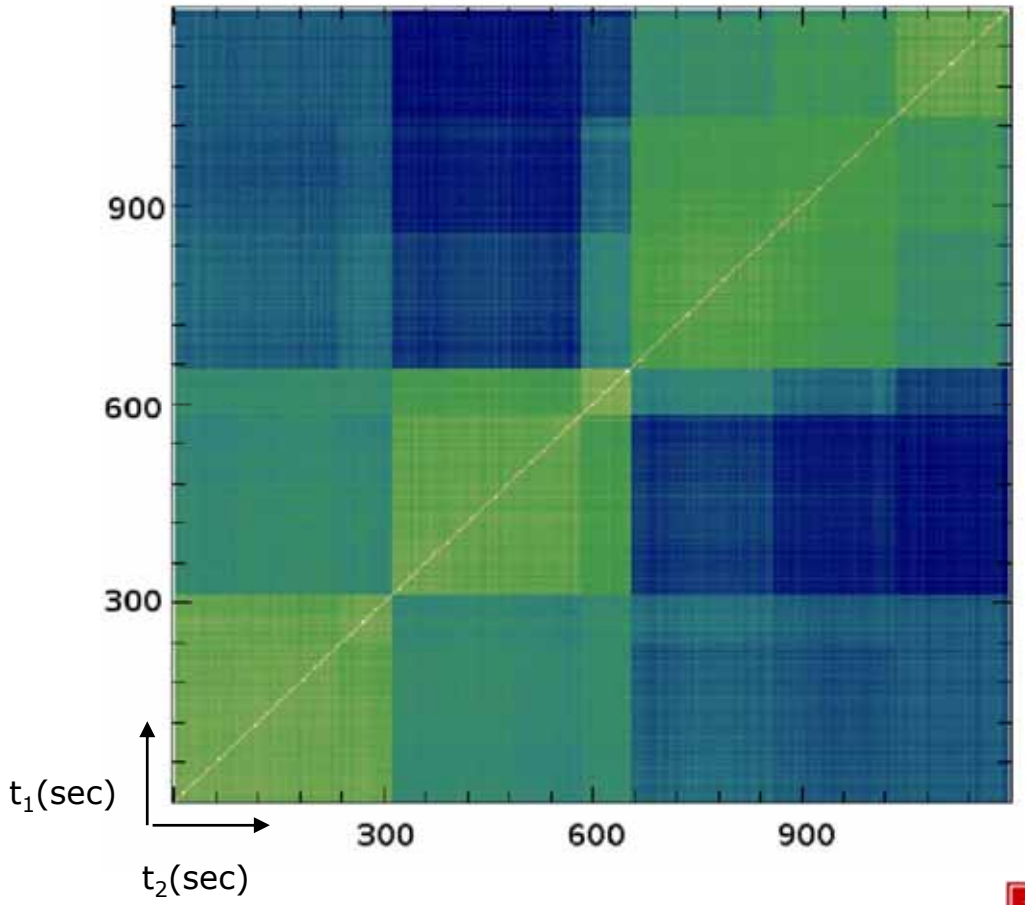
Speckles and Two-Time Correlation Function



Speckle on the HCP (01.L) rod due to stacking disorder

Avalanches in other martensitic materials previously observed by acoustic and thermal signals

Block nature of two-time correlation function points to sudden changes in local structure – “avalanches”.



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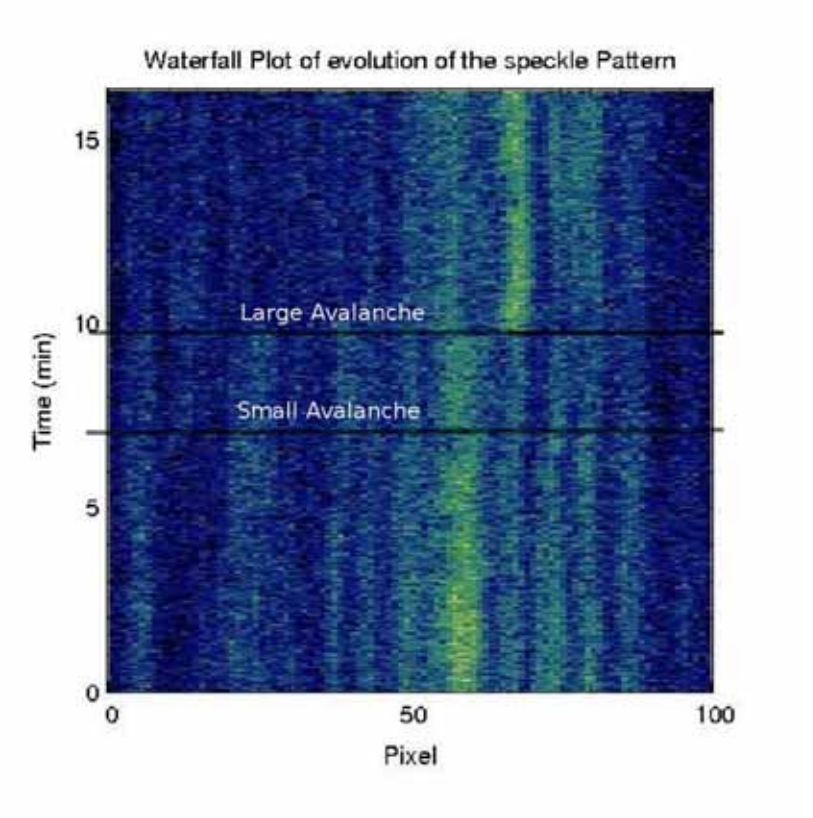
Avalanches apparent in "waterfall" plots

- Slice of 100 pixels within the speckle pattern
- What do these avalanches look like?



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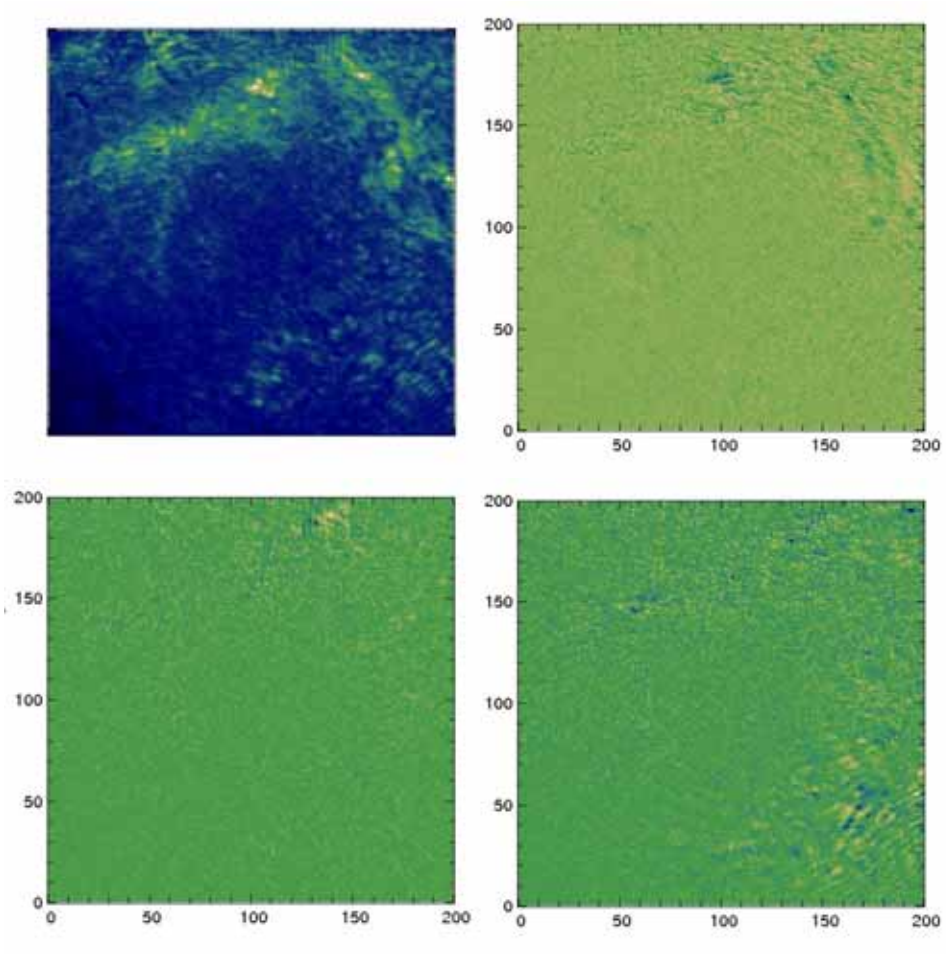
Avalanches as seen in coherent scattering

- Images
  - *Top-left:* Speckle pattern
  - *Rest:* 3 different avalanches
- Absolute difference between 10 images before and after avalanche
- Many avalanche differences somewhat similar pattern to original speckle pattern
- Avalanches occur in wide variety of sizes: large regions of detector to single pixels (i.e length scales of 100 nm to beam size of 10 μm)



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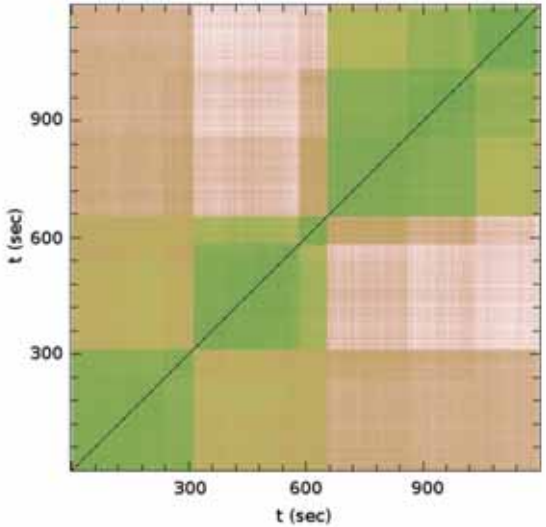
Key Issue: locating and quantifying avalanches

- Two-Time Difference
  - $D(\vec{q},t_1,t_2) = \left\langle \left| I(\vec{q},t_1) - I(\vec{q},t_2) \right| \right\rangle_{equivalent\ q}$
  - Similar to the two-time correlation function
- "Avalanche Amplitude"
  - $$A(\vec{q},t) = \sum_{j=2}^{15} D(\vec{q},t_{i-j},t_i) - D(\vec{q},t_{i-j},t_{i-1}) + \sum_{j=1}^{14} D(\vec{q},t_{i+j},t_{i-1}) - D(\vec{q},t_{i+j},t_i)$$
  - Greatly improves signal to noise ratio



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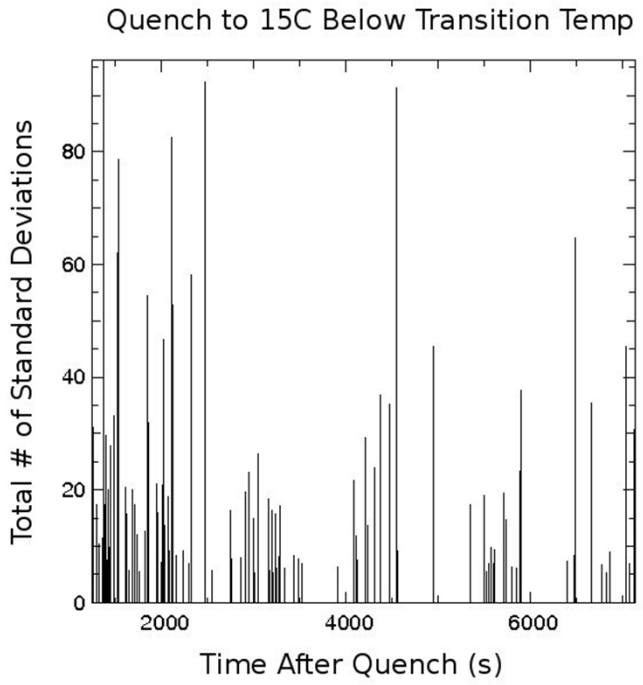
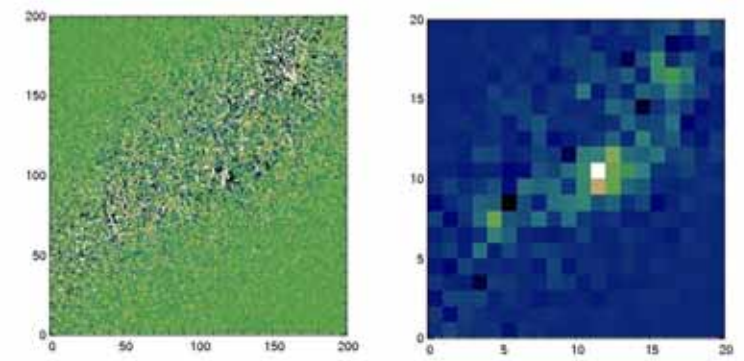
Key Issue: locating and quantifying avalanches

- Images binned into 10x10 pixel areas
  - Avalanche amplitudes calculated for all sections
- Normalize the avalanche amplitudes by standard deviation of counting statistics to find those which are statistically significant





Left: *Image of the Intensity difference between the frame before and after an avalanche*

Right: *Image of the binned avalanche amplitudes for the same avalanche*

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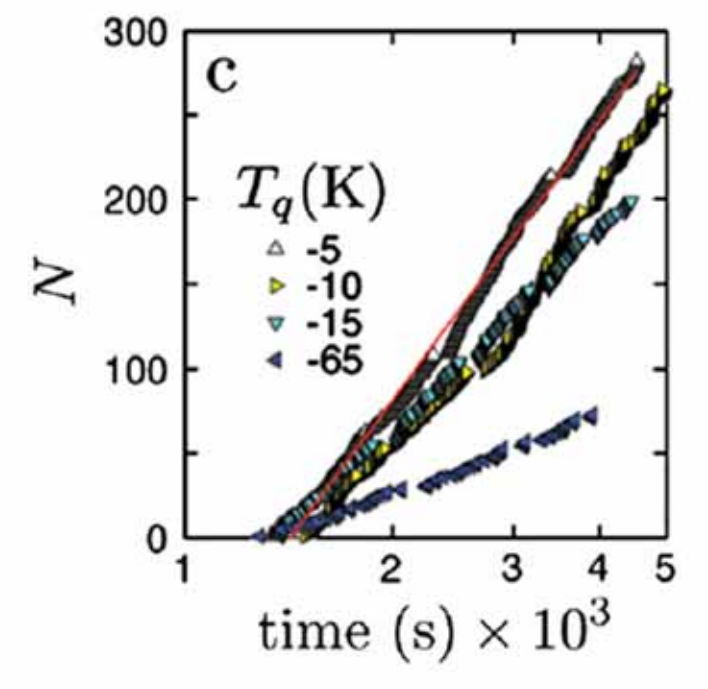
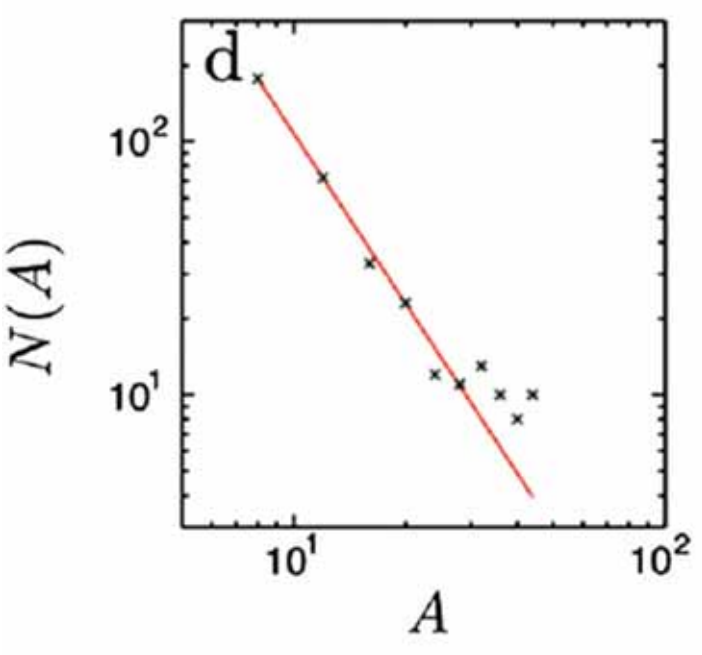
Avalanche Rates and Size Distribution





- Cumulative number of avalanches increased as log(*t*), so rate decreases as t^{-1}
- Avalanche rate decreases with temperature

- Size distribution of avalanche amplitudes follows a power law $A^{-\alpha}$ with $\alpha = 1.7 \pm 0.2$.

(Similar to Gutenberg-Richter and Omori laws for earthquake aftershocks)

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What Studies of Non-Equilibrium Processes Become Feasible with Factor of 10^3 Increased Coherent Flux?

- Dynamics during phase transformations
  - – smaller length scales L
  - – lower scattering cross section ($I \sim L^3$)
  - – shorter characteristic times (for diffusion $\tau \sim L^{-2}$)

- More fully explore length and time scales in heterogeneous dynamics (martensitic alloys, glasses, magnetic domain wall motion)

- Surface processes driven by, for example, deposition or ion bombardment

  Two possibilities suggested by our conventional *in-situ* studies at NSLS X21 (collaboration with R. Headrick – UVM):

  1) *Nanoscale self-organized structure formation during ion bombardment*

  2) *Surface morphology evolution during thin film growth*

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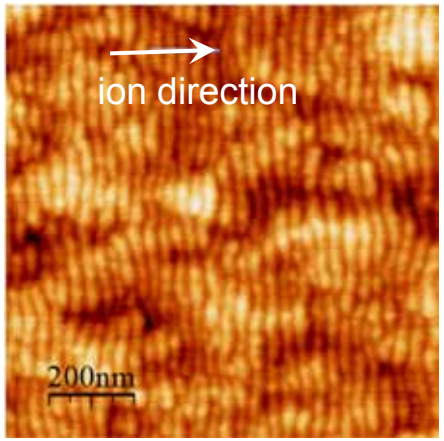
Nanoscale Self-Organized Structure Formation during Ion Bombardment

Off-Axis Bombardment –

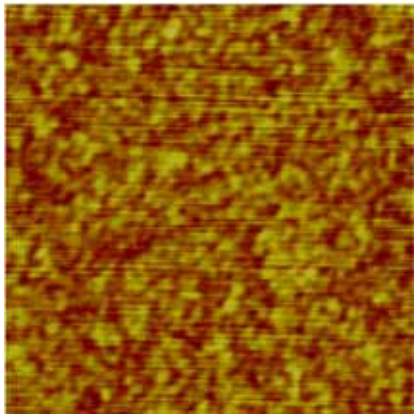
Ripples:



Si(100)

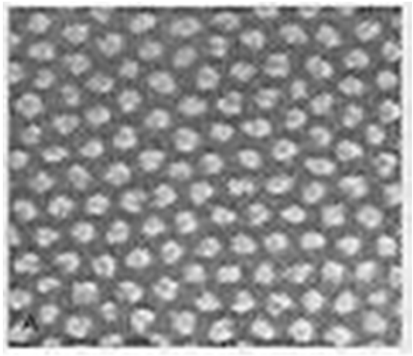
Normal Incidence Bombardment–

Smoothening:



Si(100)

Dots:



GaSb
(100)

Facsko *et al.*, Science **285**, 1551 (1999)

Key Question: What surface processes are driving pattern formation and how can we control them to make structures of interest?

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What are physical mechanisms determining nanoscale surface morphology development during bombardment?

Ion-Induced Surface Diffusion or Viscous Flow

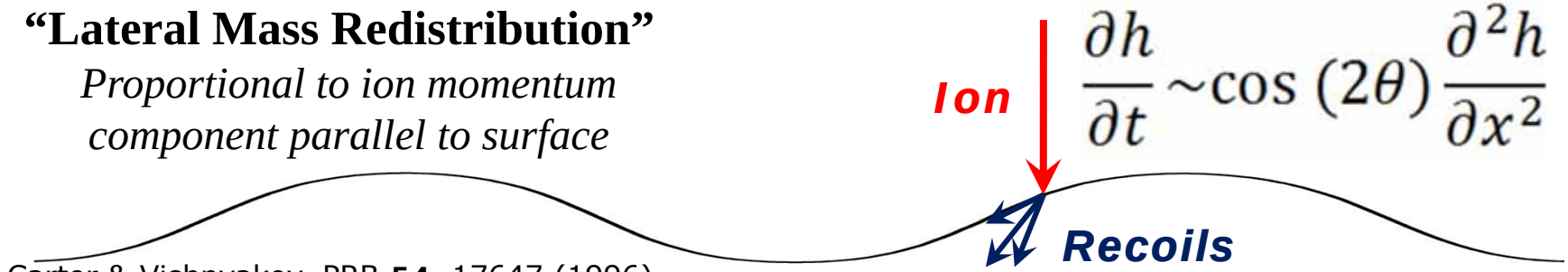
$$\left.\begin{aligned}\mu &\sim -\nabla^2 h \\ \boldsymbol{j} &\sim -\nabla\mu\end{aligned}\right\} \frac{\partial h}{\partial t} \sim -\,\mathrm{div}\boldsymbol{j} \sim -\,\nabla^4 h$$

Umbach *et al*., PRL **87**, 246104 (2001)

"Lateral Mass Redistribution"

Proportional to ion momentum component parallel to surface

$$\frac{\partial h}{\partial t} \sim \cos(2\theta)\frac{\partial^2 h}{\partial x^2}$$

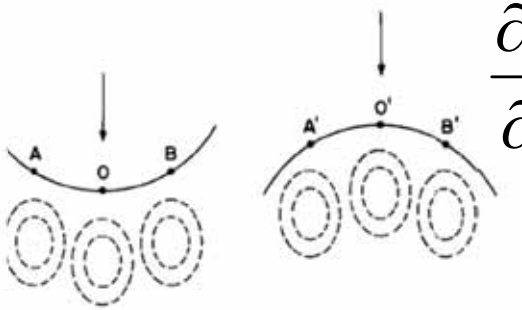


Carter & Vishnyakov, PRB **54**, 17647 (1996)

"Bradley-Harper Instability"

Theory of ripple topography induced by ion bombardment

R. Mark Bradley
Department of Physics, Colorado State University, Fort Collins, Colorado 80523
James M. E. Harper
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598



$$\frac{\partial h}{\partial t} \approx f(\theta)\frac{\partial^2 h}{\partial x^2}$$

How can we think about nanoscale surface morphology development during ion bombardment?

Linear Theory

Momentum transfer from ion knocks atoms "downhill" "Lateral Mass Redistribution"
Smoothening at $\theta = 0$
$\alpha \sim \cos(2\theta)$

Smoothening: Ion-induced diffusion or viscous flow

Stochastic nature of bombardment, relaxation

$$\frac{\partial h(x,t)}{\partial t} = -v_0 + (\alpha + \Gamma)\frac{\partial^2 h}{\partial x^2} - B\nabla^4 h + \eta(x,t)$$

Average sputter erosion rate

Roughening: Bradley-Harper term (Largest at $\theta = 0$)

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Linear theory solution for the height-height structure factor S(q,t):

$$S(q,t) = S(q,0)e^{R(q)t} + \frac{\langle \eta^2 \rangle}{-R(q)}(1 - e^{R(q)t})$$

Morphology development is governed by the amplification factor:

$$R(q) = -2\{[\Gamma(\theta) + \alpha(\theta)]q^2 + B(\theta)q^4\}$$

If $R(q) < 0$ then mode is stable to growth of surface fluctuations

If $R(q) > 0$ then mode is unstable to growth of surface fluctuations

Measuring R(q) for different incident angles can tell us much about the physical mechanisms operating during bombardment

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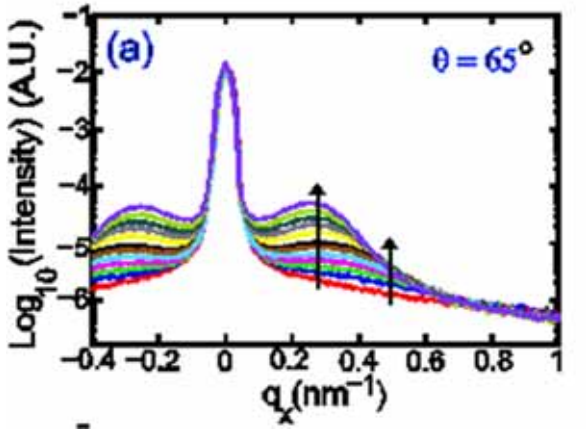
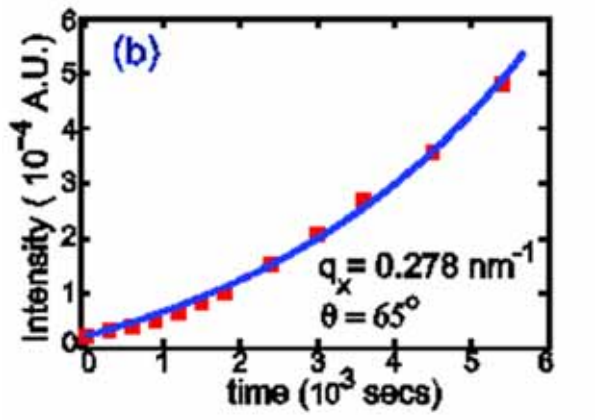
For each ion bombardment angle θ use real-time GISAXS to measure S(q,t)

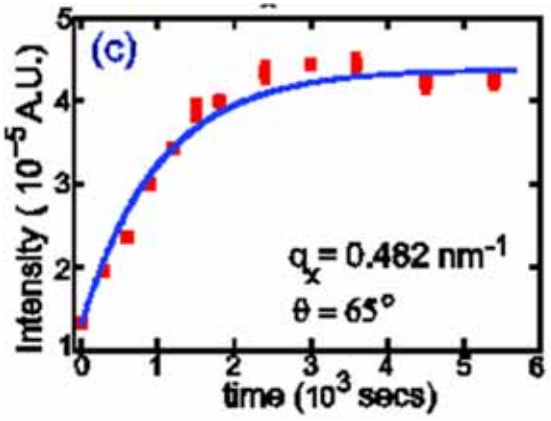
*NSLS X21: Madi, Anzenberg, Ludwig and Aziz; PRL **106**, 066101 (2011).*

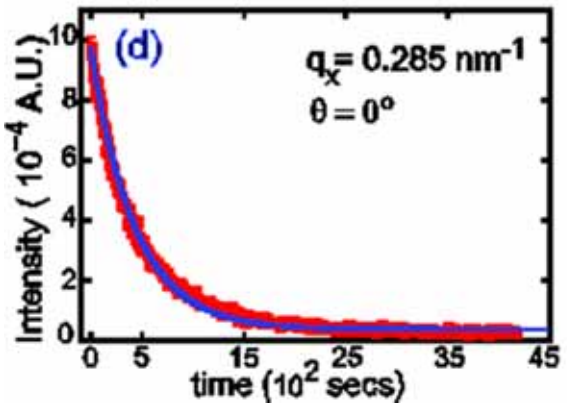


GISAXS evolution during 2 hours of 1 keV Ar^+ bombardment of Si (100)

At each wavenumber *q*, fit *S(q,t)* to determine Amplification Factor *R(q)*







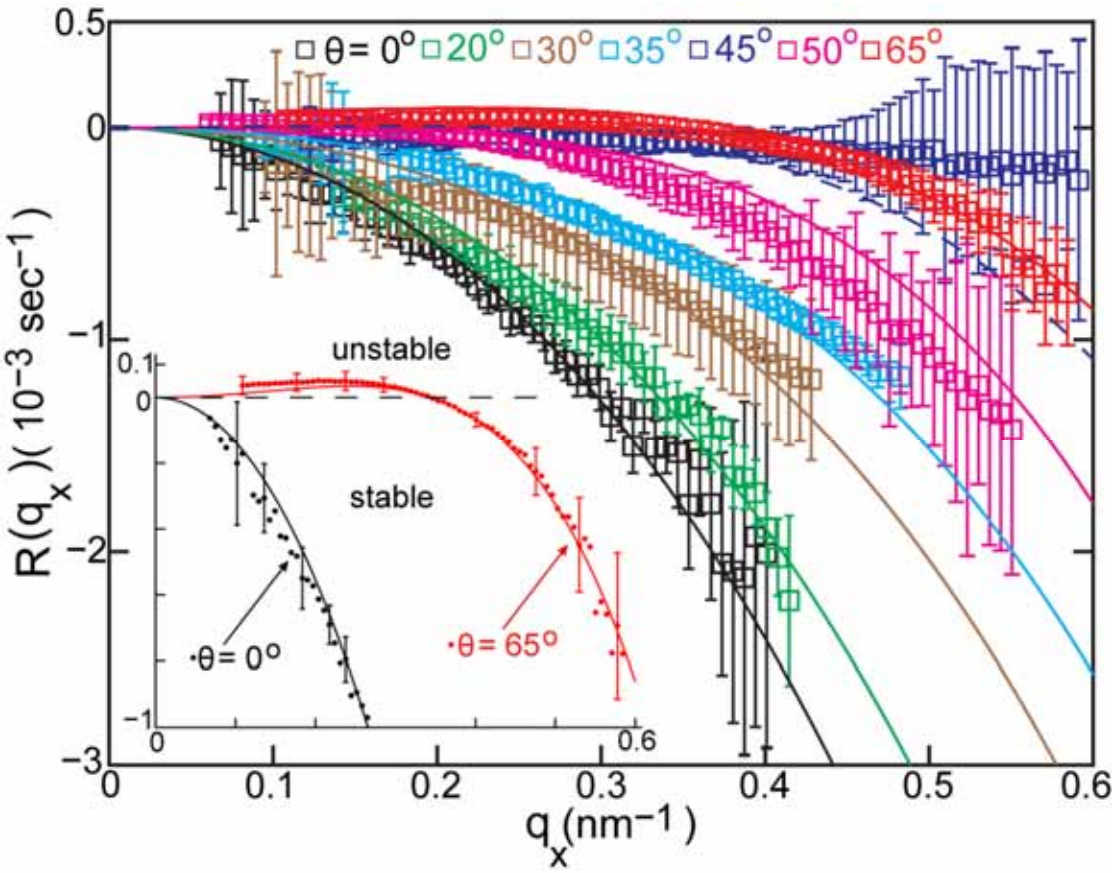
Measured Amplification Factor *R(q)*

$\theta_c \approx 45°$

For $\theta < \theta_c$:
R(q) < 0 for all *q*
(Smoothening)

For $\theta > \theta_c$:
R(q) > 0 for low *q*
(Roughening)

R(q) < 0 for high *q*
(Smoothening)



Data show complete dominance of Lateral Mass Redistribution (Ion Momentum Transfer)! Above $\theta_c \approx 45°$, ions knock atoms uphill to create nanoscale ripples.

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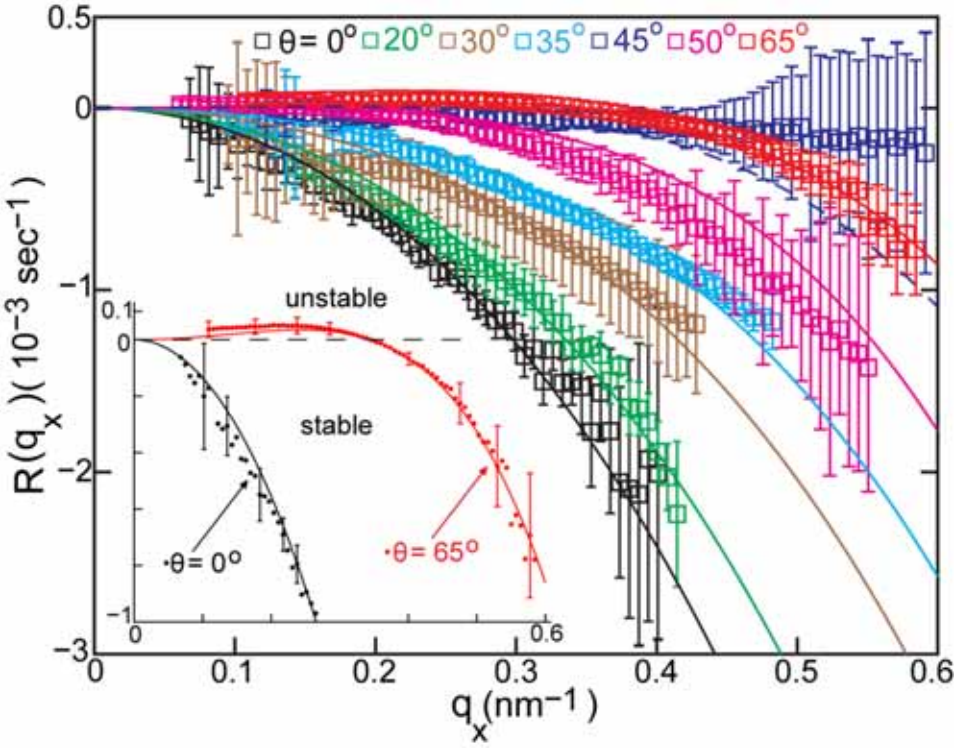
Measured Amplification Factor *R(q)*



Mystery: At θ_c theory predicts that $R(q=0) \rightarrow 0$ (i.e. unstable) but R(q > 0) should remain negative because surface still smoothened by viscous flow or surface diffusion. *However*, we see entire *R(q)* going to zero as θ_c is approached!

Conventional real-time experiments can tell us nothing more – we need XPCS to reveal underlying fluctuations!

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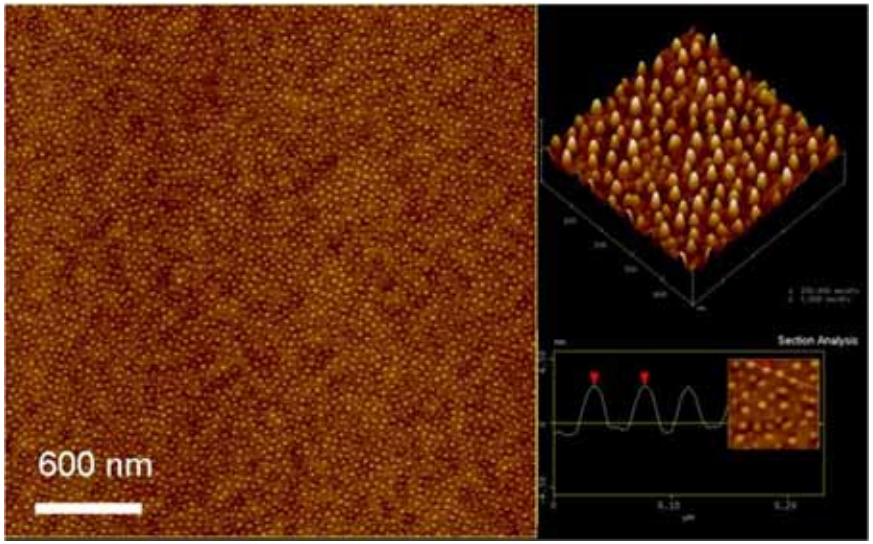
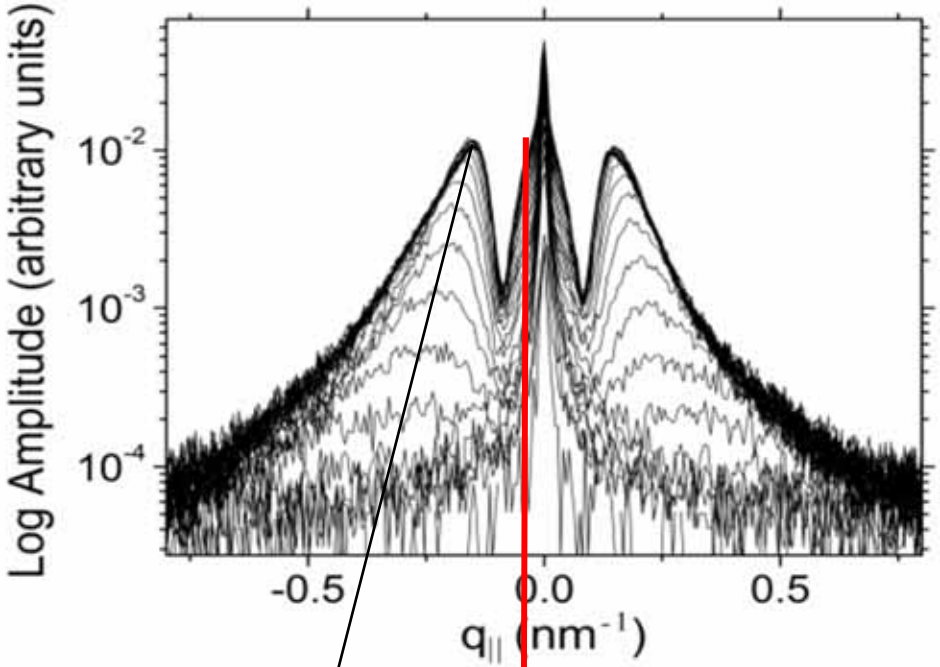
Self-Organized Nanodot Growth by Mo "Seeding" of Si Surface During Bombardment

Nanostructures form spontaneously with a period of ~ 30 nm and a height of ~ 3 nm.



Evolution of GISAXS scattering patterns



nanostructures

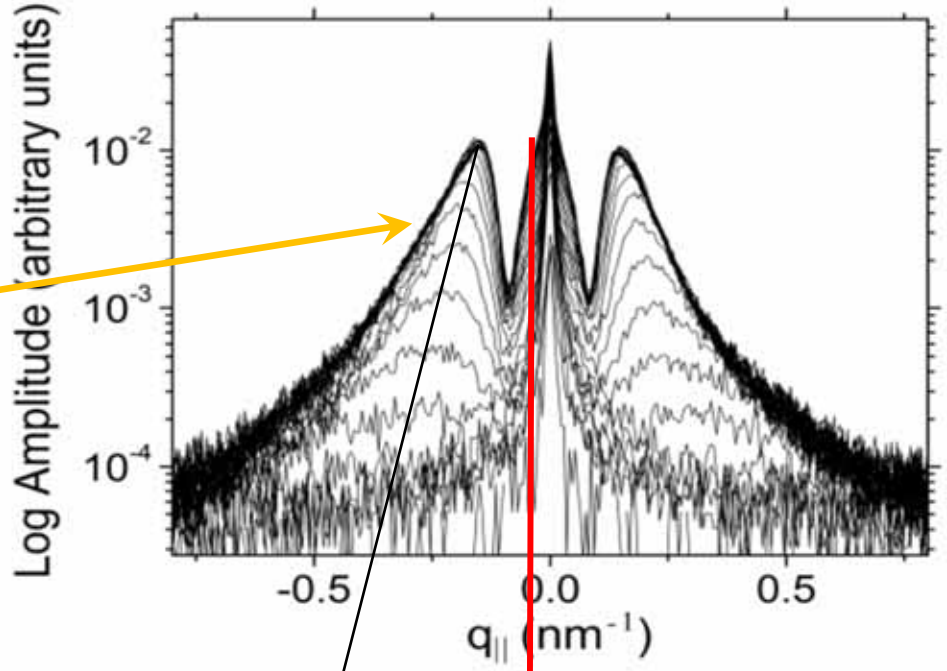
long-wavelength roughness

Self-Organized Nanodot Growth by Mo "Seeding" of Si Surface During Bombardment

At late times, surface structure saturates due to nonlinear behavior – what are dominant mechanisms driving behavior?

Conventional real-time studies show nothing more – need XPCS to understand fluctuations in this state to learn about dominant physical processes!

Evolution of GISAXS scattering patterns



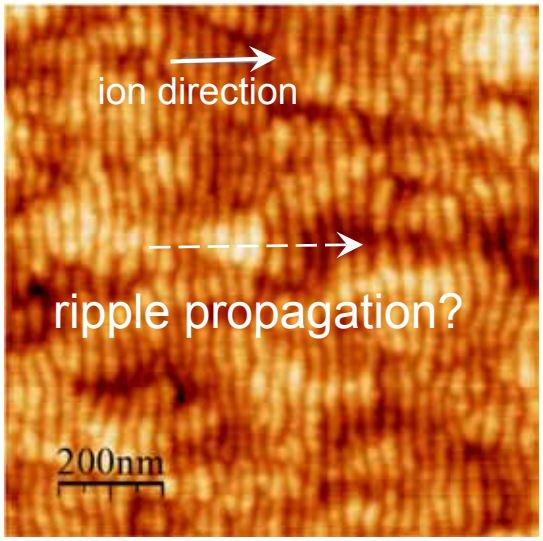
nanostructures

long-wavelength roughness

Motion of Nanoripples Across Surface during Off-Axis Ion Bombardment

One important piece of information is the direction and velocity of ripple propagation during ion bombardment. This can help reveal fundamental mechanisms operating on the surface.

Conventional scattering cannot detector ripple motion – we need XPCS. Analogous to the situation with flow, this would require the use of heterodyning.



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What Studies of Non-Equilibrium Processes Become Feasible with Factor of 10^3 Increased Coherent Flux?

There are many possibilities – but:

We probably need much more thought/theory/simulation to improve our conceptual understanding of XPCS data from non-equilibrium systems.

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