# Dynamics in Soft Matter and Biological Systems Trends and Opportunities at NSLS-II



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# Coherent Hard X-ray Scattering (CHX)

**XPCS at NSLS-II:**

- Microstructure determines most (if not all) macroscopic properties of materials.
- X-ray Photon Correlation Spectroscopy (XPCS) measures micro- and nano-scale dynamics in materials
- The unprecedented brightness of the NSLS-II source will enable studies of dynamics on *100 x faster time scales* (reaching *1 µs*) and *shorter length scales* than was ever possible before.
- Note: ERL – *10000 x faster* dynamics (?)
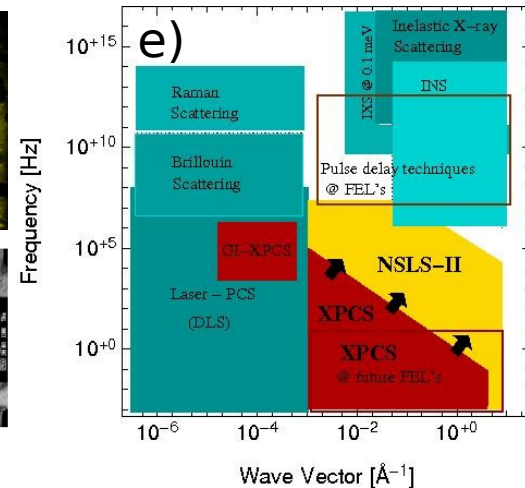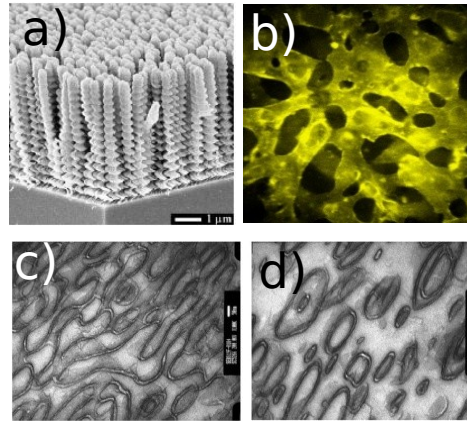


a-d Examples of microstructure: porous silicon (a); bicontinuous microstructure arrested by interfacial colloidal jamming (A. Moharaz) (b) sponge phase in a polymer blend (S. Mochrie) (c-d); e) phase space accessible today and at NSLS-II. The NSLS-II source will enable studies of dynamics on faster time scales and shorter length scales than is possible at current sources

**Examples of Science Areas**

SOFT MATTER: colloids, polymers, gels and glasses, dynamics and rheology
SOFT MATTER SURFACES and INTERFACES: polymer films and membranes, biomembranes
BIOLOGICAL MATERIALS: dynamics in protein crystals, proteins in solution; protein aggregation.
INORGANIC MATERIALS: metallic glasses, phase ordering

**Impact:**

The CHX instrument will help finding answers to important questions:

*"How do we characterize and control matter away- especially very far away- from equilibrium?"*

Directing Matter and Energy: Five Challenges for Science and Imagination (BESAC)

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# CHX Experimental Capabilities

## Beamline Capabilities:

- Coherent X-ray Diffraction XPCS, SAXS, WAXS

- Capabilities for full-field CDI

- **Source:** IVU20 Undulator

- **ENERGY RANGE:** 6 – 15 keV

- **COHERENT FLUX:**
  $>10^{11}$ ph/sec $(\Delta\lambda/\lambda)=10^{-4}$
  $>10^{12}$ ph/sec $(\Delta\lambda/\lambda)=5\times10^{-3}$

- **BEAM SIZE**
  $\approx10$ μm (SAXS)
  $\approx1$-2 μm (WAXS)

- *Consolidated end-station design* offers a unique capability for integrated studies e.g. SAXS-WAXS



B.Hsiao

A. Martel

100 μm
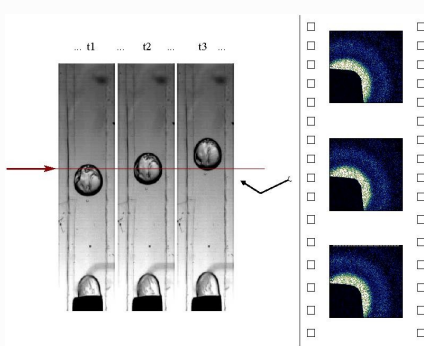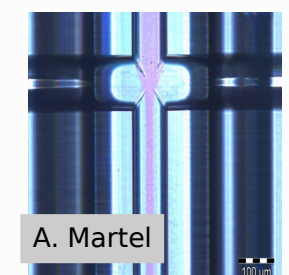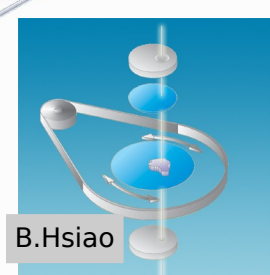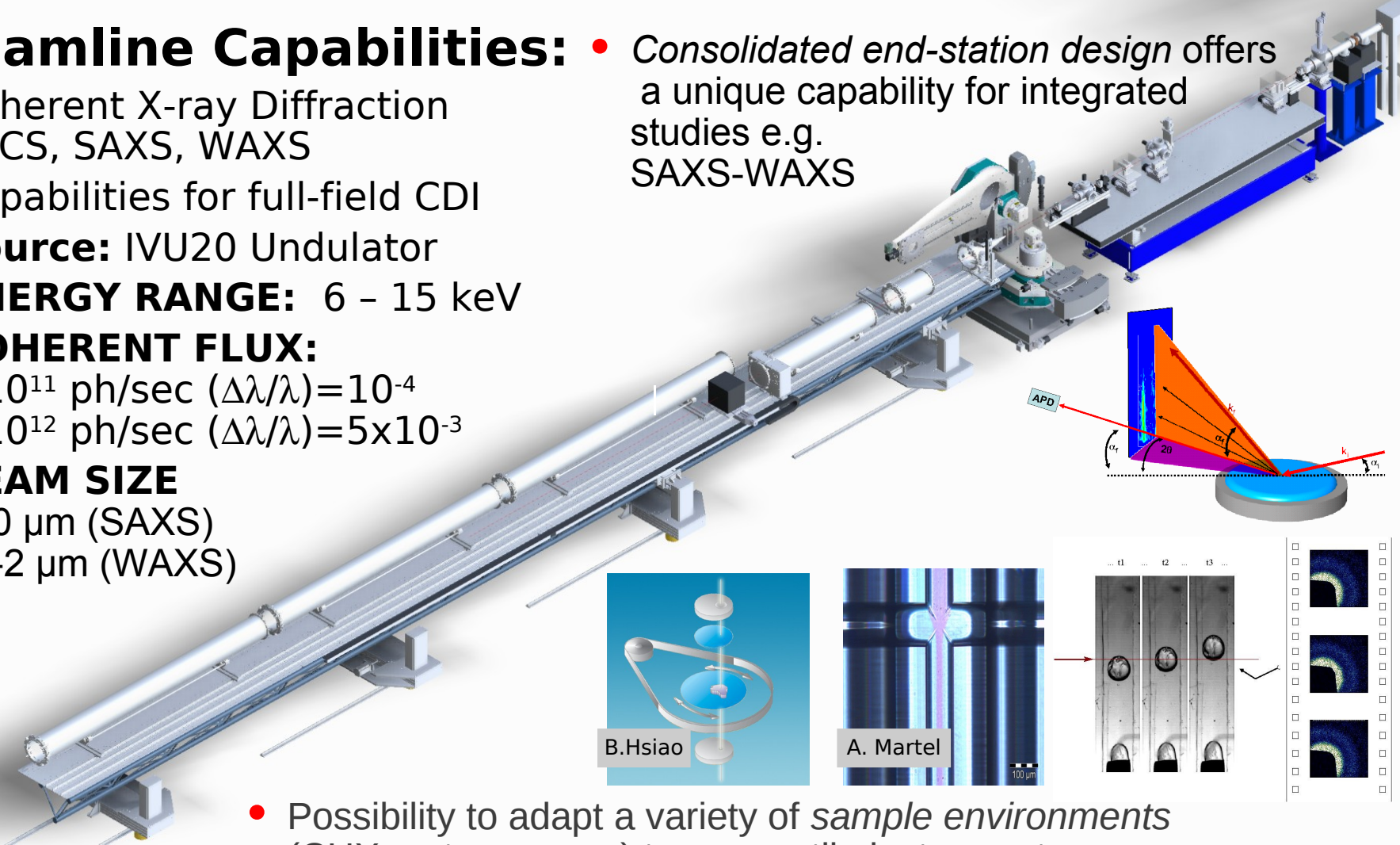
- Possibility to adapt a variety of *sample environments* (CHX mature scope) to a versatile instrument

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# NSLS-II: IVU 20 Source

- **U20 IVU (3m) Source properties**

  - Low-$\beta$ straight,
    **B=2x10$^{21}$** ph/(s·mrad$^2$·mm2·0.1% bw)
    coherent flux: $I_c = \lambda^2 B/4$

  - Working energies

| E(keV) | 6 | 8 | 10 | 12 | 15 |
|--------|-----|-----|------|------|------|
| Harmonic | 3$^{rd}$ | 5$^{th}$ | 5$^{th}$ | 7$^{th}$ | 9$^{th}$ |
| K$_{eff}$ | | 1.51 | 1.82 | 1.51 | 1.73 | 1.77 |



In-Vacuum Undulators:
IVU20: $\lambda_u$= 20 mm, K$_{max}$ = 1.83, L = 3 m (low-$\beta$)
IVU21: $\lambda_u$= 21 mm, K$_{max}$ = 1.79, L = 1.5 m (low-$\beta$)
IVU22: $\lambda_u$= 22 mm, K$_{max}$ = 1.52, L = 6 m (high-$\beta$)

EPU49 APPLE-II Undulator
$\lambda_u$ = 49 mm, L = 4 m (low-$\beta$)
K$_{max\ lin}$ = 4.34, K$_{max\ circ}$ = 3.69

DW90 Damping Wiggler
B = 1.85 T, $\lambda_w$= 90 mm
K = 15.8, $\varepsilon_c$ = 11 keV
L = 7 m  (high-$\beta$)

Three-Pole Wiggler
B = 1.14 T, $\varepsilon_c$ = 6.8 keV

Bend Magnet
B = 0.4 T, $\varepsilon_c$= 2.4 keV
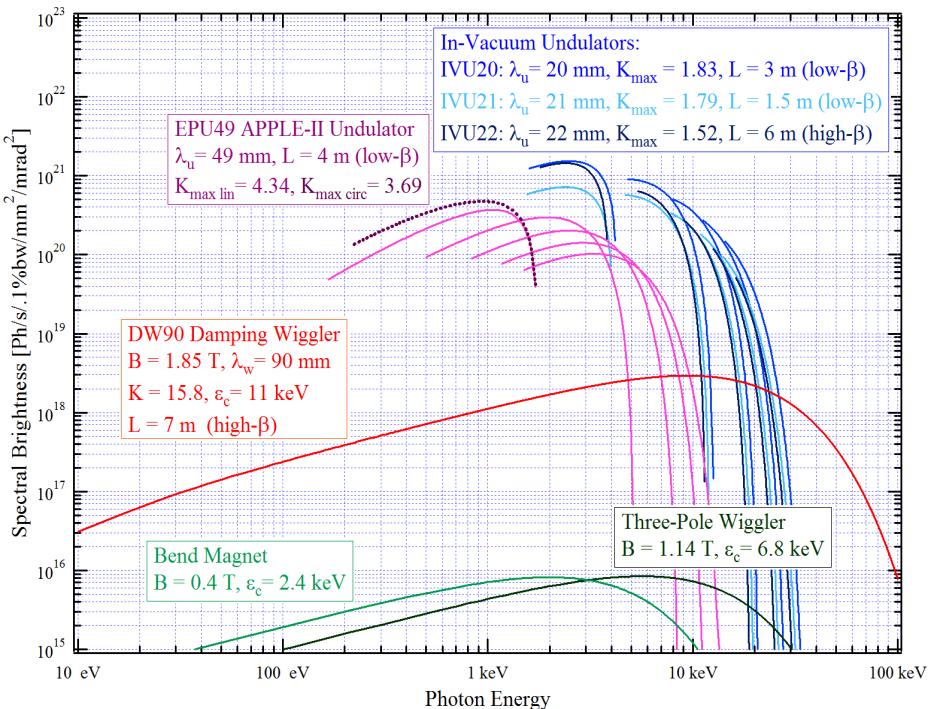
- Liouville's theorem: Phase space $\sigma\sigma'$ is conserved by propagation, focusing, diffraction, etc (not by slits!)
- For a Gaussian coherent mode
  $$\sigma\sigma'=\lambda/4\pi \text{ (in general } \sigma\sigma'\geq\lambda/4\pi)$$
  and the coherence length $\rho$ at a distance L ($\sigma'=\rho/L$) is given by
  $$\rho= \lambda L/4\pi\sigma.$$
- Phase space volume in units of "coherent modes": $M= \sigma\sigma'/(\lambda/4\pi)$, $M \geq 1$

| E (keV) | 6 | 8 | 10 | 12 | 16 |
|---------|------|------|------|------|------|
| $\sigma_h$ (μm) | 34.3 | 34.2 | 34.1 | 34.2 | 34.2 |
| $\sigma_h^{'}$ (μrad) | 18.3 | 18.3 | 18.0 | 18.2 | 18.2 |
| $\sigma_v$ (μm) | 8.8 | 8.0 | 7.5 | 7.6 | 7.4 |
| $\sigma_h^{'}$ (μrad) | 8.5 | 8.2 | 7.7 | 8.1 | 8.0 |
| **M$_h$** | 38.2 | 50.7 | 62.2 | 75.7 | 94.6 |
| **M$_v$** | 4.5 | 5.3 | 5.8 | 7.5 | 9.0 |

Optical scheme:
selects a partially coherent beam (e.g. 4 x 4 modes) and matches it to the desired spot size at the sample.

(courtesy of Oleg Chubar)

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# CHX Beamline Performance

- CHX optical scheme is designed to maximize stability, preserve the coherent wavefront and optimize the SNR via focusing

- Wavefront propagation simulations are done using the SRW (O. Chubar). This *unique* tool enables us to characterize a partially coherent wavefront along bemline components and all the way to the sample and detector

Before sample z=48.5    Before KL z=44    Before CRL z=35.5    Before SS1 z=33.5
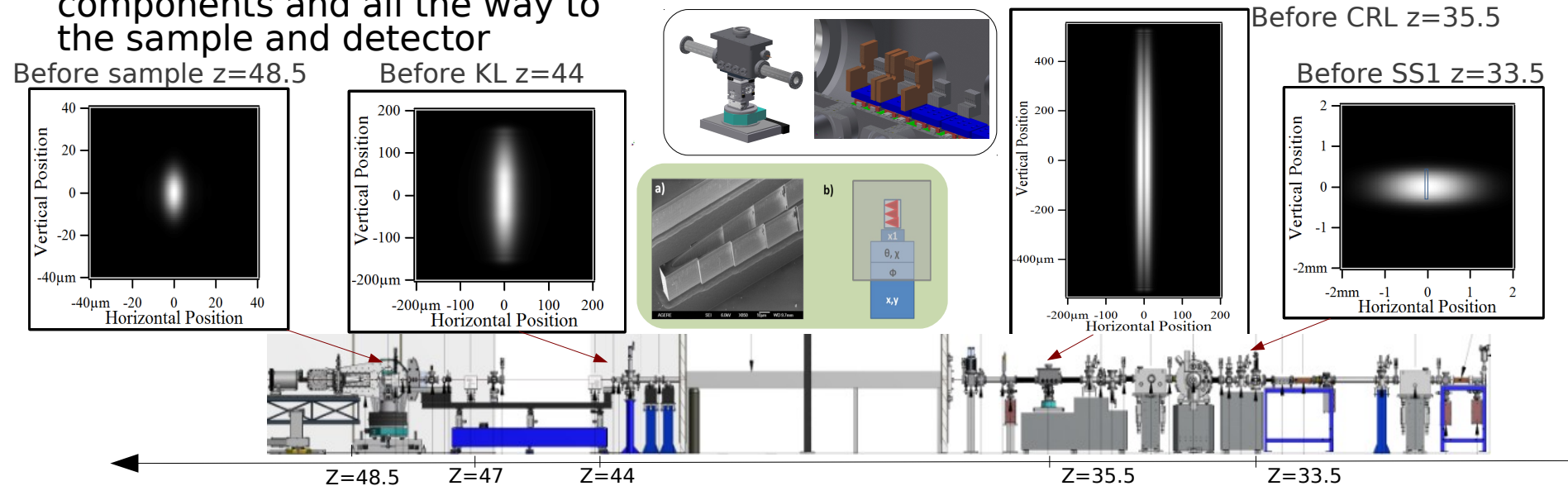


- Speckles from a static test sample[1] are used to fine-tune the beamline for XPCS and maximize:

$$SNR \text{ of } g^{(2)}(q,t) \approx (speckle\ visibility)^2 \times (coherent\ flux)$$
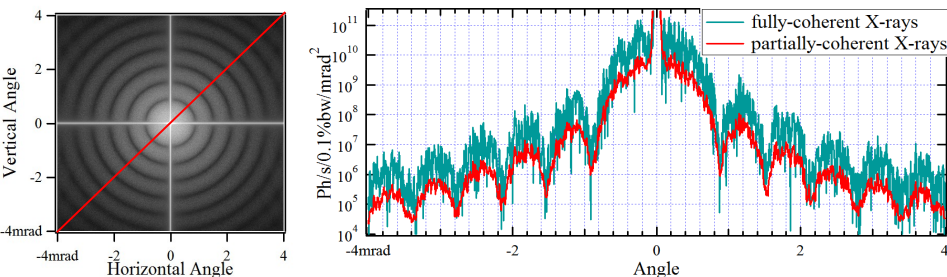


Fully coherent ($\Delta S_{1x}$=0.044 mm $\Delta S_{1y}$=0.1 mm)
  *SNR $g^{(2)}$=5.3 a.u.*

Partially coherent ($\Delta S_{1x}$=0.044 mm $\Delta S_{1y}$=1.0 mm)
  *SNR $g^{(2)}$=6.0 a.u.*

[1]Test sample: static suspension of silica spheres R=100 nm (5% polydisp.) 5000 particles in $10^3$ mm$^3$

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# Comparisons between State-of-the-Art Instruments

| | Coh. flux [ph/s] | Pink beam (flux ~ x10) | Focusing 10μm-SAXS | Focusing 2μm-WAXS | Integrated SAXS/WAXS | Fast area detector[1] |
|---|---|---|---|---|---|---|
| 8ID – APS | ~$10^9$ | ✓ | In progress | ✓ | ✗ | 100 Hz CCD |
| ID10 – ESRF | $10^{10}$ | In progress | ✓ | ✗ | ✗ | Maxipix |
| P10 - Petra III | >$10^{11}$ | In progress | ✓ | ✓ | ✗ | Maxipix & XNAP(X-ray ns resolution APD pixel det. R&D) |
| CHX | >$10^{11}$ | ✓ | ✓ | ✓ | ✓ | Maxipix and (?) EIGER[2] (24 kHz) VIPIC project (20 ns resolution) |
| ERL | $10^{14}$ | | | | | Sol Gruner |

[1] a fast pixel detector is the *single most important* instrument for XPCS

[2] EIGER Detector (24 kHz) developed by Dectris Inc. is also expected to become available 2013-2014

# High Impact Experiments: Non-equilibrium dynamics and self-organization in soft-matter systems

- Numerous processes (self-organized on induced/driven) in soft matter systems such as colloids, polymers, emulsions, surfactants, granular materials, etc. are taking place away from equilibrium state. Phenomena like jamming under flow, aging, plastic deformations under stress are important from both a fundamental view as well as for their potential applications.



Two-time correlation functions showing non-equilibrium effects ("aging") and heterogeneous dynamics (left) in colloidal gels or dynamical "rare events" in a colloidal glass (right) (AF et al.)

- Understanding how to *control* processes away and far away from equilibrium could lead to potential break-through applications in electronics (e.g. molecular devices), material science, energy, etc

- Understanding how to *describe* and *characterize non-equilibrium* states and processes is perhaps one of the most important unsolved problem in statistical physics and the science of Complexity - "*More is different* " (P. Anderson)

- **Non-equilibrium dynamics and self-organization in soft-matter systems**: studies of "Matter far beyond equilibrium" was recently identified as one of "Five challenges for science and imagination" in a report to the DOE by BESAC.

- The CHX instrument will be ideally adapted to address this challenge related to the DOE scientific program. The experiments will focus on understanding complex dynamics in non-equilibrium and driven (e.g. by flow/shear) soft matter systems and the interplay between molecular scale structure, mesoscale dynamics, and macroscopic properties such as the advective response to shear .

- Studies of heterogeneous dynamics (often associated with non-equilibrium states) will benefit tremendously from the NSLS-II source brightness (SNR dynamic susceptibility $\chi^4 \sim B^2$)

# XPCS under continuous shear flow
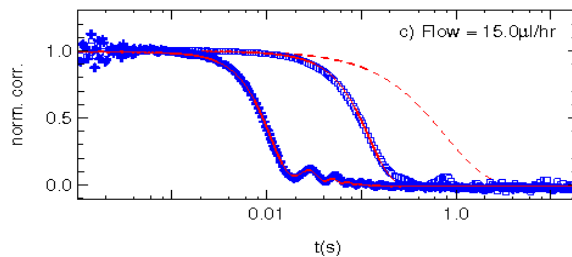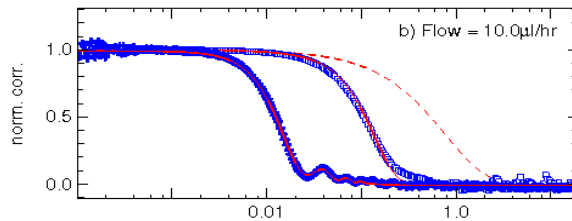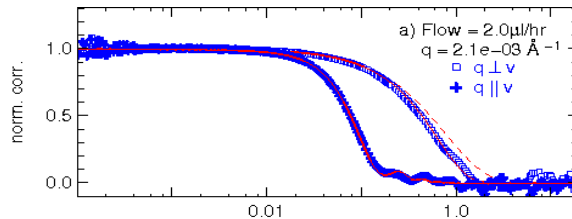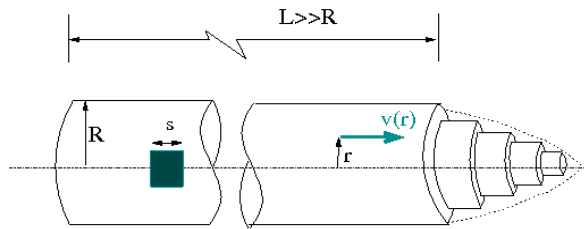




S. Busch *et al.*, *Eur. Phys. J. E.* **26**, 55 (2008)

## The importance of scale[1]

Diffusion - $\Gamma = Dq^2$

Shear rate: $\dot{\gamma} = -\frac{dv(r)}{dr}$ $(T^{-1})$

$Wi = \dot{\gamma}/\Gamma \ll 1$

Transit time effects - $\Gamma_{tr} = \frac{v_{flow}}{s}$

(s - transverse beam size)

Deborah number: $De = \frac{v}{\Gamma s} \ll 1$

Shear-induced effects - $\Gamma_S = \mathbf{v} \cdot \mathbf{q}$

Peclet number:

$Pe = \frac{\dot{\gamma} R^2}{D} \gg 1$ !!!!

Shear number:

$S = \frac{\mathbf{q} \cdot \mathbf{v}}{Dq^2} \gg 1$ !!!!

Shear-induced correlation:

$G_{shear}(q,t) = \int \int \cos[(\mathbf{q} \cdot \delta\mathbf{v})t] dr_1 dr_2$

[1]Note: assuming *homodyne* detection
heterodyne detection – M. Sutton *et al.*

G.G.Fuller *et al.*, *J. Fluid Mech.* **100**, 555 (1980)

# XPCS: Dynamics and Rheology

**XPCS:** Can measure, and study the interplay between, *dissipative dynamics* and the *advective response* to flow/shear
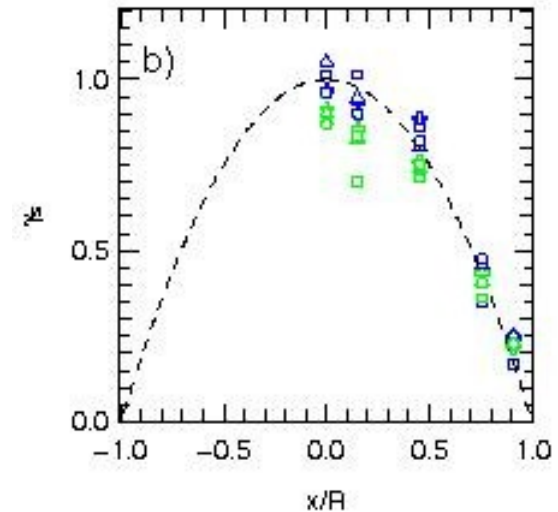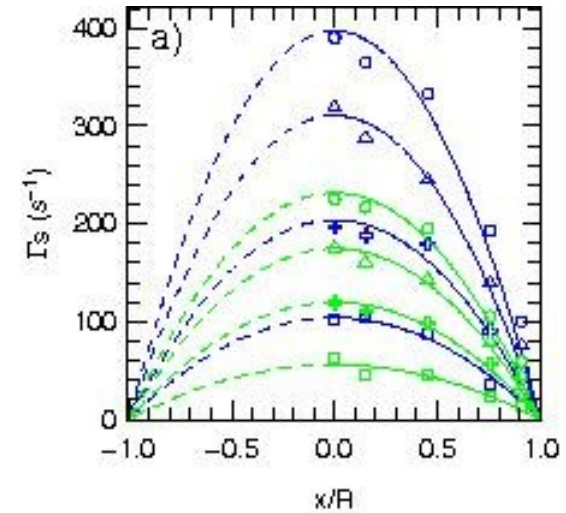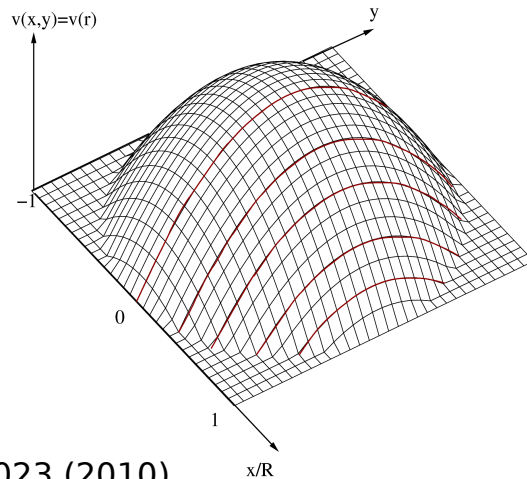
e.g. in a Poiseuille flow:

$$g^{(2)}(\mathbf{q},t) \approx 1 + \beta \exp\left[-2Dq^2t\right] \cdot \frac{\left|erf\left(\sqrt{i\mathbf{q}\cdot\mathbf{v}t}\right)\right|^2}{\mathbf{q}\cdot\mathbf{v}t} \cdot \exp\left[-(\nu_{tr}t)^2\right]$$
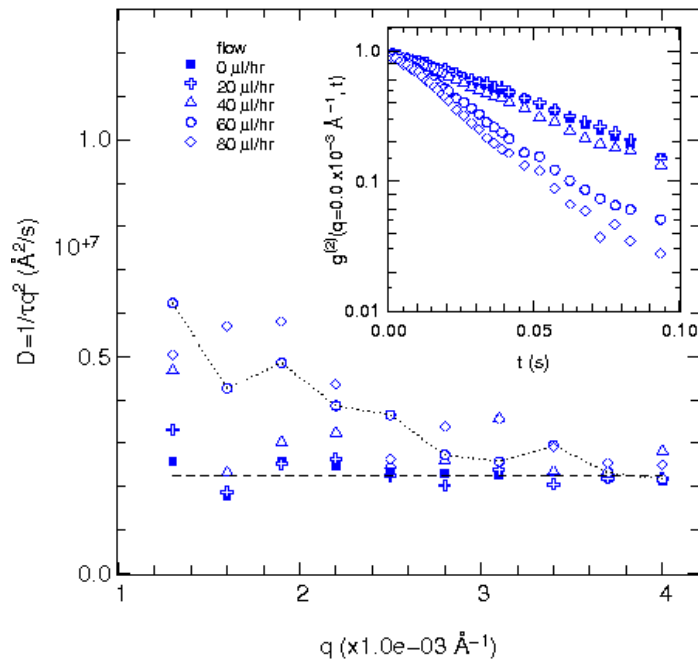
$$\Gamma_S \propto \frac{qQ}{\pi R^2}\left(1 - \frac{x^2}{R^2}\right)$$

$$\gamma_S = \frac{\Gamma_S}{qQ/\pi R^2} = 1 - \frac{x^2}{R^2}$$



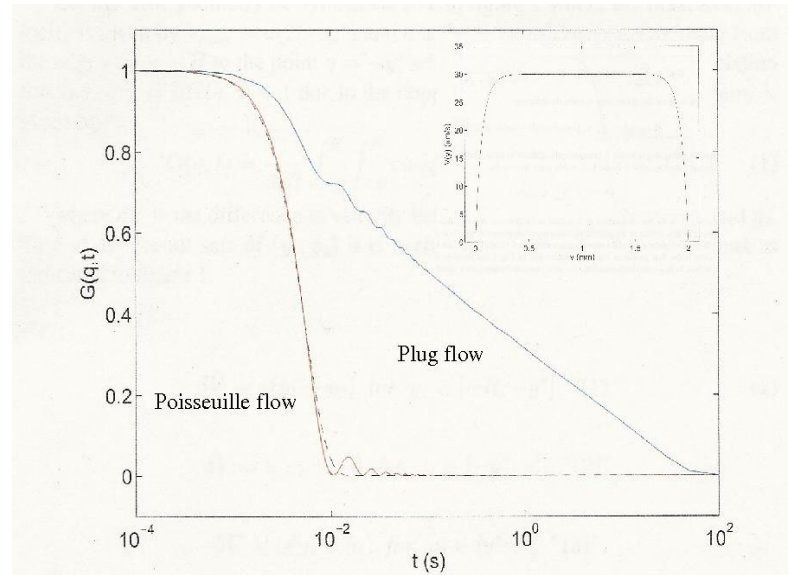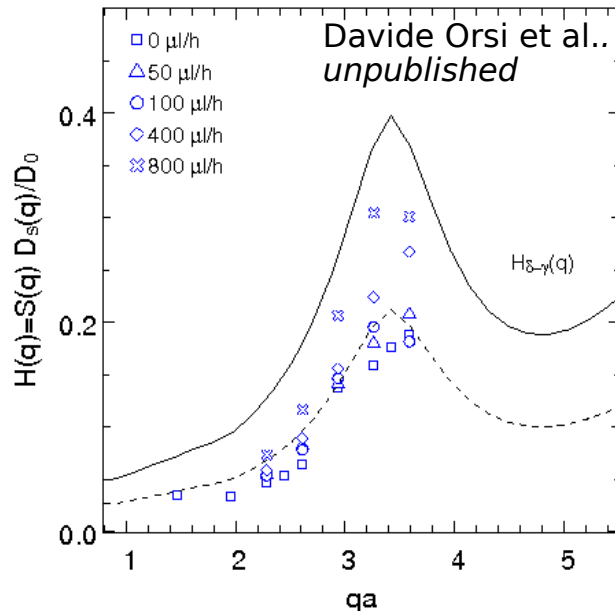AF *et al.*, *New Journal of Phys.* **12**, 035023 (2010)

# Dynamics under shear

**More interesting problems:**           ( see also W. Burghard's talk tomorrow)

- Dynamics and rheology in colloidal gels and glasses under flow



PMMA ASM361, $\Phi$=0.46, $q \perp v$

Davide Orsi et al.. *unpublished*

P.Kwasniewski et al.. *unpublished*

- Dynamics under periodic shear; Hydrodynamic reversibility

D. Pine et al., *Nature* **438**, 997 (2005)
L. Corte et al., *Nature Phys.* **4**, 420 (2008)

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# Example Experiment: Measuring Molecular Dynamics in Protein Crystals. Why?

- Protein actions are usually described in terms of static structure, but *function requires motion*.

- Protein backbones and side chains display many degrees of freedom, which allow different conformations. Collective fluctuations between different such states occur on a wide range of time scales. e.g:

> motion of backbone regions of the SpoOF - picoseconds to milliseconds
>
> V. A. Feher, J. Cavanagh, Nature 1999, 400, 289
>
> slow rotation (seconds) of aromatic rings around C-C axes in the Basic Pancreatic Tipsin Inhibitor
>
> K. Wurthrich, G. Wagner, *FEBS Lett.* 1975, **50**, 265
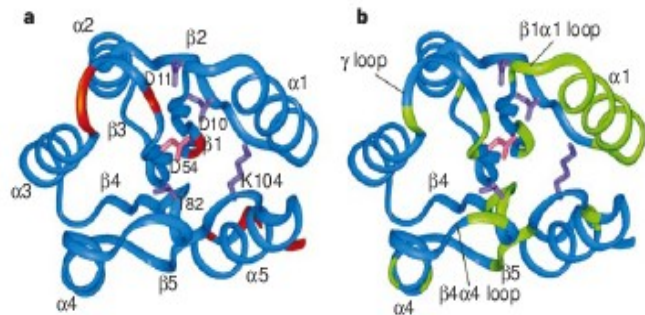


- Experimental data on the interplay between molecular mobility and biological function is in general scarce. A number of NMR studies that have measured motion of individual molecules or groups (labeled – $^{15}$N, $^{13}$C) have shown correlations between high mobility areas and surfaces and residues that are known to be critical for biological function (A. Mittermaier, L. E. Kay *Science* 2006, **312**, 224; L. E. Kay, *Nature Struct. Biol.* 1998, **5**, 513)

- "*More is different*" - from *dynamics* to *thermodynamics* i.e. bond vector motion probed by NMR vs. collective properties - changes in intramolecular fluctuations of calbindin D$_{9k}$ contribute significantly to the cooperative phenomenon of Ca ion binding (M. Akke et al. J. Am. Chem. Soc. 1993, 115, 9832).

- Allostery without conformational change (A. Cooper, D.T.F. Dryden, Eur. Biophys. J. 1984, 11, 103) "*proteins and other biological macromlecules may have evolved to take functional advantage not only on mean conformational states but also of the inevitable fluctuations about the mean.*"

# Molecular Dynamics in Protein Crystals How?

- It has been known for many years that information about the dynamics of molecules in a crystal is contained in the diffuse scattering around Bragg Peaks (see for e.g. G. U. Nienhaus et al. *Nature* (1989) **338**, 665).

- Molecular motion in protein microcrystals coupled over large scales generate coherent diffraction spots (speckles) around the Bragg peaks. We propose to quantitatively measure for the first time dynamic information about this motion from the speckle patterns obtained with coherent X-rays.

- Only a small number of the lowest frequency and largest amplitude modes dominate the diffuse scattering (L. Meinhold, J.C. Smith *Proteins* 2007, **66**, 941) hence the method can be sensitive to specific motions



from S. Boutet, I. Robinson, *J. Synchrotron Rad.* (2008) **15**, 576
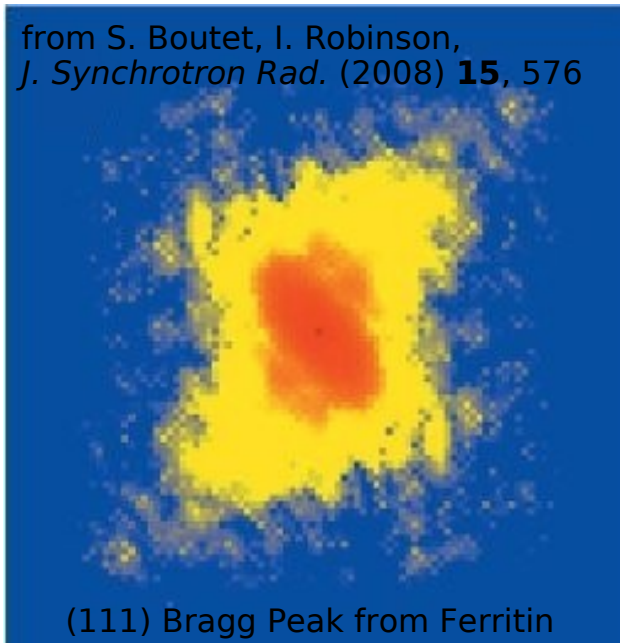
(111) Bragg Peak from Ferritin

- Speckle patterns from ferritin microcrystals were recorded and used for imaging with ~100 nm resolution (Boutet and Robinson, J. Synchrotron Rad. 15, 576, 2008) T=60s exp time with an "effective flux" (2$\mu$m crystal) of ~$10^7$ ph/s, ~$10^6$ Gy

- With an increased source brightness and by focusing the entire coherent on a (larger) microcrystal speckle patterns can be recorded in much shorter times with similar doses ESRF/APS: 6-60 ms     NSLS-II: 0.6 ms     ERL: 6-60 $\mu$s

- We propose to use *speckle visibility spectroscopy* to measure the dynamics R. Randyopadhyay, D.J.Durian et al.  J. Synchrotron Rad. 76, 093110 (2005)
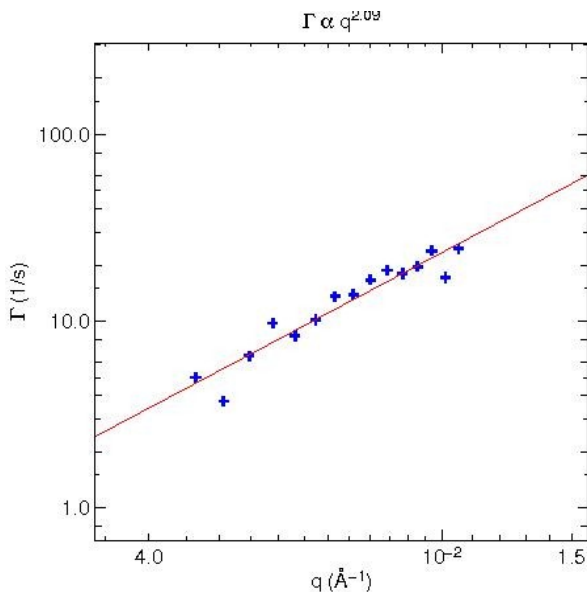
# Molecular Dynamics in Protein Crystals
# X-ray Speckle Visibility Spectroscopy

- Basic idea of XSVS (D.J. Durian et al.): The *speckle visibility* depends on the scatterer dynamics. If this is slow compared to the integration time, the speckle visibility is high. However, if the particles "move" while the diffraction pattern is recorded, the speckles will appear blurred and the speckle visibility will be low. Important information about molecular motion, e.g. mean sq. displacement vs. time, can be "extracted" from the speckle visibility function.

- Bonus #1: Reduced dose required. Only single diffraction patterns, sample can be moved between different images, etc

- Bonus #2: Can measure fast dynamics with a slow detector

$$v^{(2)}(T) = \left[\langle I^2 \rangle_T / \langle I \rangle^2 - 1\right]/\beta$$

$$v^{(2)}(T) = \frac{2}{T}\int_0^T (1 - t/T)\left|g^{(1)}(t)\right|^2 dt$$

- XSVS was used to measure dynamics in a low density colloidal suspension of hard-sphere particles and a high density suspension of hard-sphere thermosensitive core-shell particles
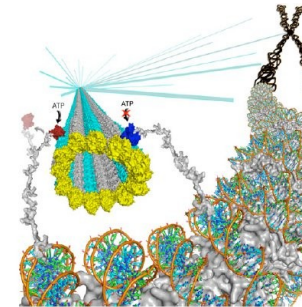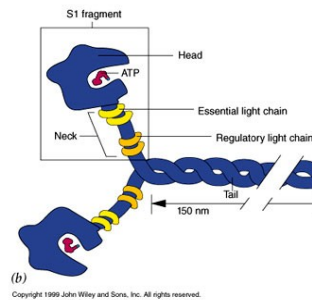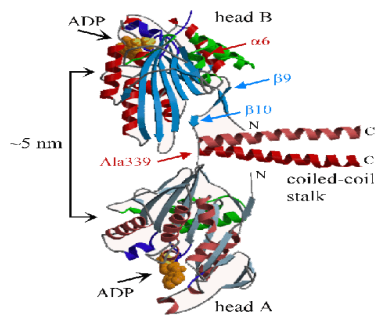
Luxi Li, Davide Orsi et al.. *unpublished*
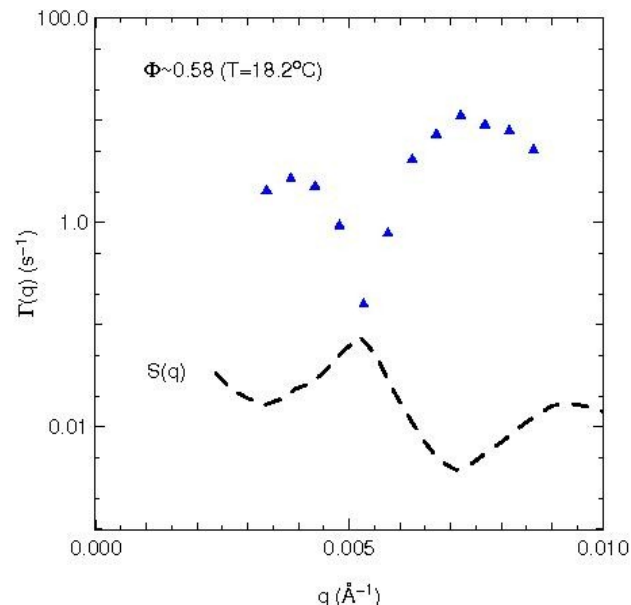
M.Siebenburger, D. Orsi et al.. *unpublished*

# Molecular Dynamics in Protein Crystals Samples and Sample handling

First experiments will focus on model systems:

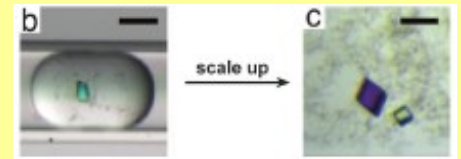proteins with large motions in their crystalline form (to enhance scattering) and (relatively) slow motion

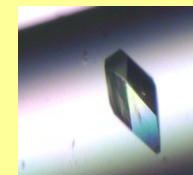Motor proteins: ideal first candidate



NOD

from J. Cohran *Cell* (2010)

- Possible technical choices for sample handling:
  - individual loops (M. Warkentin and R.E. Thorne, *J. Appl. Cryst.* 2009, **42**, 944)
  - simple flowcells
  - microfluidic chips (L. Li, R. F. Ismagilov et al., *Proc.Nat. Acad. Sci. USA* 2006, **103**, 19243).
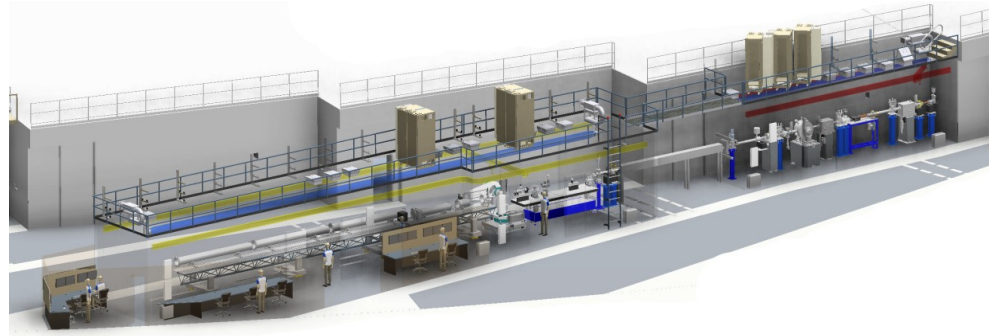  - *crystals grown in capillaries* (*Abel Moreno et al.*)



R.F. Ismagilov



Lysozyme grown in a capillary

Luxi Li, Abdel Moreno

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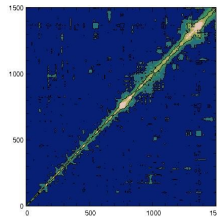BROOKHAVEN SCIENCE

# Thank You

- CHX, NSLS-II
  - Luxi Li
  - Lutz Wiegart
  - Mary Carlucci-Dayton
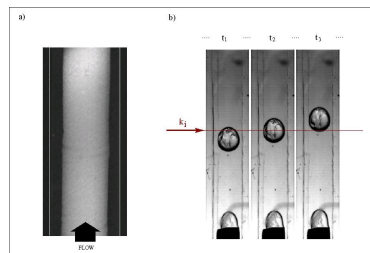  - Lonny Berman
  - BAT
- ID10, ESRF
  - A Madsen (now XFEL)
  - A. Moussaid (now UJF)
  - P. Kwasniewski
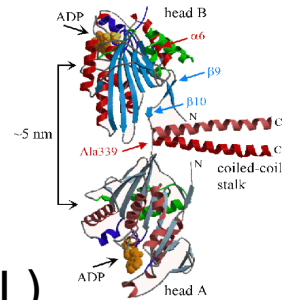  - D. Orsi (now at U. Parma)
  - S. Busch (now at TUM)
- CNRS Bordeaux
  - J. B. Salmon
  - F. Destremaut
  - J. Leng

- PX Project Team
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  - Lutz Wiegart (BNL)
  - Vivian Stojanof (BNL)
  - Jyotsana Lal (ANL)
  - Simon Mochrie (Yale)

- Funding:
  - BNL NSLS-II project
  - BNL LDRD 11-025

# High Impact Experiment: Non-equilibrium dynamics in model artificial and Biomembranes

- With a *consolidated endstation design* the CHX beamline will enable studies of dynamics and structure of artificial and biological membranes over a wide range of scales.

- A detailed understanding of the interplay between fluctuations and self-organization and transport along and across membranes is fundamental in understanding the biological function of biomembranes but can also have potential applications in designing biomimetic membranes with possible applications in sensing and separation technology, drug delivery, nanotechnology

- Recent theory has indicated that biomembrane visco-elasticity can both influence and be influenced by membrane protein conformation, leading potentially to elastically mediated interactions between proteins (Rheinstadter *et al.*, *Phys. Rev. Lett.* **103**, 128104 , 2004). By probing microsecond-scale correlations at the appropriate wave vectors, XPCS measurements at NSLS-II could potentially access the visco-elastic properties at length scales (10's of nm) matching typical protein-protein separations that are relevant to such theory.

- Fluctuations of membrane lipid rafts that could also be measured by XPCS at NSLS-II could be used as "fingerprints" to distinguish between different scenarios proposed for the raft formation (J. Fan, M. Haataja *et al.*, *Phys. Rev. Lett.* **104**, 118101, 2010).

- An objective of such work would be to establish *structure-dynamics-function relationships* for *model artificial* and *biomembranes*.
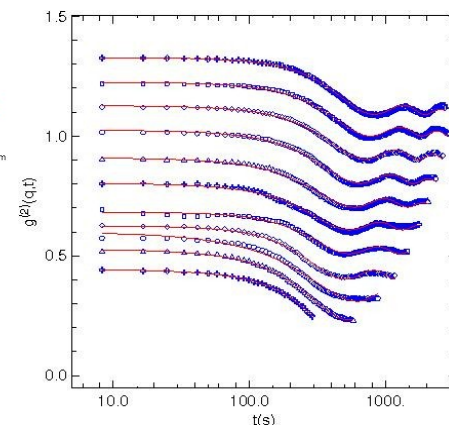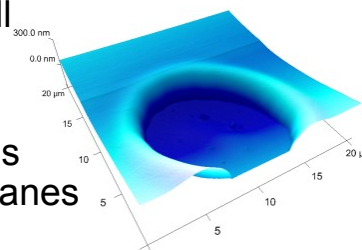




Correlation functions from a dewetting polymer film
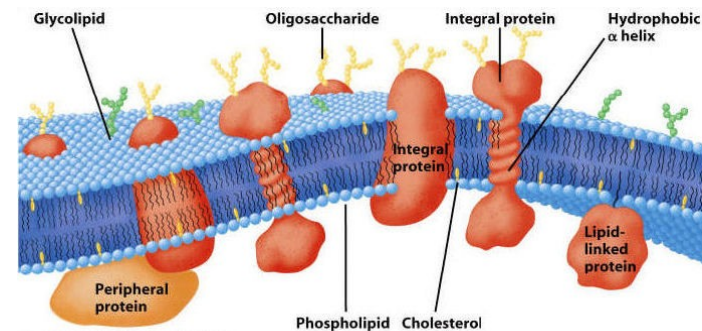J. Lal, L. Lurio, M. Sutton, AF *et al.*, unpublished



Cartoon of a biomembrane. Chracteristic length scales range from nanometers (the thickness of a biomembrane) to micrometers (the length of polymers that form the cytoskeleton). They are chemically diverse – building blocks include proteins, nucleic acids, lipids and polysaccharides – and formidably complex.

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