Opportunities in Soft Matter with High Energy X-rays at APS-U

Bob Leheny
Johns Hopkins University

Plans for the talk:

- Review some topics and issues in soft matter where the enhanced (coherent) flux at high energy provided by the APS-U should have significant impact.

- Draw on ideas from recent "*Workshop on Early Experiments and Opportunities in Soft Matter with the APS MBA Upgrade*" and related discussions.

- Key areas for opportunity in soft matter with APS-U:

1. Understanding and control of defects in ordered phases

2. Spatial and Temporal Heterogeneity of Out-of-Equilibrium Dynamics

   a) Intermittency in glassy systems
   b) Nonlinear response to mechanical stress

3. Interactions and Assembly at Fluid Interfaces

4. Structure and Dynamics of Biomembranes

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   a) Intermittency in glassy systems

   ☆ **b) Nonlinear response to mechanical stress**

☆ **3. Interactions and Assembly at Fluid Interfaces**

☆ **4. Structure and Dynamics of Biomembranes**

1. Soft materials under deformation and flow:

- Soft matter typically displays strongly nonlinear response to mechanical stress

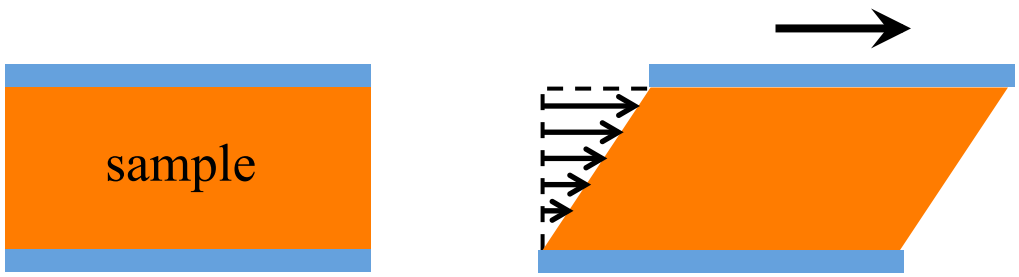
  e.g., shear thinning, shear thickening, thixotropy

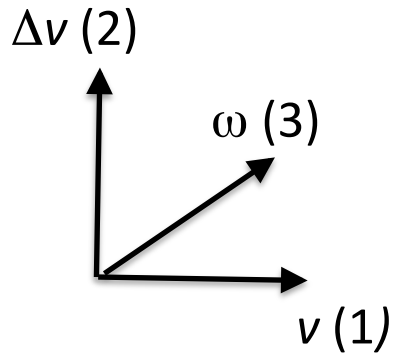
Shear thickening

- Origin of nonlinear response is stress-induced changes to microstructure.
- <u>But</u>, Identifying connections between the microscopic and macroscopic behavior remains a central challenge.

→ X-ray scattering with *in situ* stress/flow is a powerful probe.

E.g., SAXS with *In Situ* Shear

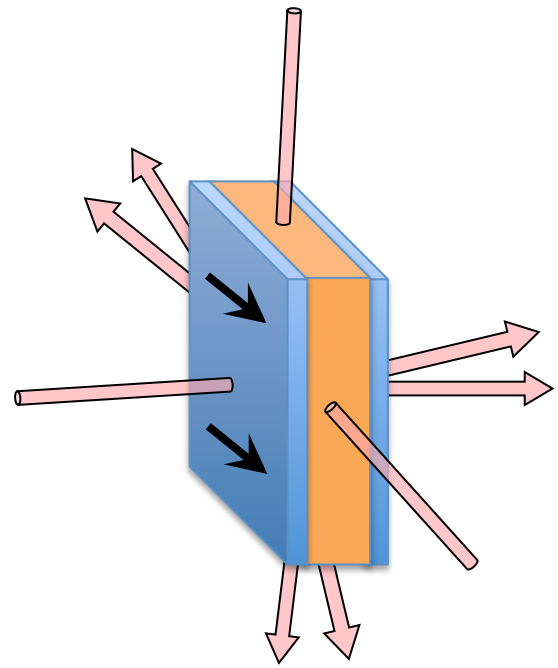




$v_1 = \dot{\gamma} x_2$

$v_2 = v_3 = 0$

$\dot{\gamma}$ = "shear rate"



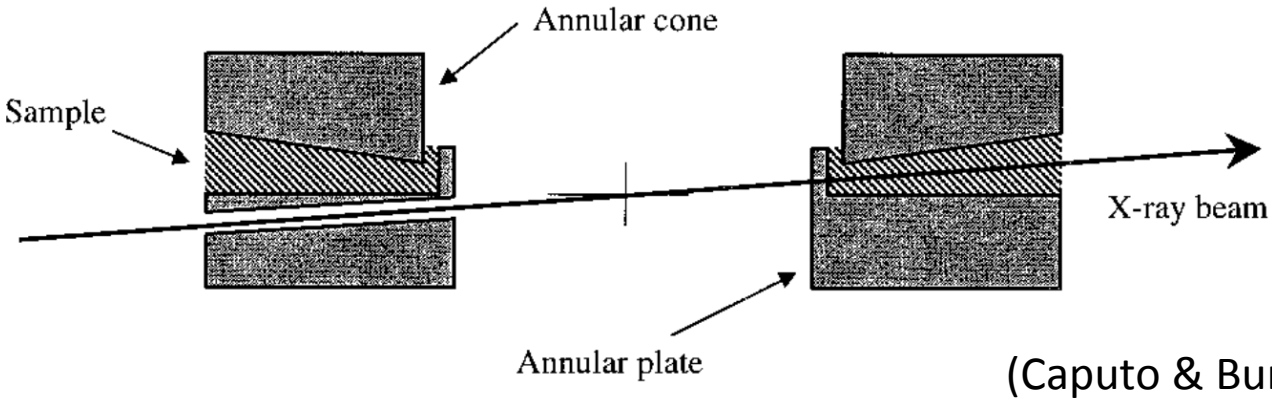
Choice of scattering plane: v-Δv, v-ω, Δv-ω leads to different information about shear-induced structure.

- SAXS in v-ω plane is easiest & most commonly realized.
  - <u>But</u>, v-Δv plane arguably most informative regarding structural changes.
  - <u>And</u>, for XPCS, Δv-ω has arguably most promise.

High energy x-rays key to realizing SAXS in v-Δv and Δv-ω planes.

SAXS in *v*-Δ*v* plane:

Example from Wes Burghardt's group:

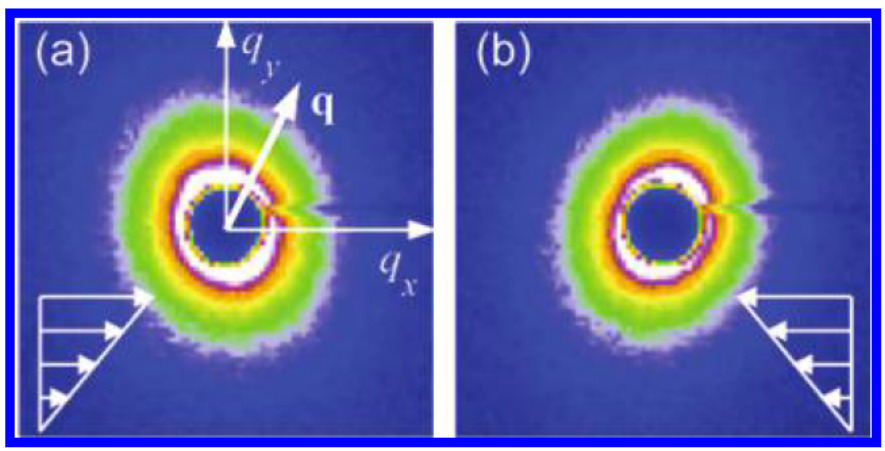


path length ≈ 1 cm

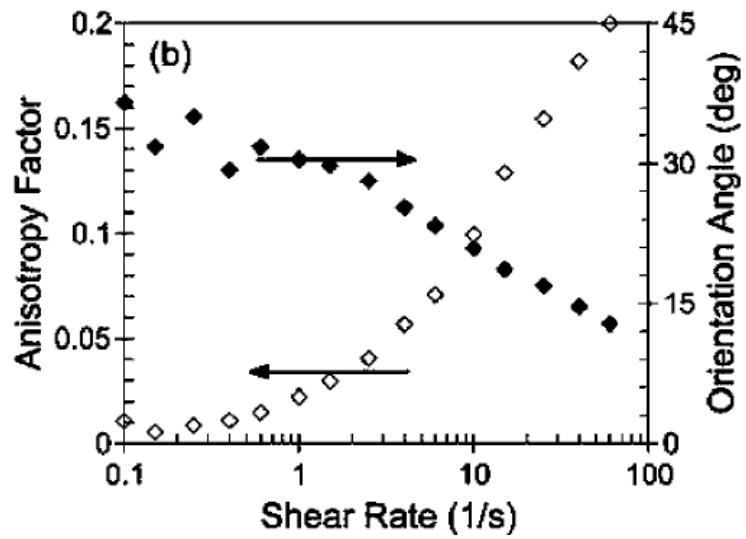
N.B., E = 15-25 keV

(Caputo & Burghardt)

Results from polymer/clay nanocomposites:



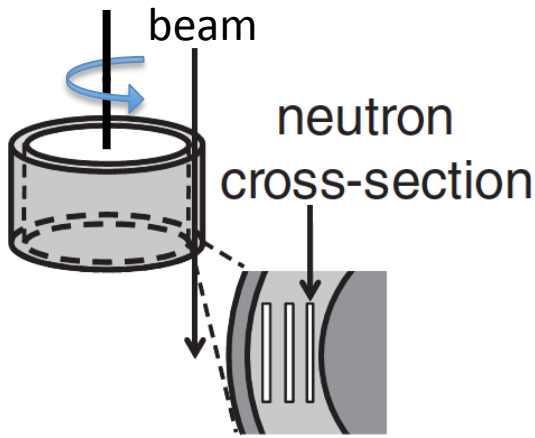
(Dykes, Torkelson, & Burghardt, Macromolecules **45**, 1622, 2012)



N.B., both degree and direction of anisotropy probed; unique capability of *v*-Δ*v* plane

Another approach to scattering in v-Δv plane: Couette geometry

concentric cylinders



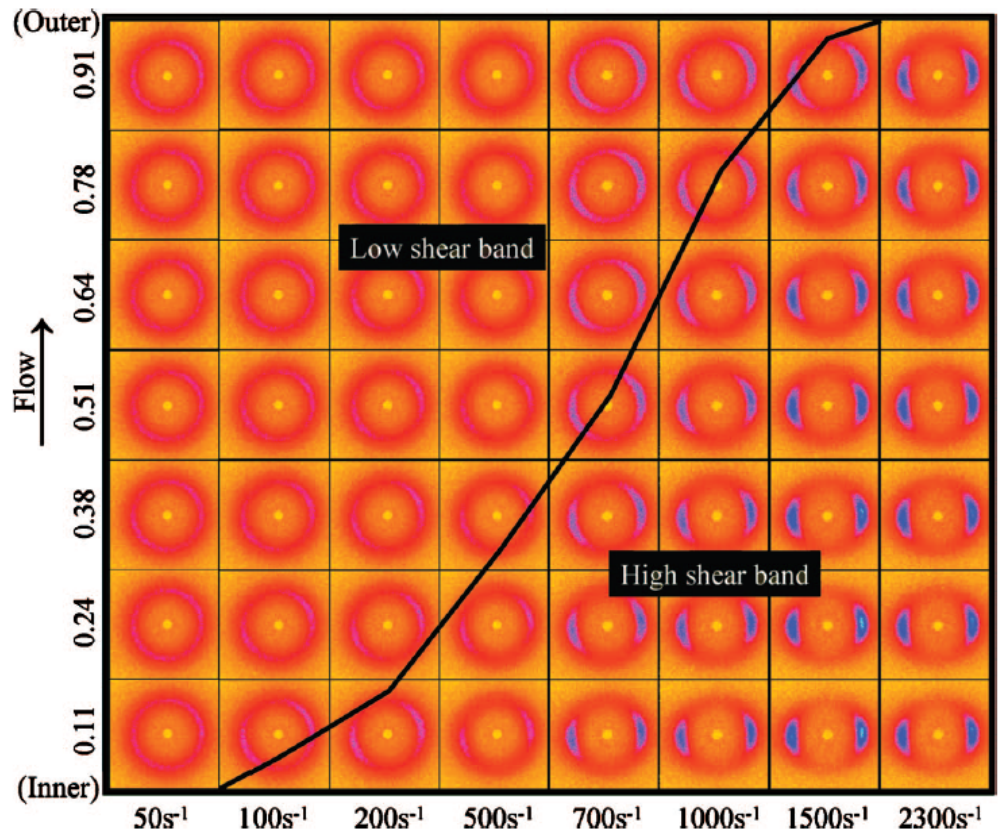
- Employed successfully with SANS.

  Path length > 1 cm.

- Advantage: spatial separation of shear instabilities/shear-induced states

  e.g., shear banding

Example: SANS on shear-induced isotropic-to-nematic transition in wormlike micelle solution



(Helgeson, Vasquez, Kaler, Wagner, J. Rheol. **53**, 727, 2009)

Key Point: Smaller, brighter high-energy beam would greatly enhance prospects for demanding SAXS experiments like these.

Rheology + XPCS:

XPCS a natural probe of microstructural dynamics relevant to rheology:

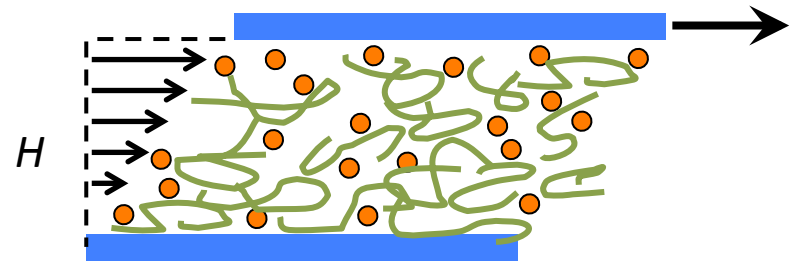
Scale of relevant structures: 1 – 100 nm

Typical time scales: 0.001 – 100 sec

"Standard" XPCS: *Equilibrium structural dynamics*, microscopic processes that govern linear response

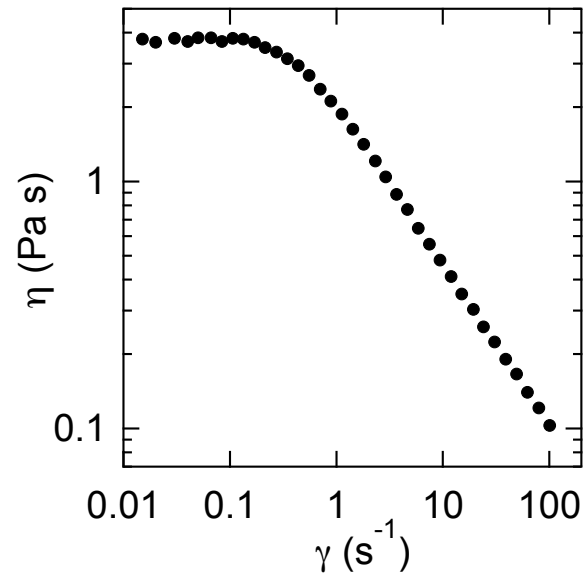
"Rheo—XPCS": *Shear-induced structural dynamics,* microscopic processes associated with nonlinear viscoelastic phenomena

Rheo-XPCS.



Consider, e.g., nanoparticle tracers in a shear-thinning polymer solution.

What is diffusivity in nonlinear regime?



Under appropriate conditions, XPCS correlation function can be factorized:

$$g_2(\mathbf{q},t) = 1 + \beta \exp\left[-2Dq^2 t\right] \times \frac{\sin^2(q_{||}\dot{\gamma}Ht/2)}{(q_{||}\dot{\gamma}Ht/2)^2} \times \exp\left[-(t/\tau_T)^2\right]$$

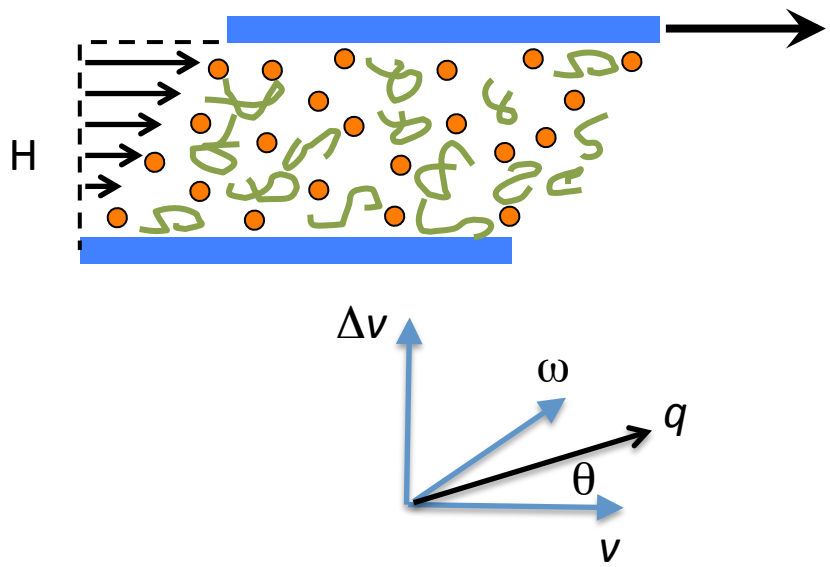
Intrinsic dynamics — Shear — Transit

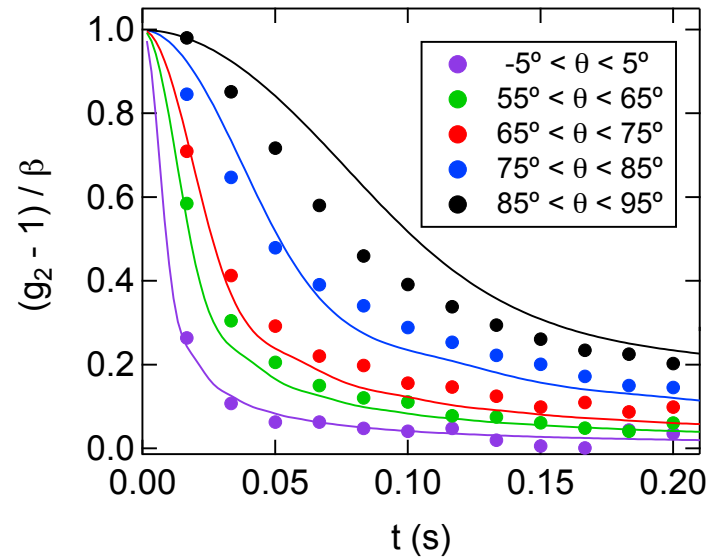
Characteristic time scales (for scattering in *v*-ω plane):

Intrinsic dynamics: $\tau_D = 1/Dq^2$

Shear term $\tau_S = (q\dot{\gamma}H\cos\theta)^{-1}$ θ = angle between mean velocity $\mathbf{v}_0$ and q

Transit term: $\tau_T = L/|\mathbf{v}_0|$ L = beam size





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Intrinsic dynamics Shear Transit

Problem:

For scattering in *v*-ω plane, correlation function determined by shear, not intrinsic dynamics.

Shear (or transit) dictates $g_2(q,t)$ except at very small Peclet numbers:

$$\mathrm{Pe} = \dot{\gamma}R^2/D \lesssim 0.01$$

→ Nonlinear effects on intrinsic dynamics inaccessible...

Possible Solution: Rheo-XPCS in different scattering geometries.

Key Point: Realizing potential of rheo-XPCS will require high-energy coherent beams.

Speckle cross-correlations in materials under deformation

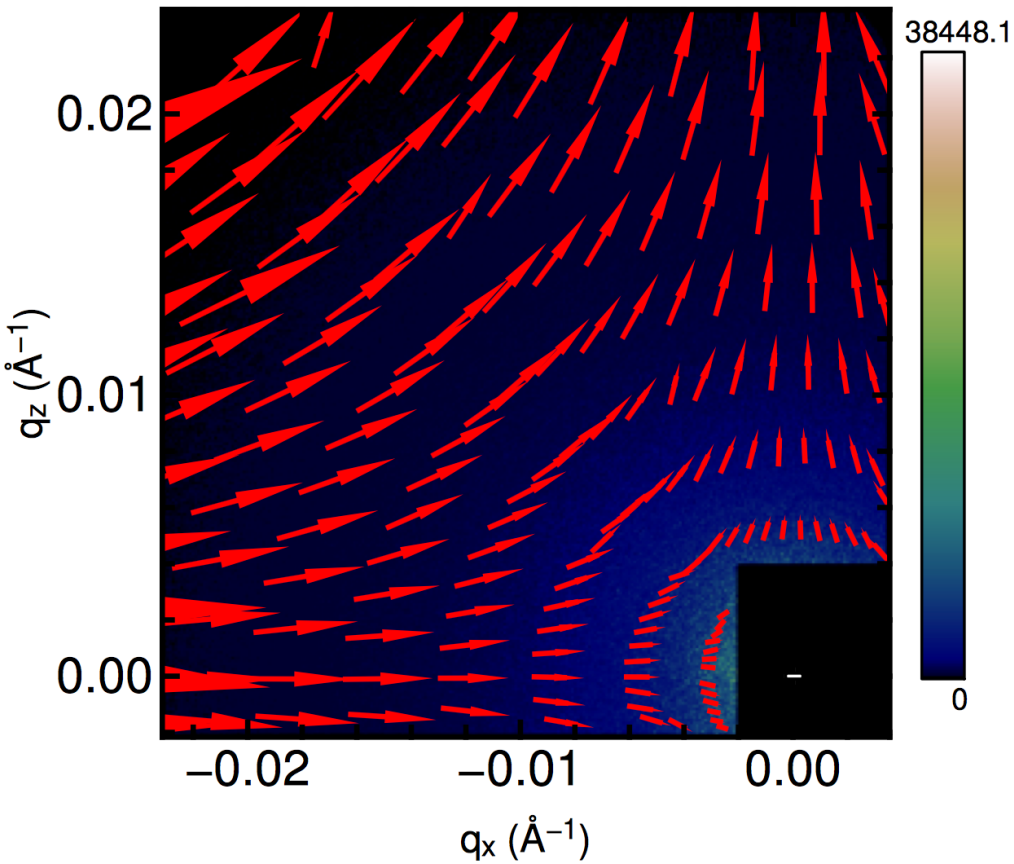
$$\frac{d\mathbf{q}}{dt} = -\dot{\mathbf{\Gamma}} \cdot \mathbf{q}$$

$\dot{\mathbf{\Gamma}}$ = local velocity gradient tensor

$$G_{\mathbf{q}}(\delta\mathbf{q}, t) = \langle I(\mathbf{q}, 0) I(\mathbf{q} + \delta\mathbf{q}, t) \rangle$$

E.g., Residual strain during stress relaxation of filled polymer under tension

M. Sutton and J. Lhermitte, unpublished.

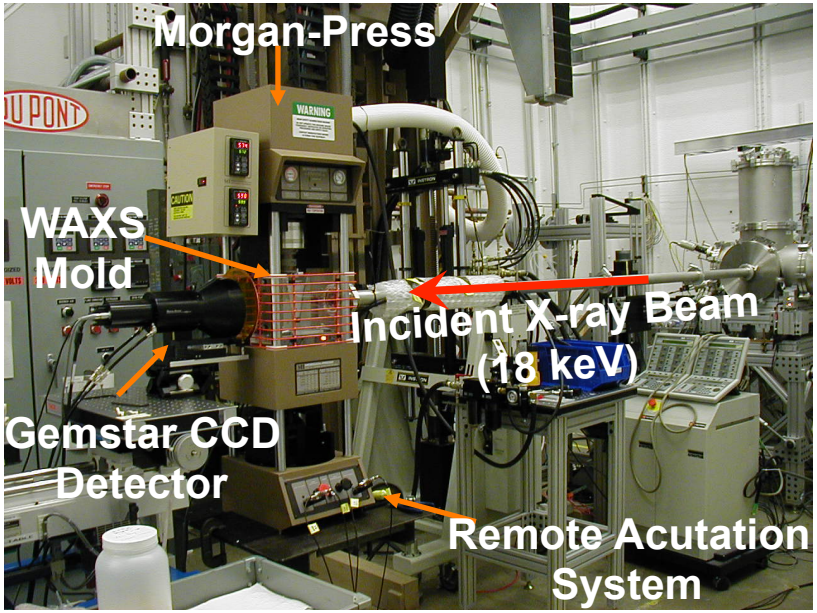


Deformation modes beyond simple shear will also benefit from brighter, high-energy beams.

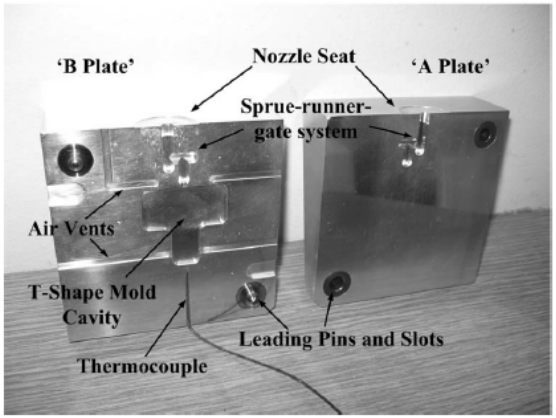
Another "Crazy" idea: Injection molding

Wes Burghardt & coworkers

Beamline 5ID-D of DND-CAT



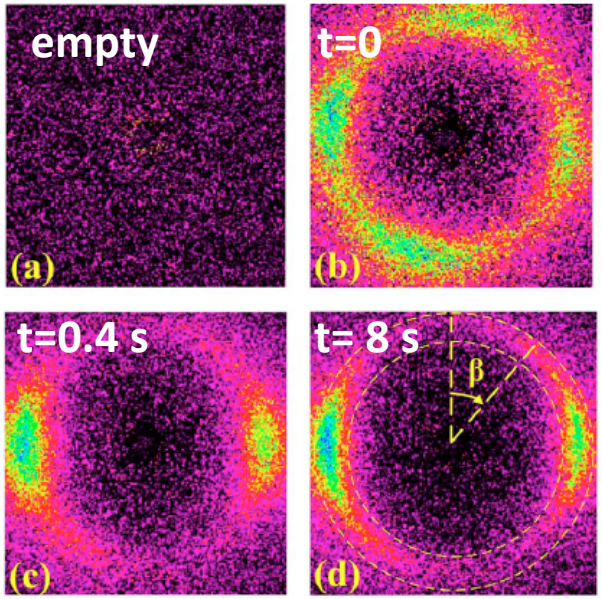
Rendon, Fang, Burghardt & Bubeck, RSI 80, 043902 (2009)



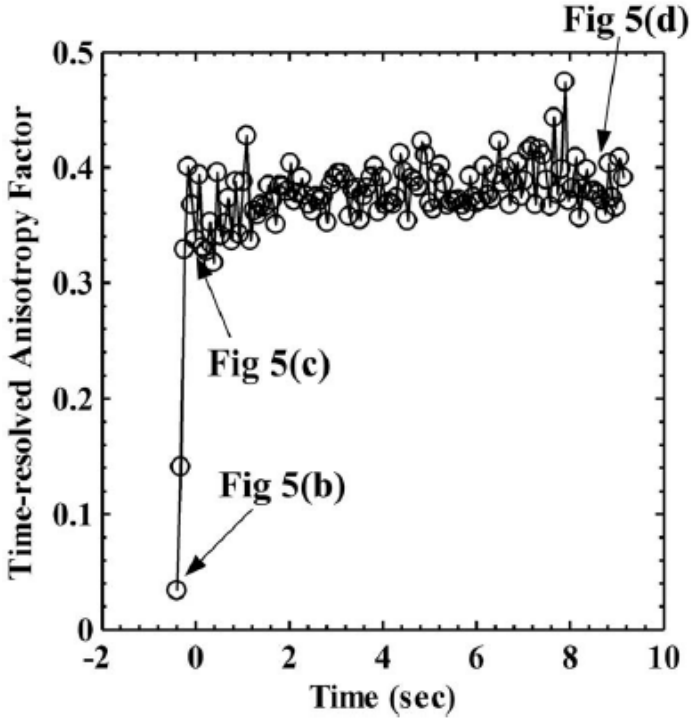
- Al mold required to support high pressures.

Transmission @ 18 keV < 25%

Time-resolved WAXS patterns during injection molding of a nematic liquid crystalline polymer:



Rendon, Fang, Burghardt & Bubeck, RSI 80, 043902 (2009)



Smaller, brighter, higher-energy beams would enable:

- Better time resolution
- Ability to probe more interesting systems (e.g. flow-induced crystallization in semi-crystalline polymers)
- Access into even more challenging sample environments

2. Interactions and Assembly at Fluid Interfaces

Assorted examples based on scientific interest and my confidence in describing.

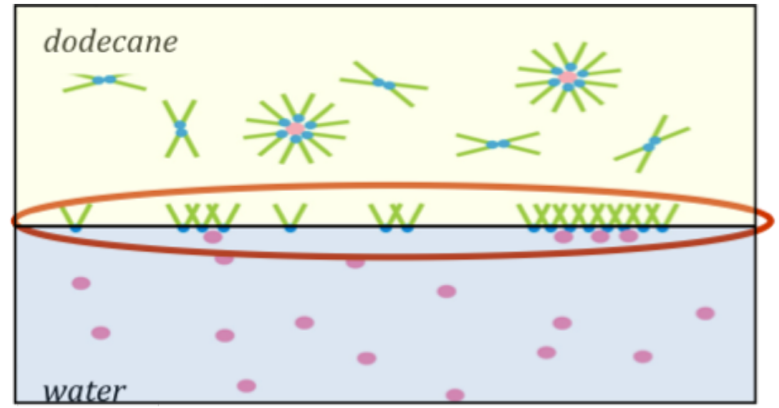
i) Molecular Assembly at Fluid-Fluid Interfaces

Mark Schlossman
Ben Ocko

E.g., Interfacial processes of solvent extraction

Soft matter meets environmental science

Surface-sensitive scattering combined with spectroscopy important



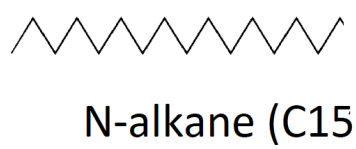
E.g., Surface freezing at buried interface

Reflectivity shows change in density consistent with transition

Taman et al., PNAS (2011).

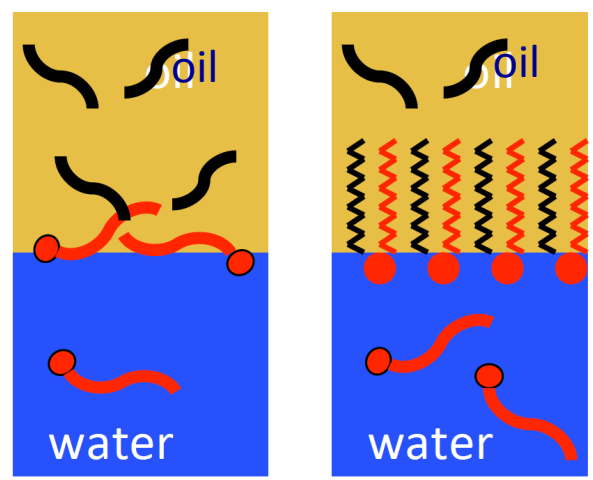
GID required for in-plane order

Need: small, bright beams to reduce background; high coherence to characterize large areas



N-alkane (C15)

Ionic surfactant (CTAB)



$T > T_s$ $T < T_s$

ii) Assembly/Organization Fluid-complex fluid interface

Nick Abbott

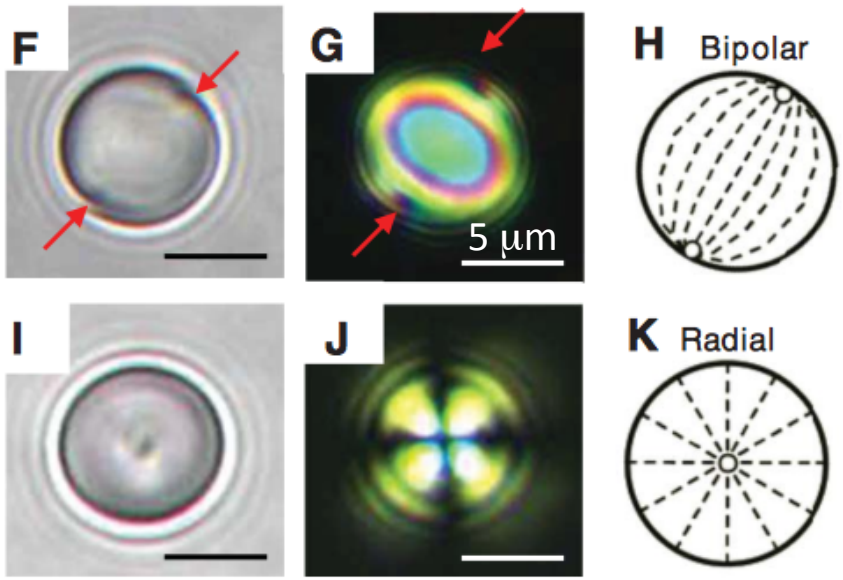
e.g. water-nematic liquid crystal interface

- Amplification of interfacial changes for exquisite sensing.

  → Topological transition in nematic order

- No experimental information regarding molecular-scale changes to interface.

E.g., Endotoxin-Induced Structural Transformations in Liquid Crystalline Droplets



Lin, Miller, Bertics, Murphy, de Pablo, Abbott, Science **332**, 1297 (2011).

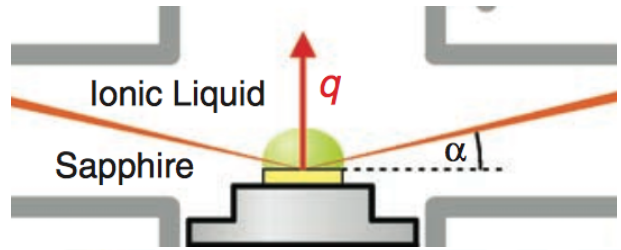
iii) ionic liquids at solid surface

Ben Ocko

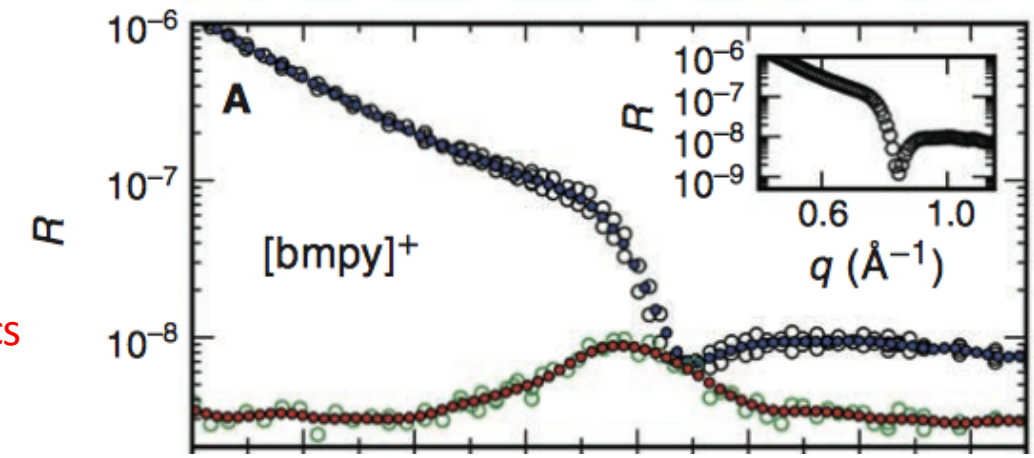
Relevant to applications, e.g., environmentally friendly solvents, supercapacitors, etc.

$[bmpy]^+[FAP]^-$ on Al_2O_3

- Near surface layering demonstrated with high-E x-ray reflectivity.

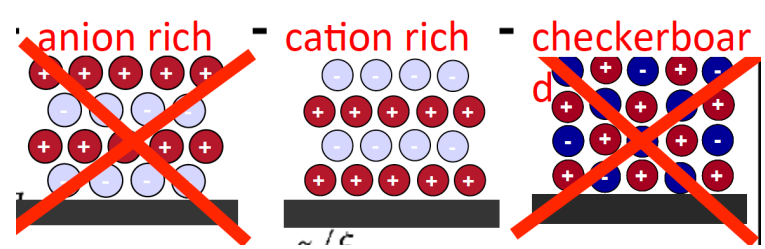


ESRF
E = 72 keV



Possible studies with APS-U

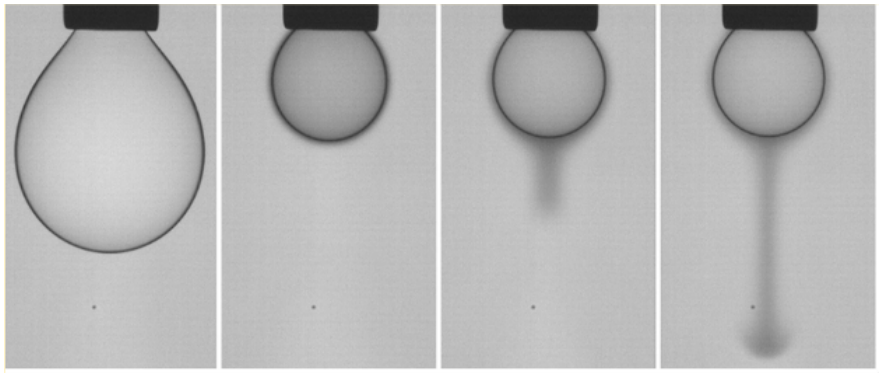
- Time-resolved structural response to potential step.
- Near-surface dynamics
  → IL diffusivity suggests dynamics accessible to XPCS.



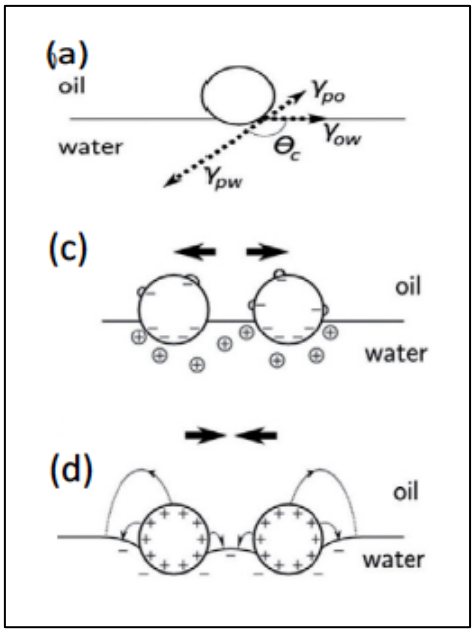
Mezger et al., Science 322, 424 (2008)

iv) Nanoparticle Assemblies at Fluid-Fluid Interfaces: Nanoparticles are "different"

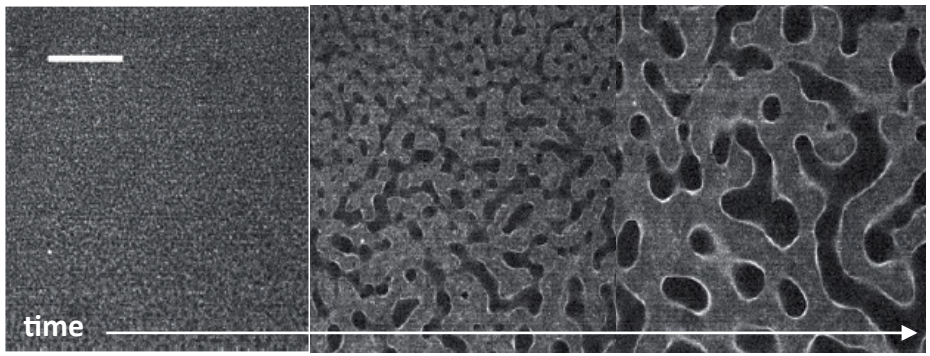
Ben Ocko
Tom Russell



Garbin, Crocker, and Stebe., *Langmuir* **28**, 1663 (2011)



Bijel formation



Herzig *et al., Nat. Mater.* **6**, 966 (2007)

Complex Interactions (poorly understood)

1) Van Der Waals Attraction
2) Electrostatic and dipole-dipole
3) Steric
4) Capillary

Lots of theory; no clean experiments

Small, bright high-energy beams could enable access to:

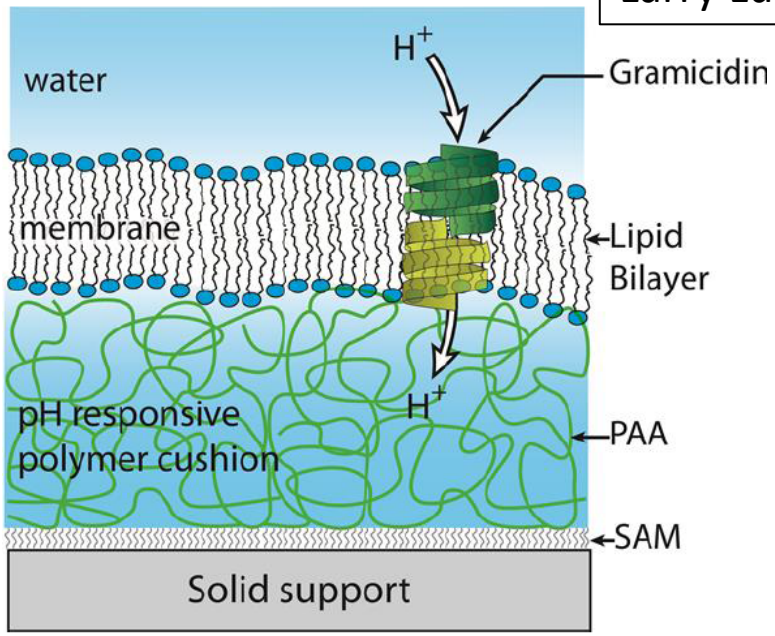
1) interfacial dynamics of NPs through XPCS
2) in-plane ordering through GID

v) (Single) lipid bilayer membranes

Tonya Kuhl
Larry Lurio

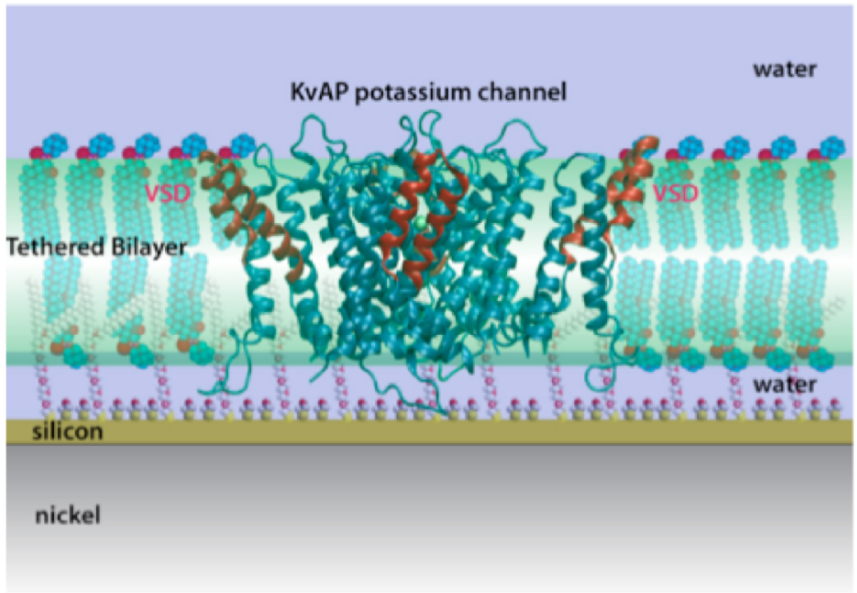
a) Polymer-cushioned membrane platforms

- Mimic nanostructured chemical and physical environment of cell membrane.
  - GID for in-plane structure.
  - XPCS for membrane fluctuations → viscoelasticity.



b) Supported membranes with controlled electrochemical potential

- Structure of ion pumps and gated ion-channels upon opening/closing.



3. Soft Matter and X-Ray Beam Damage Considerations

Larry Lurio

- Radiation damage a continual challenge for x-ray studies of soft matter.
- Damage expected to be lower at higher energy.

E.g., Absorption dose in carbon

For E $\lesssim$ 20 keV:

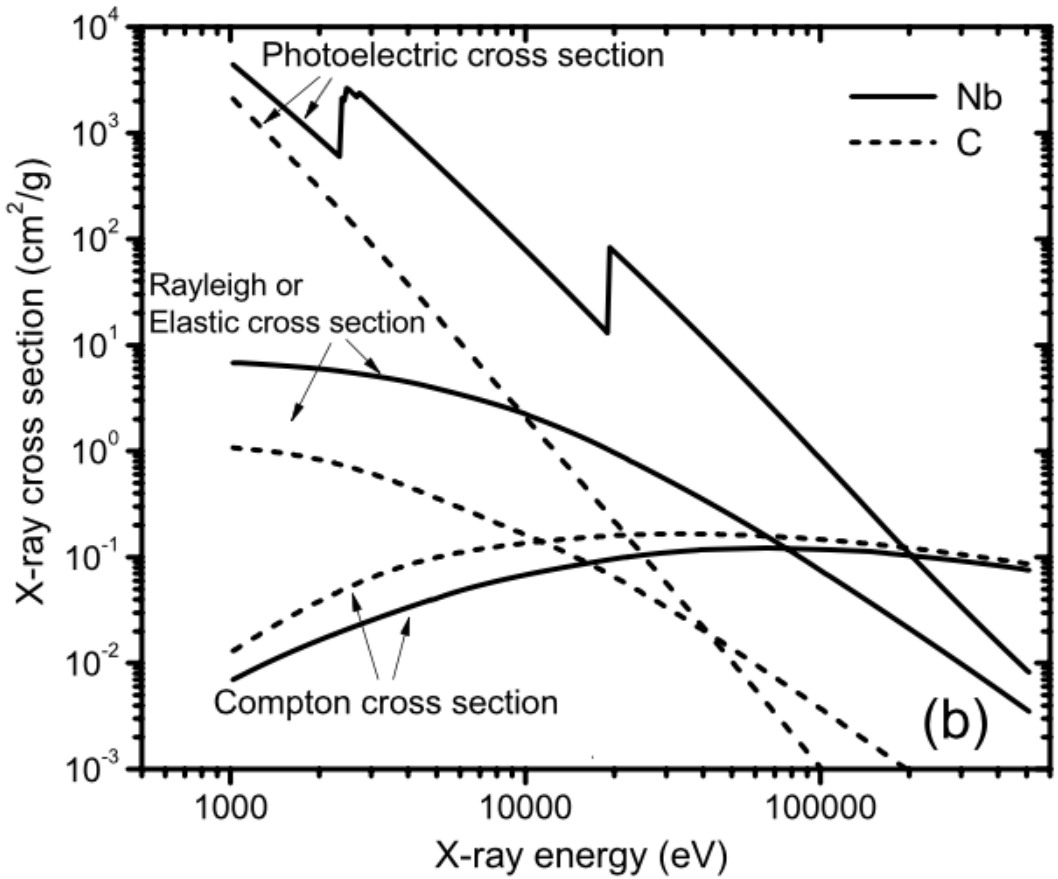
$\sigma \sim E^{-3}$ (approx.)

due to photoelectric absorption

For E > 20 keV:

$\sigma \sim$ constant (approx.)

due to Compton scattering

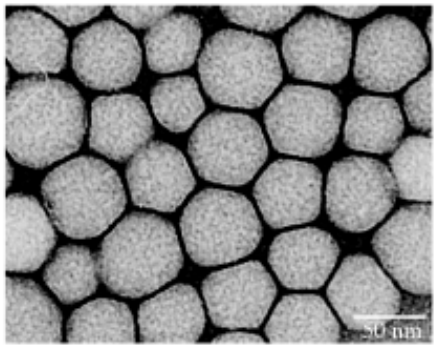


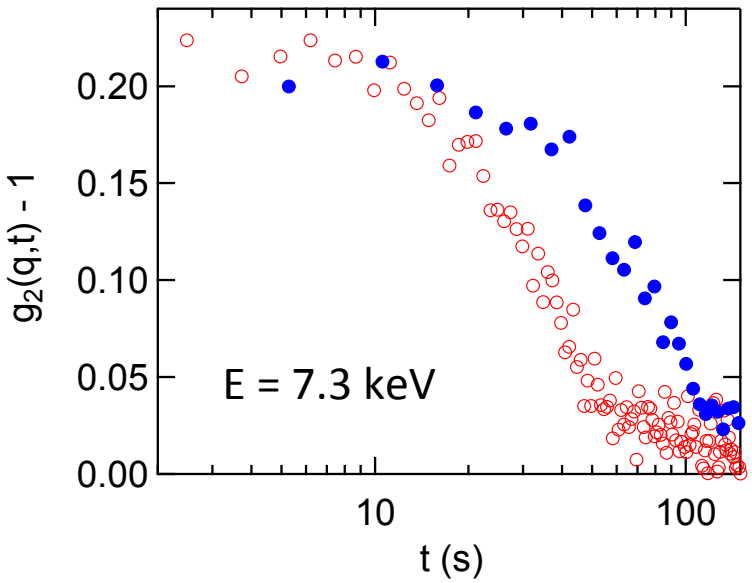
Tiwari & Sawhney, JPCM (2010).

Example of dependence of beam damage on energy:

XPCS measurements on a nanoemulsion:

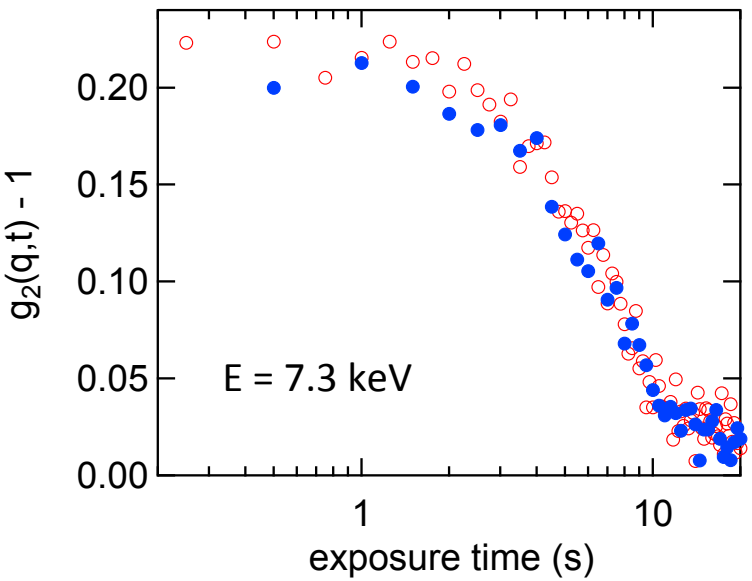
Silicone oil droplets in SDS solution





- Decay in correlation function apparently frame-rate dependent!
- Correlation time depends on exposure time!

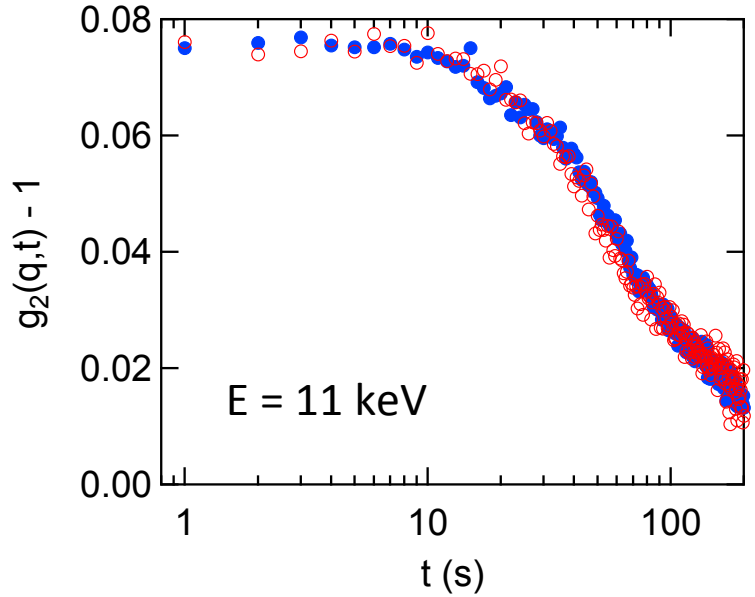
→ Obvious beam damage.



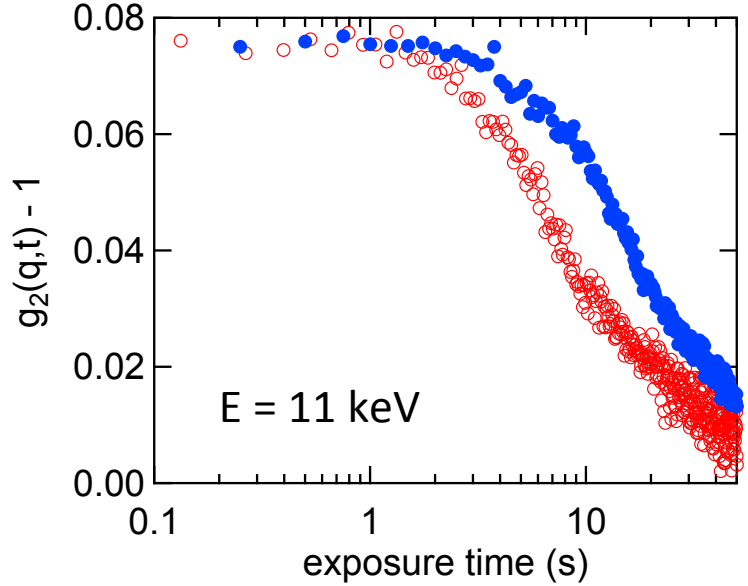
Beam damage to nanoemulsions mitigated at higher E:

- Correlation time independent of exposure time.

- Apparent intrinsic microscopic dynamics recovered.



Coherent flux at 20 keV at APS-U should exceed that at 7 keV today.



Thanks to:

Alec Sandy, APS
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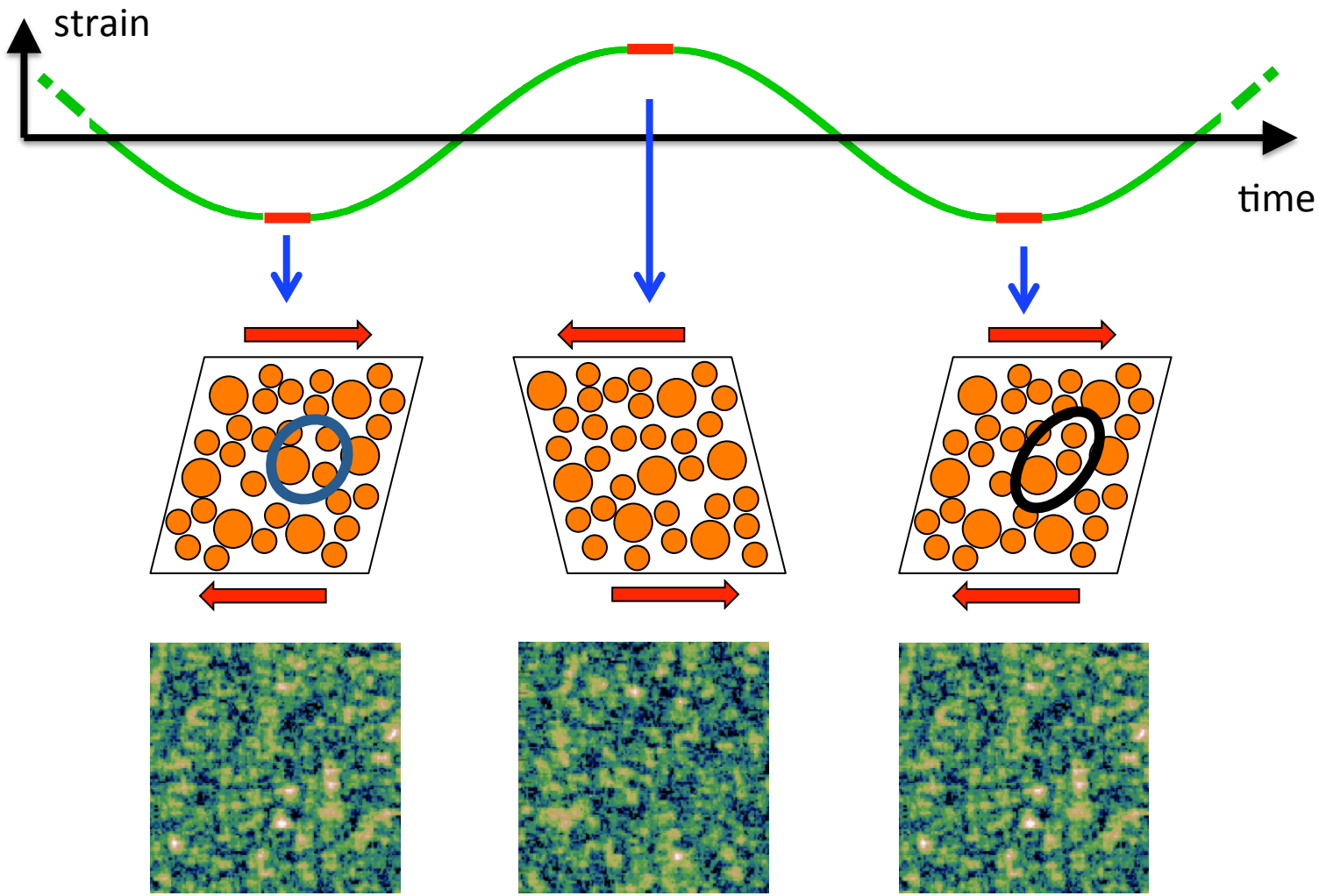
Jin Wang, APS

Jim Harden, Ottawa
Michael Rogers, Ottawa
Kui Chen, JHU
Tom Mason, UCLA
Suresh Narayanan, APS

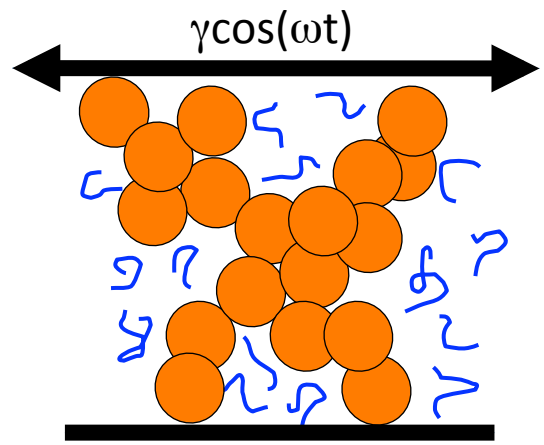
Wes Burghardt, Northwestern
Mark Schlossman, UIC
Tony Kuhl, UC Davis
Ben Ocko, BNL
Nick Abbott, Wisconsin
Tom Russell, U Mass, Amherst
Andrea Liu, U Penn
Sam Sprunt, Kent State
Paul Nealey, U Chicago
Oleg Gang, BNL
Robert McFarlane, Cal Tech

Related opportunity: XPCS with *in situ* Large Amplitude Oscillatory Shear (LAOS)



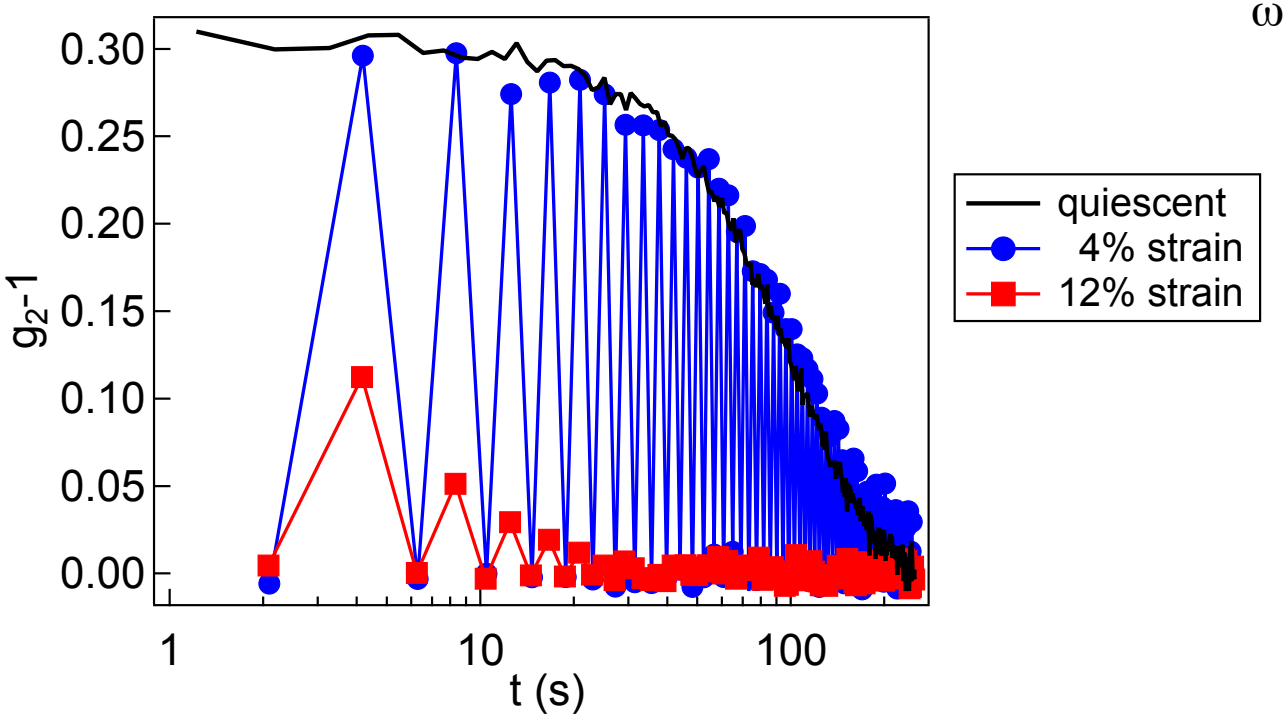
Echoes in x-ray speckles from nanocolloidal gel:

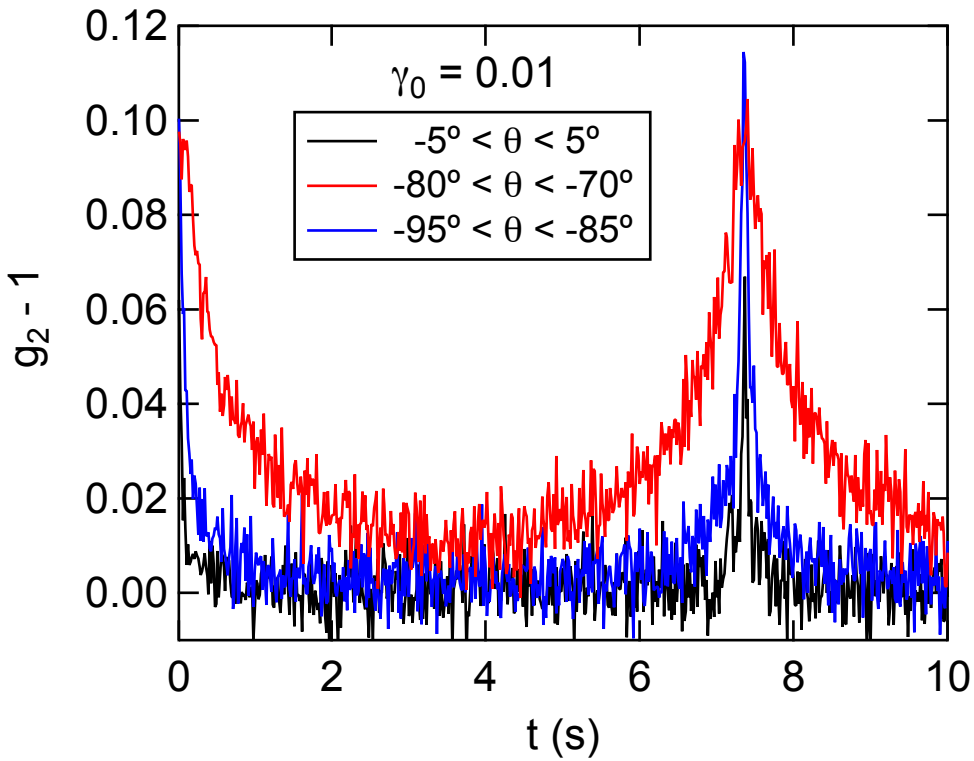
T = 4.1 s



$\phi = 0.3$ $c_p/c_p^* = 0.2$

$\omega = 2\ s^{-1}$




γ_0 = 0.01
-5º < θ < 5º
-80º < θ < -70º
-95º < θ < -85º
g_2 - 1
t (s)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
2
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