XPCS at NSLS-II

Coherence for studies of Soft- and Bio- Materials

Oleg Shpyrko, UC San Diego,

NSLS-II Early Science Workshop, Aug 12, 2013

X-ray Coherence:

- X-ray Photon Correlation Spectroscopy (XPCS)

  Coupling to Fluctuations

- Coherent X-ray Diffractive Imaging (CXDI)

  Real-space microscopy based on phase retrieval

  * Discussed tomorrow!

Early Future Science Ideas?

Past Experiments that fail miserably

*(We have plenty of those)

Never underestimate the joy people derive from hearing something they already know.

-- Enrico Fermi

Prediction is very difficult, especially about the future.

-- Niels Bohr

30

* Increase in brightness over APS, etc

1,000

* Decrease in timescales accessible with XPCS

1ms

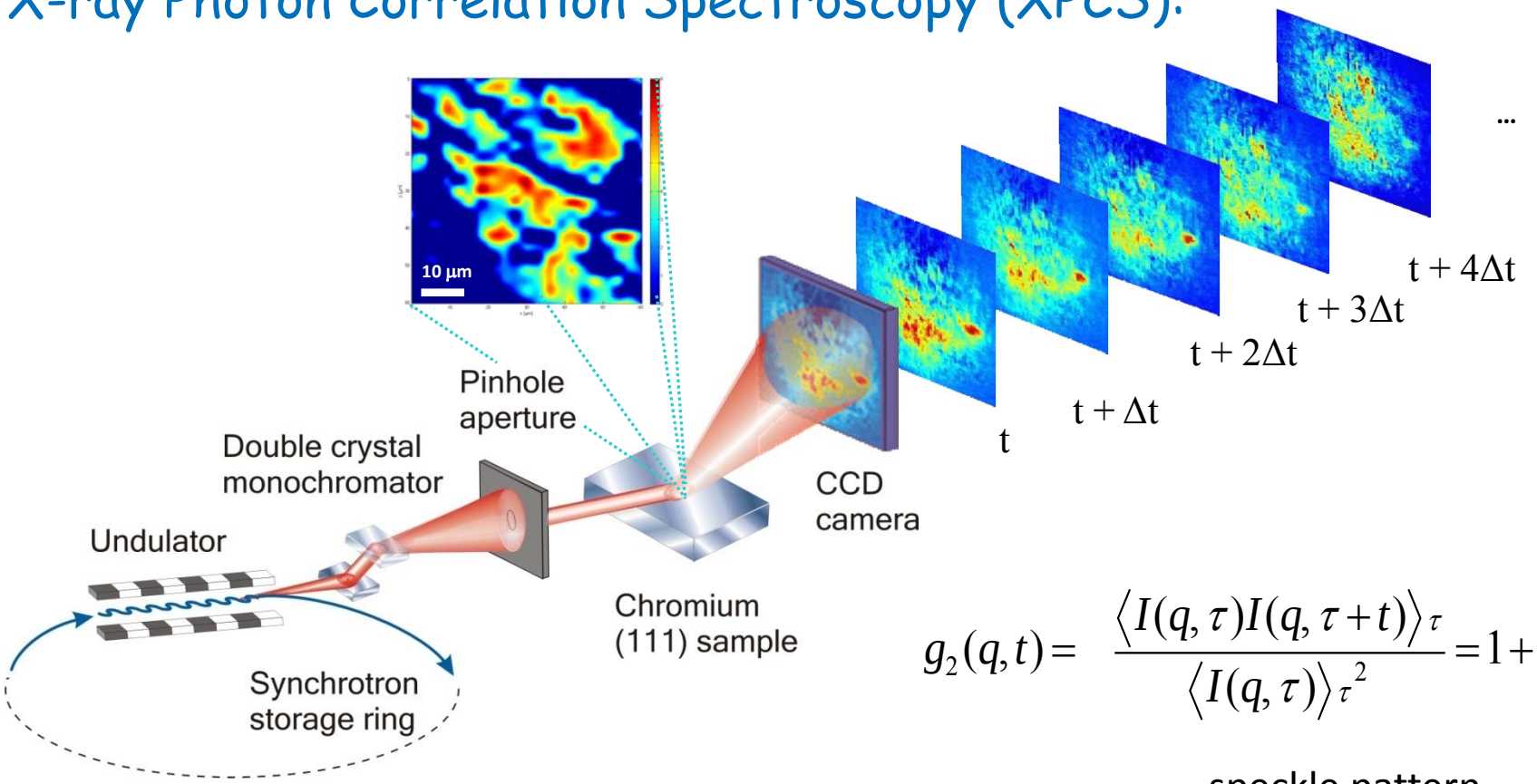
1μs

2ns? (maybe)

* Decrease in timescales accessible with XPCS

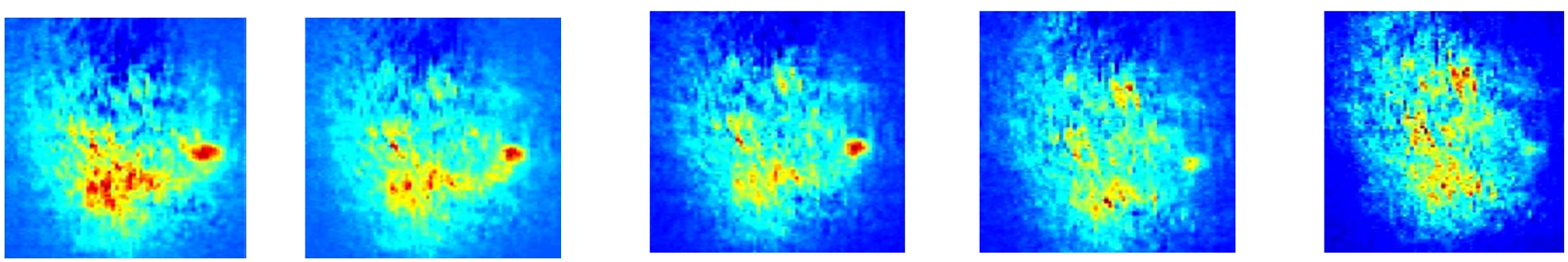
MATERIALS SYSTEMS (SCIENTIFIC FIELD)	TIMESCALES	LENGTHSCALES
Liquids, Glasses, Polymers, Thin films, Colloids. Glass Transition. Ageing. Surface Fluctuations. (SOFT MATTER)	ns - hours	Ångström – 100 µm
Biomembranes, Protein Folding, Bio and Chem. Self-assembly, Phase Separation/Segregation (BIOPHYSICS, CHEMICAL ENGINEERING)	µs - hours	Ångström – 10 µm
Crystalline solids and alloys: Dislocations and other defects, Diffusion, Nucleation and Growth, Strain-induced avalanches. In-situ characterization of growth, processing, failure modes: corrosion, defect formation, crack propagation (MATERIALS SCIENCE)	ns- hours	Ångström – 100 µm
Ferromagnetic, Ferroelectric Domains, Helical Antiferromagnets, Superconductivity, Avalanches (CONDENSED MATTER PHYSICS)	100 ps – seconds	10 nm – 10 µm
Energy transfer (buried interfaces) and storage; ionic diffusion; electrochemical processes, charge transfer and separation (ENERGY SCIENCES AND TECHNOLOGY)	ps - hours	10 nm – 10 µm

X-ray Photon Correlation Spectroscopy (XPCS):



$$g_2(q,t) = \frac{\langle I(q,\tau) I(q,\tau+t) \rangle_\tau}{\langle I(q,\tau) \rangle_\tau^2} = 1 + \beta \left| f(q,t) \right|^2$$

speckle pattern



t t + Δt t + 2Δt t + 3Δt t + 4Δt

O. G. Shpyrko et al., *Nature* **447**, 68 (2007)

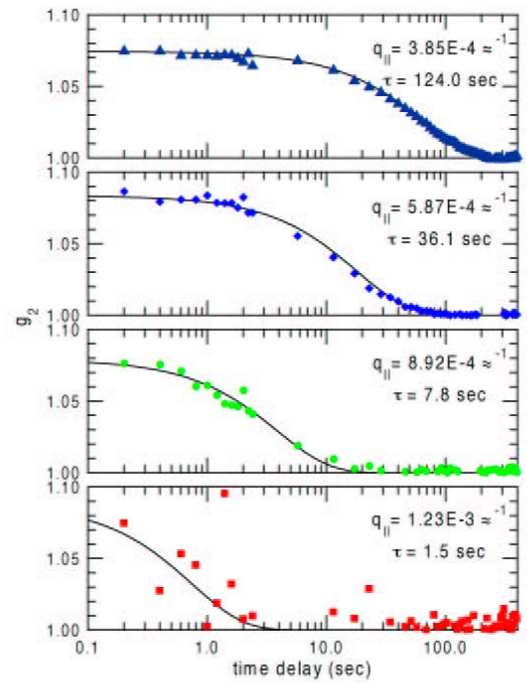
Measure: intensity autocorrelation function, $g_2(q, t)$

Intensity autocorrelation function, $g_2(q, t)$:

$$g_2(q,t) = \frac{\langle I(q,\tau) I(q,\tau+t) \rangle_\tau}{\langle I(q,\tau) \rangle_\tau^2} = 1 + \beta \left| f(q,t) \right|^2$$

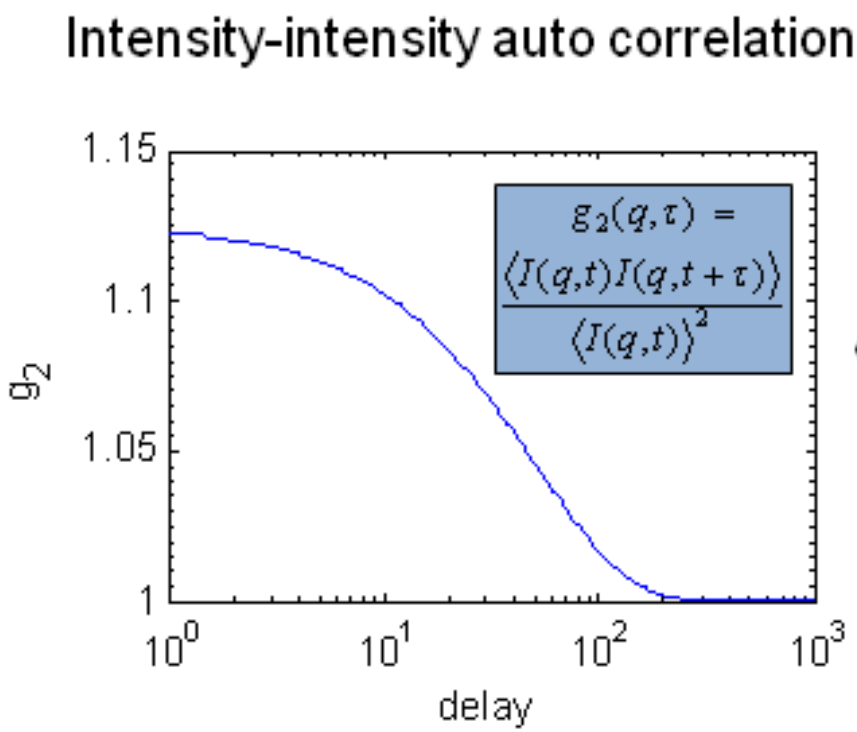
Intermediate Scattering Function (ISF):

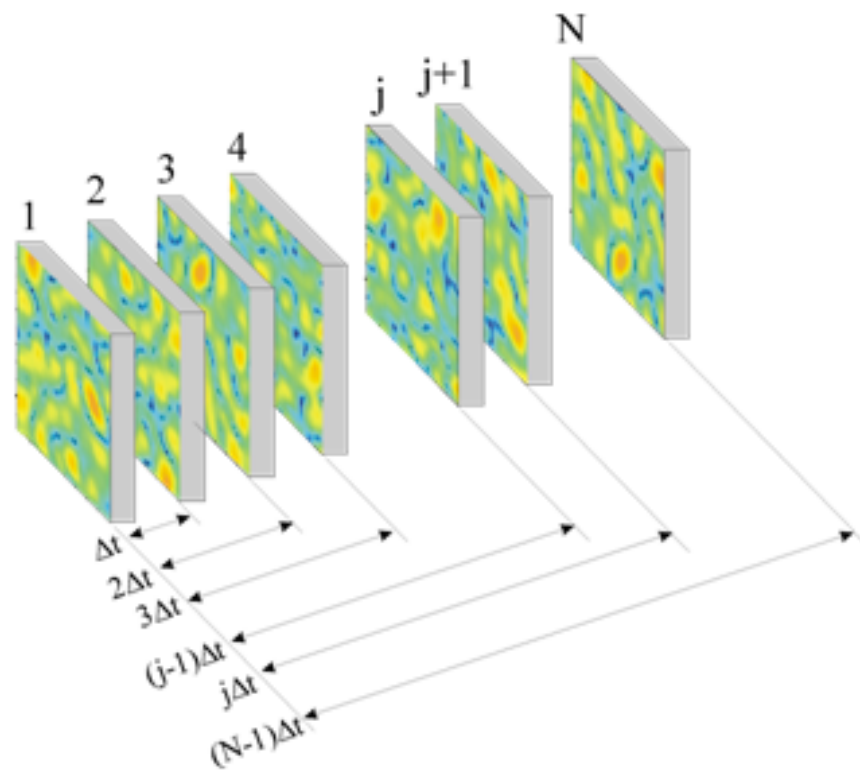
$$f(q,t) = \frac{S(q,t)}{S(q,0)} = g_1(t) = \exp[-(t/\tau_0)^\alpha]$$



β: speckle contrast (Siegert factor)
α: stretching exponent; often $\alpha \cong 1$
τ_0: relaxation time constant

Sequential XPCS:
multi-tau, multi-Q in one measurement
SNR improves with larger number of speckles

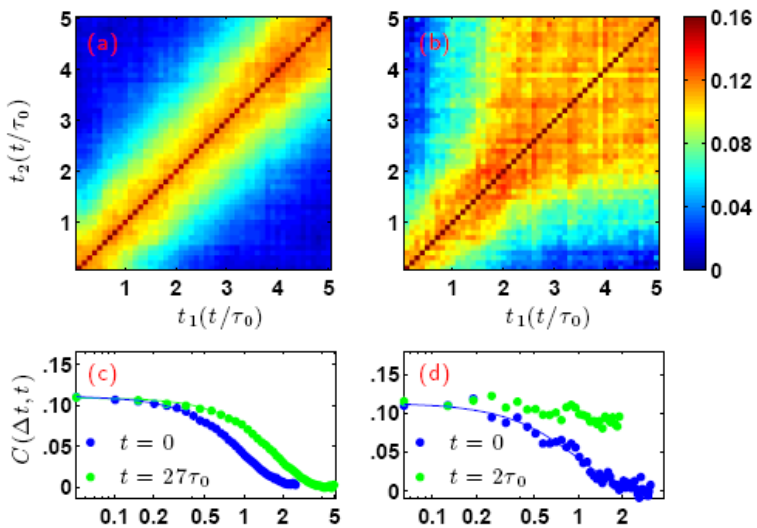




Charge Density Wave Systems

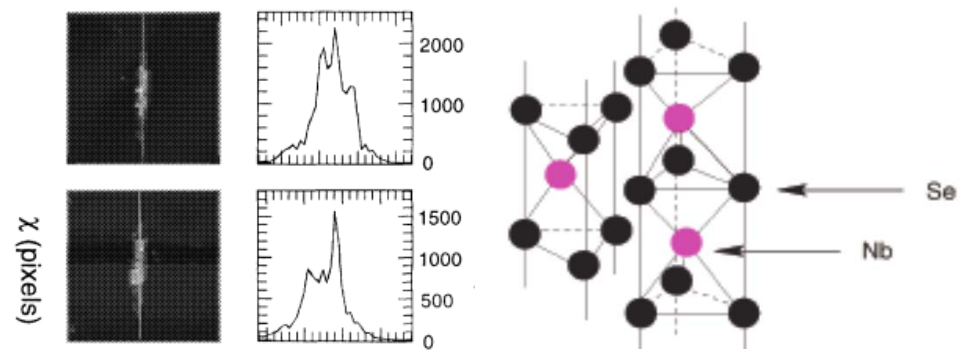
CDW in 1T-TaS2,

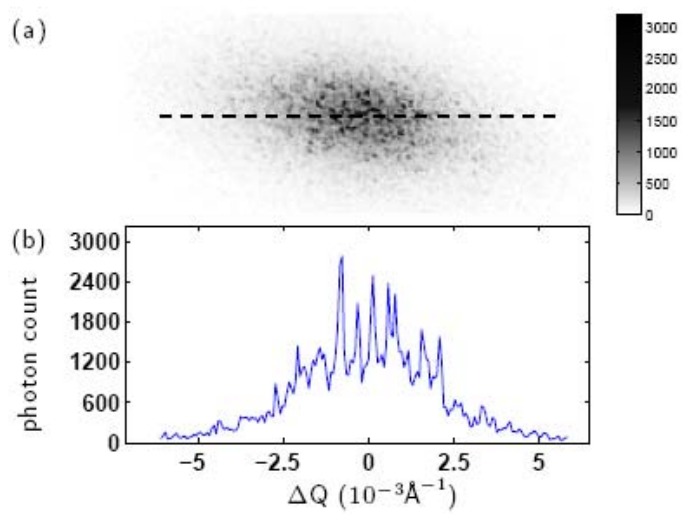
with J.-D. Su, M. Sutton, A. R. Sandy



Nb_3Se (classic CDW system)

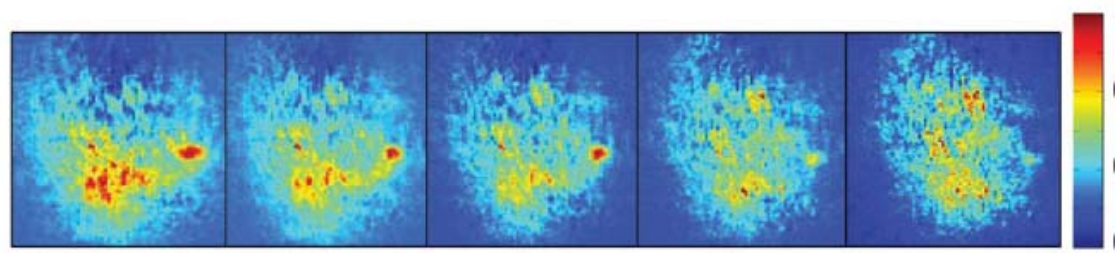
Sutton, Brock, Thorne et al., J. Phys. 2002, PRB 2001



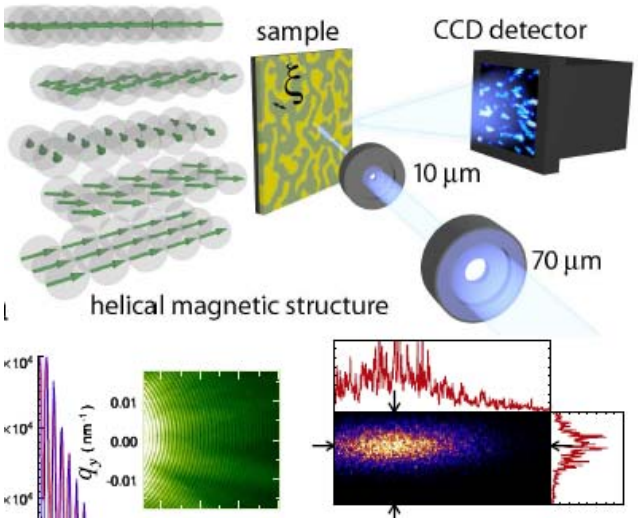


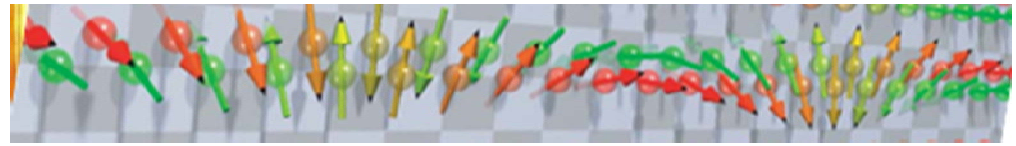
Cr (CDW/SDW Antiferromagnet)

Shpyrko, Isaacs et al., Nature 447, 68 (2007)



Helical Magnets:



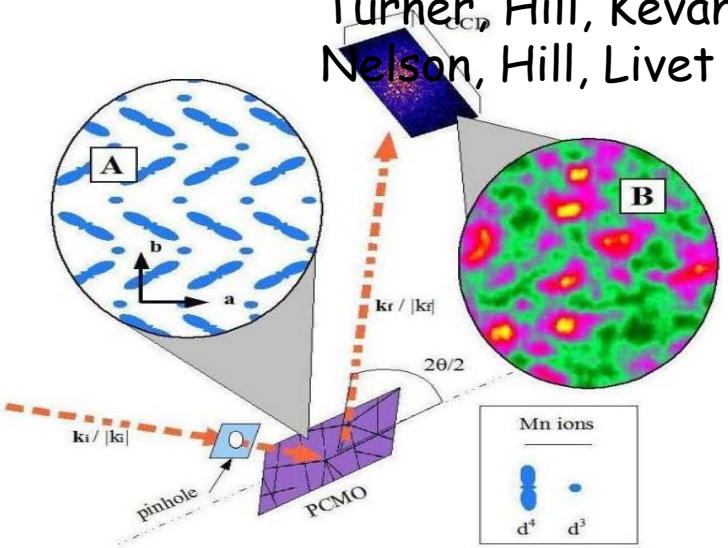


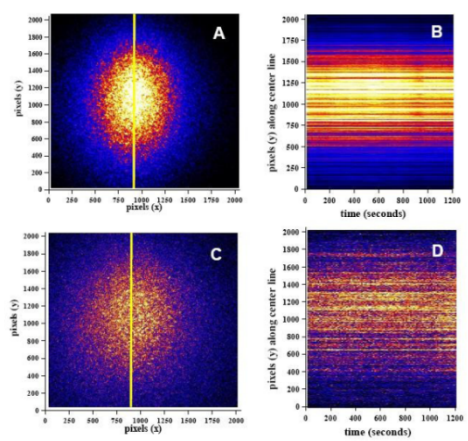
Holmium (helical antiferromagnet)
S. Koning et al., PRL 106, 077402 (2011)

Dysprosium, Holmium
Work with Sunny Sinha (UCSD)

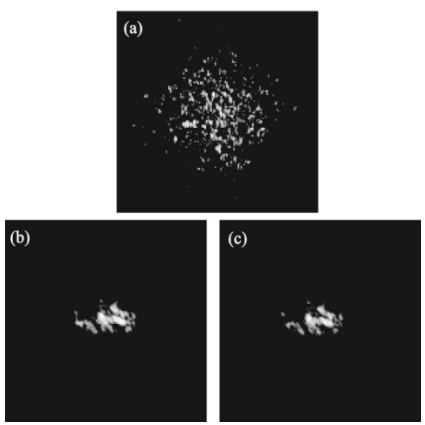
Manganites (Charge- & Orbital-Order):

Turner, Hill, Kevan et al., New J. Phys. 10, 053023 (2008)
Nelson, Hill, Livet et al., PRB 2002

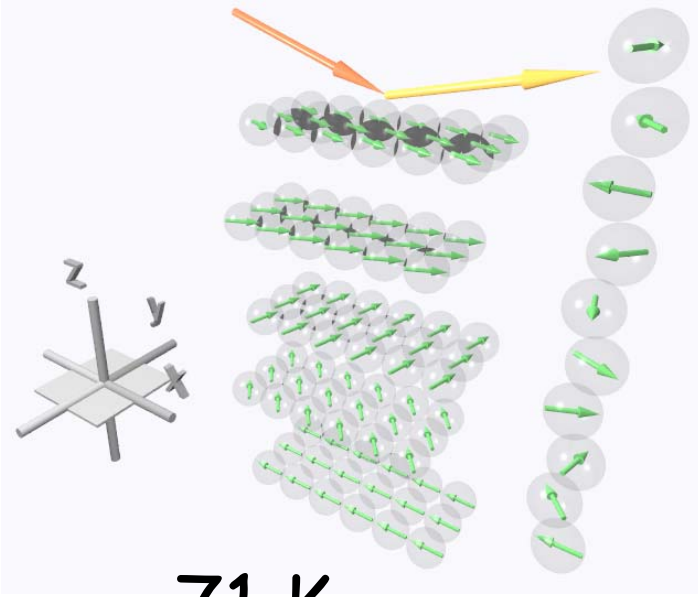




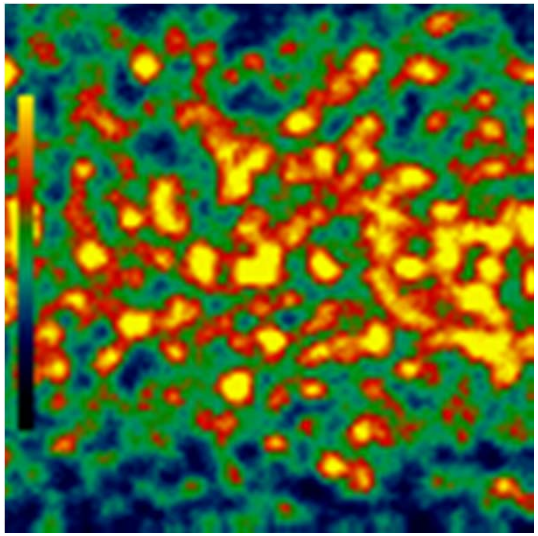
$Pr_{0.6}Ca_{0.4}MnO_3$, T = 150 K



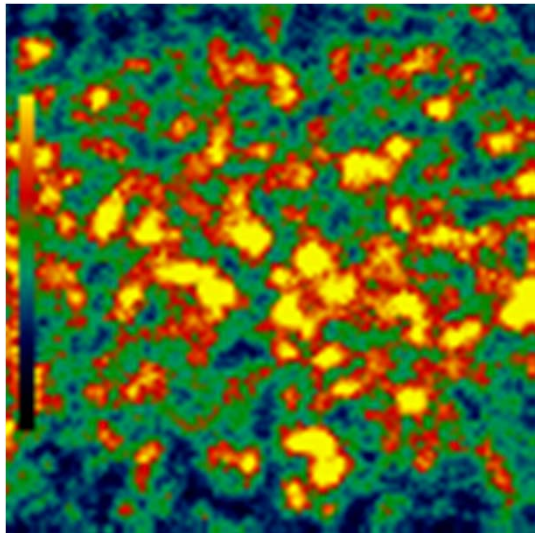
Example: "glassy" Fluctuations in antiferromagnetic Ho



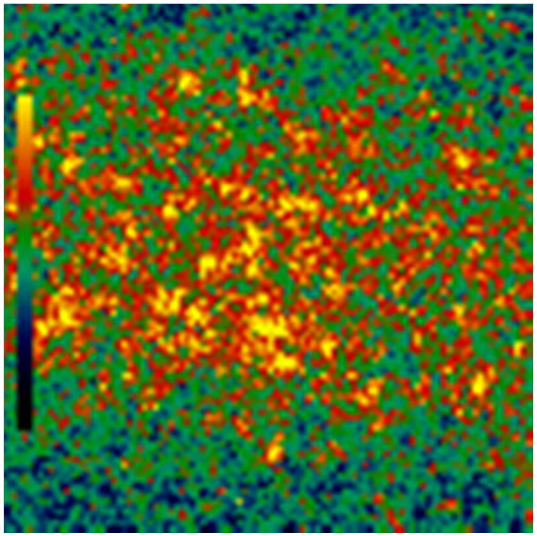
52K



64K



71 K



S. Koning et al., PRL 106, 077402 (2011)

Selected XPCS highlights

- Diffusion of colloids:
  - S. B. Dierker et al., **PRL** 75, 449 (1995)
  - T. Thurn-Albrecht et al., **PRL** 77, 5437 (1996)
  - L. B. Lurio et al., **PRL** 84, 785 (2000)
  - D. Pontoni et al., **PRL** 90 (2003)
  - M. Sikorski et al., **PRL** 106, 188301 (2011)
- Complex Fluids: polymer blends, clays
  - S. G. J. Mochrie et al., **PRL** 78, 1275 (1997)
  - D. Lumma et al., **PRL** 86, 2042 (2001)
  - P. Falus et al., **PRL** 94, 16105 (2005)
  - P. Falus et al., **PRL** 97, 66102 (2006)
  - R. Bandyopadhyay et al., **PRL** 93, 228302 (2004)
  - T. Koga, **PRL** 107, 225901 (2011)
- Capillary fluctuations of liquid surfaces
  - H. Kim et al., **PRL** 90, 68302 (2003)
  - Z. Jiang et al., **PRL** 98, 227801 (2007)
  - A. Madsen et al., **PRL** 92, 96104 (2004)
  - C. Gutt et al., **PRL** 91, 76104 (2003)
  - S. Streit et al., **PRL** 98, 047801 (2007)
  - S. Prasad et al., **PRL** 104, 137801 (2010)
- Langmuir Monolayers:
  - A. Duri et al., **PRL** 102, 145701 (2009)
  - Orsi et al., **PRL** 108, 105701 (2012)
- Liquid Crystal membranes
  - A. C. Price et al., **PRL** 82, 755 (1999)
  - A. Fera et al., **PRL** 85, 2316 (2000)
  - I. Sikharulidze et al. **PRL** 88, 115503 (2002)
- Charge- ,Spin-, Orbital- ordered domains
  - O. G. Shpyrko et al., **Nature** 447, 68 (2007)
  - J. Turner et al., **New J. Phys**. 10, 053023 (2008)
  - S. Koning et al., **PRL** 106, 077402 (2011)
- Non-equilibrium dynamics, Binary alloys:
  - A. Fluerasu et al., **PRL** 94, 055501 (2005)
  - S. Bauer et al., **PRL** 74, 2010 (1995)
  - M. Leitner et al., **Nat. Mat.** 8, 717 (2009)
  - L. Muller et al., **PRL** 107, 105701 (2011)
  - C. Sanborn et al., **PRL** 107, 015702 (2011)
- Metal/polymer nano-composite
  - S. Streit et al., **PRL** 98, 47801 (2007)
  - S. Narayanan et al., **PRL** 98, 185506 (2007)
  - C. Caronna et al., **PRL** 100, 055702 (2008)
  - H. Guo et al., **PRL** 102, 075702 (2009
- Phasons in Quasicrystals:
  - S. Francoual, et al., **PRL** 91, 225501 (2003)

Capillary Fluctuations

gravity waves
(long-wavelengths)

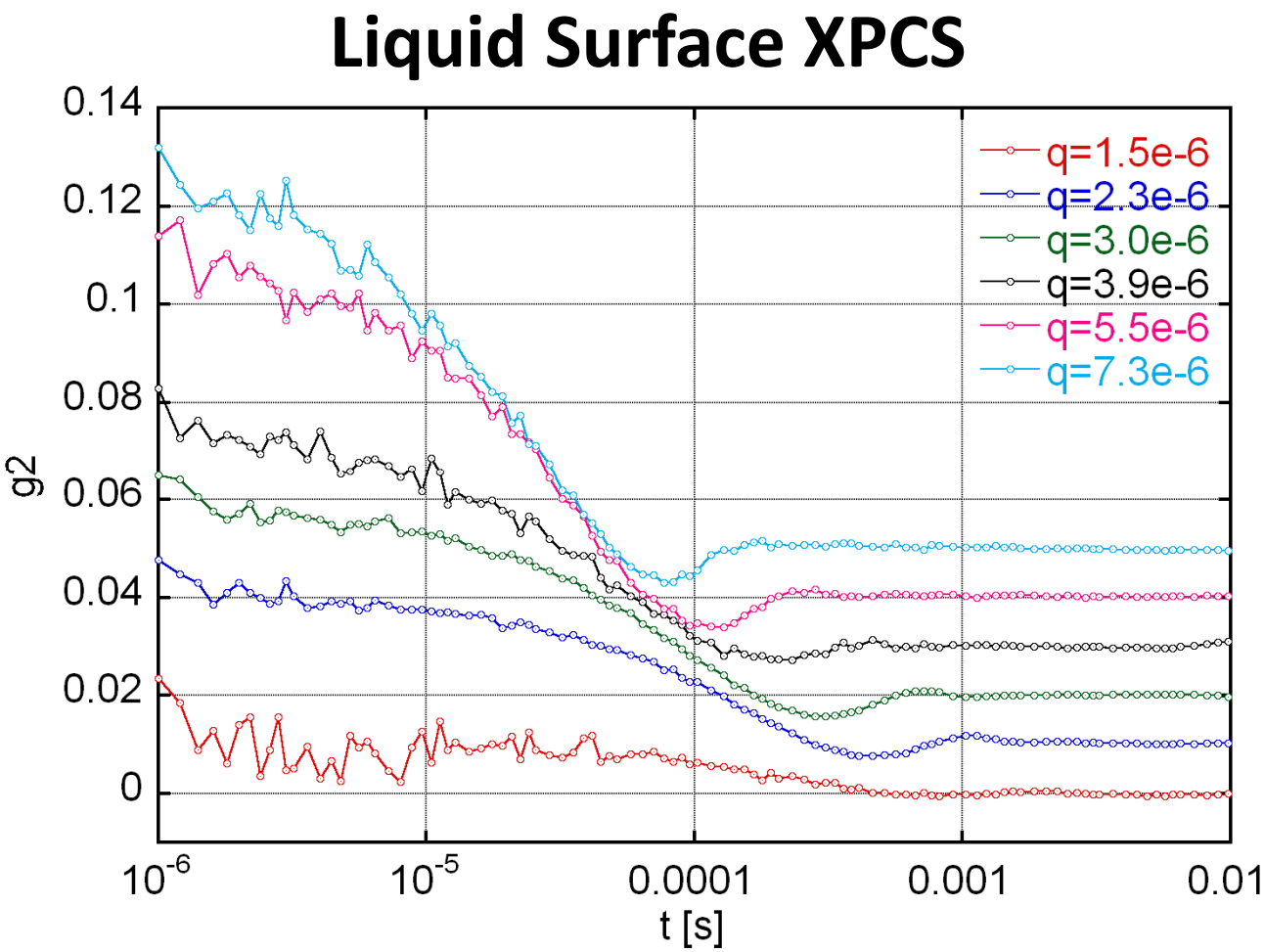
capillary waves
(short-wavelengths)

Surface tension γ [energy/L^2] vs. Thermal energy $k_B T$ [energy]

Crossover at lengthscale $\xi \sim \sqrt{\frac{\gamma}{\rho g}}$ (~3mm for water)

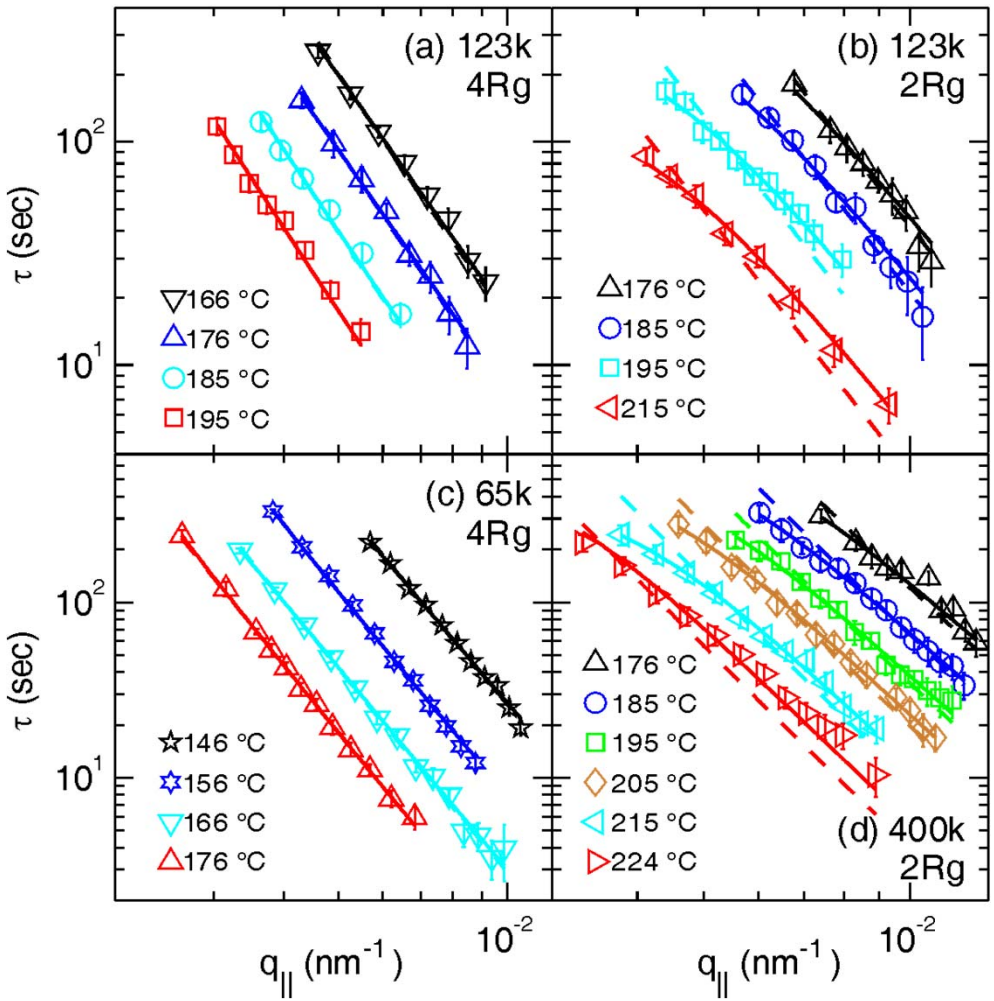
Characteristic length scale (amplitude) $\sigma \sim \sqrt{\frac{k_B T}{\gamma}}$ (~2.4Å for water at room T)

Soft matter XPCS: colloids, polymers, gels, clays, liquid surfaces, nanoparticles, liquid crystals, microfluidics, biomembranes



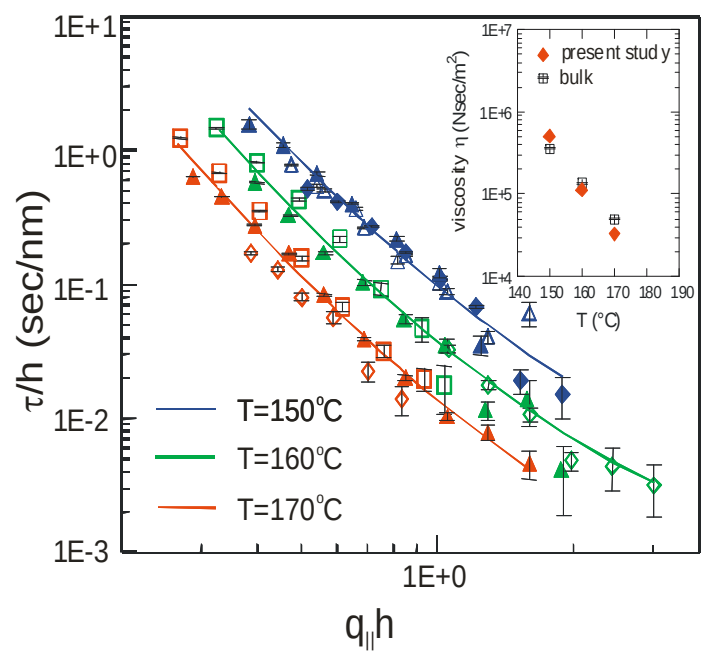
M. Sprung et al. (unpublished)

Relaxation Time Constants



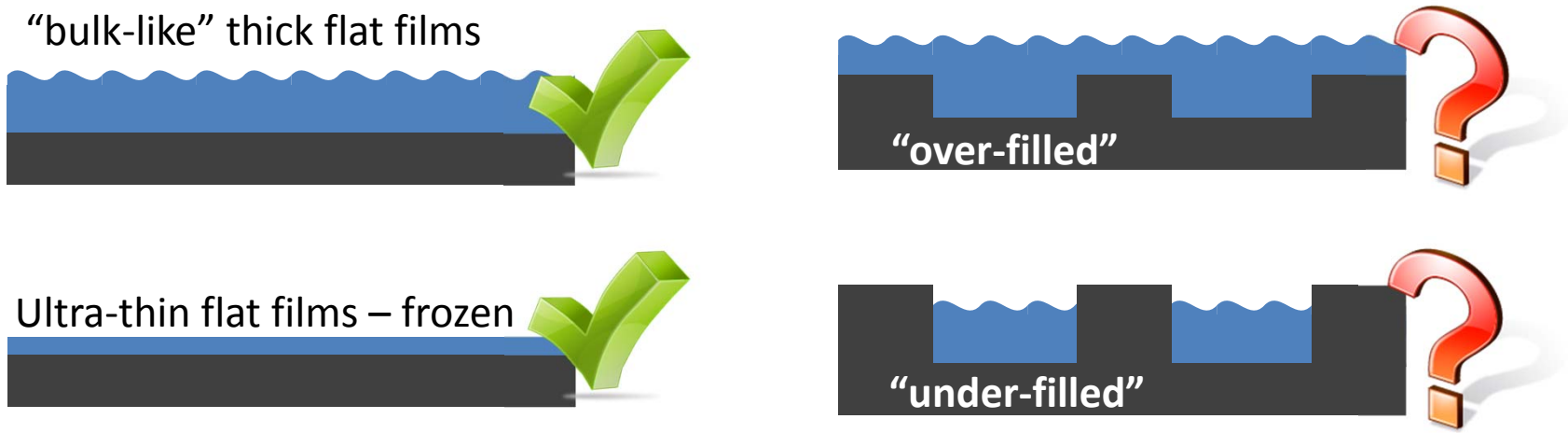
- Viscoelastic model:

$$\tau(q_{||}) = \frac{\tau_0(q_{||})}{1+\tau_0(q_{||})(\mu/\eta)}$$

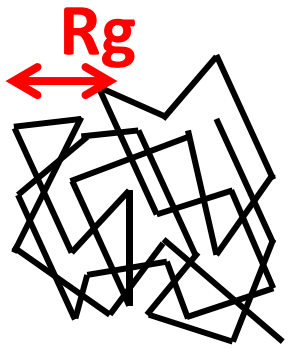


Z. Jiang, et al., Phys. Rev. Lett. 98, 227801 (2007)

Dynamics of Capillary Waves in Patterned Structures



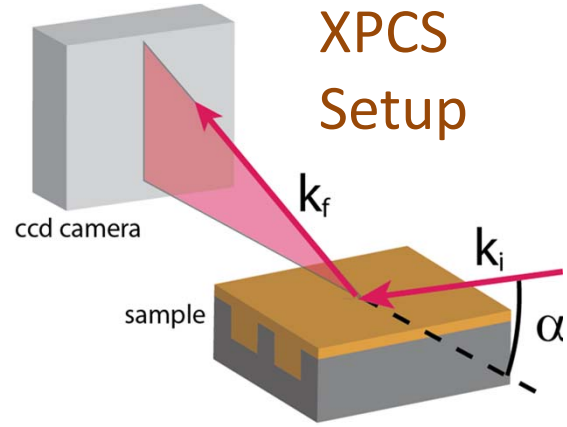
- Thermally induced height fluctuations = capillary waves
- Sinha's group* has shown:
  - Flat films – overdamped capillary waves = excellent model
  - 1-3 Rg thick = significant damping
- Lateral confinement?
- "Over-filled"/"Under-filled"



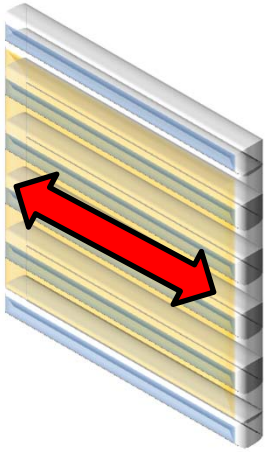
Polymer chain

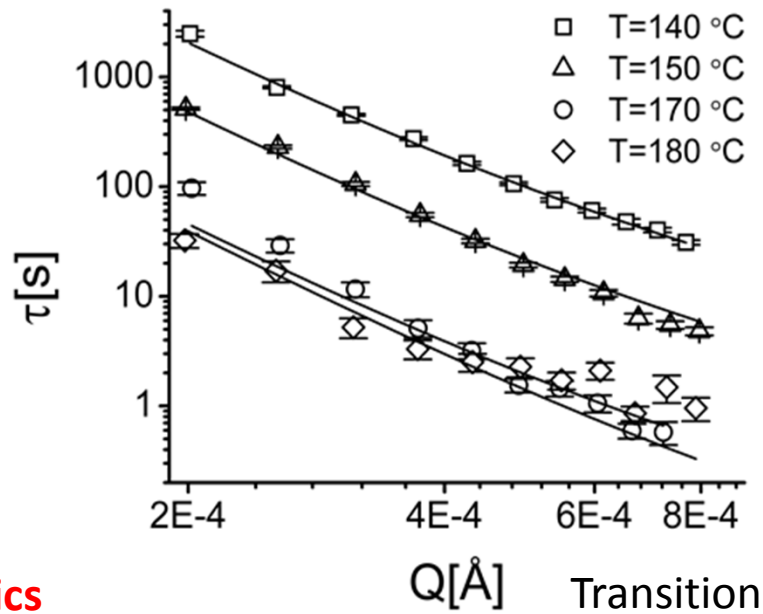
Kim, H. *et al. PRL* (2003)
Kim, H. *et al. Physica* (2003)
Jiang, et al. PRL (2007)

Capillarity in confinement

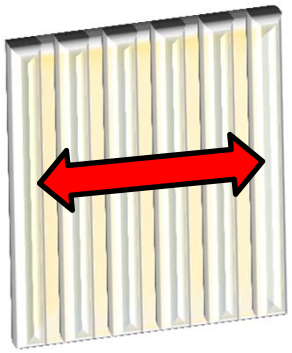


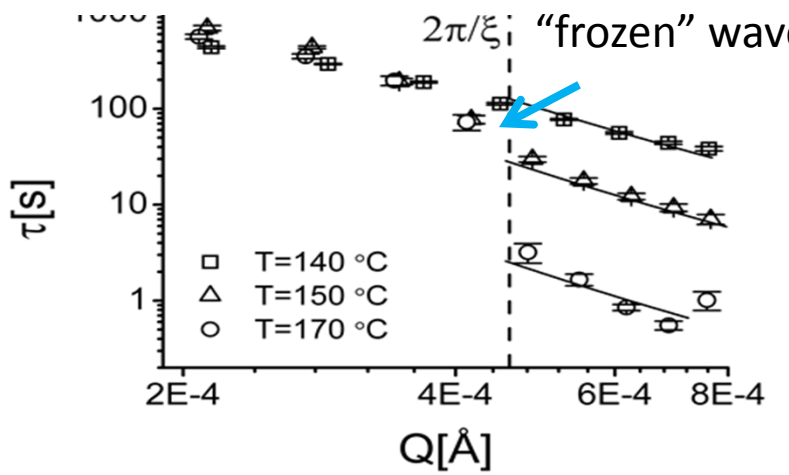
Parallel Dynamics





Perpendicular Dynamics





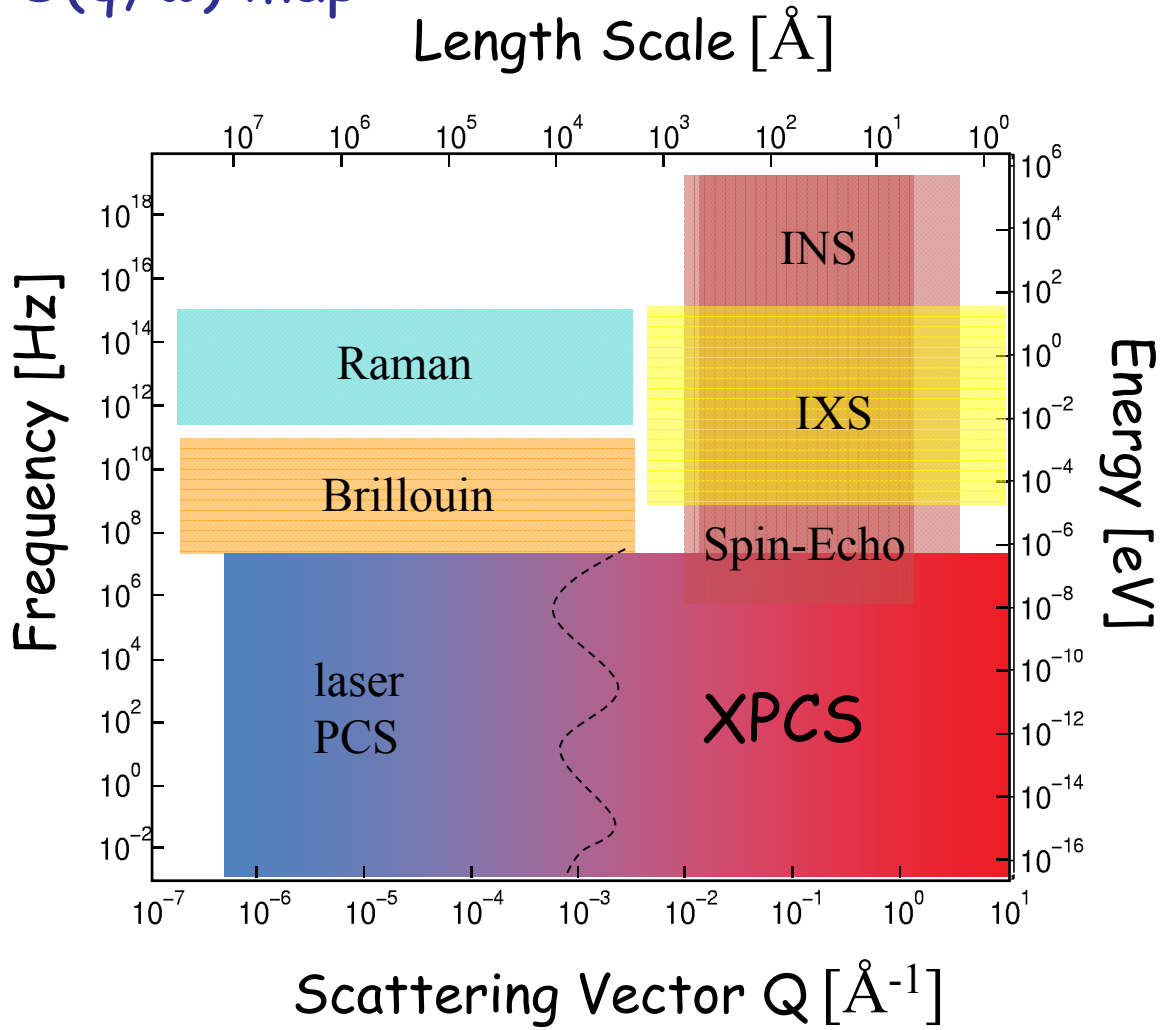
Transition to "frozen" waves

$$\xi = d^2 \left(\frac{2\pi\gamma}{A_{eff}} \right)^{1/2}$$

K. Alvine, ..., O.S., PRL 109, 207801 (2012)

XPCS and other spatio-temporal probes

S(q, ω) map:



XPCS is the extension of dynamic light scattering probe (laser PCS)

Pros:

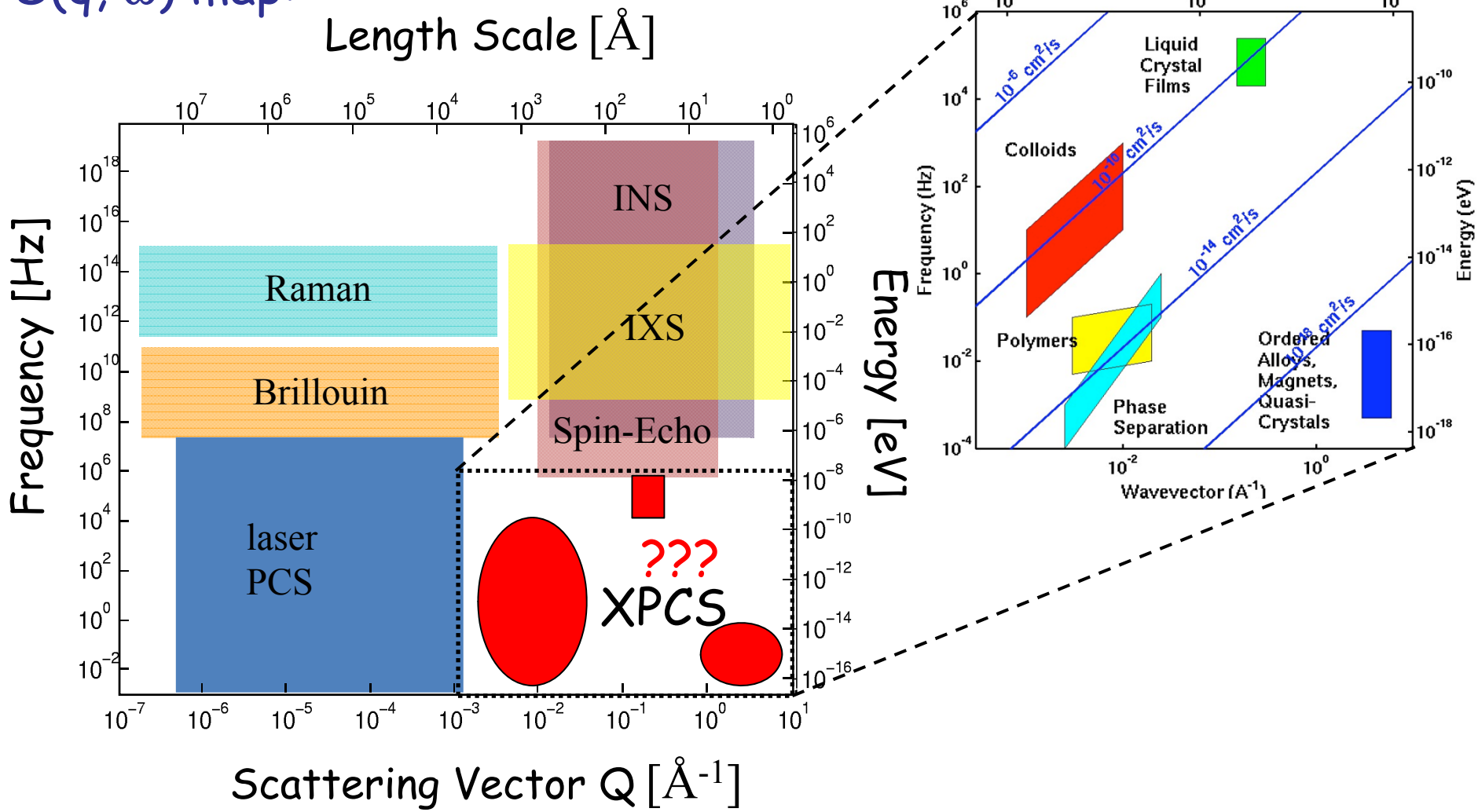
- Smaller lengthscales
- Non-transparent materials
- Charge, Spin, Chemical and atomic structure sensitivity

Cons:

- Need fully coherent x-ray sources!

XPCS and other spatio-temporal probes

S(q, ω) map:



What limits XPCS timescales?

Problems

Short Timescales:

- Low Coherent Flux

(nothing to correlate)

- Detector readout times

(seconds for conventional CCD)

Long Timescales:

- Beam/components stability

(10s-10,000s)

Solutions:

- Brighter Sources

(NSLS-II)

- Faster Detectors

- Stable source

and components

Signal to Noise in XPCS:

$$R_{\mathrm{sn}} = A\bar{I}\left(T\tau n_x n_z\right)^{1/2}$$

P. Falus, et al., J. Synchrotron Rad. 13, 253–259 (2006)

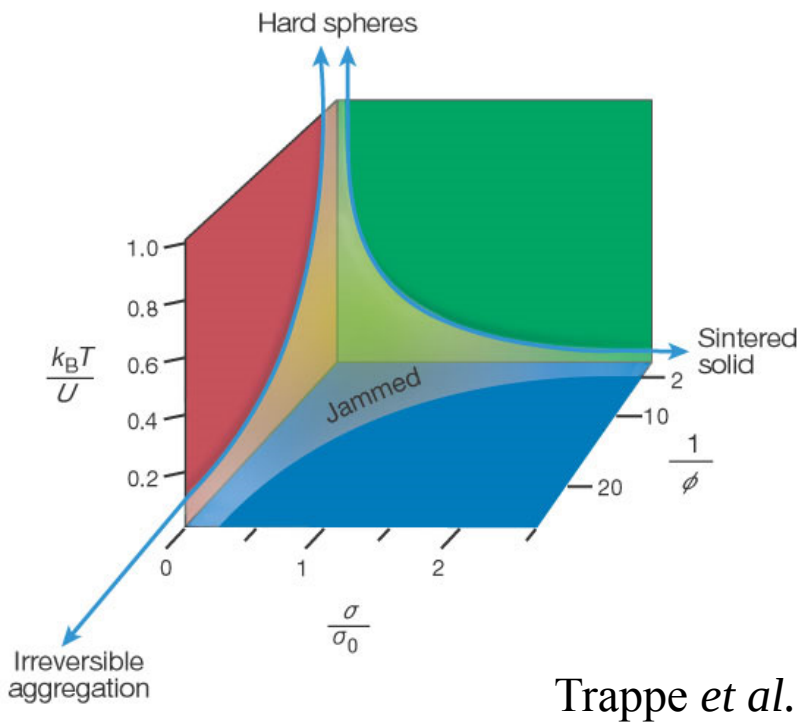
More speckles helps! (Need 2D detectors)

Unusual that SNR scales as Coherent Flux (not square root)

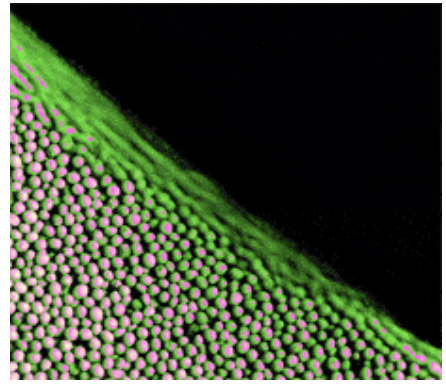
For a fixed Brightness, RSN and Coherent flux scales as E^{-2} (softer x-rays help, up to a point)

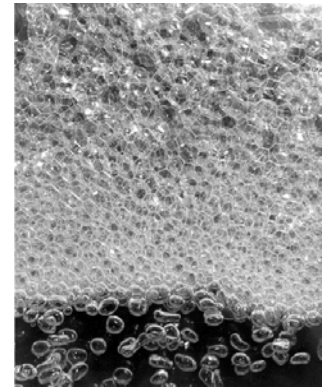
If Coherent Flux increases by a factor of N, one can measure timescales N^2 faster with the same SNR

Structural arrest, glasses and jamming

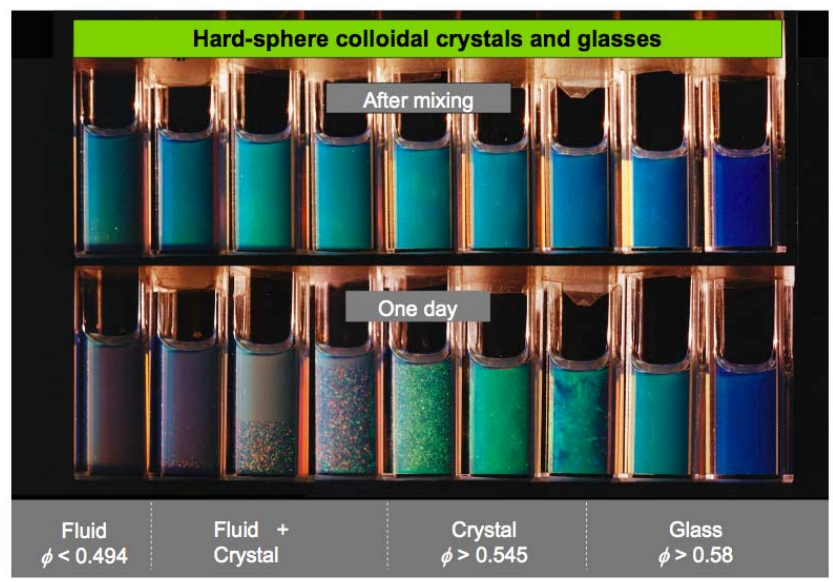


Trappe *et al.*





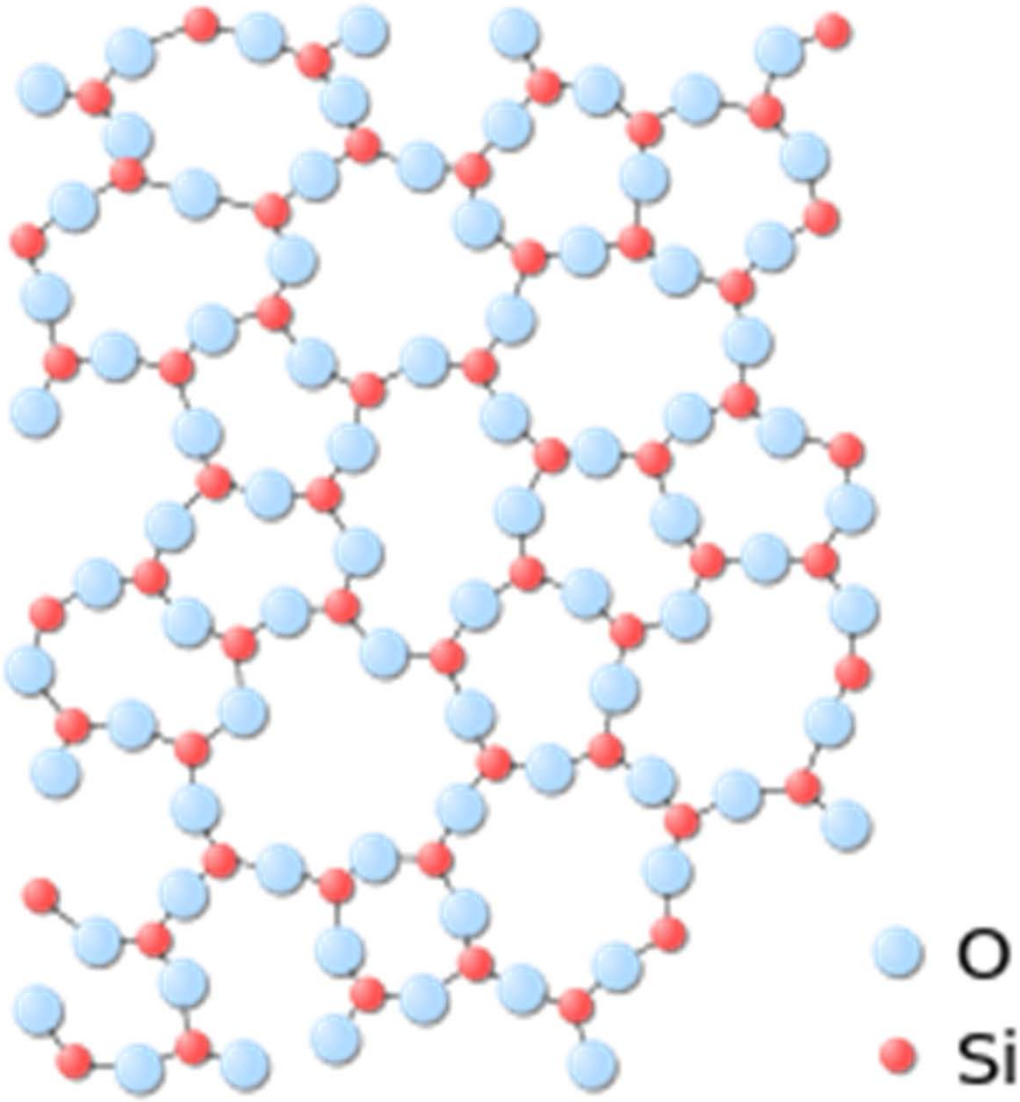
Heinrich Jaeger

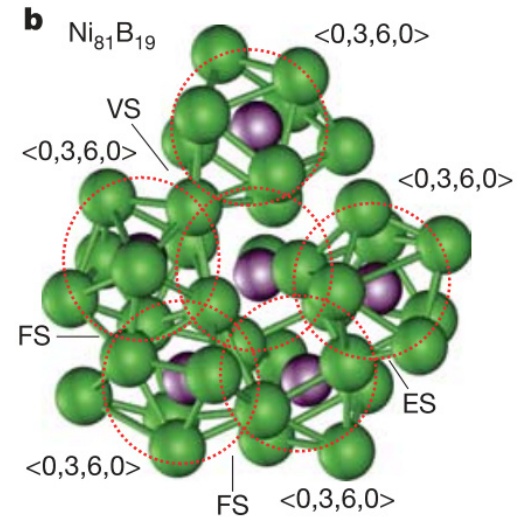


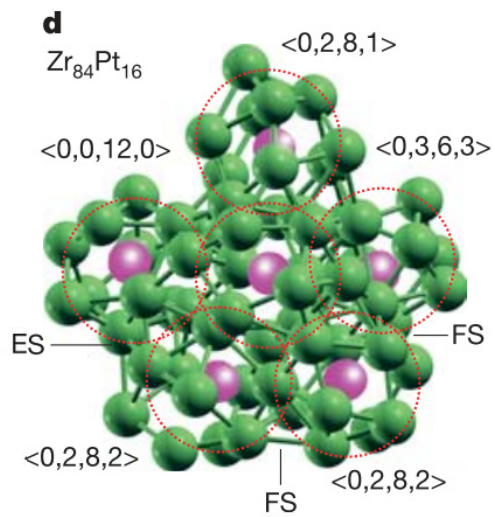
Peter Pusey

Andrea Liu and Sid Nagel, Nature
"Jamming is not just cool any more"

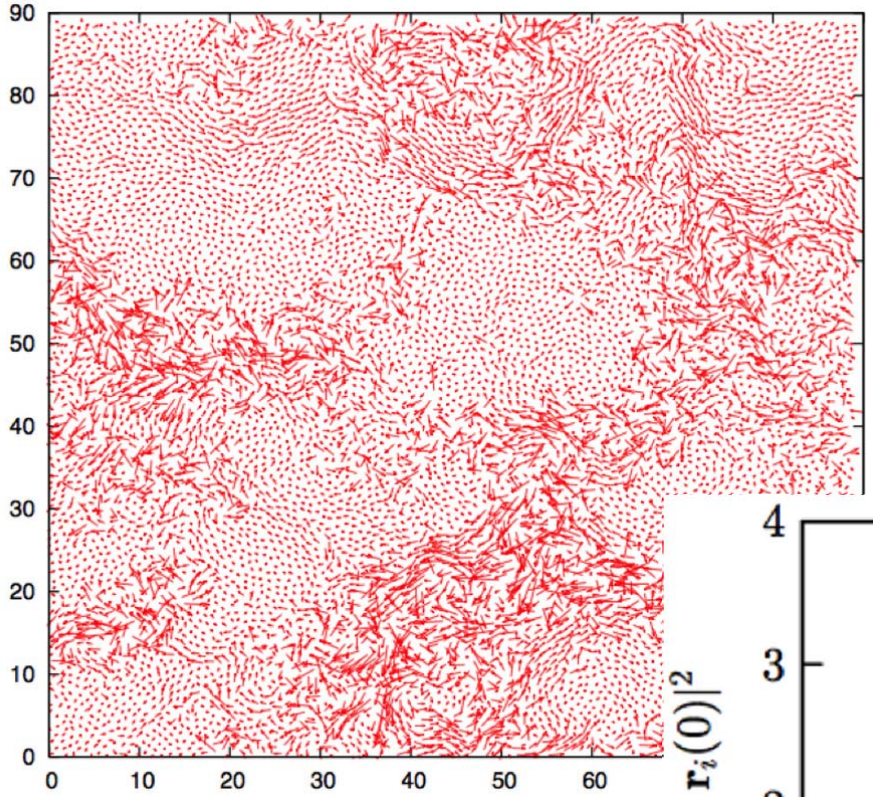
What is the nature of glassy state?

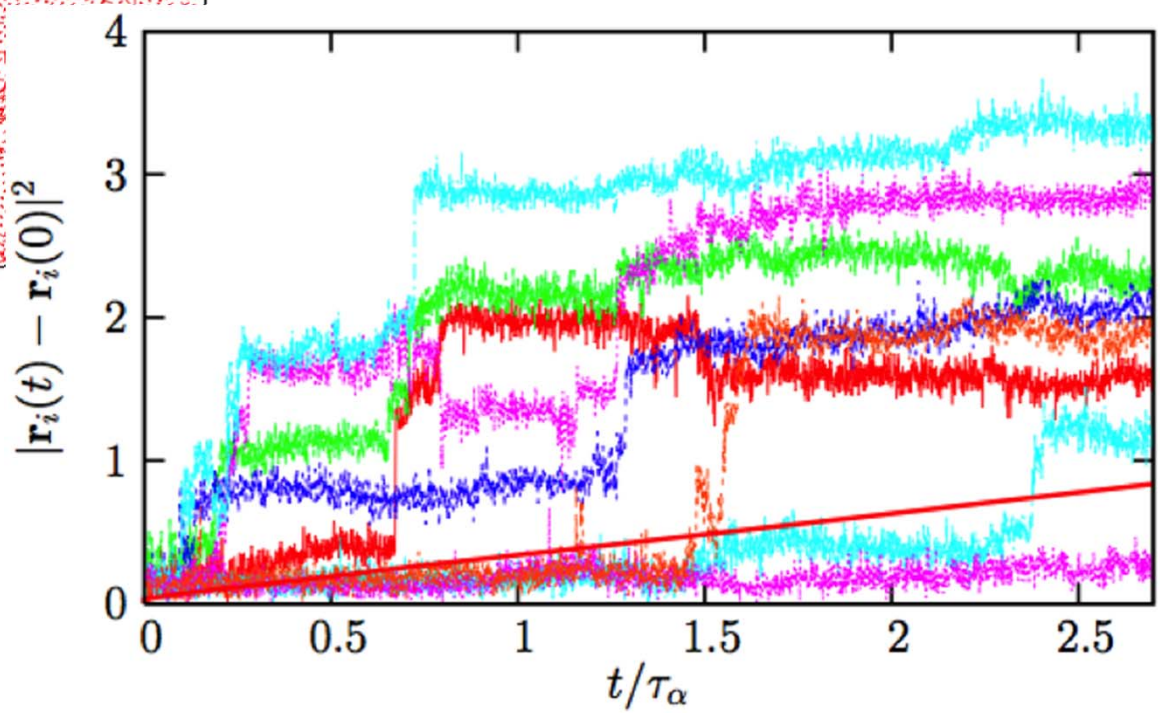






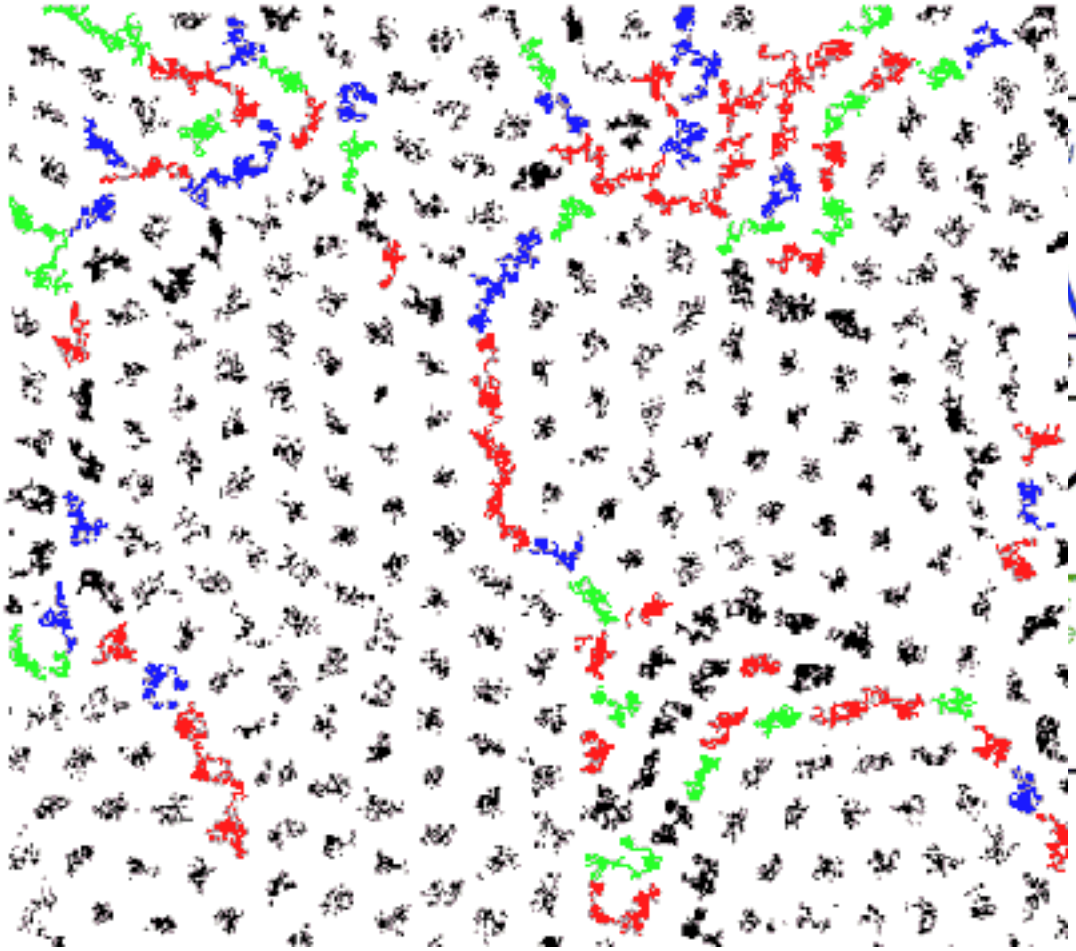
Dynamical Heterogeneities in Glasses



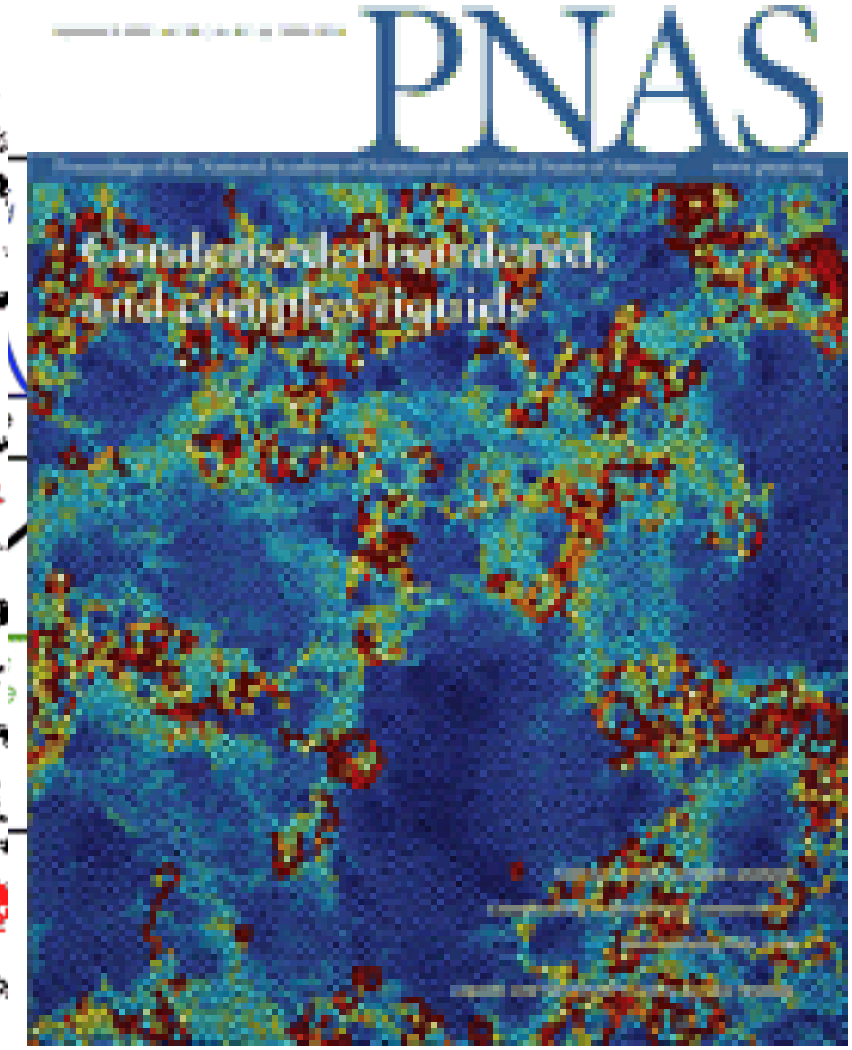


L. Berthier, Physics 4, 42 (2011)

Dynamic Heterogeneities

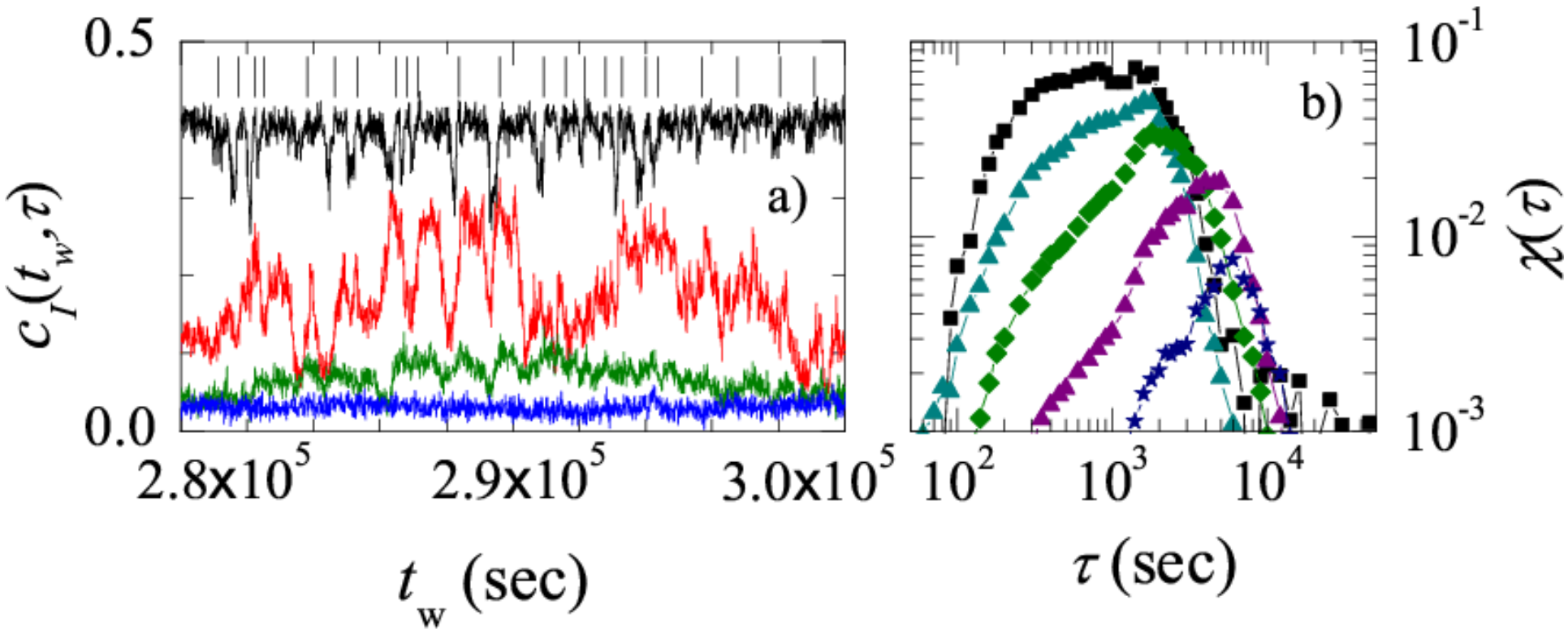


B. Cui, B. Lin, S. Rice



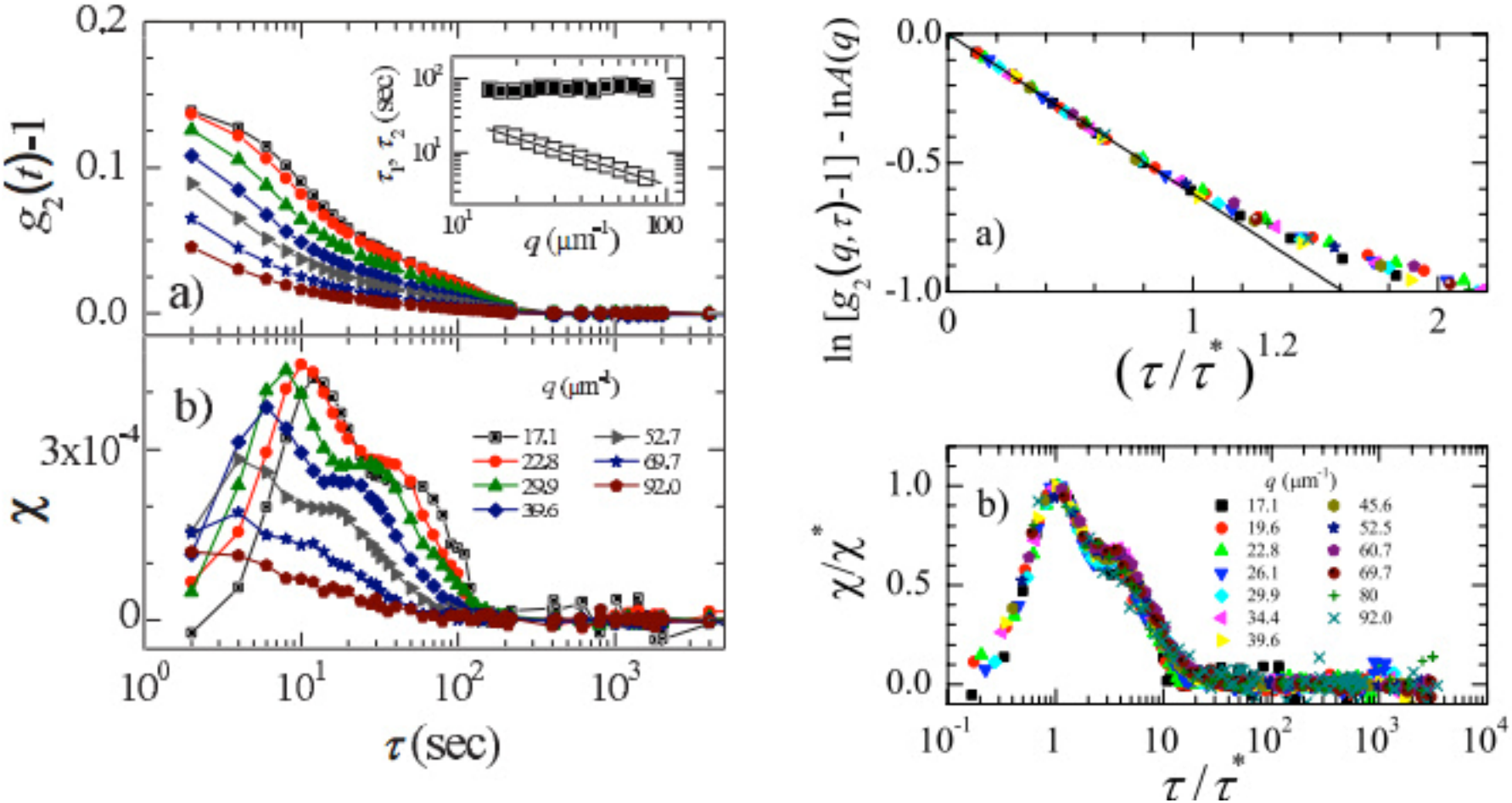
Lester Hedges, UCB

Dynamical Heterogeneities in fractal gels



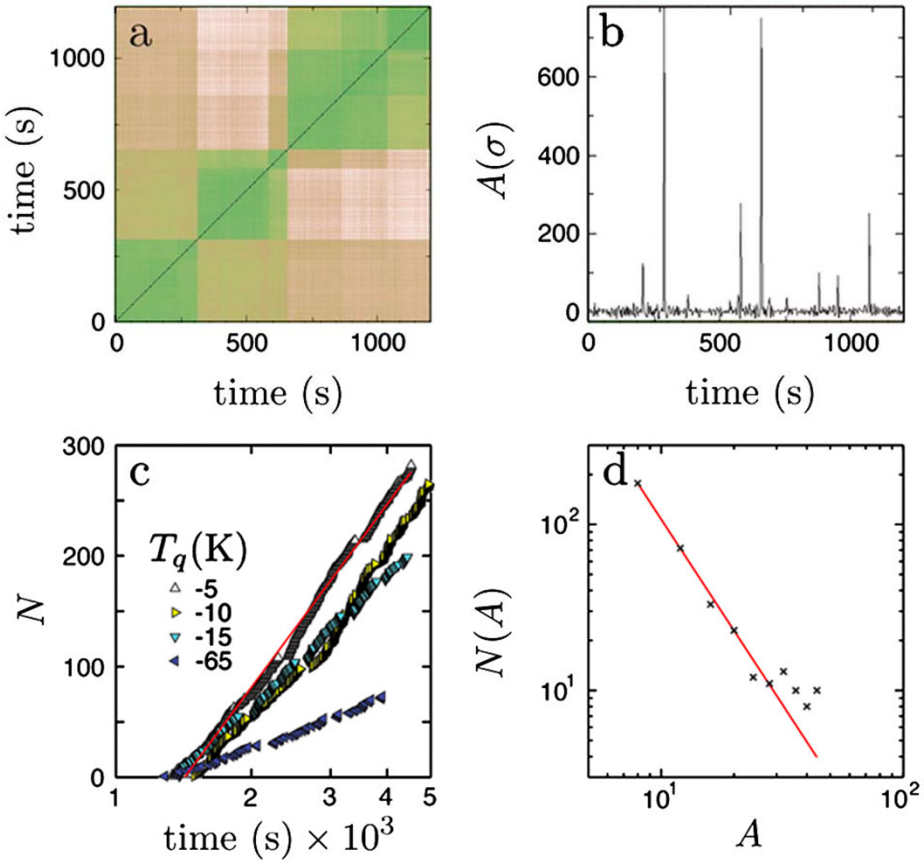
A. Duri - L. Cipelletti, Europhys. Lett., 76 (5), p. 972 (2006)

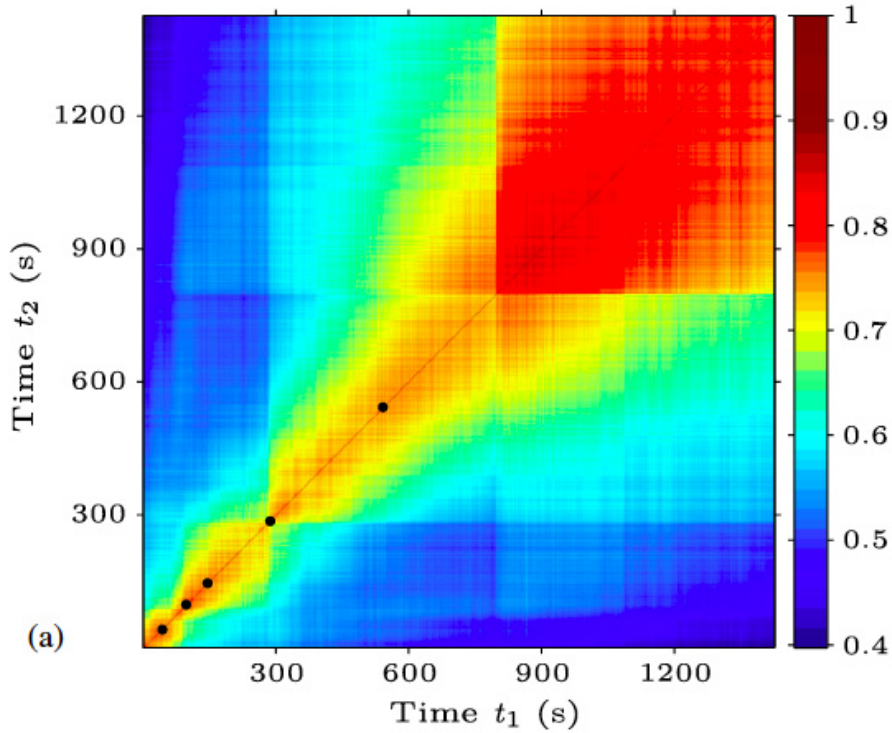
Dynamical Heterogeneities in fractal gels



V. Trappe, A. Robert et al., PHYSICAL REVIEW E 76, 051404 (2007)

Intermittency, Avalanches and Higher Order Correlation Functions:





Structural Avalanches in Cobalt
C. Sanborn et al., PRL 107, 015702 (2011)

Structural Avalanches in AuCd Alloy
L. Muller et al., PRL 107, 105701 (2011)

Membrane Fluctuations

Dynamics of lipid and other small-molecule-surfactant membranes. Time scales needed 10 μs to 10 ms.

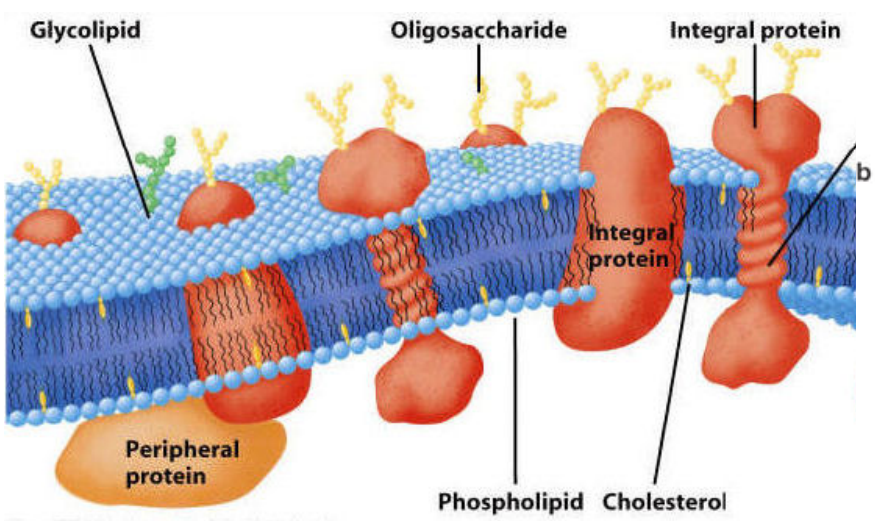
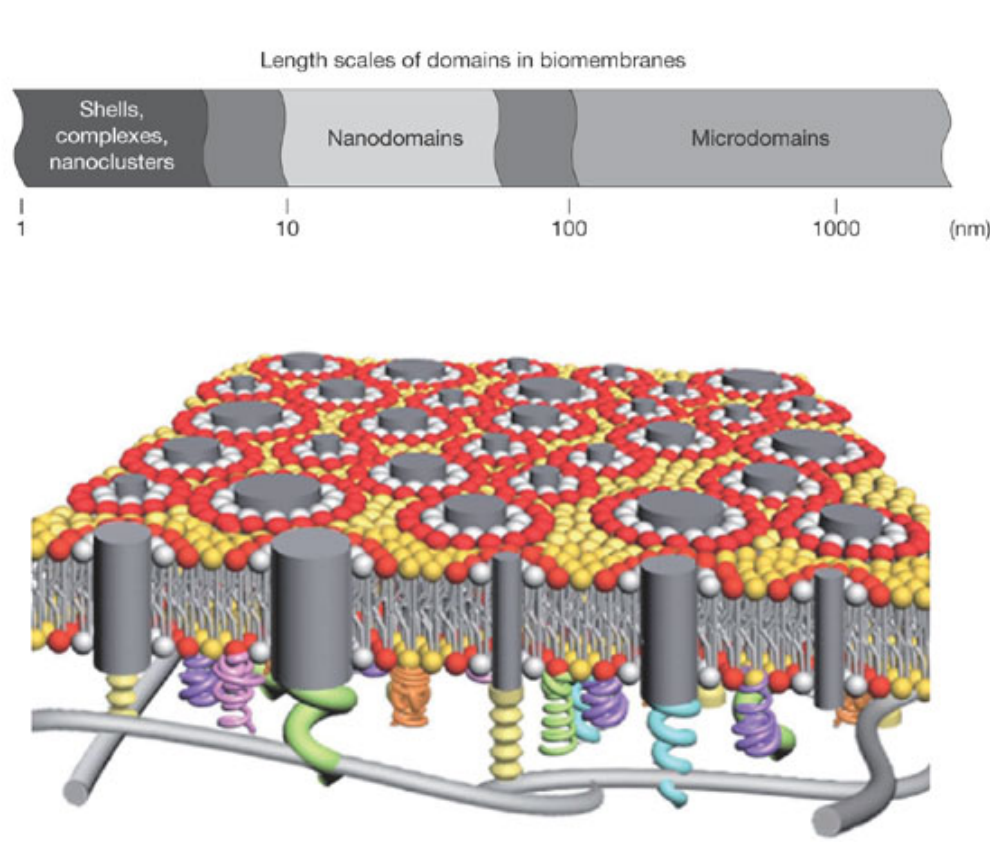
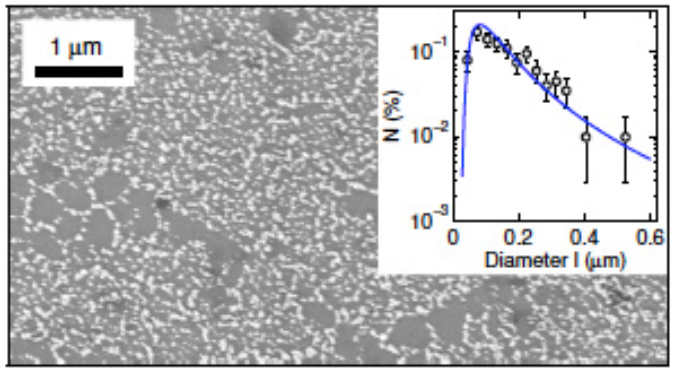
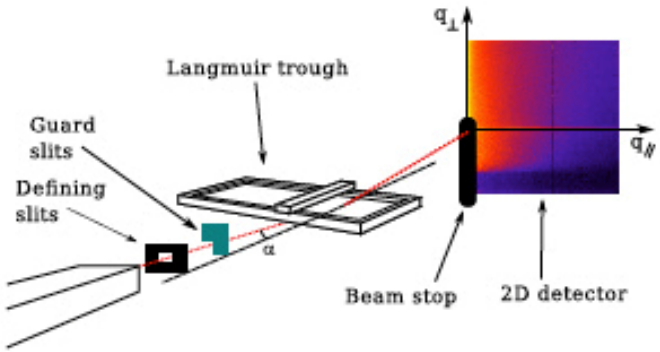


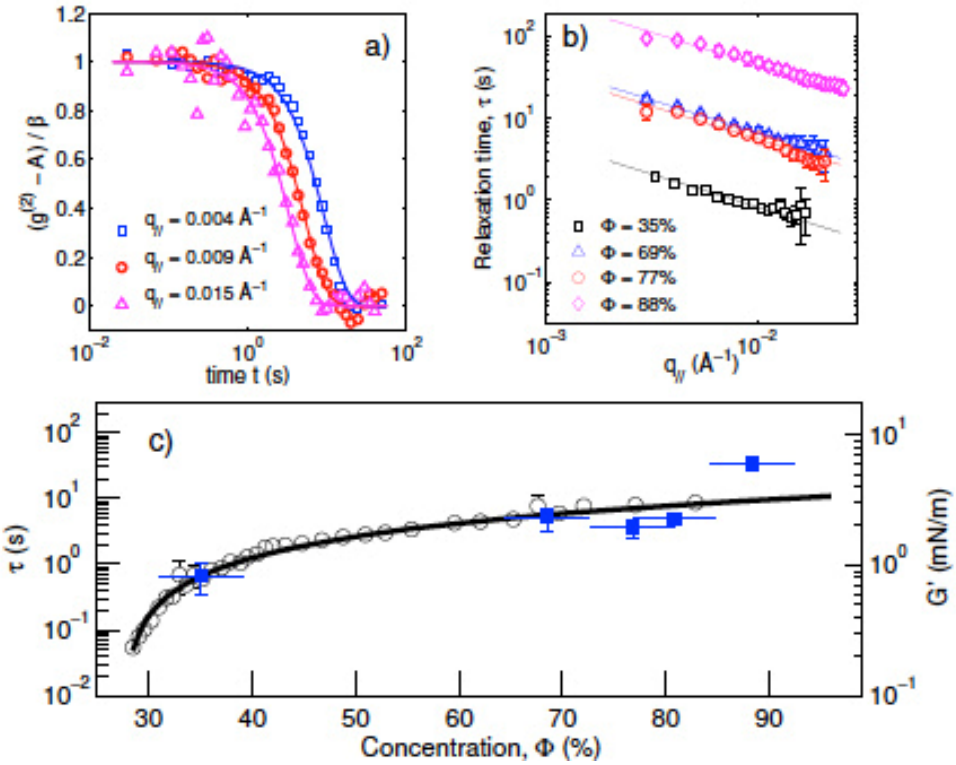
Figure 9-26 Fundamentals of Biochemistry, 2/e
© 2006 John Wiley & Sons



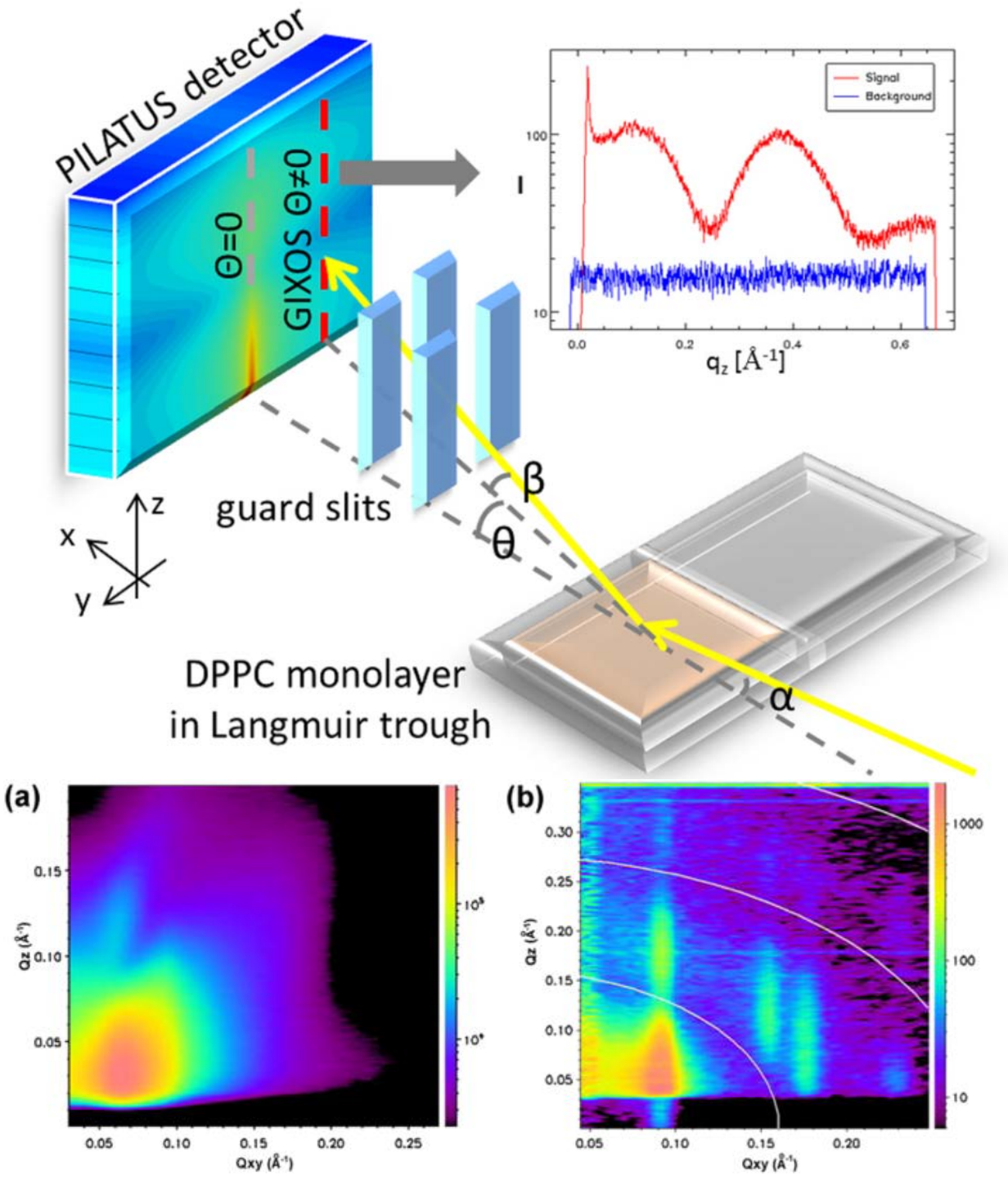
Lateral diffusion in 2D gel



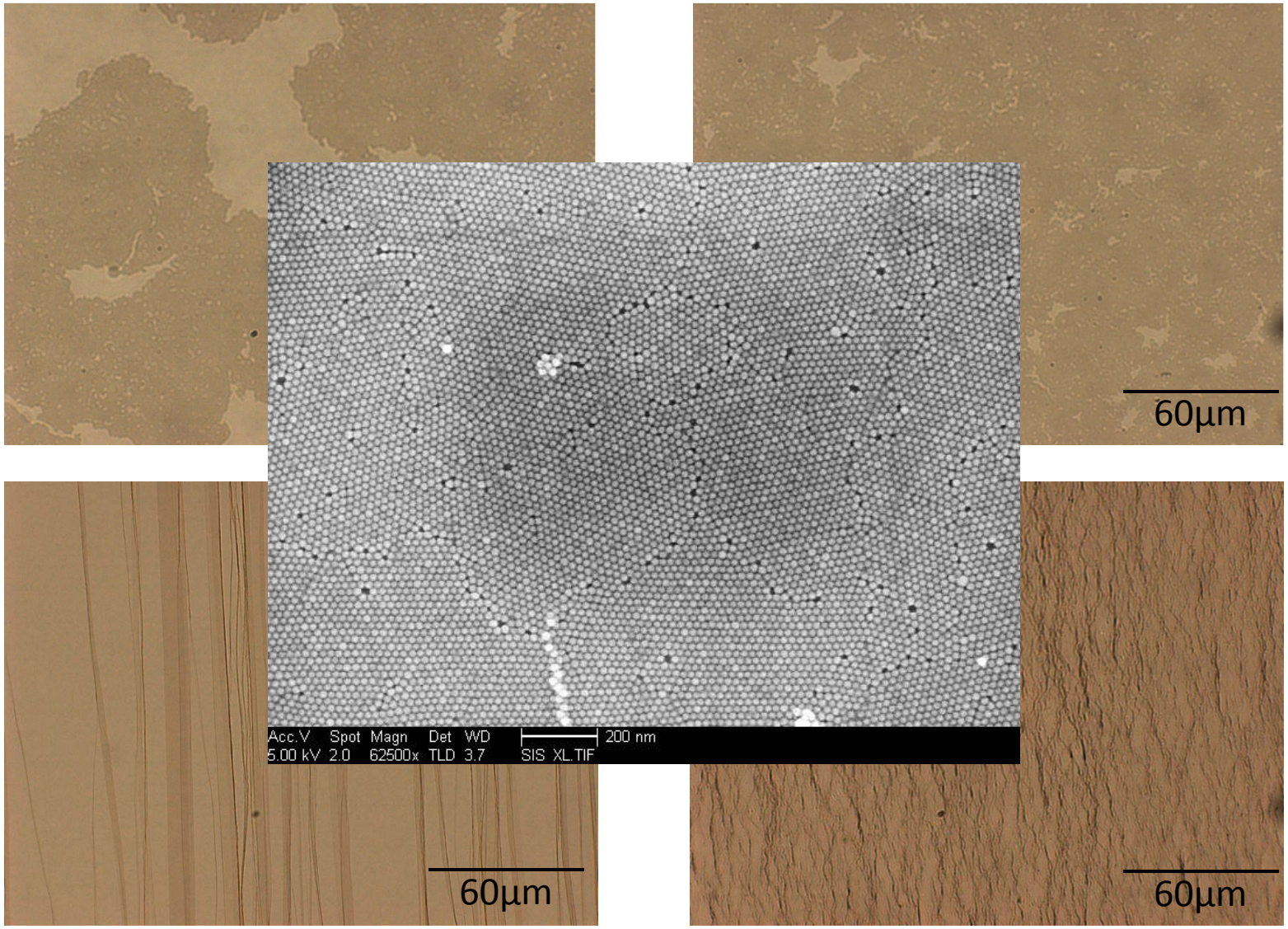




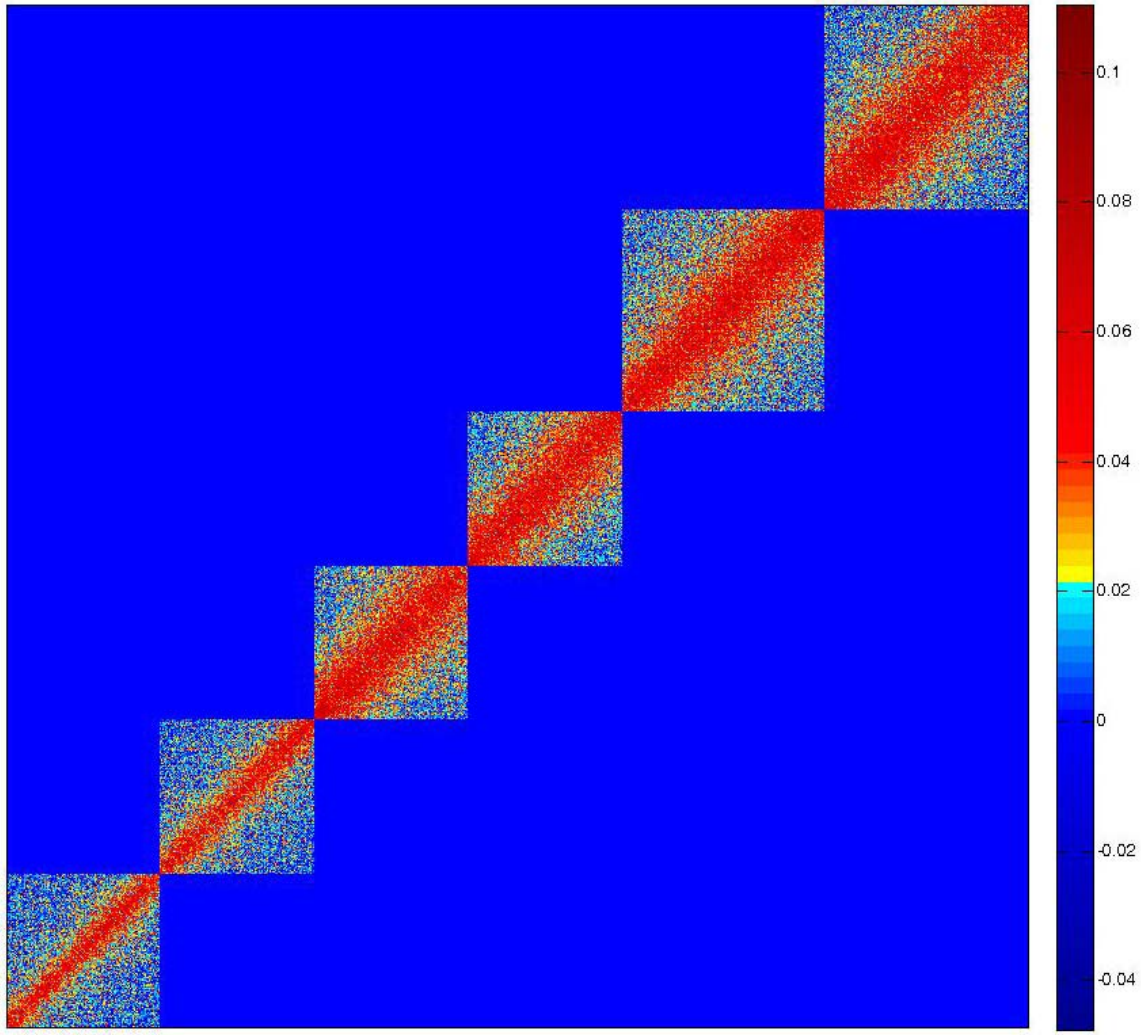
Orsi et al., PRL (2012)


PILATUS detector
Θ=0
GIXOS Θ≠0
Signal
Background
I
100
10
0.0
0.2
0.4
0.6
q_z [Å^{-1}]
guard slits
β
θ
α
z
x
y
DPPC monolayer
in Langmuir trough
(a)
(b)
Qz (Å^{-1})
Qxy (Å^{-1})
0.05
0.10
0.15
0.20
0.25
0.30
1000
100
10

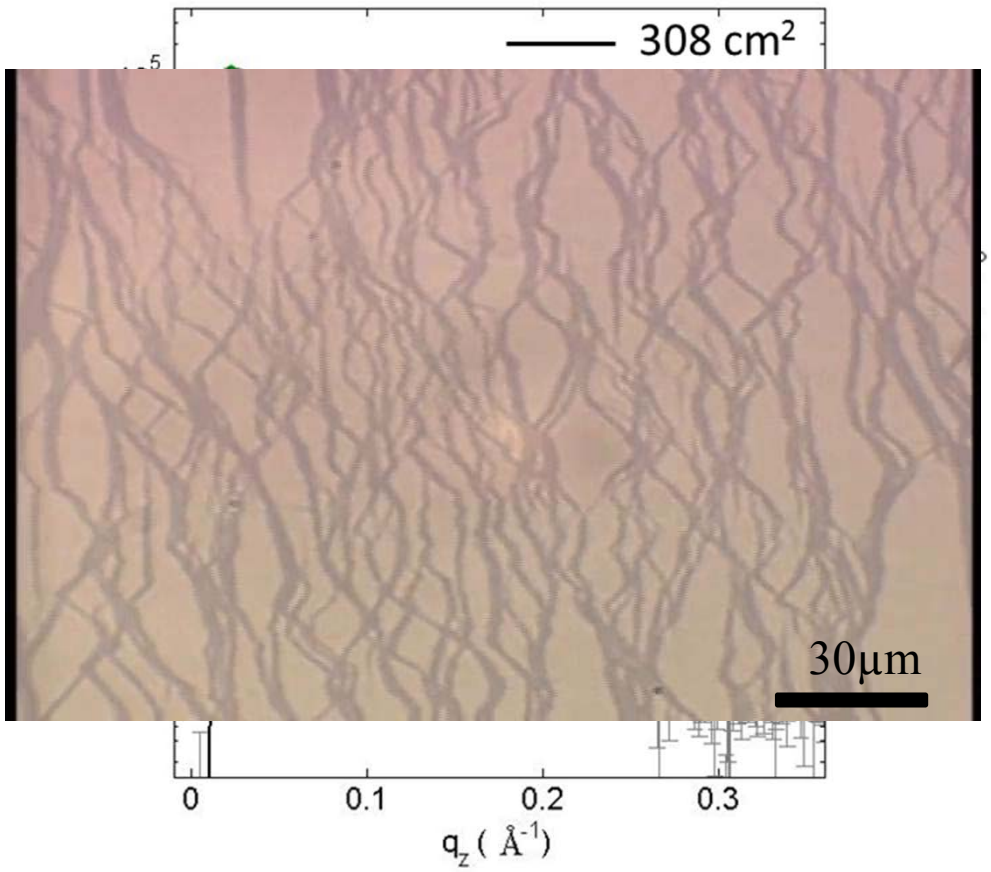
The Macroscopic Picture

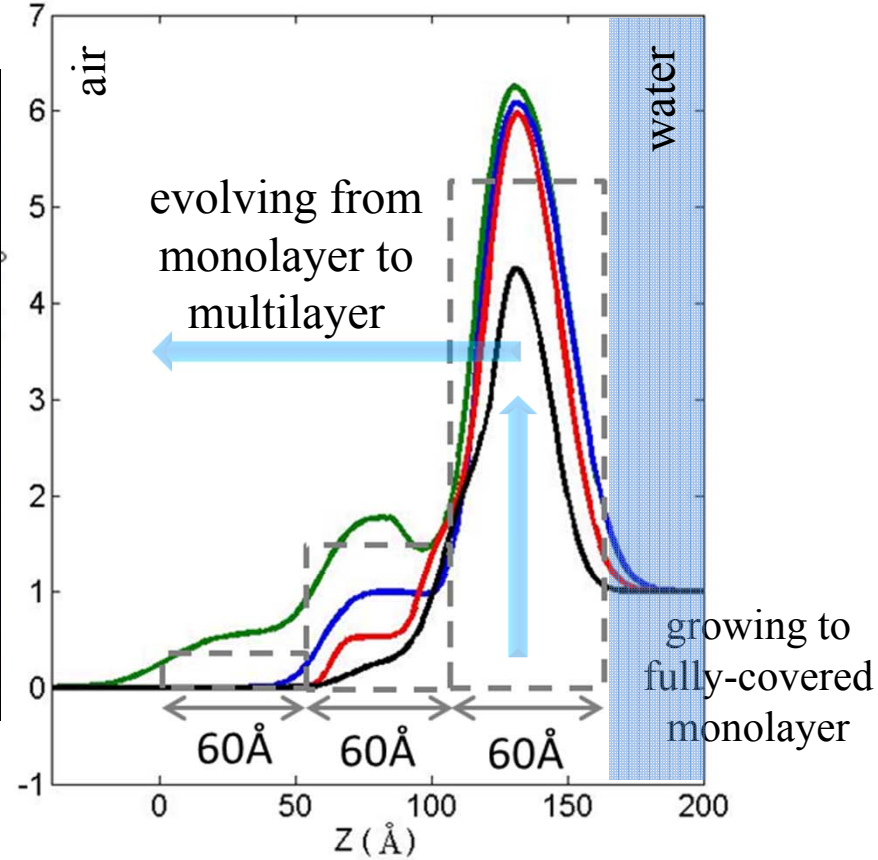


2-Time Correlation



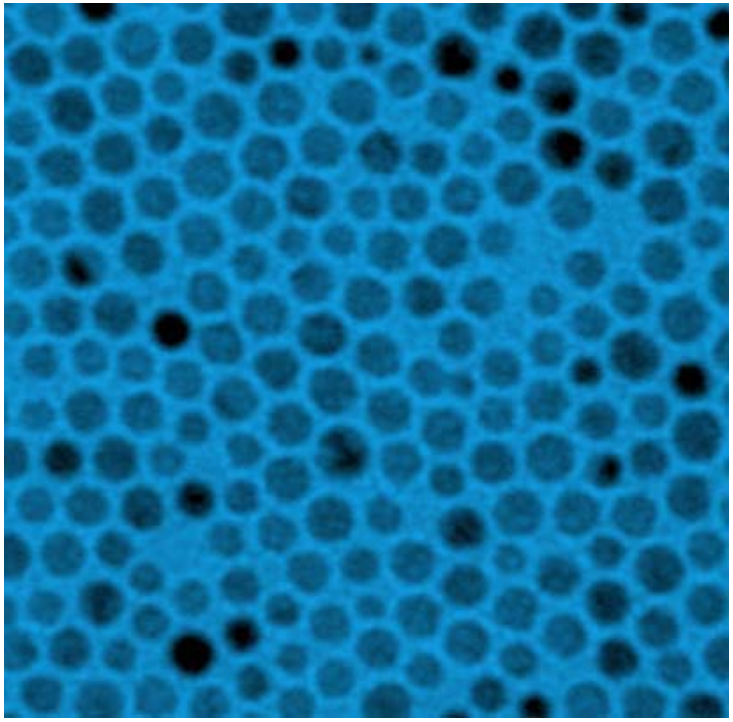
GIXOS data



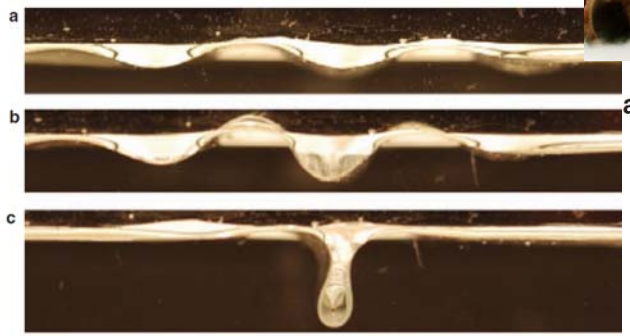


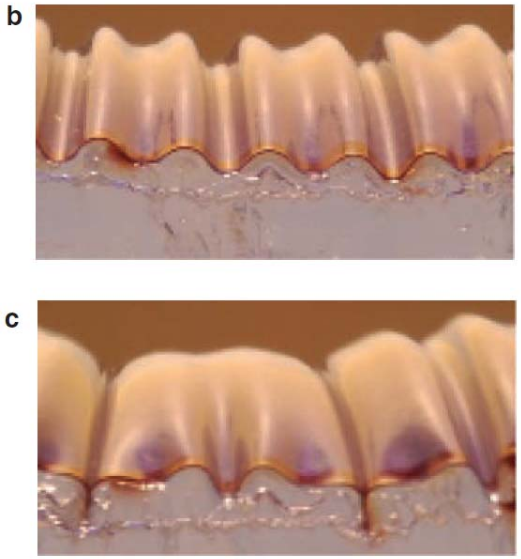
The data and fits were shifted for clarity

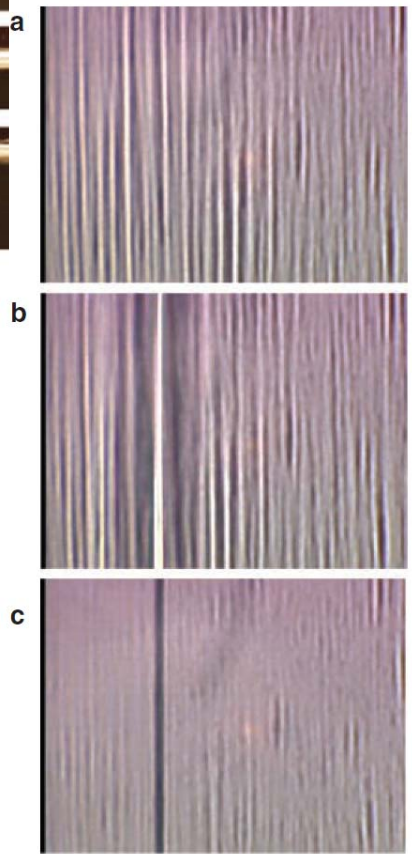
Buckling, Folding, Mechanical instabilities in thin films



Nanoparticle monolayer films







Limiting Factors for XPCS:

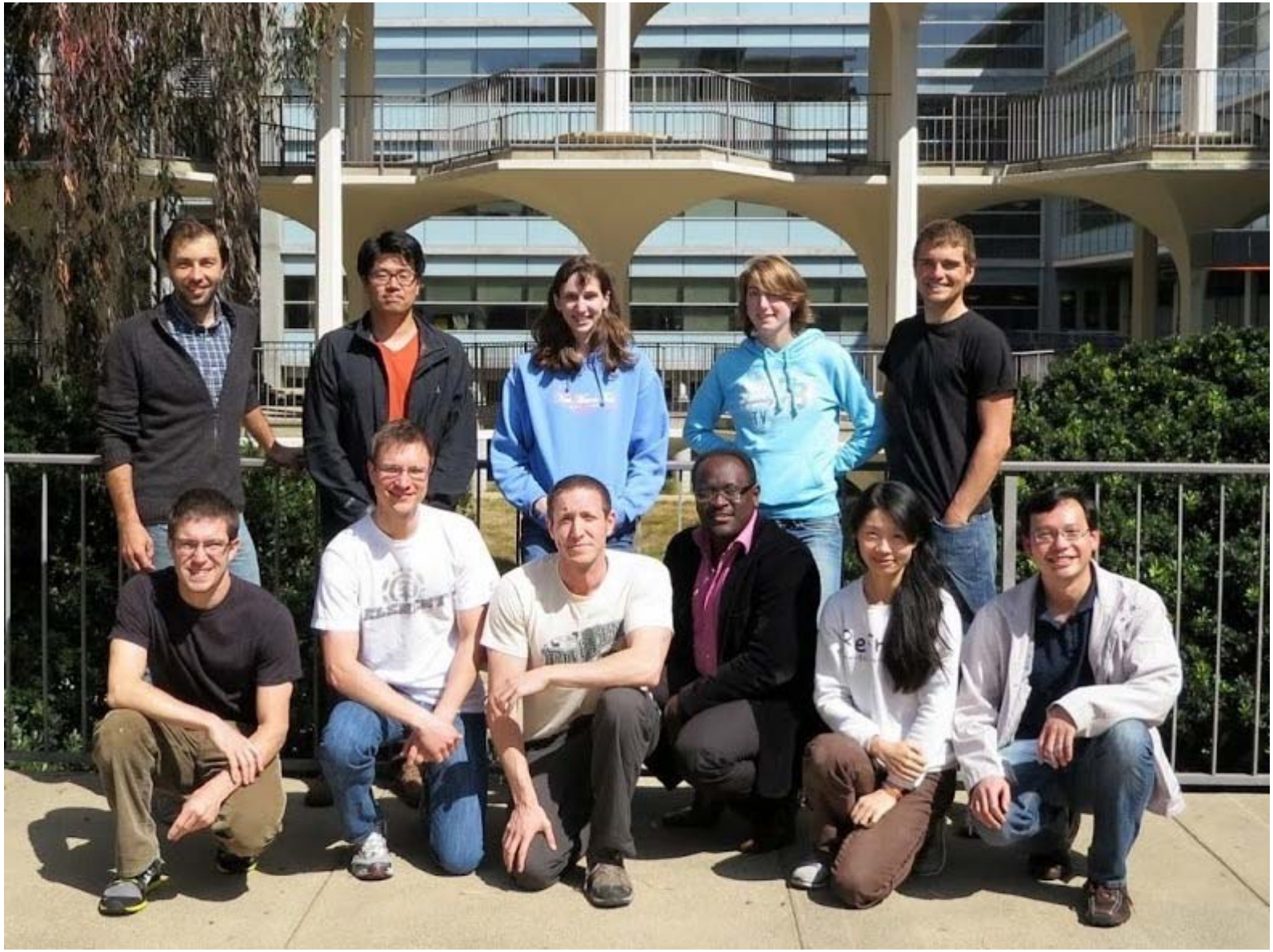
- Coherent Flux
- Detectors
- Beamline Stability (at Slow timescales)
- Quality of Optical Elements

(Talk by Andrej Singer tomorrow)

Other ideas for early science:

- De-wetting, flow, turbulence, critical fluctuations
- Driven, non-equilibrium fluctuations, “random” or non-reversible processes (defect formation, propagation, etc.)
- Ionic diffusion (energy sciences)
- Self-assembly, diffusion – e.g. block copolymers, going beyond R_g
- Lipid bilayers, biological membrane fluctuations
- Dynamics of motor proteins (e.g. kinesin), Growth and Dynamic Instabilities in microtubule, actin bundles
- Protein folding (?)

Our Group at UC San Diego



Acknowledgments:

UC San Diego:

Yeling Dai
Ash Tripathi
Leandra Boucheron
Jacob Stanley
Sebastian Dietze
Moses Marsh
Edwin Fohtung

UChicago:

Binhua Lin & group

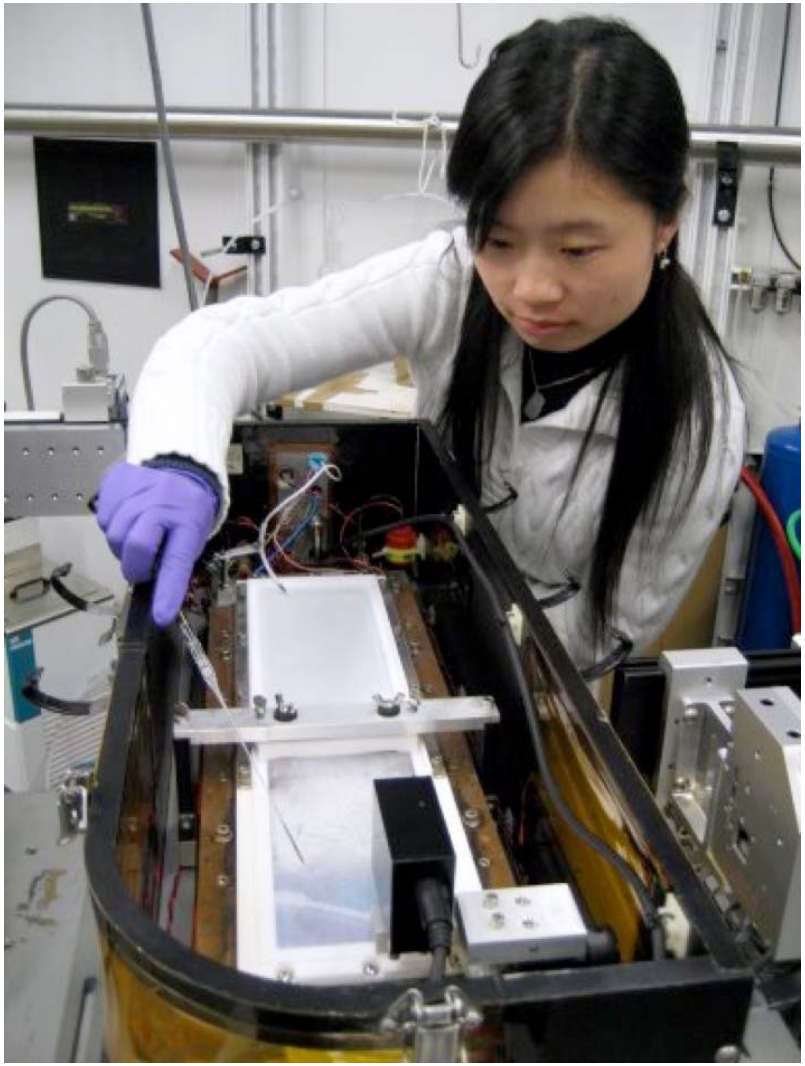
Argonne:

Suresh Narayanan,
Alec Sandy

PNNL: Kyle Alvine

Supported by
DOE-BES,
NSF CAREER

Yeling Dai, PhD, Fall’2013



Please Hire Yeling!