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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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.
Overview

• XPCS studies of equilibrium 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*
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*
**XPCS studies of non-equilibrium systems: Domain Coarsening Dynamics**

Langevin equation describing kinetics is highly nonlinear

<table>
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<th>Material</th>
<th>Reference</th>
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<tbody>
<tr>
<td>AlLi Alloy (phase separating)</td>
<td>Livet et al. PRE 63, 036108 (2001)</td>
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<tr>
<td>Cu₃Au Alloy (phase ordering)</td>
<td>Fluerasu et al. PRL 94, 055501 (2005)</td>
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<tr>
<td>Cu₃Pd Alloy (phase ordering)</td>
<td>Ludwig et al. PRB 72, 144201 (2005)</td>
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<td>Al-Zn/Al-Ag (phase separating)</td>
<td>Stadler et al. PRB 68, 180101 (2003)</td>
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<td>Ni-Al-Mo (phase separating)</td>
<td>Pfau et al. PRB 73, 180101 (2006)</td>
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<td>Al-Zn/Al-Ag (phase separating)</td>
<td>Stadler et al. PRE 74, 041107 (2006)</td>
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Comparison with specially developed scaling theory
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

\[
\overline{d} \propto t^{1/\alpha} \\
q_0 \propto t^{-1/\alpha}
\]

\[\alpha = 2 \text{ nonconserved OP (phase ordering)}
\]
\[\alpha = 3 \text{ conserved OP (phase separating)}
\]

Dynamic Scaling: \[
I(q,t) \propto q_0^{-d} F\left(\frac{q}{q_0}\right) \propto t^{d/\alpha} F(qt^{1/\alpha})
\]
Two-time correlation function:

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

\[ \Delta t = t_2 - t_1 \]
\[ t_m = (t_1 + t_2) / 2 \]

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

Scaling variable: \( x = q^2 t \)

Two Regimes of Correlation Decay:

- \( x_m \) small: \( x_t \sim x_m \)
- \( x_m \) large: \( x_t \sim x_m^{1/2} \)
Persistent speckles develop as predicted by theory
Normalized Two-Time Correlation Function

Contours:

\[ C_{\text{norm}}(q,t_1,t_2) \]

\[ t_m = 5676 \text{ s} \]
\[ t_m = 17286 \text{ s} \]
\[ t_m = 30440 \text{ s} \]

Series 2

30440 fit
17286 fit

Fits to theoretical form:

\[ C(z) = \left( \frac{z^2 K_2(z)}{2} \right)^2 \]

\[ z = A\Delta t/t_m^{1/2} \]
Comparison with Scaling Predictions

- As predicted by the theory and simulations:
  \[ x_T \sim x_m \]
  i.e. the speckles’ persistence increases linearly with mean coarsening time.

- Although \( x_T \sim x_m \), the dimensionless slope (ratio) between them is much smaller than expected –
  \[ 0.5 \text{ (experiment)} \text{ vs. } \sim 1.4 \text{ (theory)} \]
  Importance (or not) still unclear….
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.

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

Two regimes in FCC $\rightarrow$ HCP transformation:
- Growth of strained HCP regions form with stacking faults
- Strain redistribution accompanying local stacking changes
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”.

Center Pixel (-0.15, 0.96, 2.98)
Avalanches apparent in “waterfall” plots

- Slice of 100 pixels within the speckle pattern
- What do these avalanches look like?
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)
Key Issue: locating and quantifying avalanches

- **Two-Time Difference**
  - \( D(\bar{q}, t_1, t_2) = \langle |I(\bar{q}, t_1) - I(\bar{q}, t_2)| \rangle \)_{equivalent q}
  - Similar to the two-time correlation function

- **“Avalanche Amplitude”**
  - \( A(\bar{q}, t) = \sum_{j=2}^{15} D(\bar{q}, t_{i-j}, t_i) - D(\bar{q}, t_{i-j}, t_{i-1}) \)
    + \( \sum_{j=1}^{14} D(\bar{q}, t_{i+j}, t_{i-1}) - D(\bar{q}, t_{i+j}, t_i) \)

- Greatly improves signal to noise ratio
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
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)
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*
Nanoscale Self-Organized Structure Formation during Ion Bombardment

Off-Axis Bombardment –
Ripples:

Normal Incidence Bombardment –
Smoothening:
Dots:

Si(100)

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

**Ion-Induced Surface Diffusion or Viscous Flow**

\[ \mu \sim - \nabla^2 h \]
\[ j \sim - \nabla \mu \]
\[ \frac{\partial h}{\partial t} \sim - \text{div} j \sim - \nabla^4 h \]

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

**“Lateral Mass Redistribution”**

Proportional to ion momentum component parallel to surface

Carter & Vishnyakov, PRB 54, 17647 (1996)

**“Bradley-Harper Instability”**

Theory of ripple topography induced by ion bombardment

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\[ \frac{\partial h}{\partial t} \approx f(\theta) \frac{\partial^2 h}{\partial x^2} \]
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 $\theta = 0$)
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:

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

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


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 $R(q)$

$\theta_c \approx 45^\circ$

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 $\theta_c \approx 45^\circ$, ions knock atoms uphill to create nanoscale ripples.
**Mystery**: At $\theta_c$ 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 $\theta_c$ is approached!

Conventional real-time experiments can tell us nothing more – we need XPCS to reveal underlying fluctuations!
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!
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 detect ripple motion – we need XPCS. Analogous to the situation with flow, this would require the use of heterodyning.
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.*