Nanoscale Dynamics in Condensed Matter

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Why is Nanoscale Important in Dynamics?

→ Often determines mechanism of dynamics during materials processing

Misfit-Strain-Induced Domain Walls in Ferroelectric Thin Film

Magnetically-Induced Inversion Domain Wall in Nematic Liquid Crystal

C.M. Foster et al., J. Applied Physics 81, 2349 (1997)


Can be difficult to image during processing
Atomic- and nano-scale (<100nm) of great importance in dynamics
- Basic dynamic processes occur at atomic scale
- Overall dynamics mediated by defects and collective mechanisms at the nanoscale

Would like to observe equilibrium dynamics:
- Non-equilibrium mechanisms are typically based on microscopic processes which occur, and are simpler to understand, at equilibrium
- Many useful properties are inherently dynamic
To understand dynamics, need *in-situ* techniques which resolve both *length* and *time*

Determining nature of rate-limiting step from wavenumber \((Q)\) dependence of rate:

\[
\text{Rate } \propto Q^2 : \\
\text{e.g. composition change by diffusion} \\
\text{(conserved quantity)}
\]

\[
\text{Rate indep. of } Q : \\
\text{e.g. deformation by viscous flow} \\
\text{(non-conserved quantity)}
\]
Scattering Techniques for Equilibrium Dynamics

Existing techniques

**Probe thermal fluctuations:**

- Visible
- Raman Scattering
- Visible Brillouin Scattering
- Visible Photon Correlation Spectroscopy

**Excite and probe fluctuations:**

- Inelastic Scattering: X-ray, Neutron
- Visible Transient Grating Spectroscopy
Scattering Techniques for Equilibrium Dynamics

XPCS and XTGS

Probe thermal fluctuations:

Excite and probe fluctuations:
Example: Test of Reptation Model

Dynamics of Long-Chain Polymers

Neutron spin-echo has been used to observe Rouse motions.

\[ \tau \propto Q^{-3} \]

\( \tau = \) "disentanglement time"

Independent of \( Q \)

XPCS at LCLS would allow test of reptation model.
Experiment 1: X-ray Photon Correlation Spectroscopy (XPCS)

In milliseconds - seconds range:
Uses high average brilliance

transversely coherent X-ray beam from LCLS

monochromator

sample

\[ g_2(\Delta t) \equiv \frac{\langle I(t) I(t + \Delta t) \rangle}{\langle I \rangle^2} \]

\[ \tau^{-1}(Q) = \text{Rate}(Q) \]

"movie" of speckle recorded by CCD

\[ I(Q, t) \]
Experiment 2: XPCS Using Split Pulse

In picoseconds - nanoseconds range:
Uses high peak brilliance

transversely coherent X-ray pulse from LCLS

variable delay $\Delta t$

splitter

sample

sum of speckle patterns from prompt and delayed pulses recorded on CCD

$I(Q, \Delta t)$

Analyze contrast as $f(d)$elay time

$10 \text{ ps} \Leftrightarrow 3 \text{ mm}$

Contrast

$\Delta t$
Experiment 3:
X-Ray Transient Grating Spectroscopy

In **picoseconds - nanoseconds** range:
Uses high peak intensity

X-ray pulse from LCLS

\[ \alpha = 0.1 - 10^\circ \]
\[ Q = 0.05 - 5 \text{nm}^{-1} \]

\[ S(Q, \Delta t) \]

**Drive system with chosen Q**, observe response as \( f(\text{delay time}) \)
Is there enough signal from a single LCLS pulse?  
Is sample heating by x-ray beam a problem?

Available photons per pulse:

\[ N_{AVAIL} = f(E, \Delta E, A) \]

Minimum photons per pulse to give sufficient signal:

\[ N_{MIN} = \frac{2 \pi A E^2 \sigma_{abs}}{h c^2 \sigma_{el} M_{corr}} N_{SPECKLE}^{MIN} \]

Maximum photons per pulse to give \(1^\circ\) temperature rise:

\[ N_{MAX} = \frac{3 k_B A}{E \sigma_{abs}} \Delta T_{MAX} \]
• **Simple Liquids** – Transition from the hydrodynamic to the kinetic regime.

• **Complex Liquids** – Effect of the local structure on the collective dynamics.

• **Polymers** – Entanglement and reptative dynamics.

• **Glasses** – Vibrational and relaxational modes in the mesoscopic space-time region.

• **Dynamic Critical Phenomena** – Order fluctuations in alloys, liquid crystals, *etc.*

• **Charge Density Waves** – Direct observation of sliding dynamics.

• **Quasicrystals** – Nature of phason and phonon dynamics.

• **Surfaces** – Dynamics of adatoms, islands, and steps during growth and etching.

• **Defects in Crystals** – Diffusion, dislocation glide, domain dynamics.

• **Ferroelectrics** – Order-disorder *vs.* displacive nature; correlations and size effects.