X-ray Photon Correlation Spectroscopy

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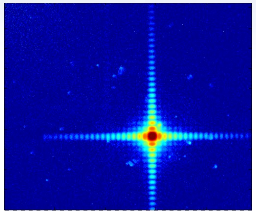
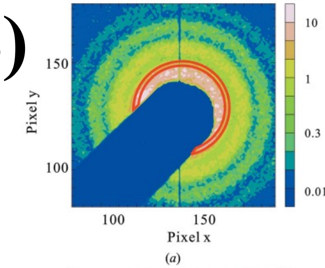
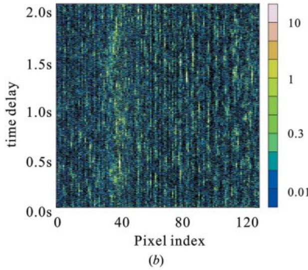
National School on Neutron and X-ray Scattering, Aug. 2016

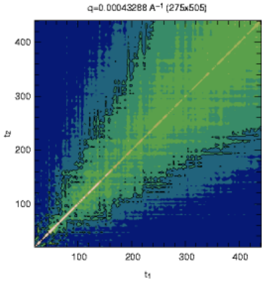
Outline

- **Introduction**
  - Why (oportunities for mesoscale science) and How (cohernece and speckles)
  - Speckle fluctuations, dynamics
  - Speckle Statistics
- **X-ray Photon Correlation Spectroscopy (XPCS)**
  - Time autocorreltion functions, equilibrium dynamics
  - Signal-to-Noise
  - Two-time correlation functions, non-equilibrium dynamics
  - Higher order correlation functions, dynamical heterogeneities
  - X-ray Speckle Visibility Spectroscopy
  - A mini user guide to XPCS
- **XPCS examples**
  - Dynamics of concentrated hard-sphere suspensions. Is there a colloidal glass transition?
  - "Anomalous" relaxations in "jammed" systems
- **Conclusions**





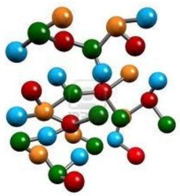


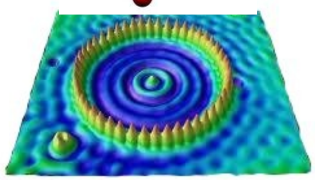


The Next "Big Thing"

- Opportunities for "Mesoscale Science" DOE BESAC report Sept 2012
  http://www.meso2012.com

"Nano" nm



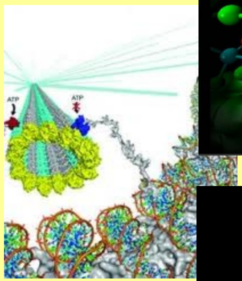


Reductionist Science
"Theory of Everything"

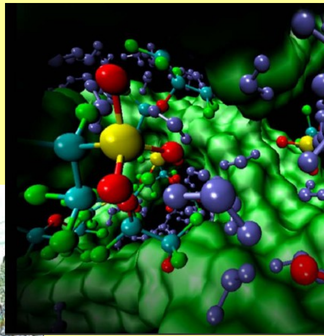
$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$$

Not practical....

Kinesin

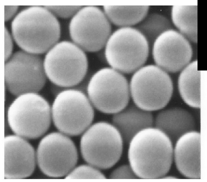


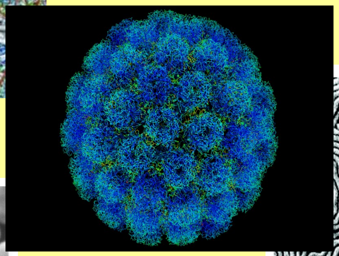
Biomembrane



Cu_3Au

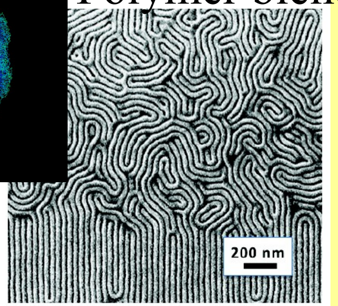
Colloids





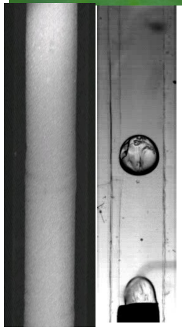
SP40 virus

Polymer blend



"Meso"
in-between

"Macro"
µm, mm, m, ...
hydrodynamics
rheology
...

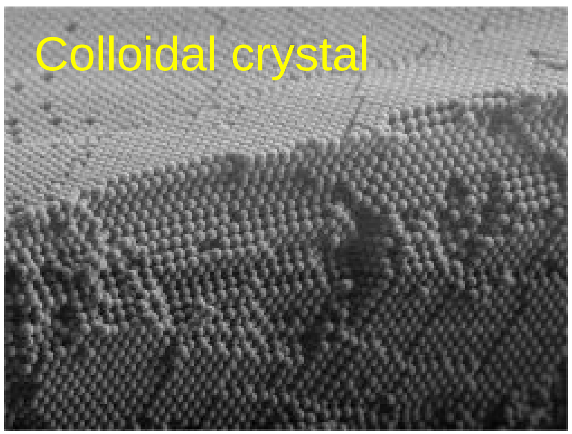


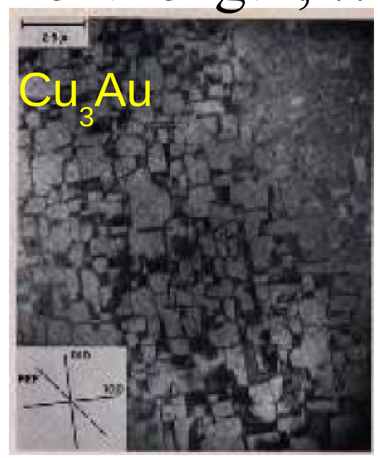
10^{-10} 10^{-9} (1nm) 10^{-8} 10^{-7} **length [m]** 10^{-6} (1µm) 10^{-5} 10^{-4} 10^{-3} (1 mm)

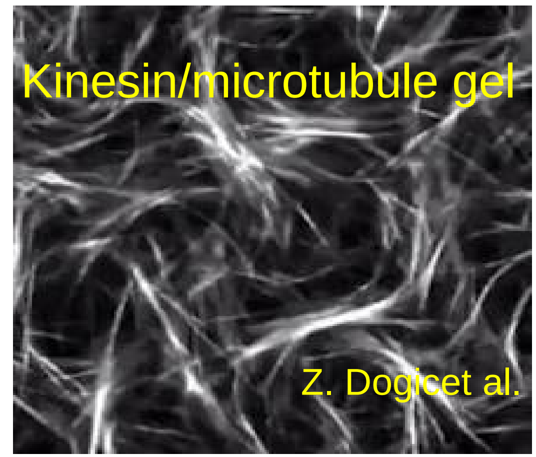
"More is Different"

P.W. Anderson, *Science* **177**, 393 (1972)

- Most *macroscopic properties* of *complex disordered materials emerge* at the *mesoscale* (nm to μm):
  - Mesoscale structure: defects, grain size, macromolecule shape/size, entanglement length, …







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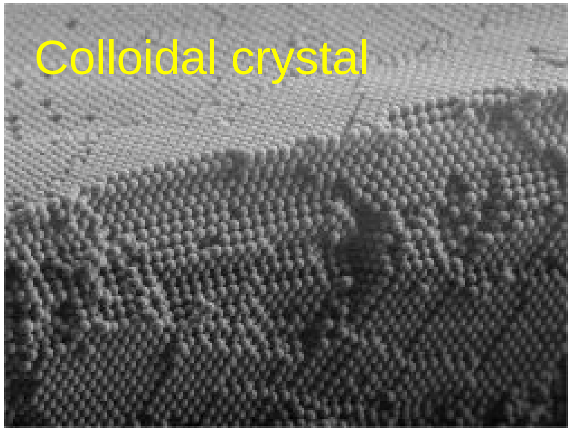
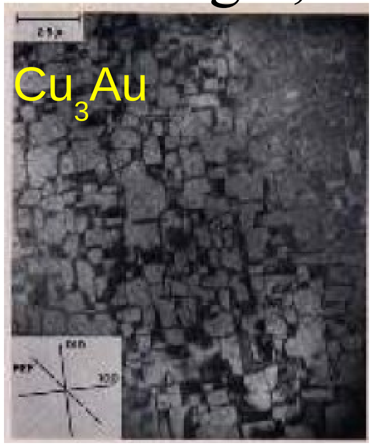
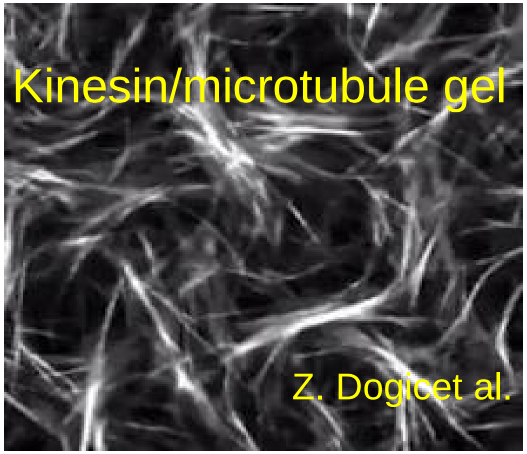




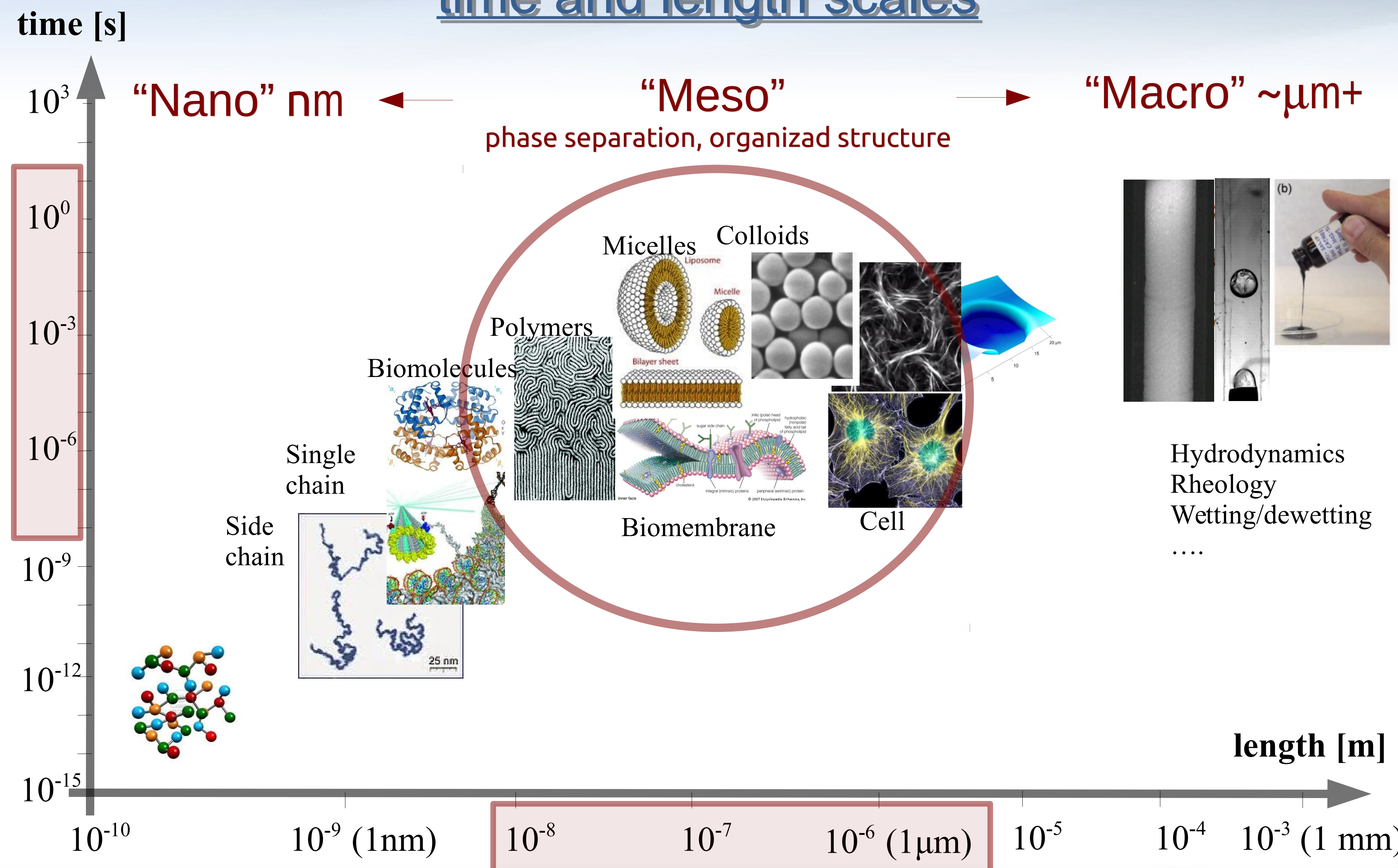


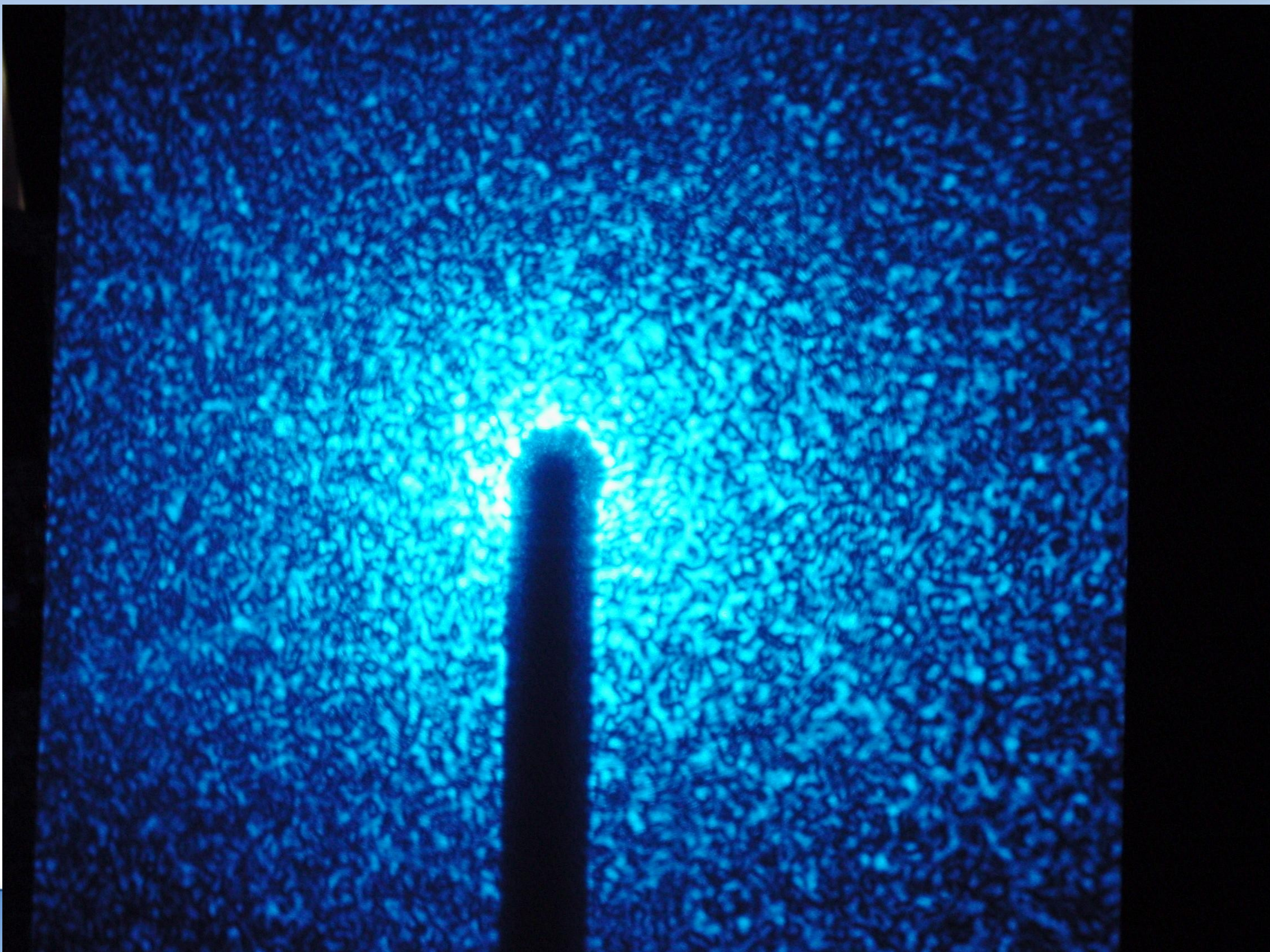
But things are not static !

- Mesoscale Dynamics

Z. Dogic (Brandeis Univ.)
Dynamics of bundled active networks

Dynamics of Materials (soft- and bio-): time and length scales



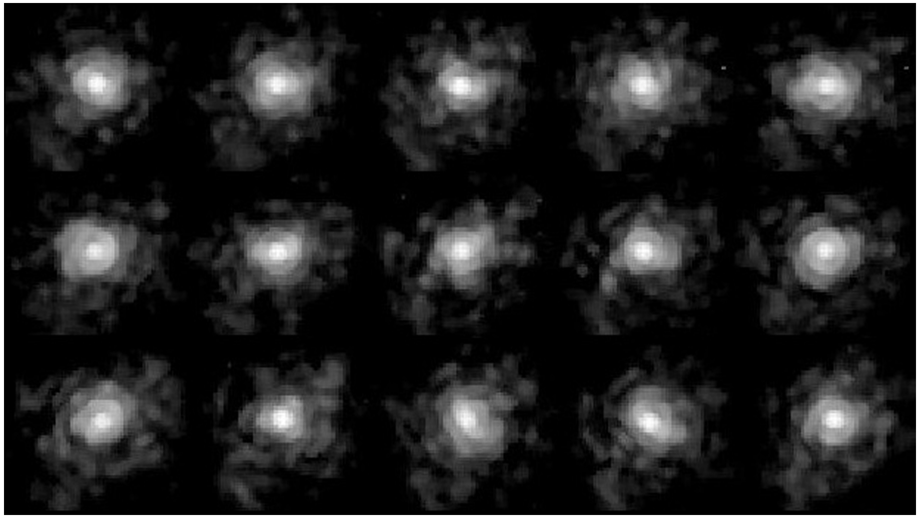


Speckles

Sunset in Alaska

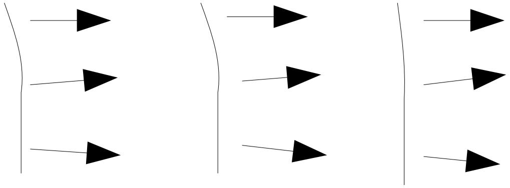
From S. Mochrie

Images of a Stars in a Telescope



J. Codona

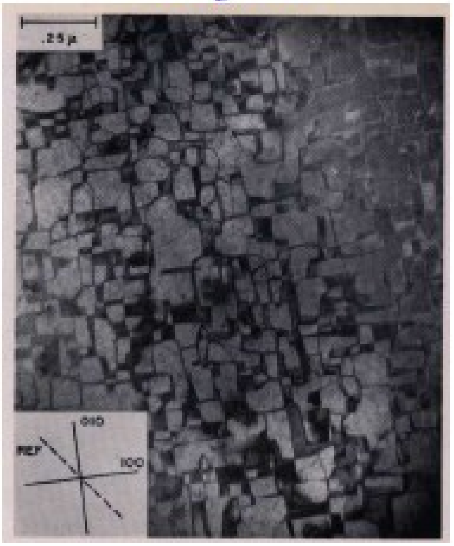
- Stars (far away) = nearly coherent "point-like" sources + fluctuations

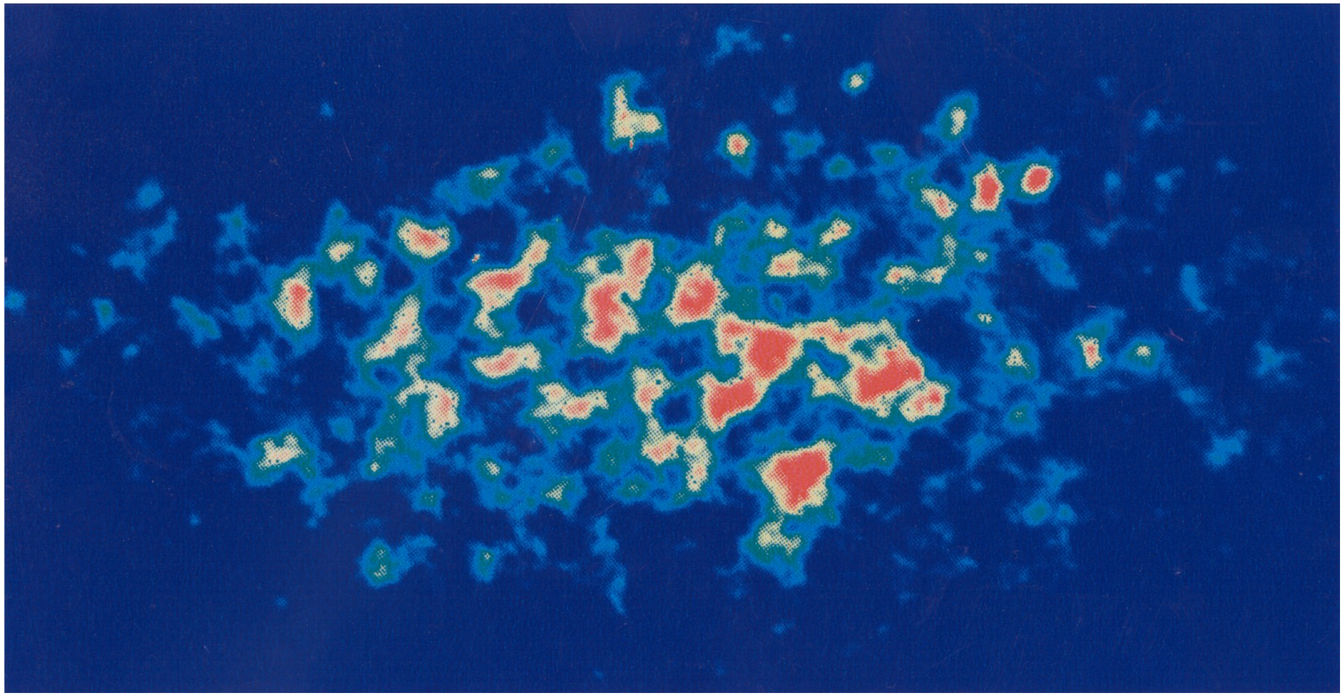


Speckles with (partially) coherent X-rays

Speckles from Cu_3Au

Cu_3Au



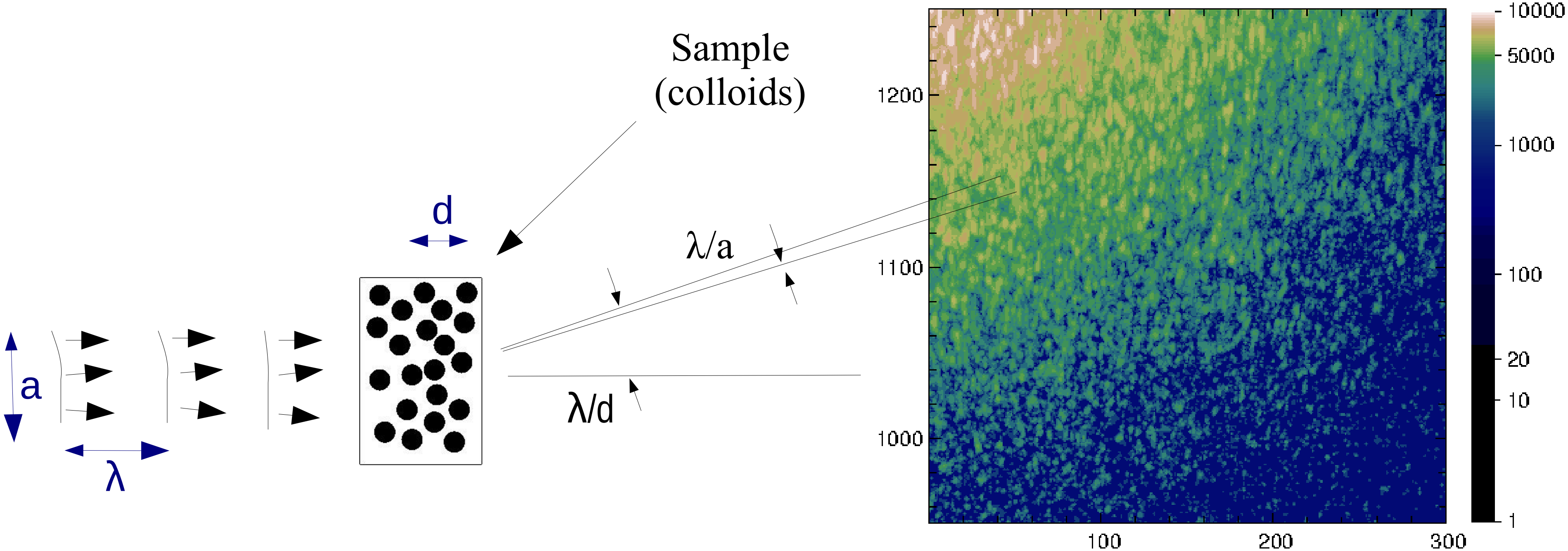


Recorded at X25, NSLS on Kodak film

M. Sutton, *et al. Nature* **352**, 608 (1991)

Speckles with (partially) coherent X-rays

Speckles from colloidal suspensions

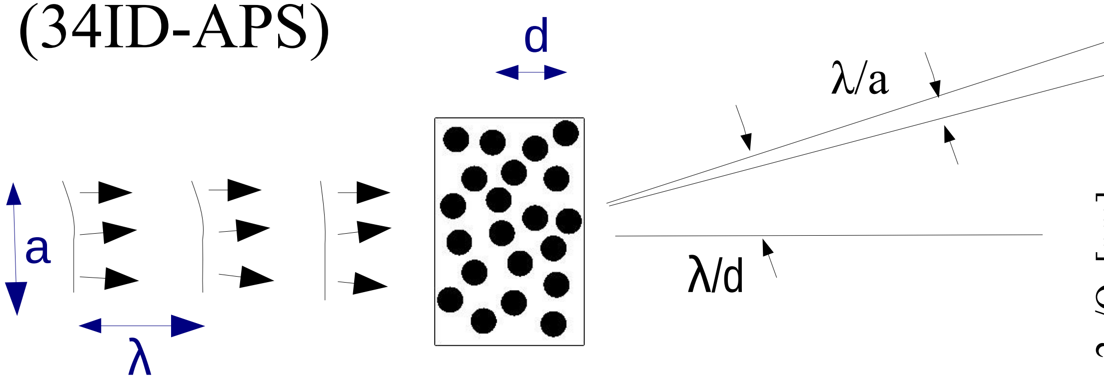


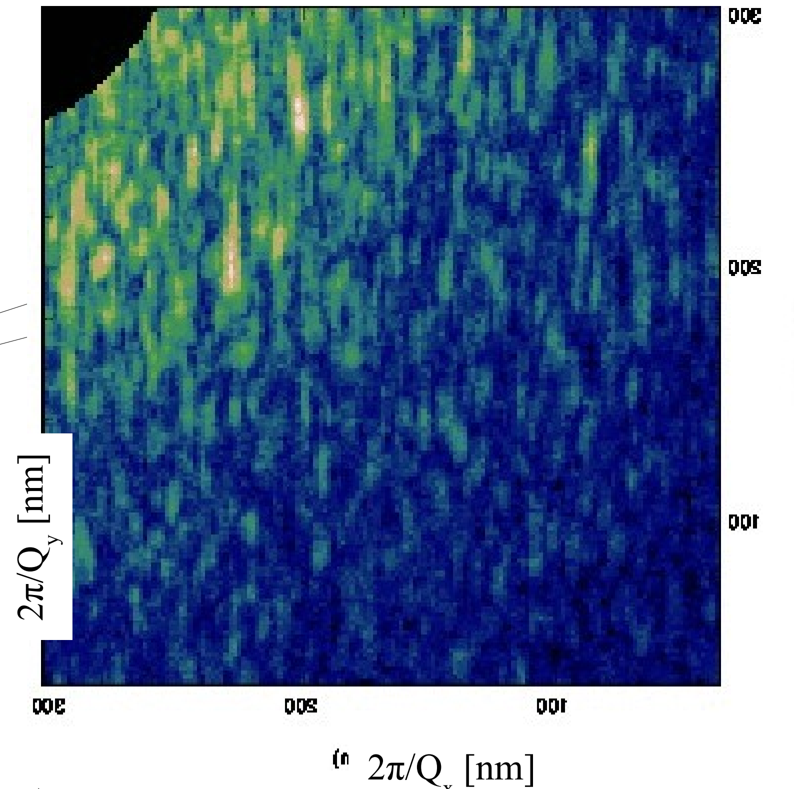
Measured at 34ID with a CCD detector

Speckle Fluctuations & Dynamics

- At high brightness light sources (APS, ESRF, Petra-III, NSLS-II ...) it is possible to measure dynamics by recording “speckle movies”

Partially Coherent X-rays
(34ID-APS)



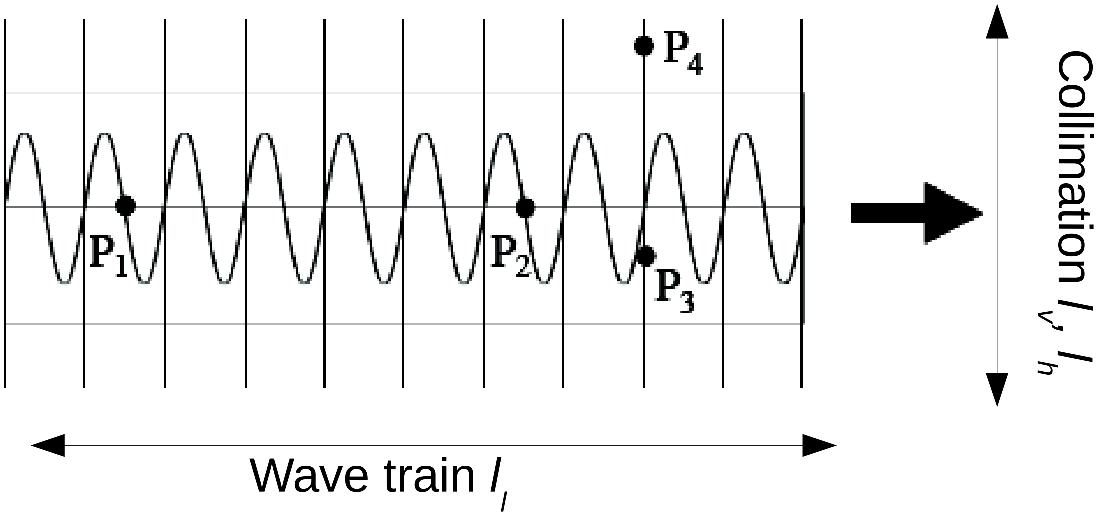


$$g^{(2)}(t) \propto \langle I(t)\, I(0) \rangle$$

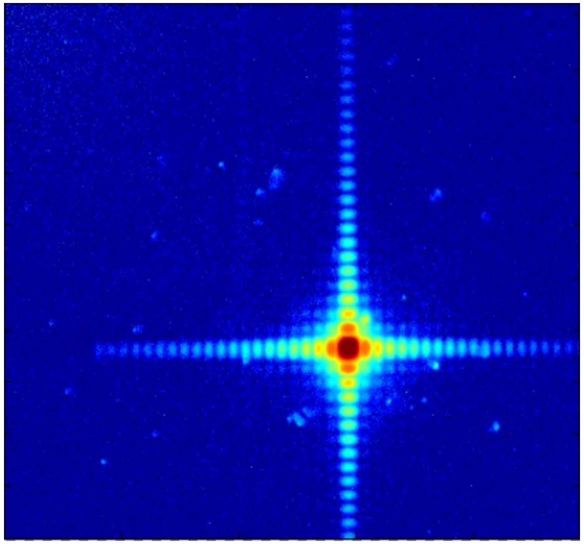
Mini-introduction to coherence

(for more details see D. Mills' lectures tomorrow)

- Coherence =ability to create interference fringes w. good contrast
  - i.e. exists whithin a region where the phase difference between any pair of points is well defined and constant in time
  - Transverse coherence: $\Delta\Phi$(P3:P4)
  - Longitudinal(temporal) coherence: $\Delta\Phi$(P1:P2)



Malcolm Howells, Lecture Notes, ESRF 2007

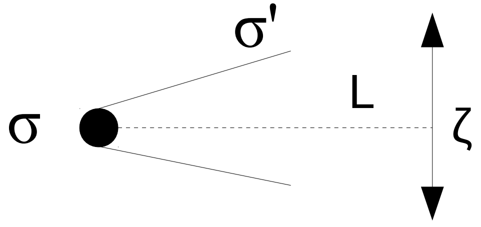


L. Wiegart, CHX, NSLS-II

Transverse coherence

- Ideal *coherent* (Gaussian) source:
  - a source cannot be arbirarily small and arbitrarily well collimated at the same time (diffraction limit)

$$\sigma \cdot \sigma' \simeq \frac{\lambda}{4\pi}$$



  - A transverse coherence length (@ distance L from the source) can then be defined as:

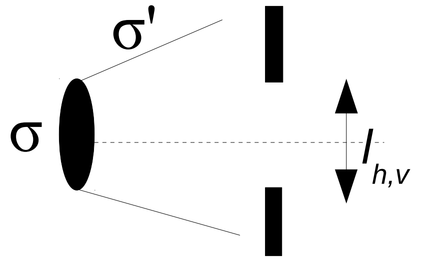
$$l_{h,v} = \frac{\lambda L}{4\pi\sigma_{h,v}}$$

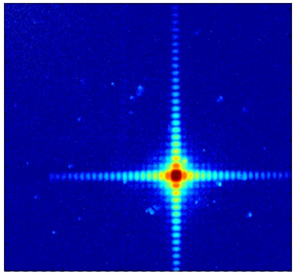
Transverse coherence

- Real Source:
  - The degree of coherence is determined by the phase space volume σσ'; "Heisenberg's inequality":

$$\sigma \cdot \sigma' \geqslant \frac{\lambda}{4\pi}$$

  - "Liouville's theorem": the phase space is conserved by propagation, (ideal) crystal optics, (ideal) focusing, etc.
  - To obtain a more coherent beam (at the expense of flux!), the phase space can be limited/reduced by collimation (a set of slits)



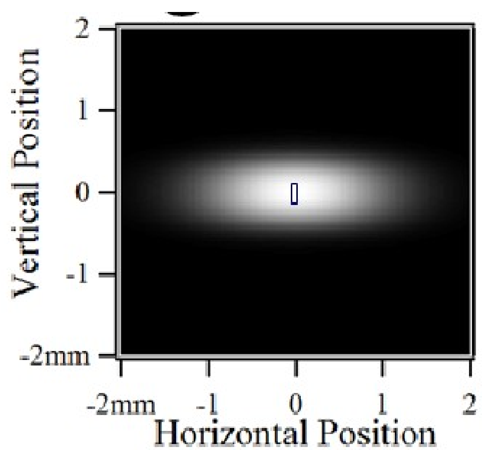


Coherence of (NSLS-II) Sychrotron Sources

- Real Source:
  - Number of coherent modes:

$$\sigma \cdot \sigma' = N \frac{\lambda}{4\pi}, N \geqslant 1$$

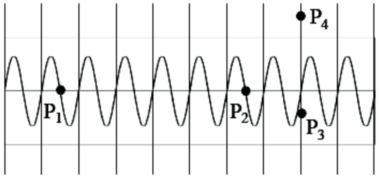
  - E.g. IVU20 undulator source at CHX, NSLS-II



E (keV)	6	8	10	12	16
σ_h (μm)	34.3	34.2	34.1	34.2	34.2
σ_h' (μrad)	18.3	18.3	18.0	18.2	18.2
σ_v (μm)	8.8	8.0	7.5	7.6	7.4
σ_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

Longitudinal coherence

- Longitudinal (temporal) coherence:



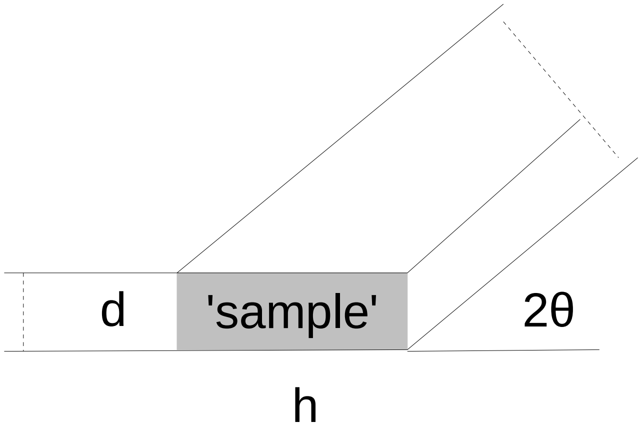
$$\frac{\delta\lambda}{\lambda} \approx \frac{1}{N}, l_l = \lambda N \qquad l_l \approx \frac{\lambda^2}{\delta\lambda}$$

- Experimental requirement:

  max optical path diff. < l_l

- In a transmission geometry
  - Sample thinckness *h*, beam size *d*

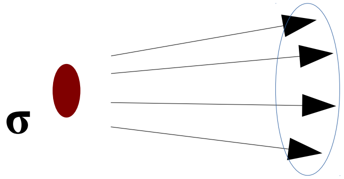
$$h \sin^2(2\theta) + d \sin(\theta) \leqslant l_l$$



A. Madsen, A. Fluerasu, B. Ruta, Structural Dynamics of Materials probed by X-ray Photon Correlation Spectroscopy, Springer, 2014

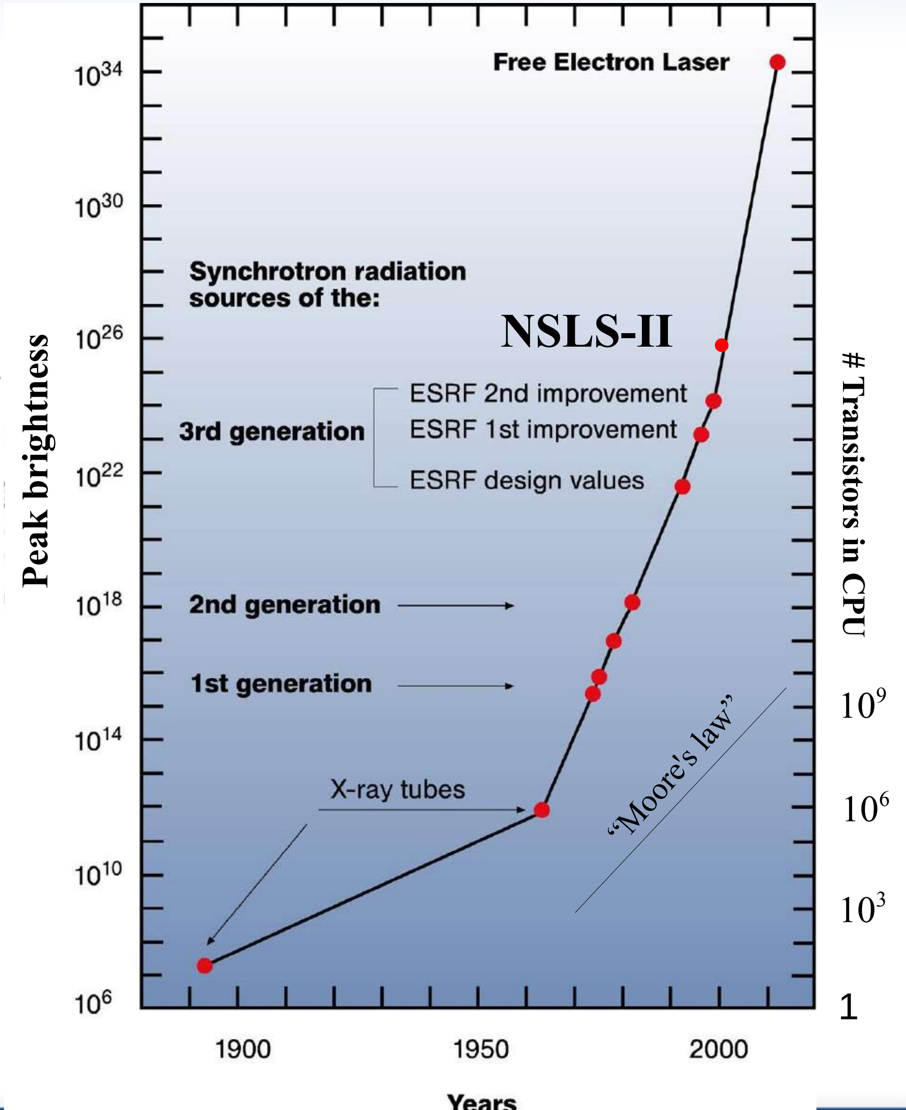
Synchrotron Source Brightness

- Key for XPCS: **Brightness**



$$\frac{\textit{Spectral Power}}{\textit{phase space volume}}$$

Brightness=Coherence
increased faster than Moore's law!!



- Coherent Flux $I \propto B\,\lambda^2$
- CHX, NSLS-II (~10 keV)
  - $B \sim 10^{21}$ ph/s/%bw/mm^2/mrad^2
  - $I \sim 10^{11}$ ph/s

Correlation Functions

- Coherence → measures dynamics

$$\langle I(q,t)\,I(q,t+\delta t)\rangle = \langle I(q)\rangle^2 + \beta(q)(\ldots)|S(q,t)|^2$$

- Intensity autocorrelation function, dynamic structure factor & Siegert relationship

$$g^{(2)}(q,t) = \frac{\langle I(q,t)\,I(q,t+\delta t)\rangle}{\langle I(q)\rangle^2} = 1 + \beta(q)\left|\frac{S(q,t)}{S(q,0)}\right|^2$$

- Intermediate Scattering Function

$$g^{(1)}(q,t) = \left|\frac{S(q,t)}{S(q,0)}\right| \propto \iint \rho_n(q)\,\rho_m(q)\exp\left(iq\left[r_n(0) - r_m(t)\right]\right)$$

Correlation Functions

- Signal-to-noise (of $g^{(2)}$) – it's complicated!!

$$R_{sn} = K(T\tau\Omega_x\Omega_z)^{1/2}\Sigma W \exp(-W\Lambda)\tilde{B}(\Delta E/E) r_{snx} r_{snz}$$

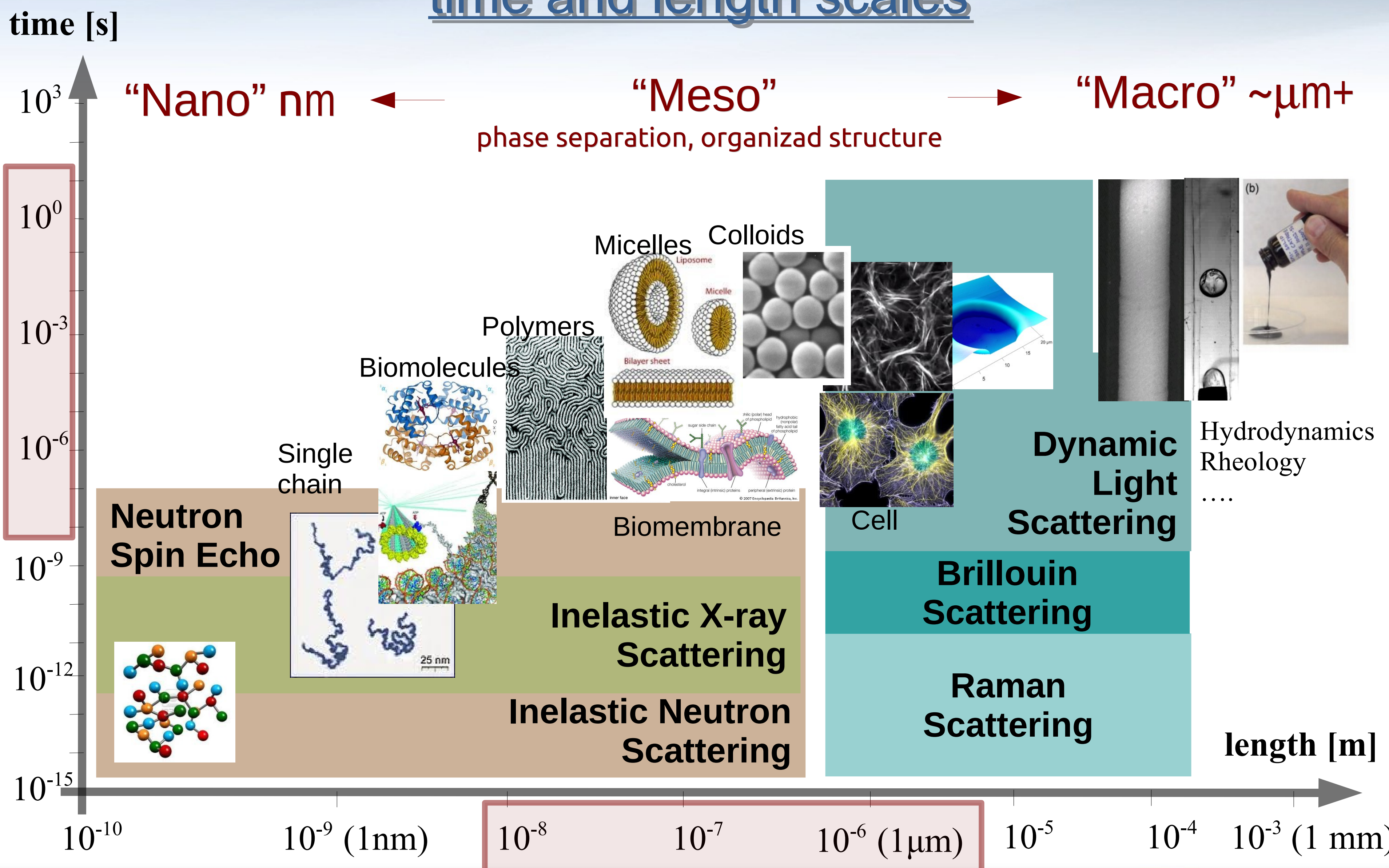
K = detector efficiency
T = total experiment duration
τ = accumulation time
Ω = angle subtended by Q of interest
Σ = scattering cross section per unit volume
W = sample thickness
Λ= 1/attenuation length
B = source brilliance
ΔE/E = normalized energy spread
r = factor depending on source size, pixel size, and slit size

- SNR ~ $B\tau^{1/2}$...
- Need an area det
- ~small pixels
- fast frame rates

Eiger 1M detector (Dectris)

Lumma *et al. Rev. Sci. Instrum.* 71, 3274 (2000)
Jackeman *et al.* J. Phys. A, 5, 517 (1971)

Dynamics of Materials (soft- and bio-): time and length scales



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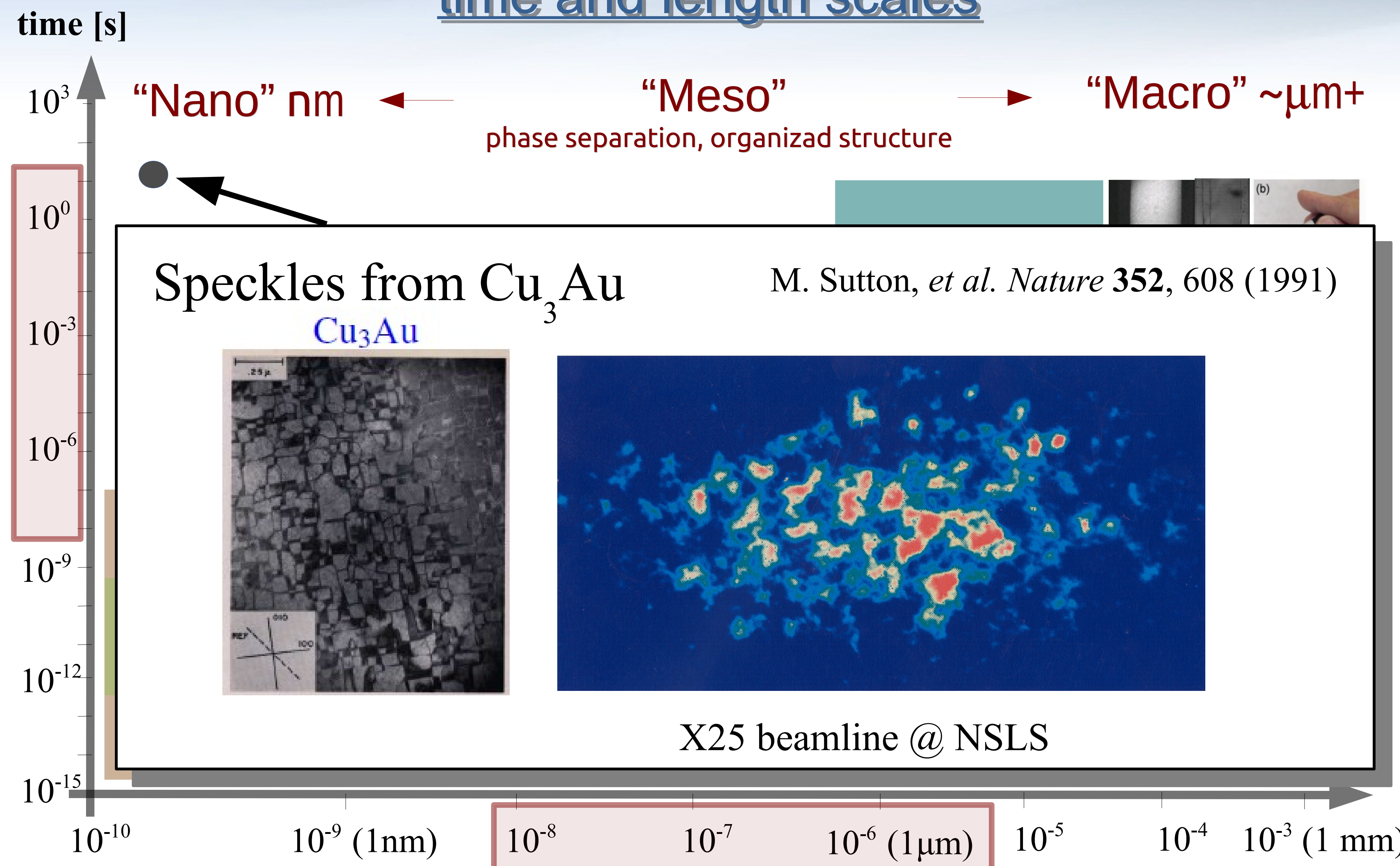

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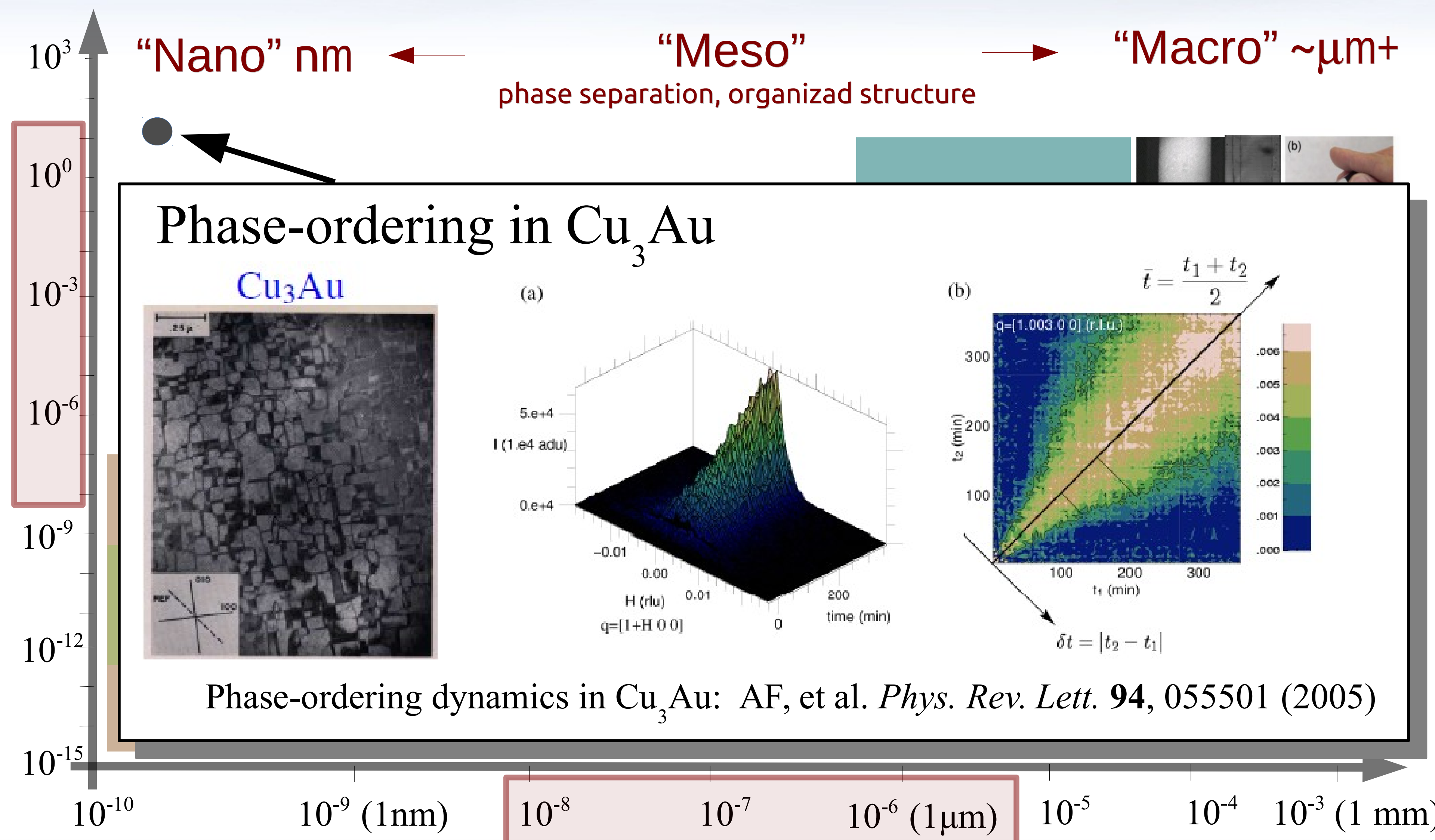


Phase-ordering dynamics in Cu_3Au: AF, et al. *Phys. Rev. Lett.* **94**, 055501 (2005)

Dynamics of Materials (soft- and bio-): time and length scales

time [s]

10^{3}

10^{0}

10^{-3}

10^{-6}

10^{-9}

10^{-12}

10^{-15}

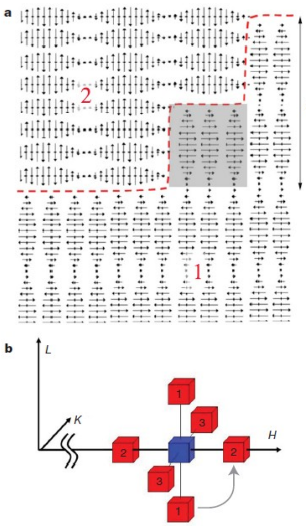
"Nano" nm ← "Meso" → "Macro" ~µm+

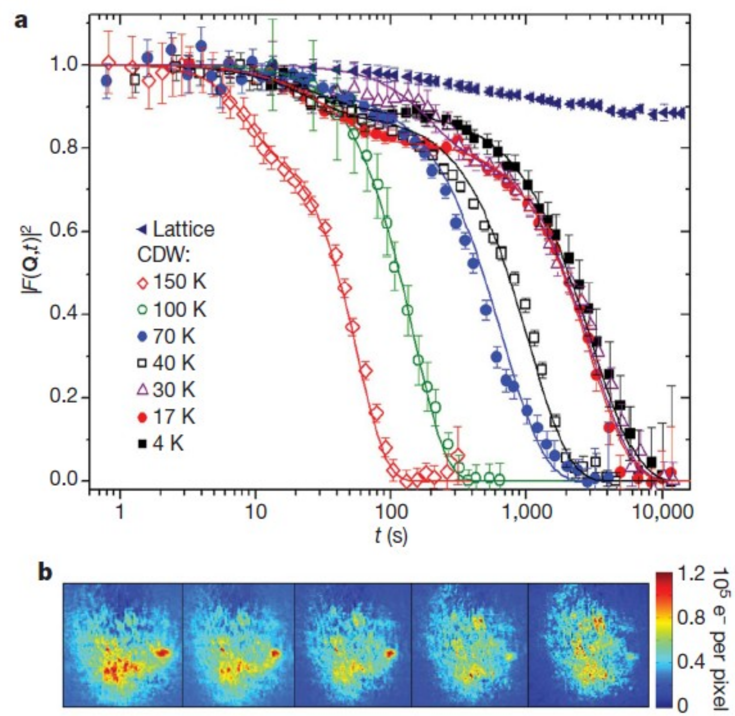
phase separation, organizad structure

Antiferromagentic domain fluctuations in Chromium

8-ID, APS

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





10^{-10} 10^{-9} (1nm) 10^{-8} 10^{-7} 10^{-6} (1µm) 10^{-5} 10^{-4} 10^{-3} (1 mm)

Dynamics of Materials (soft- and bio-): time and length scales

time [s]

10^{3} “Nano” nm ← “Meso” → “Macro” ~µm+

phase separation, organizad structure

10^{0}

10^{-3}

10^{-6}

10^{-9}

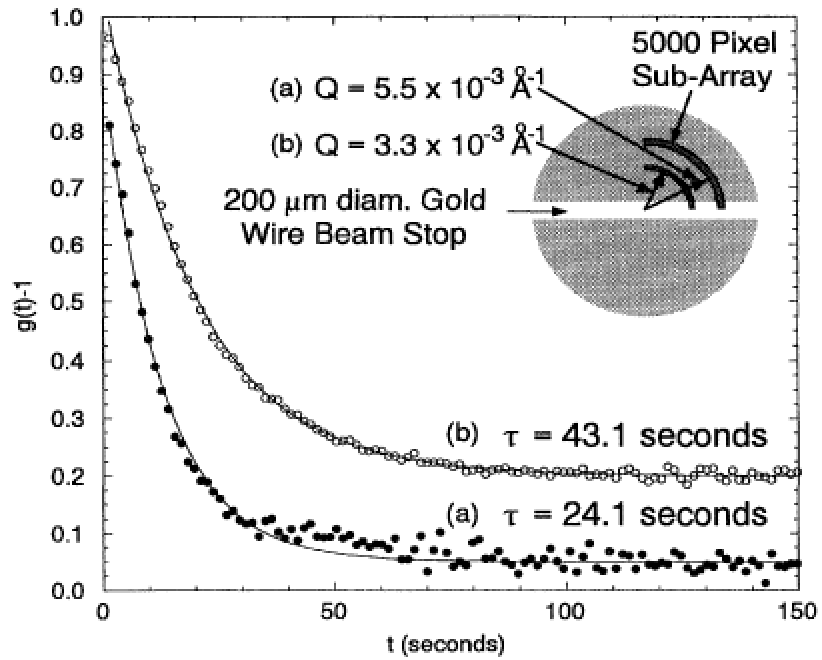
10^{-12}

10^{-15}

Brownian motion: Au colloids in glycerol

S.B. Dierker, R. Pindak *et al.*
Phys. Rev. Lett. **75**, 449 (1995)

X25 beamline @ NSLS



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Dynamics of Materials (soft- and bio-): time and length scales

time [s]

10^{3} 10^{0} 10^{-3} 10^{-6} 10^{-9} 10^{-12} 10^{-15}

"Nano" nm ← "Meso" → "Macro" ~µm+

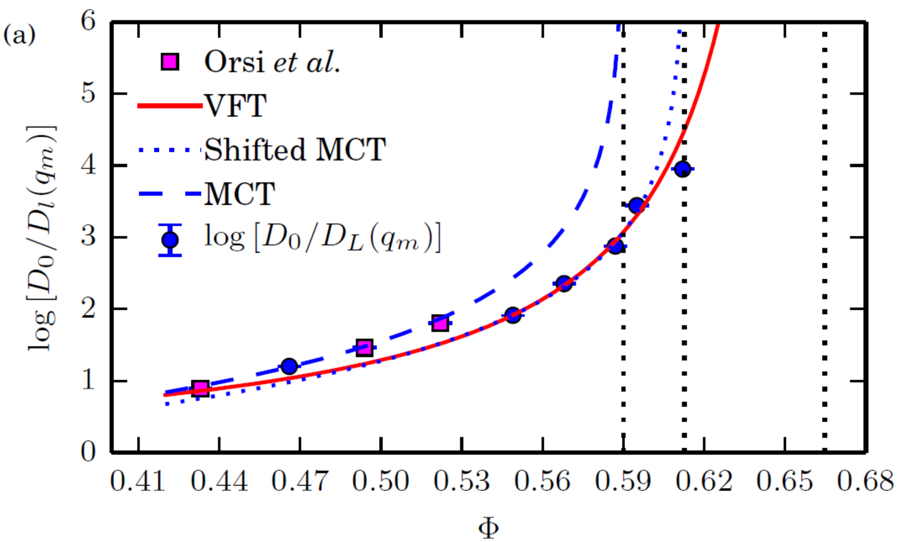
phase separation, organizad structure

Micell… Colloids

Brownian motion: high density PMMA colloids

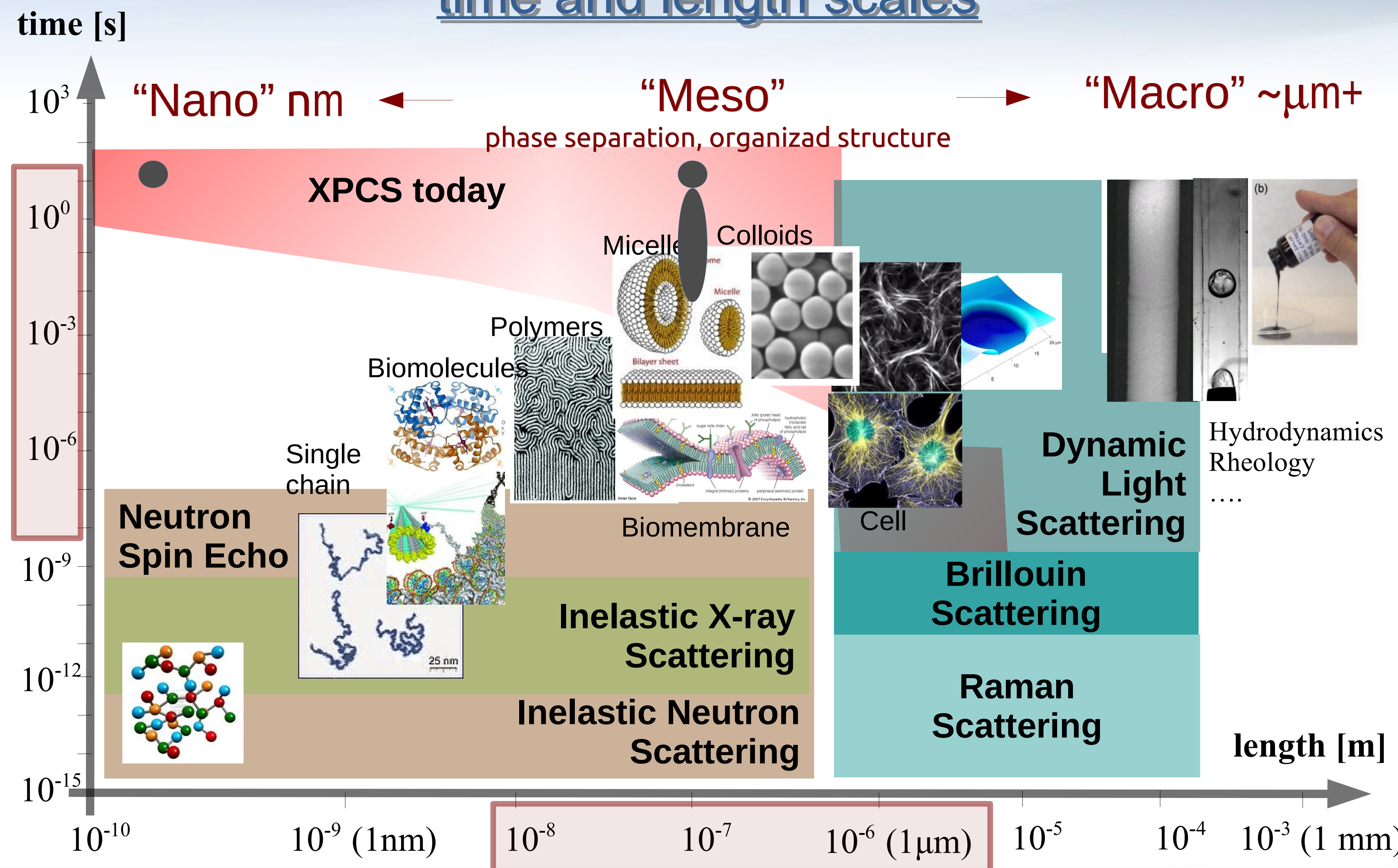
P. Kwasniewski *et al.*
Soft Matter. **10**, 8698 (2014)

ID10 beamline @ ESRF

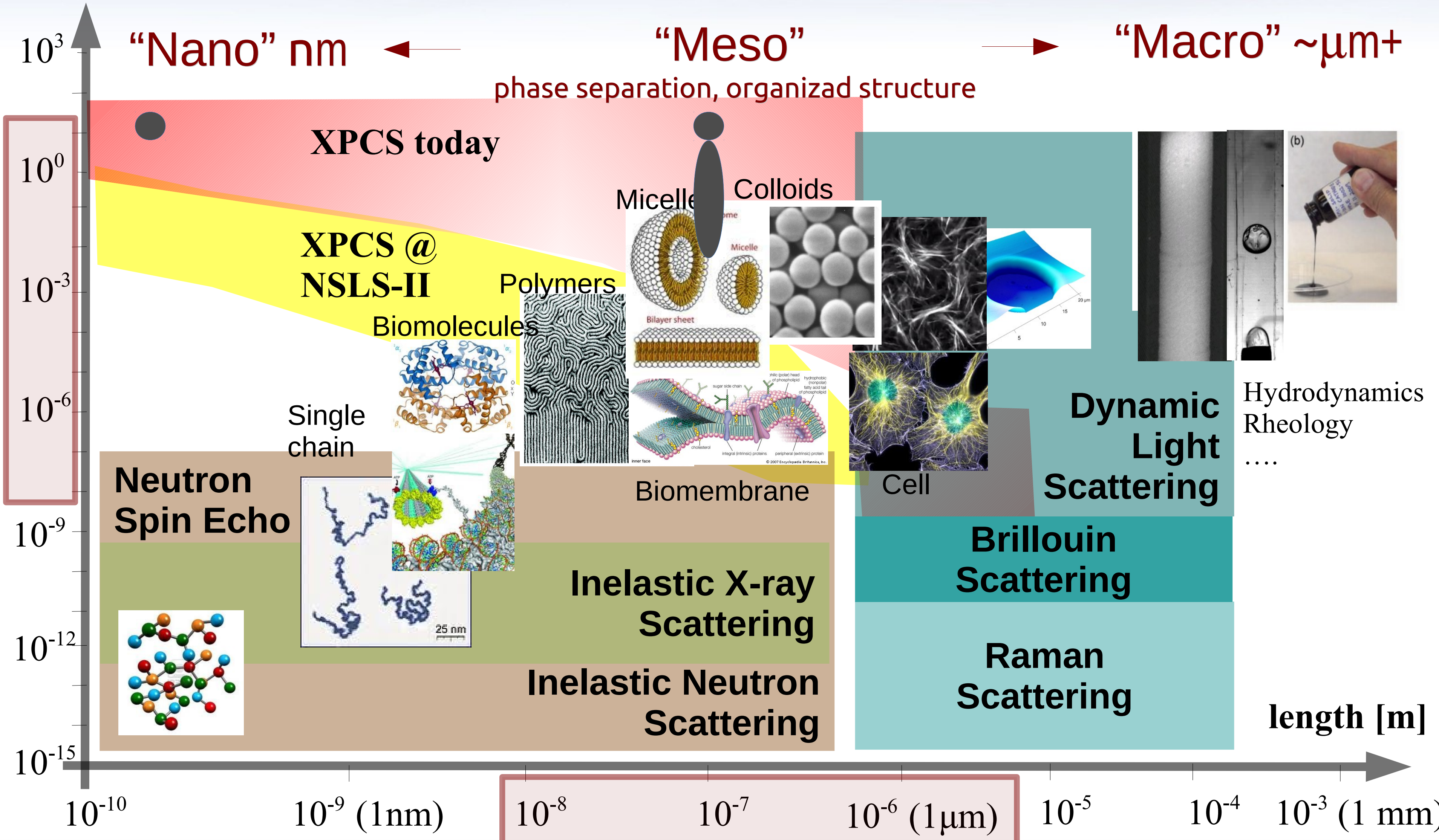


10^{-10} 10^{-9} (1nm) 10^{-8} 10^{-7} 10^{-6} (1µm) 10^{-5} 10^{-4} 10^{-3} (1 mm)

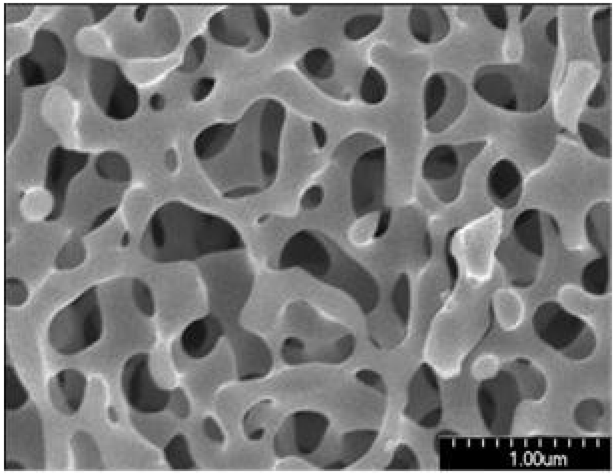
Dynamics of Materials (soft- and bio-): time and length scales



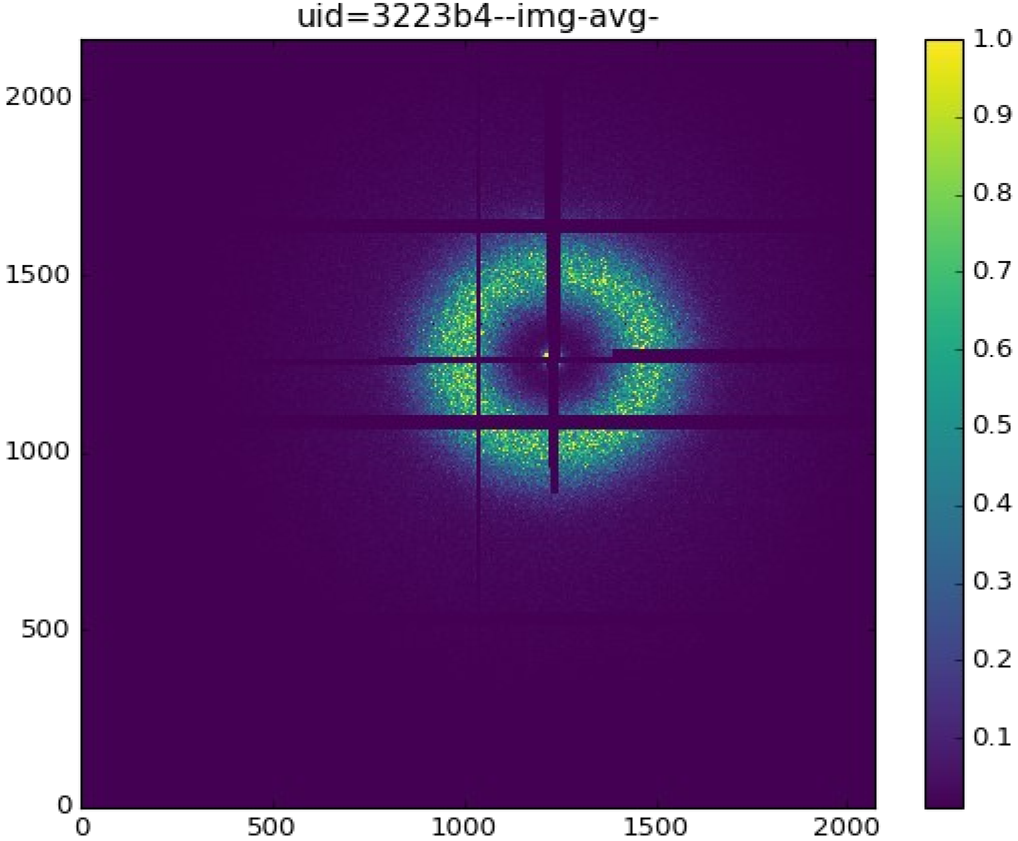
Dynamics of Materials (soft- and bio-): time and length scales



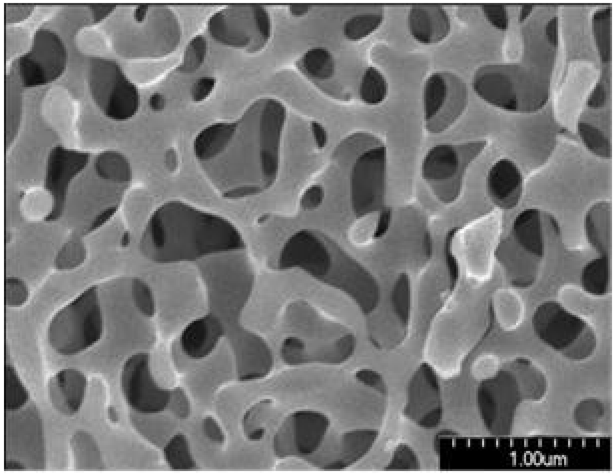
Speckles



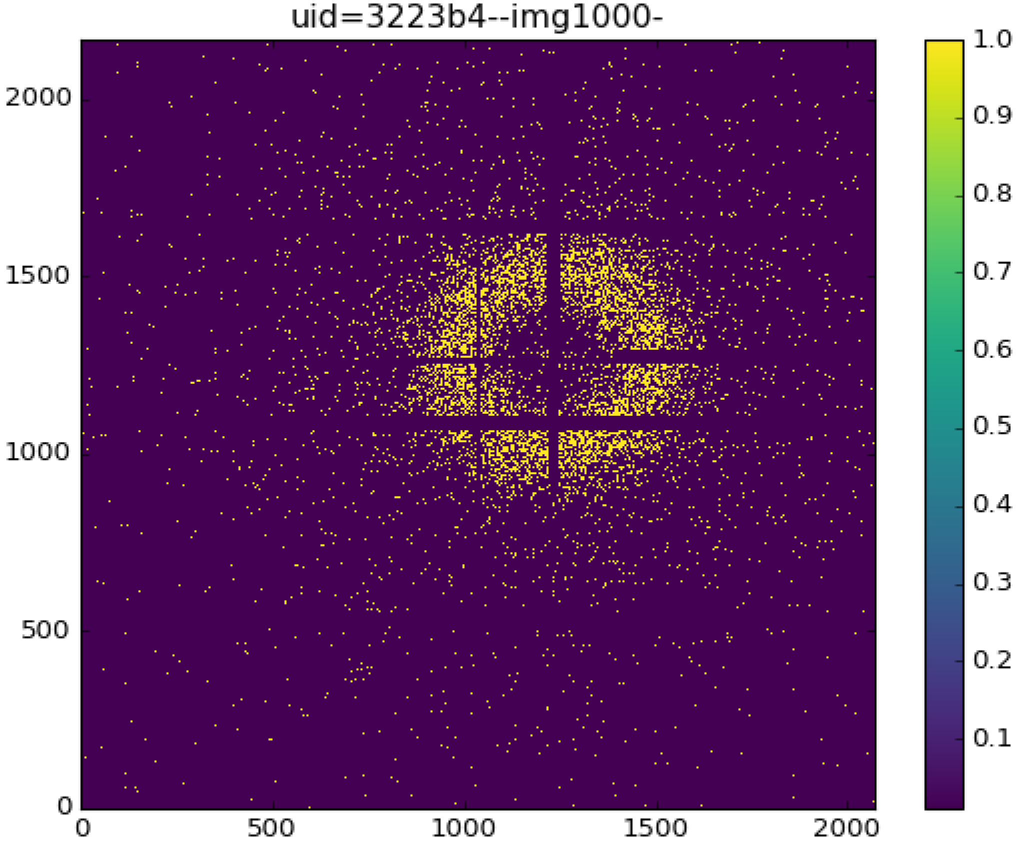
Schott CoralPor porous glass sample and scattering image recorded with the Eiger 4M detector and averaged over 10,000 fr recorded at 750 Hz (1.33 ms)



Speckles

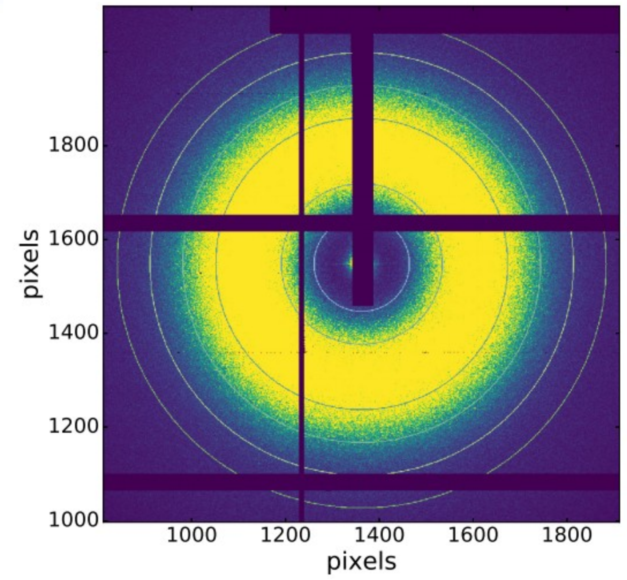


Schott CoralPor porous glass sample and scattering image recorded with the Eiger 4M detector in ***1.33 ms*** !

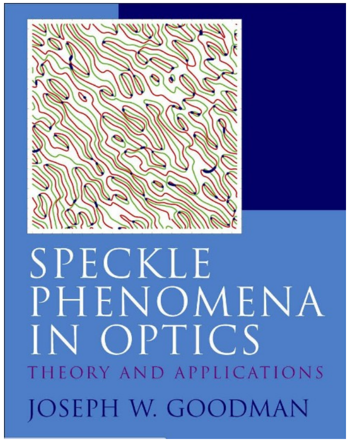


Speckles

- Speckle statistics is described by the negative binomial distribution with
  - $M=M(q,T)$: # of coherent modes
  - $K=K(q,T)$: avg # of counts at a given q/ring



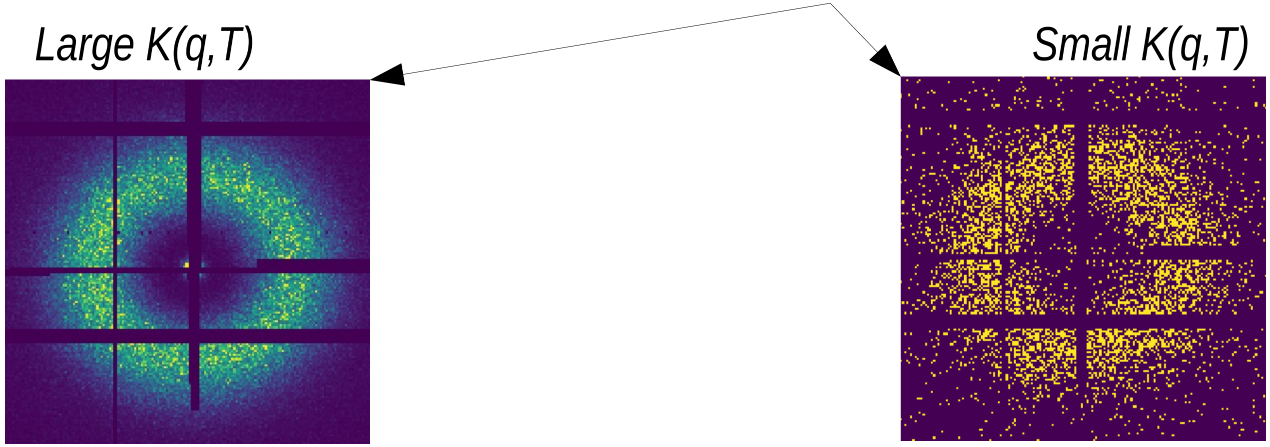
$$P(K) = \frac{\Gamma(K+M)}{\Gamma(K+1)\Gamma(M)} \left(\frac{M}{\langle K\rangle + M}\right)^M \left(\frac{\langle K\rangle}{M+\langle K\rangle}\right)^K$$



Speckles

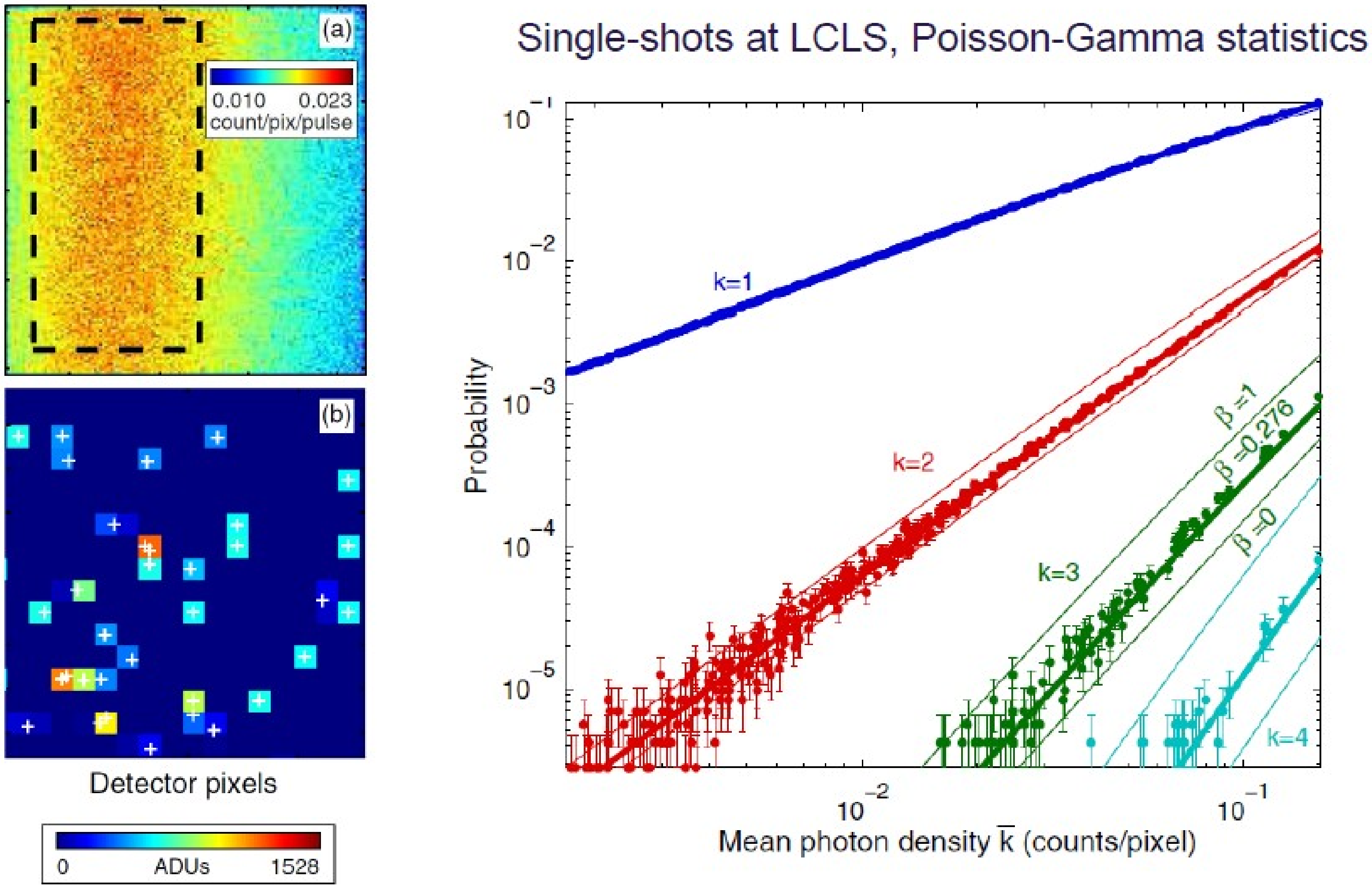
- Normalized variance becomes:

$$var_K(q,T) = \frac{1}{M(q,T)} + \frac{1}{K(q,T)}$$



Mandel, L. (1958). *Proc. Phys. Soc.* **72**, 1037.
Mandel, L. (1959). *Proc. Phys. Soc.* **74**, 233.
Goodman, J. W. (2007). *Speckle Phenomena in Optics: Theory and Applications*. Englewood: Roberts and Company.

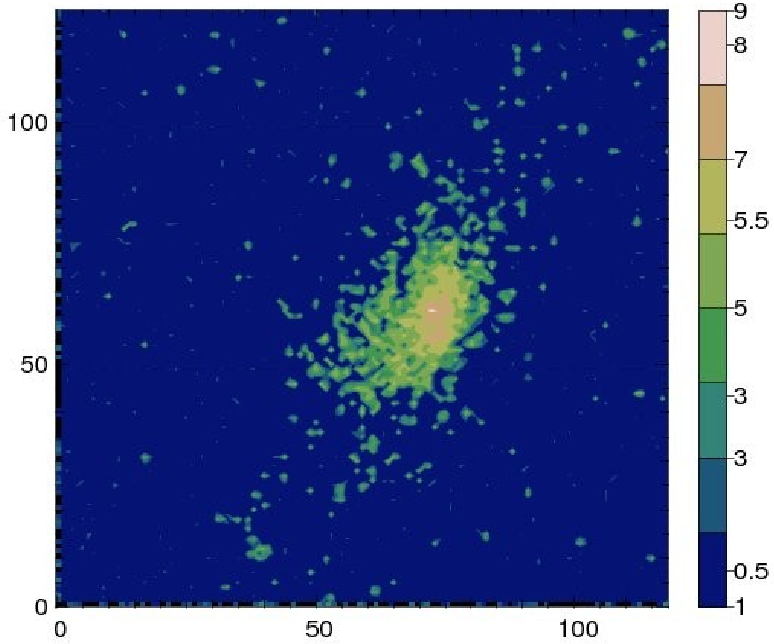
Speckles from single shot LCLS pulses

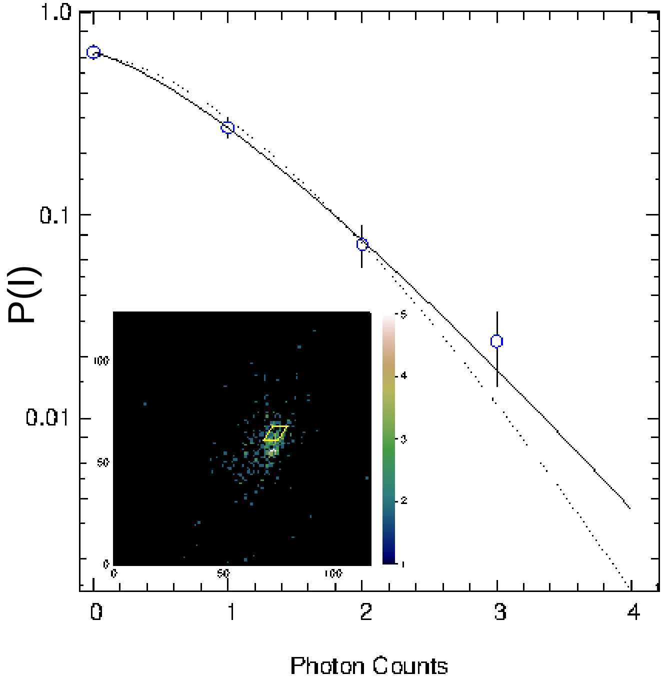


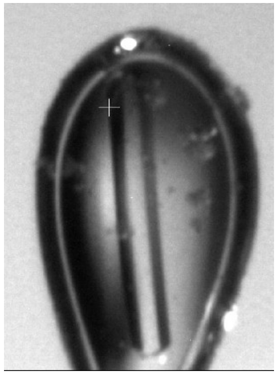
S. O. Hruszkewycz et al., PRL**109**, 185502 (2012)

X-ray Speckles come to life

- Molecular motion in protein microcrystals coupled over large scales generate diffuse scattering around the main Bragg peaks.





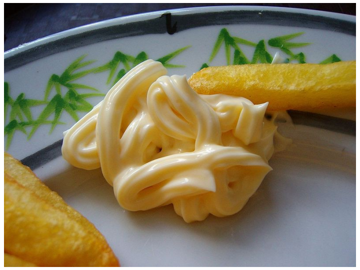


L. Li *et al.*, unpublished

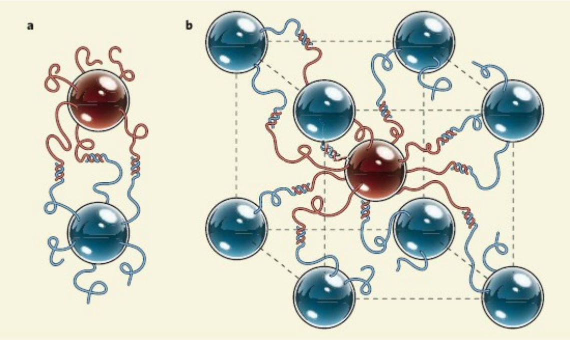
Colloids

- Colloids are ubiquitous:
  - Particles (1-1000 nm) of dispersed phase in dispersion medium






- Phase behavior;
  The "magic" of self-assembly ...
  - Opals are dried "polycrystalline" colloids"patchy colloids" can be elementary blocks for programmable self-assembly of "colloidal materials"
    (O. Gang, BNL & Columbia)
  - etc

Colloids: simple diffusive dynamics

- Intermediate Scattering Function

$$g^{(1)}(q,t) \propto \sum_{i=1}^{N} \sum_{i=1}^{N} \exp(iq[r_i(0) - r_j(t)])$$

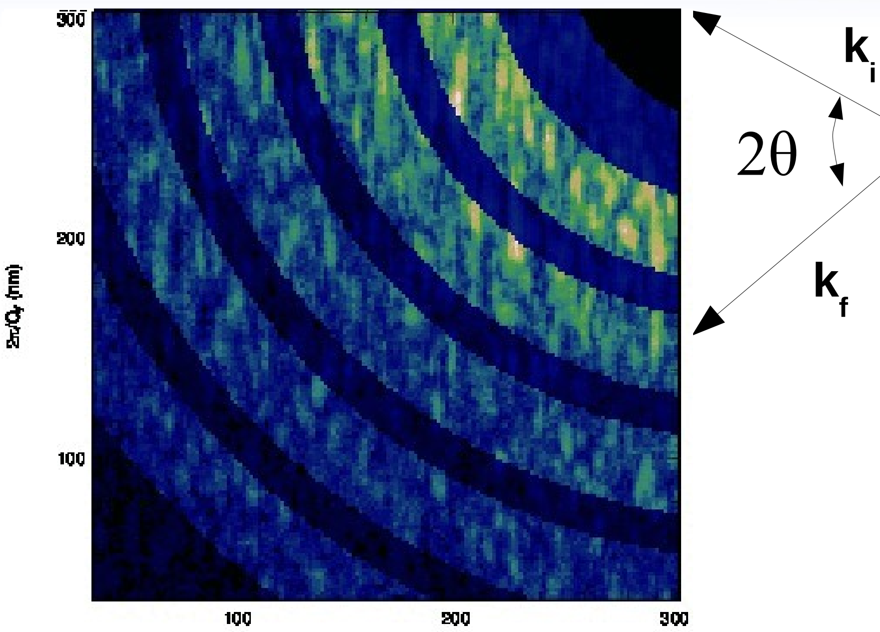
- Mean square displacement

$$\langle [r_i(0) - r_j(t)]^2 \rangle = 6 D_0 t \qquad D_0 = \frac{k_B T}{6 \pi \eta a}$$

- Intermediate Scattering Function

$$g^{(1)}(q,t) = \exp(-D_0 q^2 t)$$

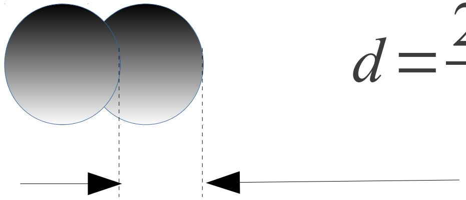
Colloidal Dynamics with XPCS



$2\pi/Q_x$ [nm]

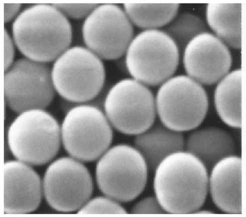
$$q = \frac{4\pi}{\lambda}\sin\left(\frac{2\theta}{2}\right)$$

- Measures time scale associated with displacement of colloids



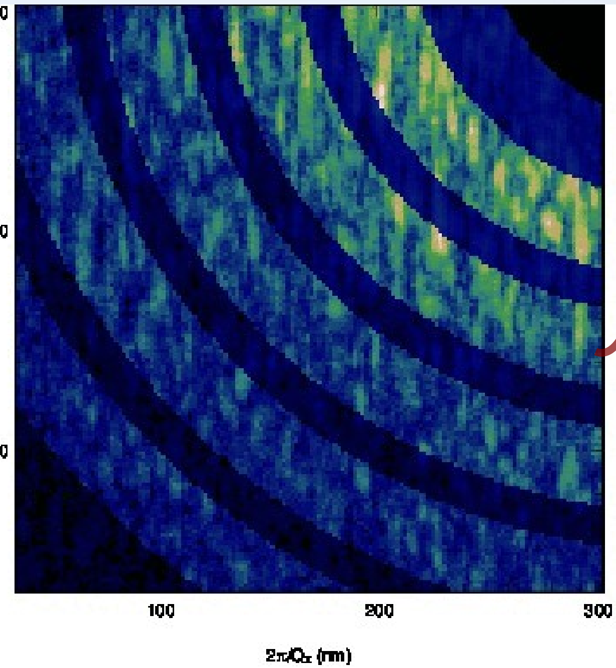
$$d = \frac{2\pi}{q}$$

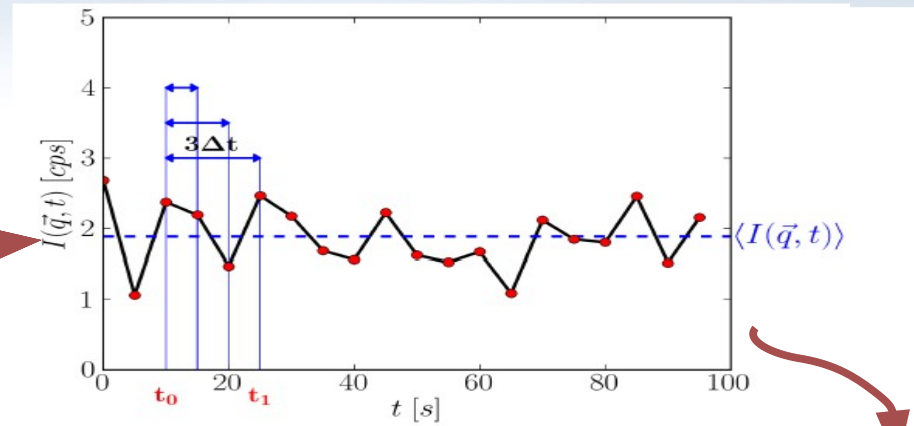
- i.e. measures dynamic structure factor *S(q,t)*
- By averaging over ~10^{11} particles

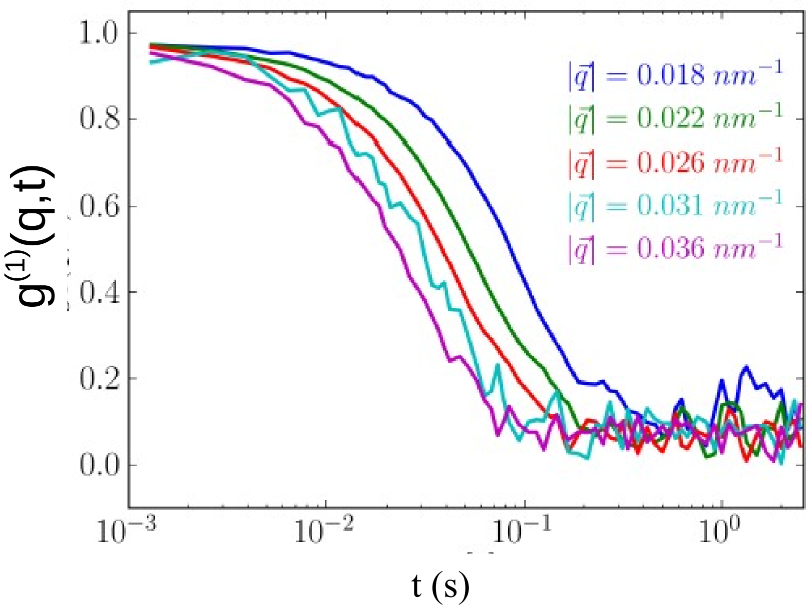


- For different *q* values

Colloidal Dynamics with XPCS



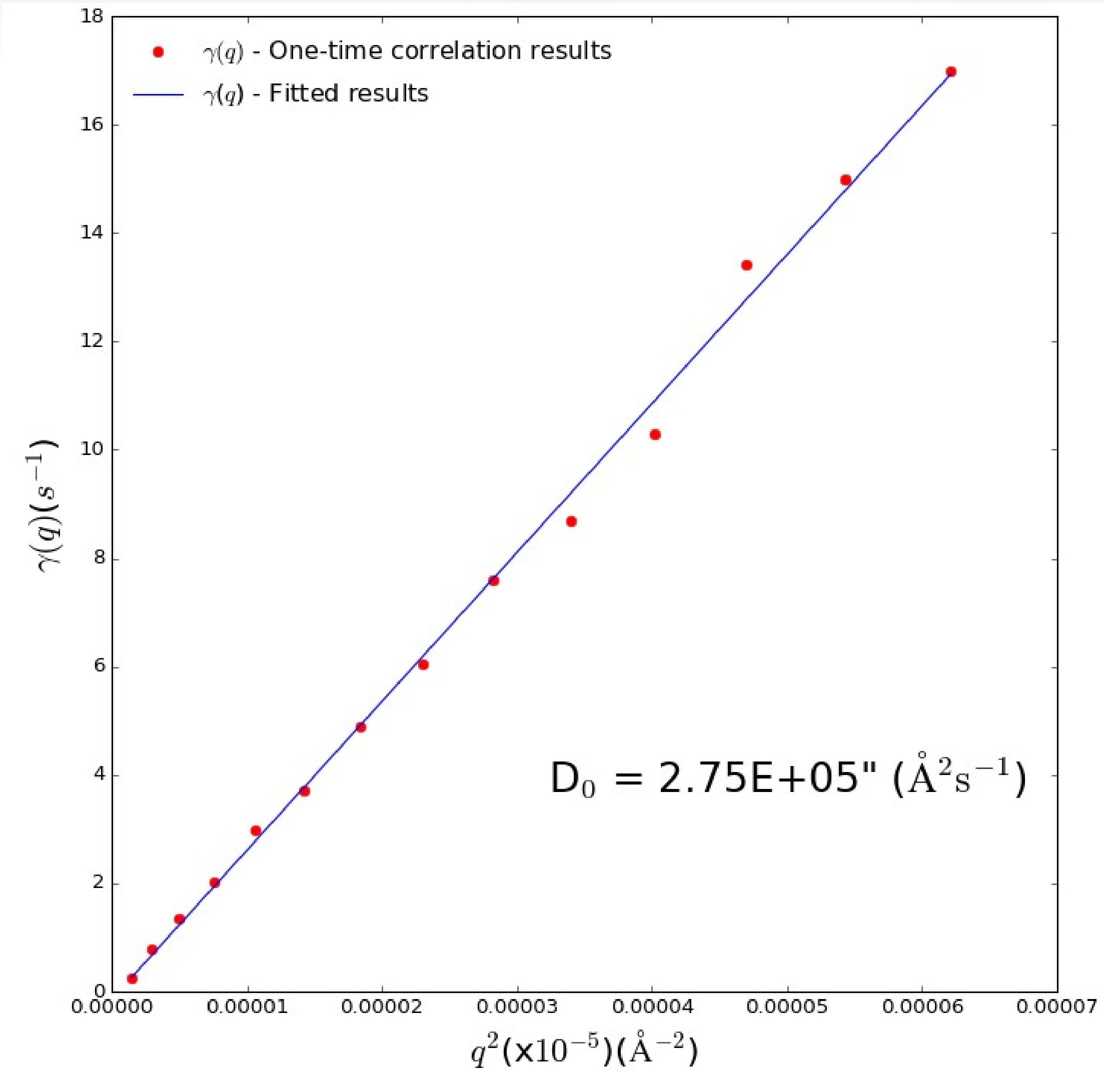




$$g^{(2)}(q,t)=\frac{\langle I(q,t)\,I(q,t+\delta t)\rangle}{\langle I(q)\rangle^2}$$

$$g^{(2)}(q,t)=1+\beta(q)[g^{(1)}(q,t)]^2$$

Colloidal Dynamics with XPCS



Here 500 nm Silica spheres suspended in a water/glycerol mixture

ISF:

$$g^{(1)}(q,t) \propto \exp[-Dq^2 t]$$

Relaxation rate:

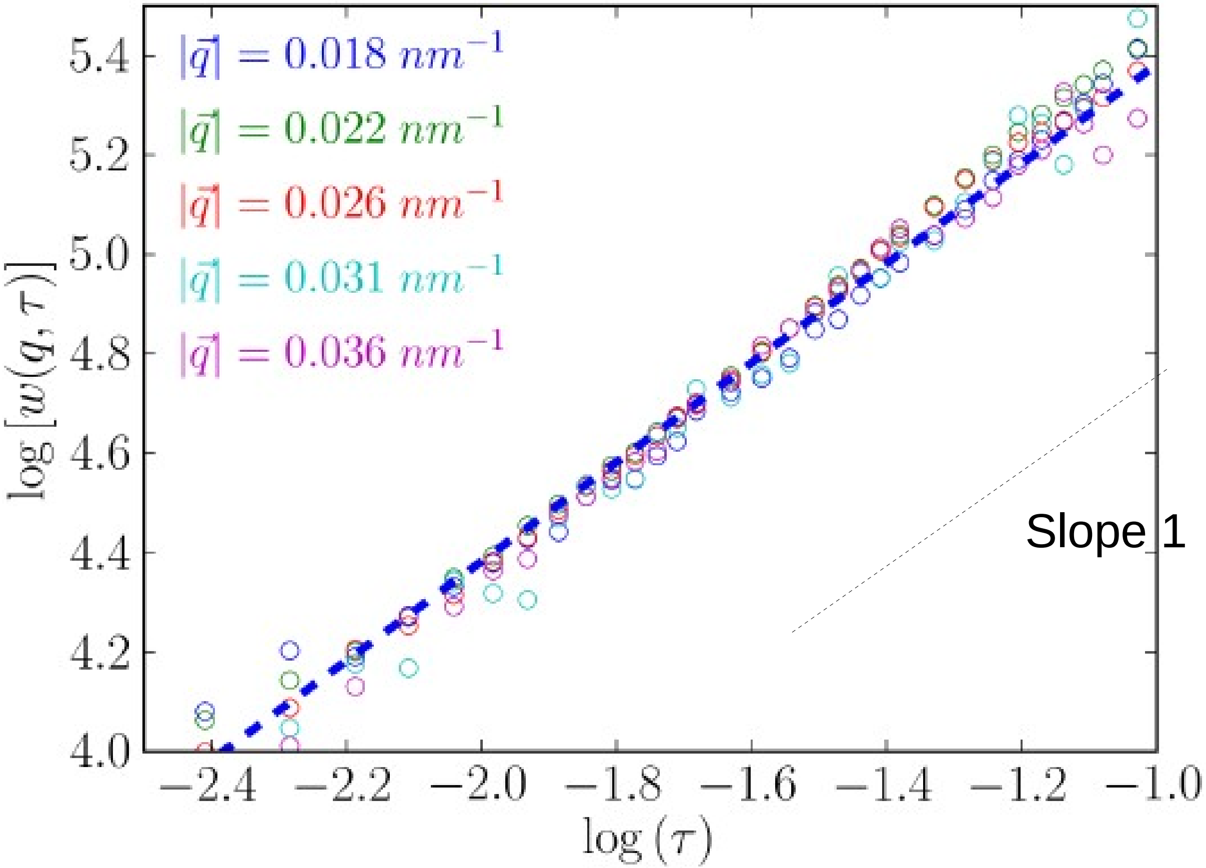
$$\Gamma = Dq^2$$

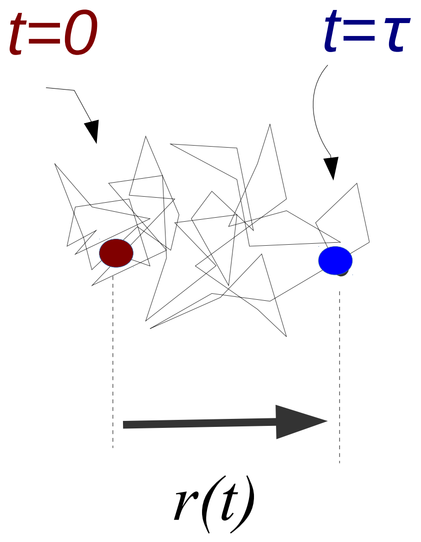
CHX Analysis Pipeline!

Colloidal Dynamics with XPCS

- Width function analysis
  (Martinez, Van Megen *et al.* JCP 2011)

$$w(q,t) = -\log[g^{(1)}(q,t)/q^2] \propto Dt \propto \langle r^2(t) \rangle$$





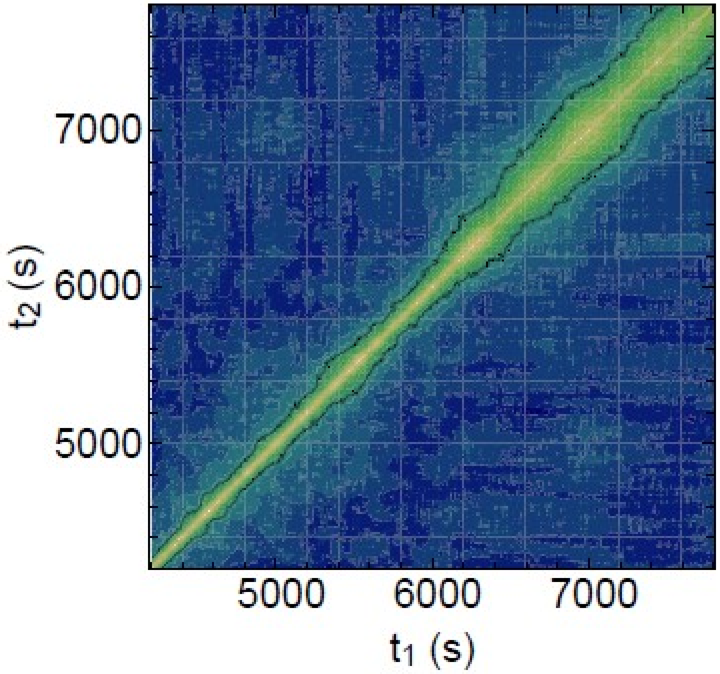
Free diffusion at low - Φ

$< r^2(t) > \sim Dt$

Two-time analysis

Non-equlibrium dynamics in colloidal depletion gels (colloid/polymer mixtures):

Two-time correlation functions: $C(Q,t_1,t_1) = \frac{\langle I(Q,t_1) I(Q,t_2)\rangle_{pix}}{\langle I(Q,t_1)\rangle_{pix}\langle I(Q,t_2)\rangle_{pix}}$



average time ("age"):
$t_a = \frac{t_1+t_2}{2}$

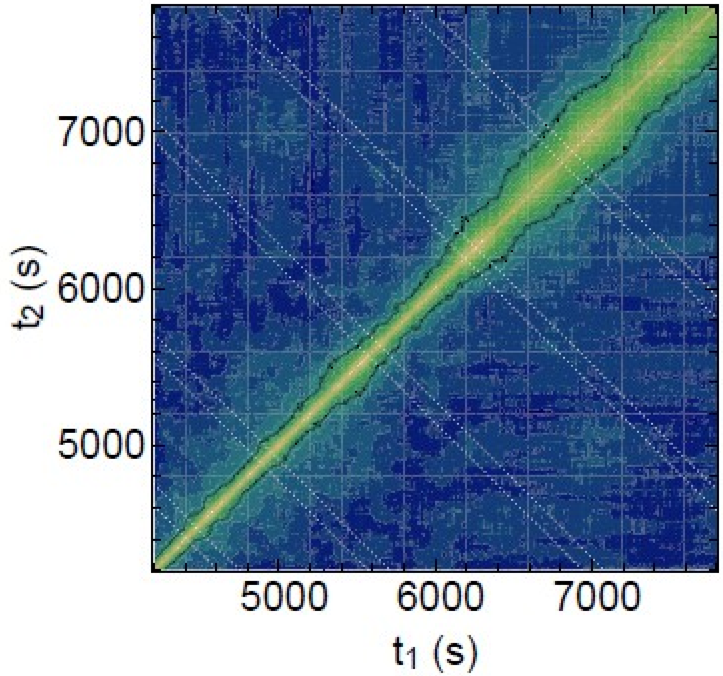
time difference:
$t = \delta t = |t_1 - t_2|$

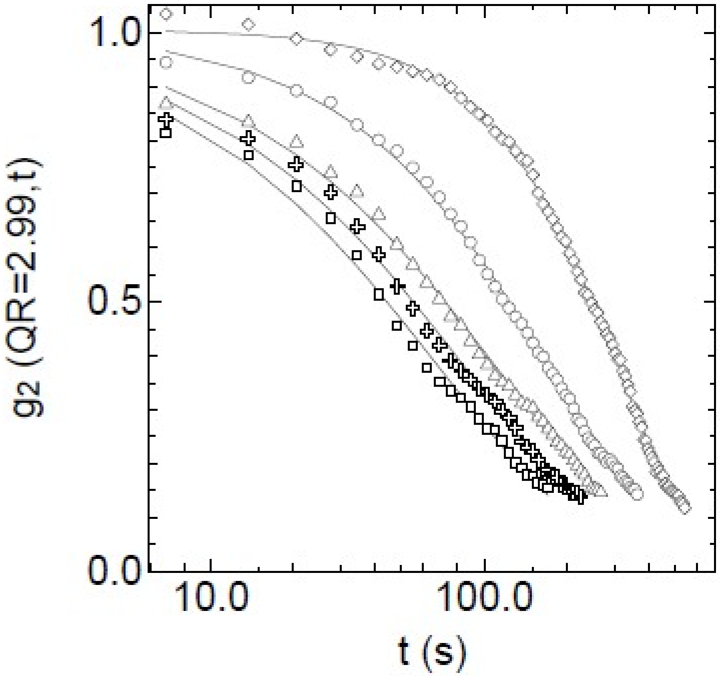
* M.Sutton et al., Optics Express **11**, 2268 (2003).

AF *et al.*, *Phys. Rev. E*, **76**, 010401(R) (2007)

Two-time analysis

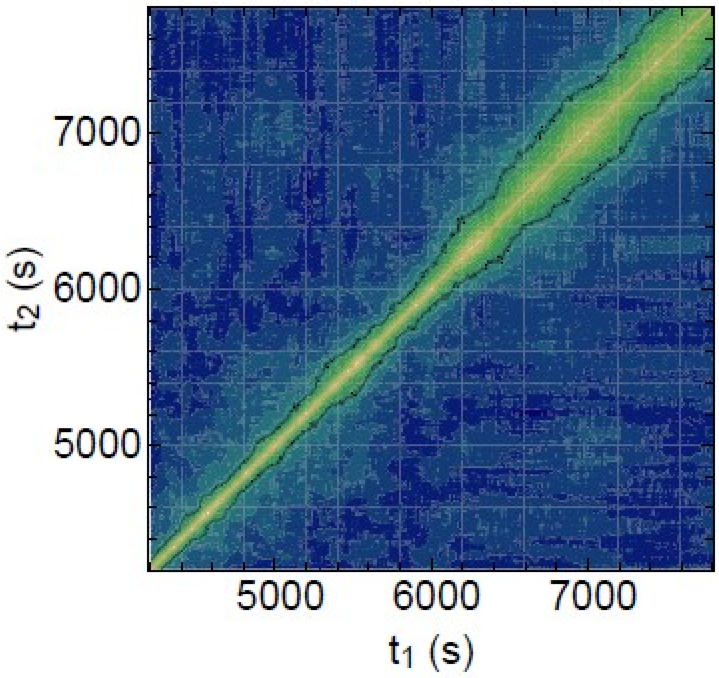
Two-time correlation functions: $C(Q,t_1,t_1) = \frac{\langle I(Q,t_1)I(Q,t_2)\rangle_{pix}}{\langle I(Q,t_1)\rangle_{pix}\langle I(Q,t_2)\rangle_{pix}}$

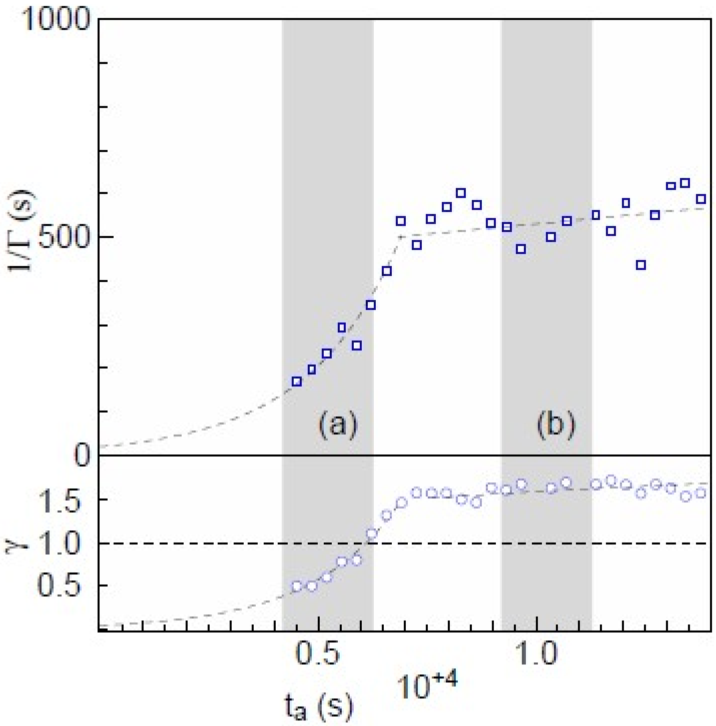




Two-time analysis

Two-time analysis: $g_2(Q, t_a, t) = \beta exp\left(-(\Gamma t)^{\gamma}\right) + g_{\infty}$

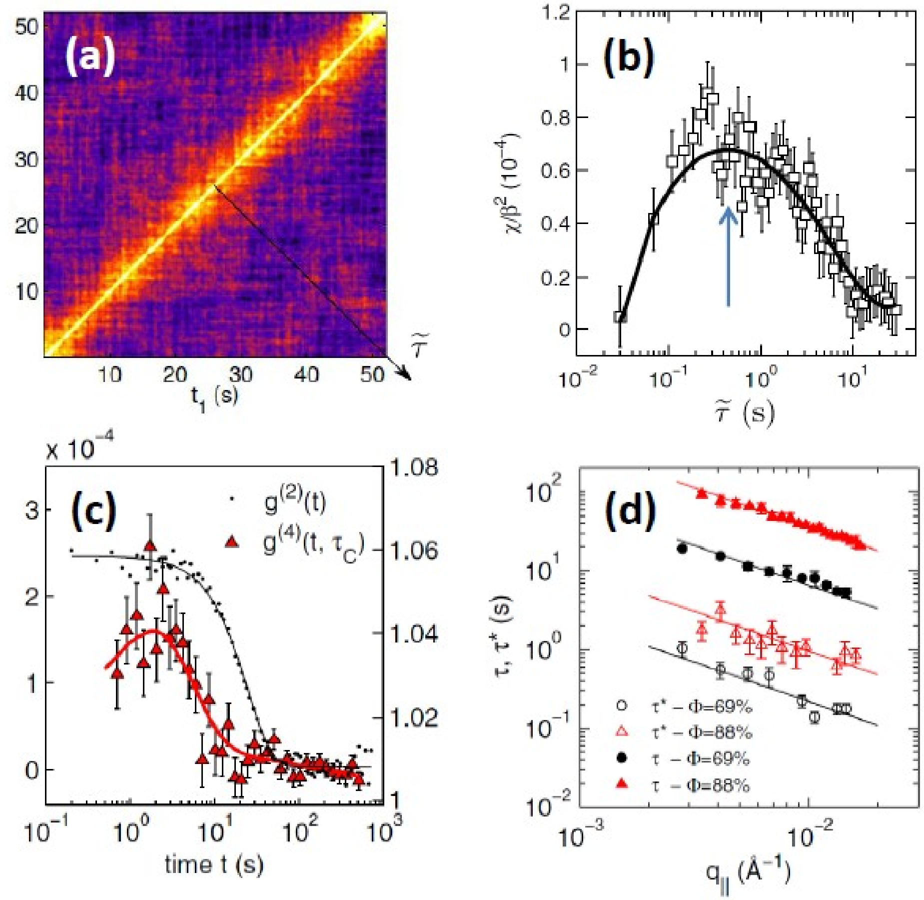




4^{th} order correlations: dynamical heterogeneities

- Orsi et al. - dynamics in langmuir monolayer of nanoparticles using Grazing Incidence (GI)-XPCS
- Heterogeneities (correlations of correlations)

$$g^{(4)}(t,\widetilde{\tau}) = \langle C(t_1,t_1+\widetilde{\tau})C(t_1+t,t_1+t+\widetilde{\tau})\rangle_{t_1}$$
$$= \langle I(t_1)I(t_1+\widetilde{\tau})I(t_1+t)I(t_1+t+\widetilde{\tau})\rangle_{t_1}$$



A. Duri *et al.*, *Phys. Rev. E* **72**, 051401 (2005)
D. Orsi *et al.*, *Phys. Rev. Lett.* **108**, 105701 (2012)

How can we go faster than the frame rate?

- X-ray Speckle Visibility Spectroscopy

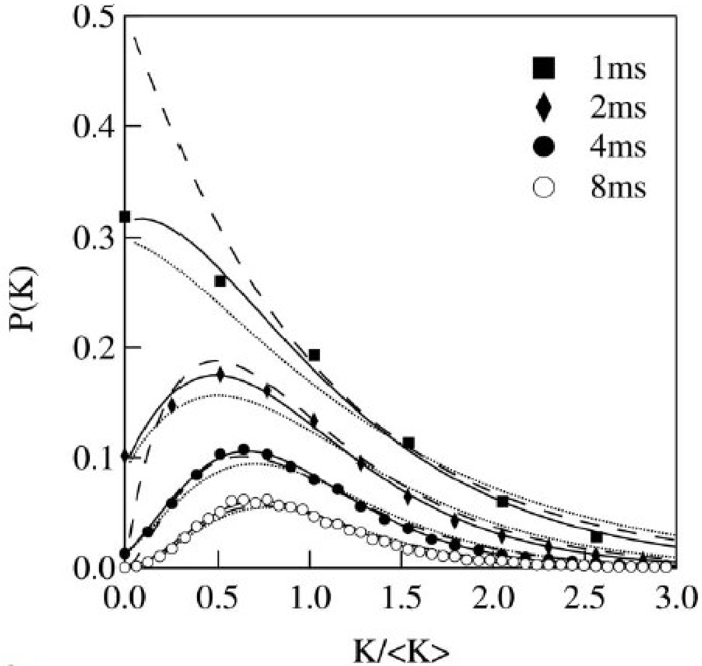


Figure 2
Photon count statistics analysis performed over an ensemble of pixels marked in the circular region in Fig. 1(*a*) for four integration times. Markers represent the photon count probability density $P(K)$ from the experiments, and solid lines are the fitting curves using the negative-binomial distribution function [equation (11)], dashed lines are the fitting curves using the gamma distribution function [equation (5)] and dotted lines are the fits using equation (11) with M as the only fitting parameter, while $\langle K \rangle$ is calculated from the measured photon counts. The results are plotted as a function of reduced count $K/\langle K \rangle$, so that $P(K)$ values with different integration times can be stacked in the same figure.

L. Li, P. Kwasniewski, D. Orsi, L. Wiegart, L. Cristofolini, C. Caroma and A. Flerasu, *Photon statistics and speckle visibility spectroscopy with partially cohernt X-rays.*, J. Synchrotron Rad., 21, 1288-1295, 2014.

C. DeCaro, V. N. Karunaratne, S. Bera, L. B. Lurio, A. R. Sandy, S. Narayanan, M. Sutton, J. Winans, K. Duffin, J. Lehuta, N. Karonis, *X-ray speckle visibility spectroscopy in the single-photon limit*, J. of Synchrotron Rad., 20, 332–338, 2013.

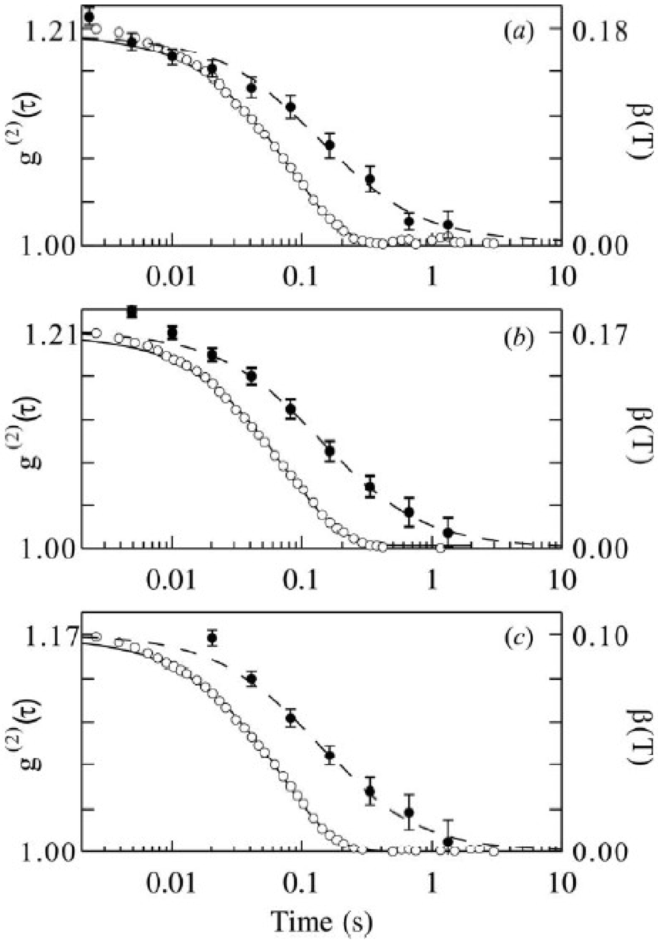
I. Inoue, Y. Shinohara, A. Watanabe, Y. Amemiya, *Effect of shot noise on X-ray speckle visibility spectroscopy*, Opt. Express 20, 26878–26887, 2012.

S. O. Hruszkewycz, M. Sutton, P. H. Fuoss, B. Adams, S. Rosenkranz, K. F. Ludwig, W. Roseker, D. Fritz, M. Cammarata, D. Zhu, S. Lee, H. Lemke, C. Gutt, A. Robert, G. Grübel, G. B. Stephenson, *High Contrast X-ray Speckle from Atomic-Scale Order in Liquids and Glasses*, Phys. Rev. Lett., 109, 185502, 2012.

R. Bandyopadhyay, A. S. Gittings, S. S. Suh, P. K. Dixon and D. J. Durian, *Speckle-visibility spectroscopy: A tool to study time-varying dynamics*, Rev. Sci. Instrum. 76, 093110 ,2005.

How can we go faster than the frame rate?

- X-ray Speckle Visibility Spectroscopy



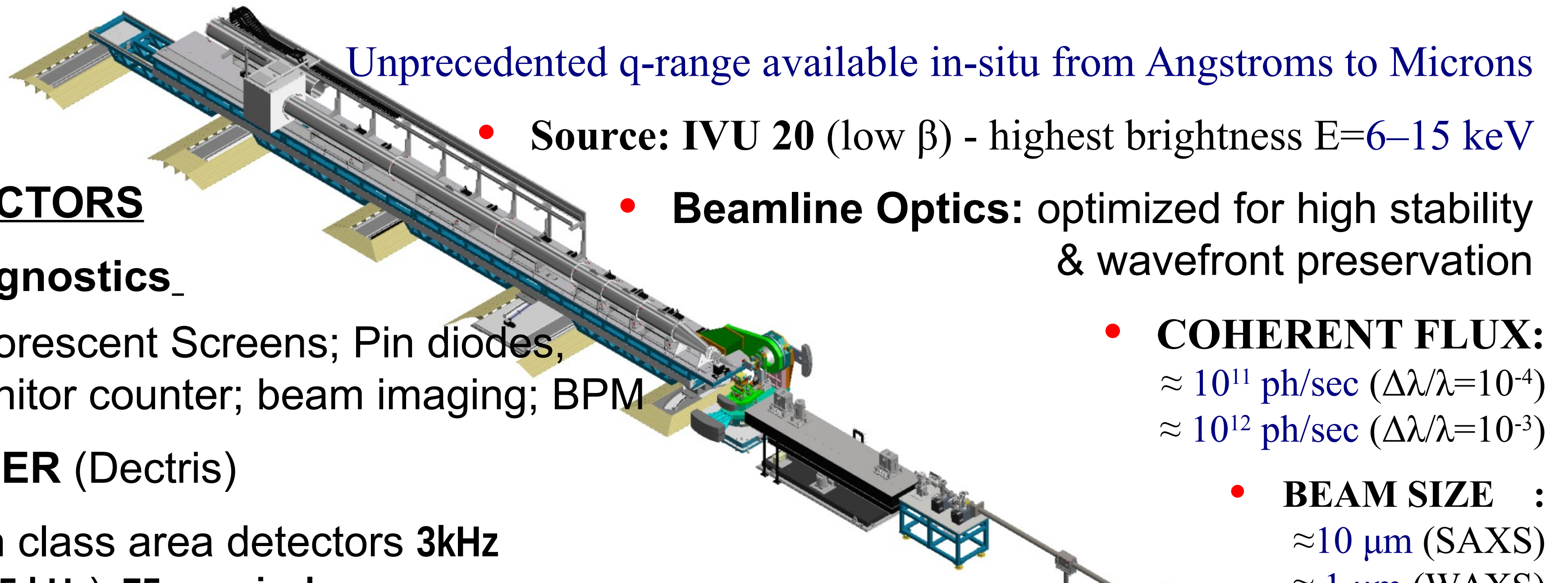
Luxi Li et al. J. Synch. Rad. 2014

Dixon, Durian et al.

$$\beta(q,T) = \beta_1 \int_0 2(1 - t/T)\left[g^{(1)}(q,t)\right]^2 \mathrm{d}t/T + \beta_\infty$$

A "User Guide" to XPCS

- **CHX optimized for Coherent X-ray Diffraction - *XPCS*, *(GI-)SAXS*/*WAXS*, *CDI***



Unprecedented q-range available in-situ from Angstroms to Microns

- **Source: IVU 20** (low β) - highest brightness E=6–15 keV
- **Beamline Optics:** optimized for high stability & wavefront preservation
- **COHERENT FLUX:**
  $\approx 10^{11}$ ph/sec ($\Delta\lambda/\lambda = 10^{-4}$)
  $\approx 10^{12}$ ph/sec ($\Delta\lambda/\lambda = 10^{-3}$)
- **BEAM SIZE :**
  ≈10 μm (SAXS)
  ≈ 1 μm (WAXS)

DETECTORS

1. Diagnostics

- Fluorescent Screens; Pin diodes, Monitor counter; beam imaging; BPM

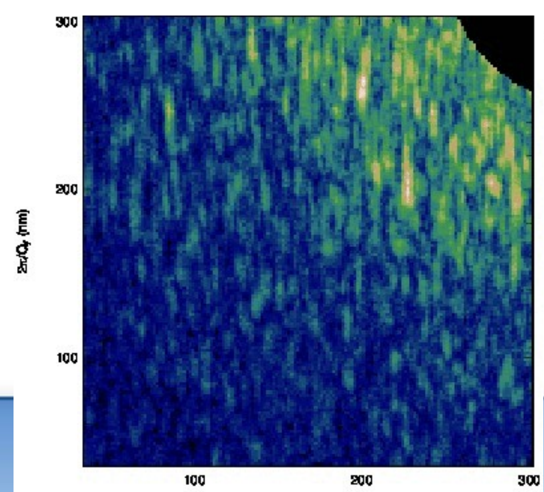
2. EIGER (Dectris)

best in class area detectors **3kHz** (up to **15 kHz**), **75 μm pixels**

- **Eiger 1M** for c – WAXS
- **Eiger 4M** for c - S AXS

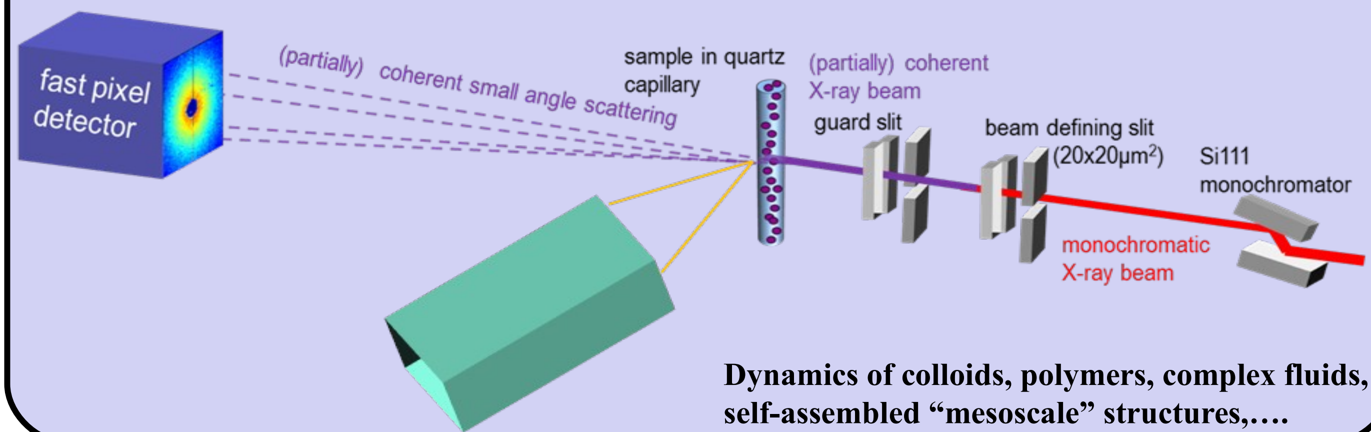
3. Point Detectors (FMB Oxford)

- Scintillator detector systems;
- Avalanche Photodiode (APD)



Example Scattering Geometries

(Transmission) SAXS / WAXS



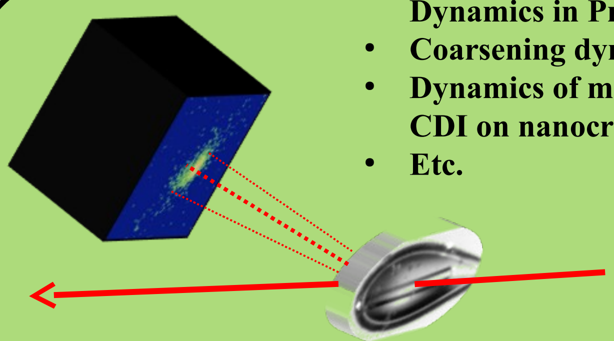
Dynamics of colloids, polymers, complex fluids, self-assembled "mesoscale" structures,….

Next deadline for Experiment proposals: ***Sept 30, 2016***

https://pass.bnl.gov

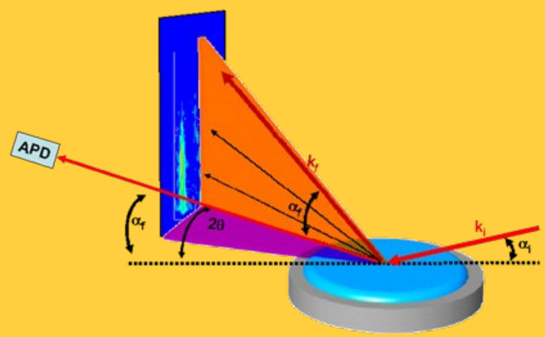
Dynamics in Protein Crystals

- **Coarsening dynamics in alloys**
- **Dynamics of metallic glasses CDI on nanocrystals**
- **Etc.**



Coherent WAXS

GI-SAXS / GI-WAXS, XRR (solid)



In-plane structure/diffusion, capillary waves, electron density profile

A "User Guide" to XPCS

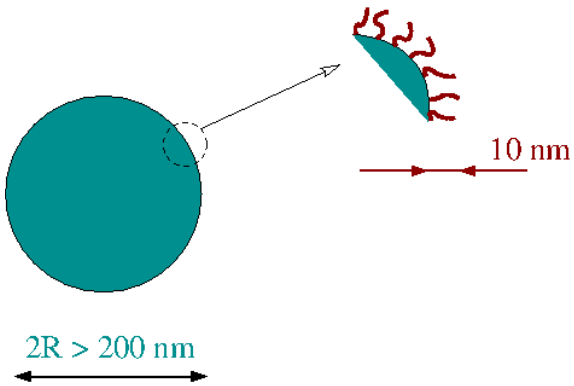
Questions:

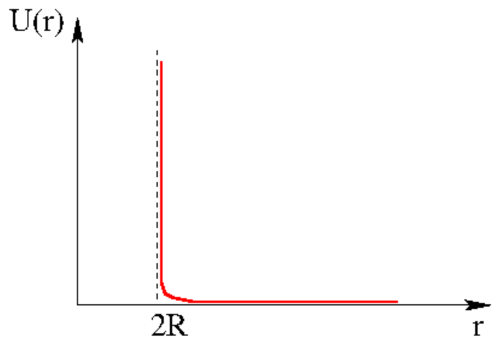
- What is the optimal flux/coherence balance?
- How much does the sample scatter?
  - we need $\sim 10^{-N}$ ph/correlation time/speckle(pixel) - $g^{(2)}$
  - We need ~1/ph/correlation time/speckle(pixel) – $C(t_1,t_2)$
- What time scales are we expecting?
- What is the radiation limit?
- Is the sample homogeneous? i.e can we build an ensemble by averaging information recorded from differnet locations?
- Think about optimizing sample thinckness ~1 absorption length
- An analysis pipeline capable of producing 'quasi-real-time' results is basically needed

Example of XPCS & XSVS analysis (Open Source) on GitHub:

CHX Analysis Pipeline!

High density hard-sphere suspensions



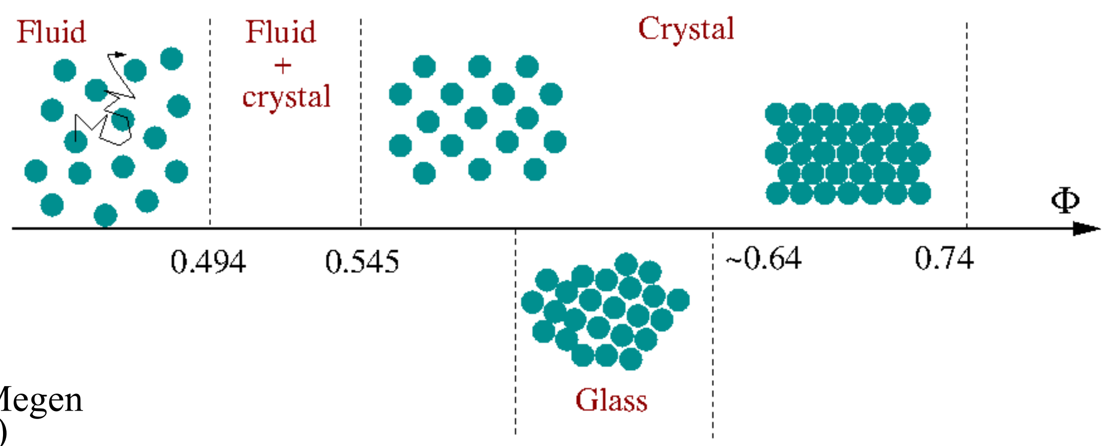


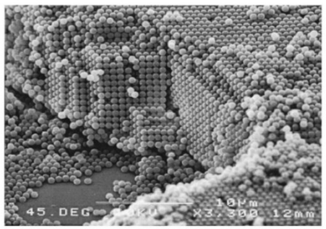
Hard-sphere colloids:

- Spherical PolyMethylMethacylate (PMMA) particles coated with 12 hydroxystearicacid in cis-decalin (A. Schofield, Edinburgh)
- Entropic forces between polymer coating layers → infinite "hard-sphere-like" repulsions

- The phase behavior depends on the *particle volume fraction Φ*

$$\Phi = \frac{N\, V_{colloid}}{V_{total}}$$

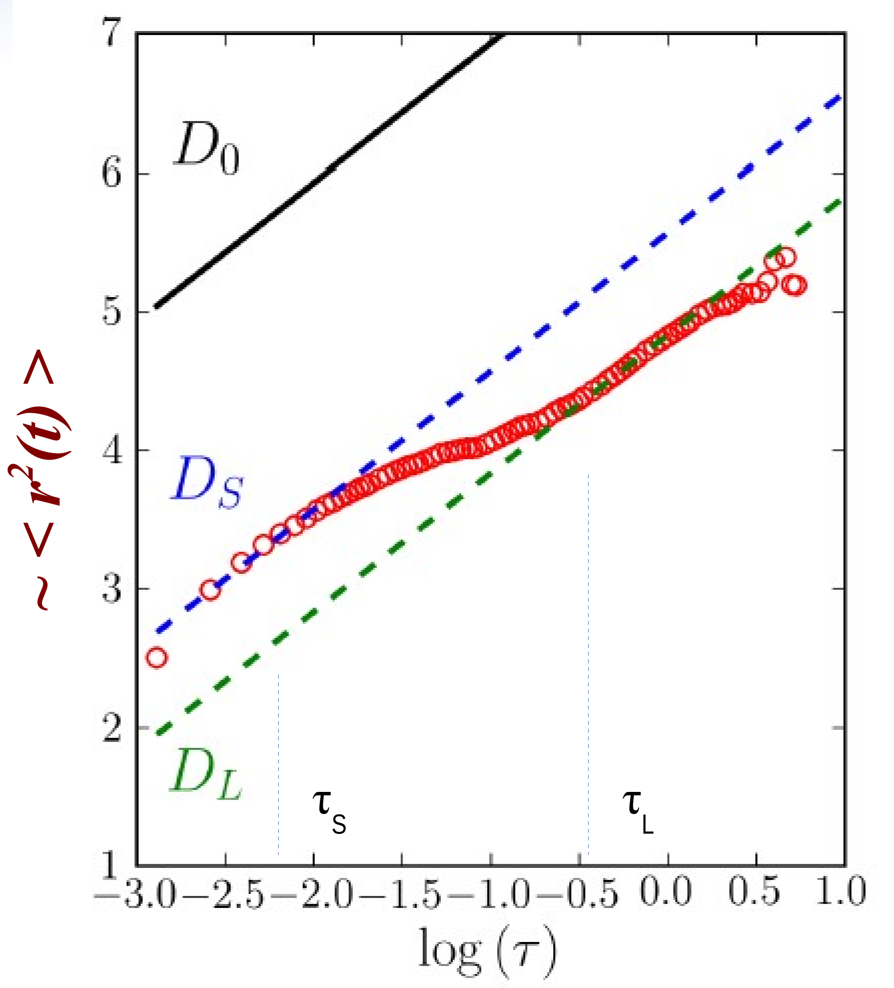




(b) R.M. Amos et al., PRE **61**, 2929 (2000)

P.N. Pusey & W. Van Megen
Nature **320**, 340 (1986)

Dynamics in high density hard-sphere suspensions



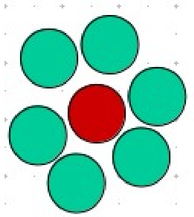
P. Kwasniewski, PhD Thesis 2012

Short-time diffusion D_s ($t<\tau_S$)

Motion of particles inside of "cages" created by other particles

Slowed down (compared to D_0) by *hydrodynamic interactions*

D. Orsi, AF et al. *Phys. Rev. E* 2012



Long-time diffusion D_L ($t>\tau_L$)

Structural rearangements i.e. "Rearrangements of cages"

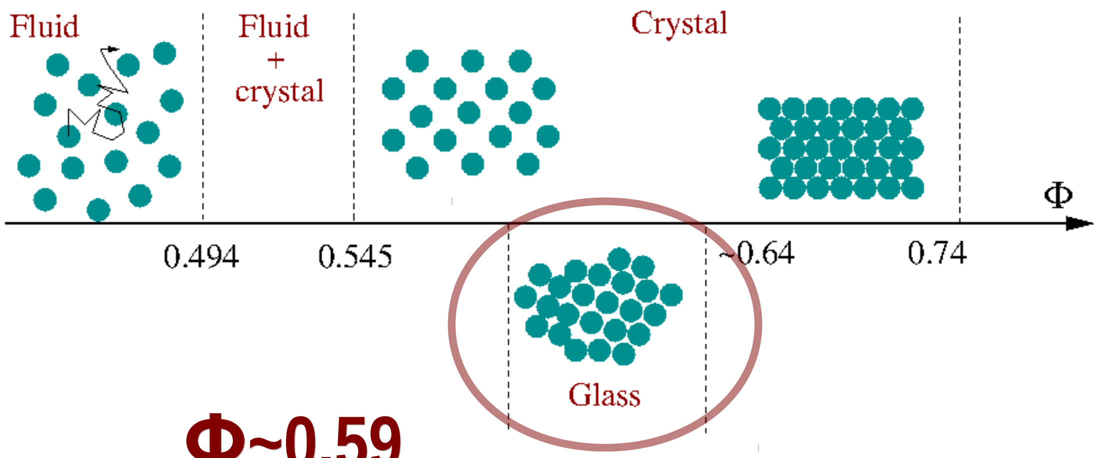
Slowed down (compared to D_S) by *direct interactions*

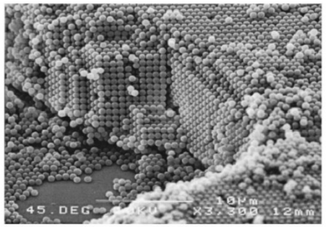
P. Kwasniewski, AF, A. Madsen, Soft Matter, 2014, **10**, 8698-8704

The Colloidal Glass Transition

- What happens here?

$$\Phi = \frac{N\, V_{colloid}}{V_{total}}$$

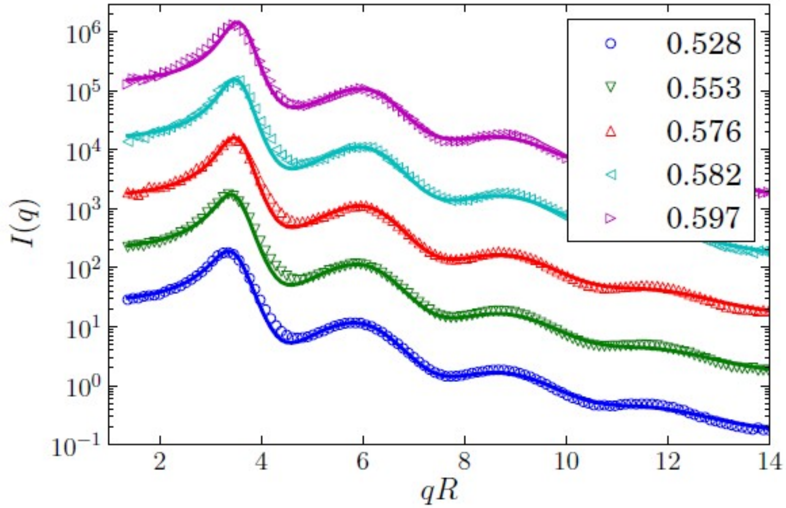




(b) R.M. Amos et al., PRE **61**, 2929 (2000)

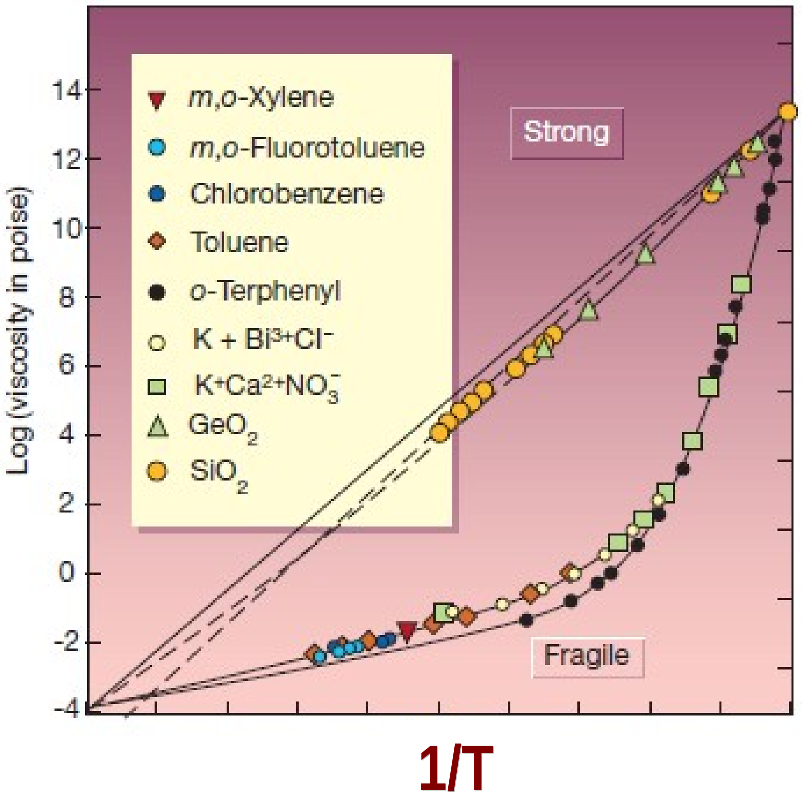
Φ~0.59

- From SAXS / static scattering: pretty much *nothing* ...

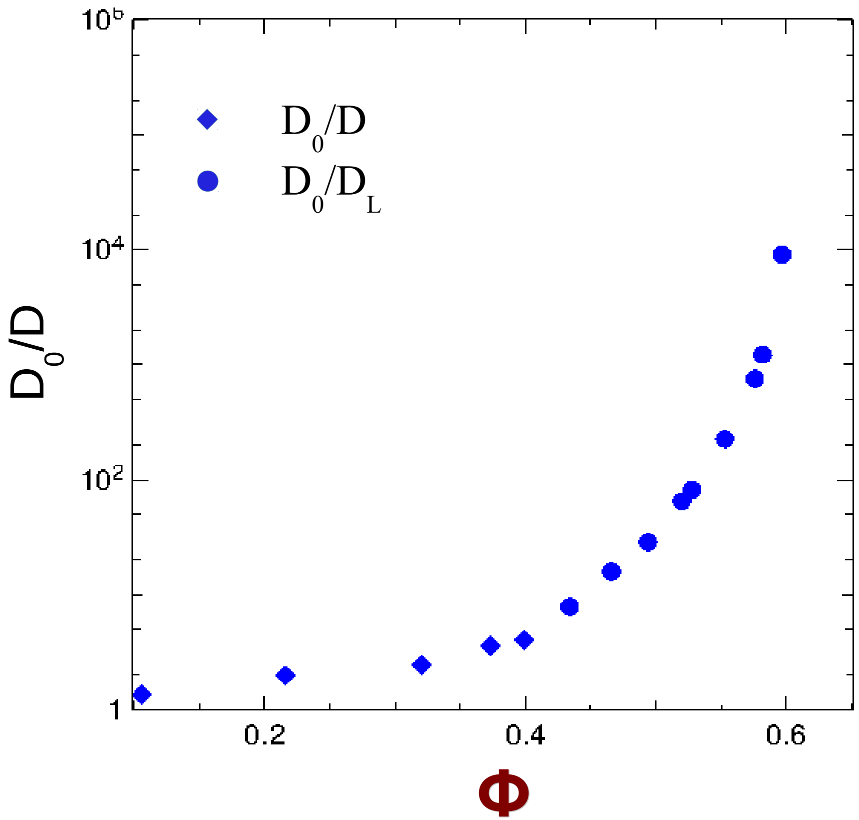


Supercooled Liquids vs. Hard-Sphere Colloids

- In addition to being interesting/useful in their own right, colloids are an excellent model system for supercooled liquids and molecular glassformers



Denenedetti, Stillinger, *Nature* 2001

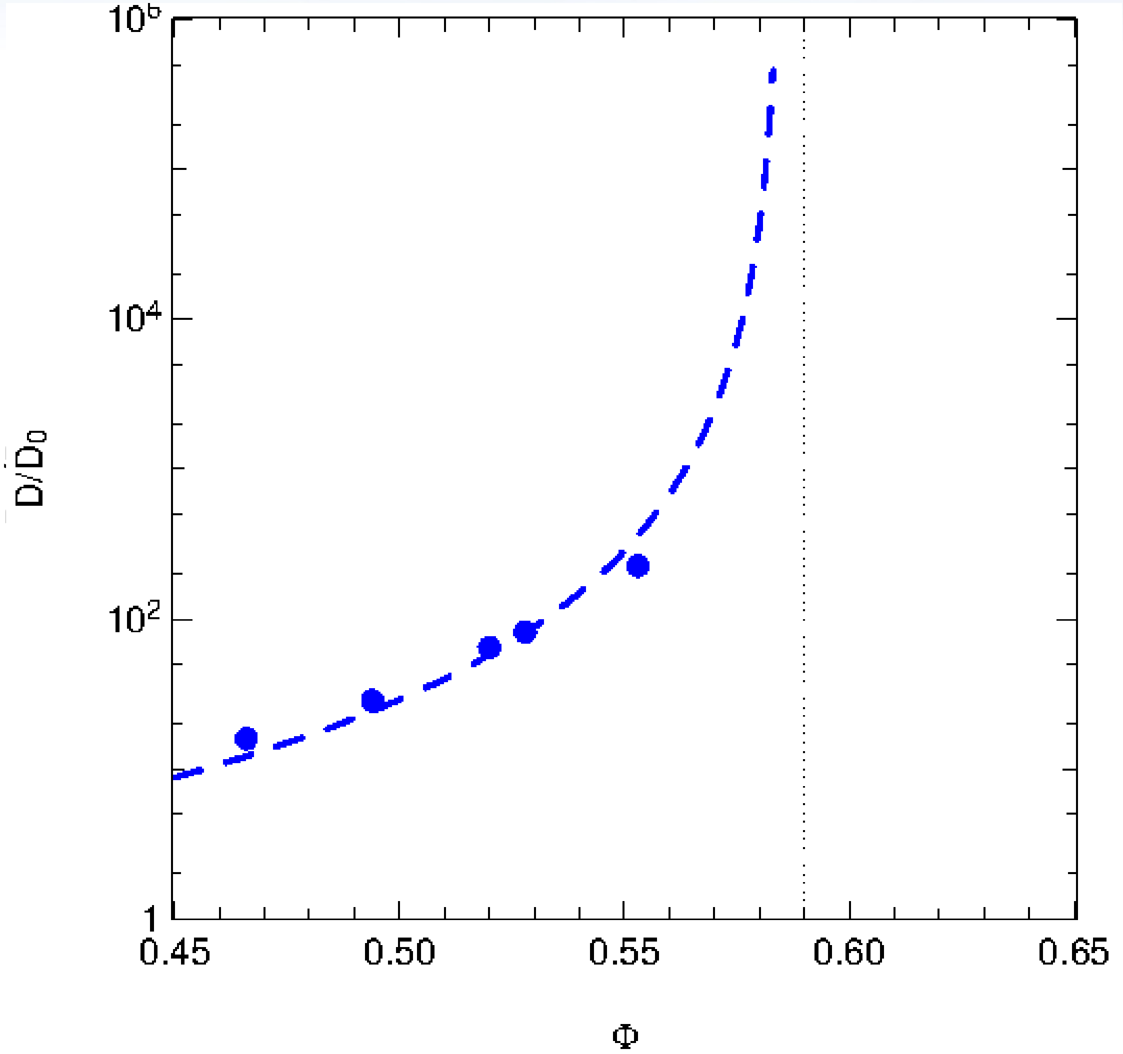


D. Orsi, AF et al. *Phys. Rev. E* 2012

P. Kwasniewski, AF, A. Madsen, *Soft Matter* 2014

$\eta/\eta_0 \rightarrow D_0/D_L$ (Segre *et al.*, *Phys. Rev. Lett* 2001)

Structural Relaxations near the Hard-Sphere Glass Transition

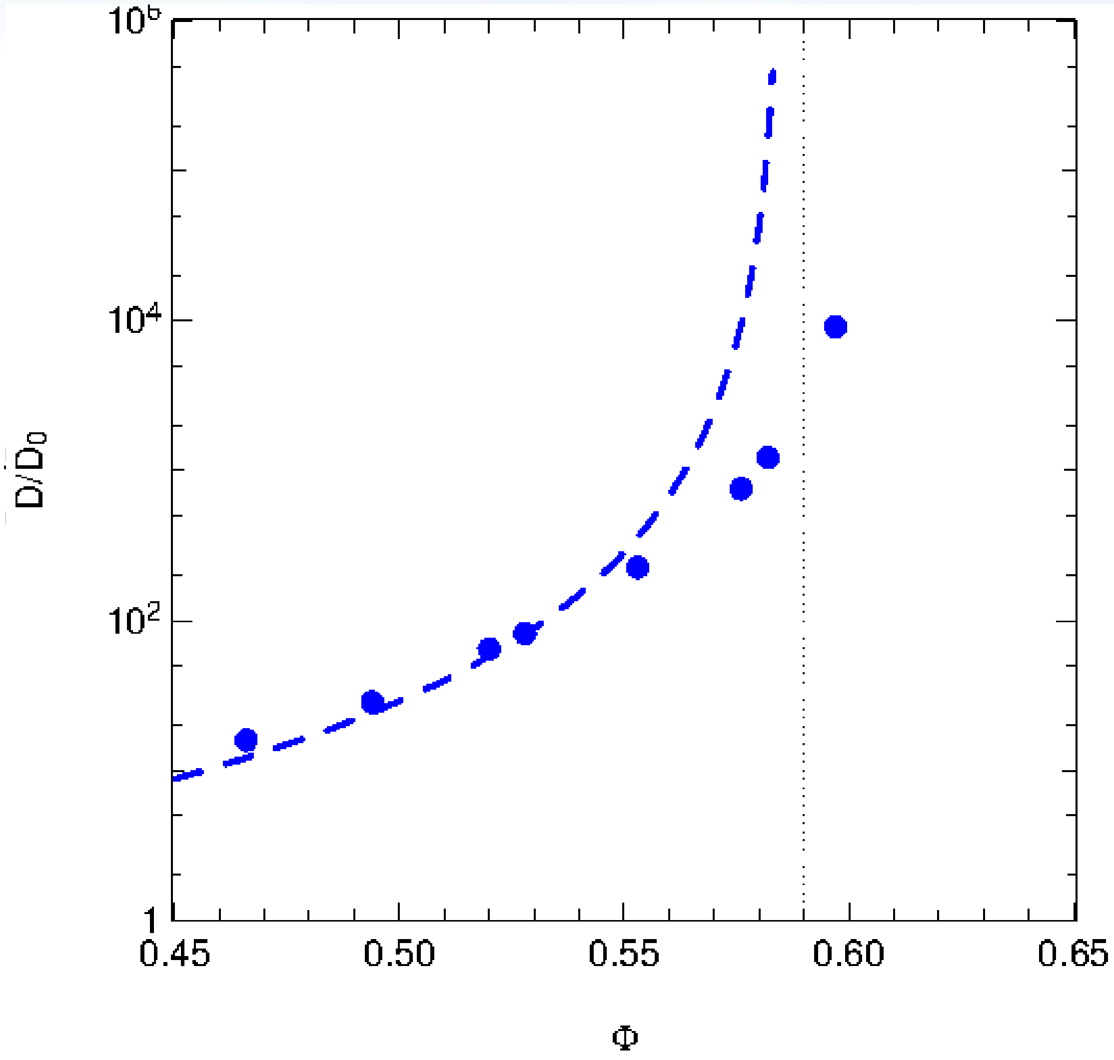


Structural relaxations:

- Structural relaxations slow-down with increasing **Φ**
- And are expected to *diverge* at the colloidal glass transition concentration Φ_g **-** "Mode Coupling Theory" (MCT)
- $D_0/D_L \rightarrow \infty$ at Φ_g~0.59

$$\frac{D_0}{D_l(q_m)} \propto \left|\frac{\Phi_g - \Phi}{\Phi_g}\right|^{-\gamma}$$

Structural Relaxations near the Hard-Sphere Glass Transition



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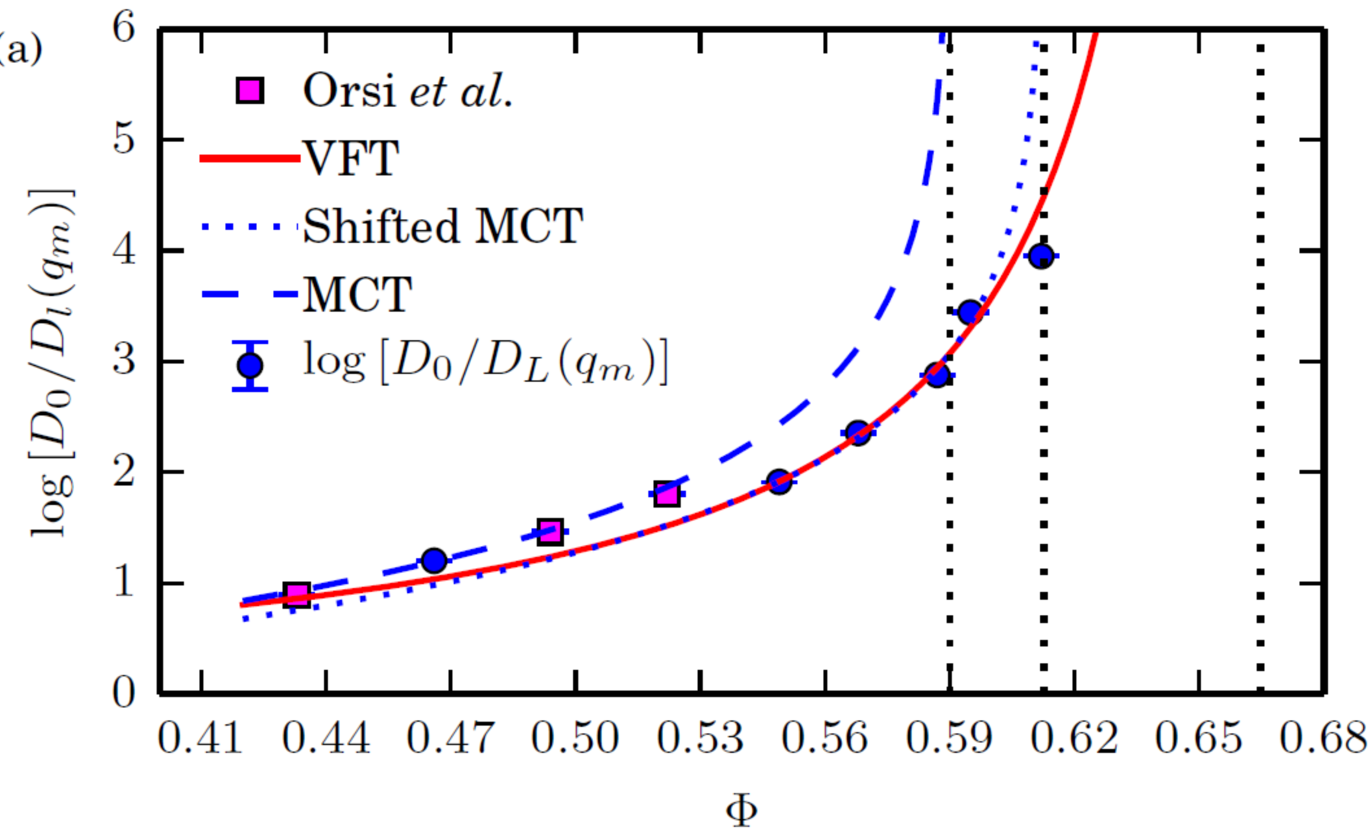
$$\frac{D_0}{D_l(q_m)} \propto \left| \frac{\Phi_g - \Phi}{\Phi_g} \right|^{-\gamma}$$

Not so simple:

- Instead of diverging the relaxations remain finite (but slow!) above $\mathbf{\Phi_g}$

Structural Relaxations near the Hard-Sphere Glass Transition



MCT:

$$\frac{D_0}{D_l(q_m)} \propto \left|\frac{\Phi_g - \Phi}{\Phi_g}\right|^{-\gamma}$$

g~2.58

VFT:

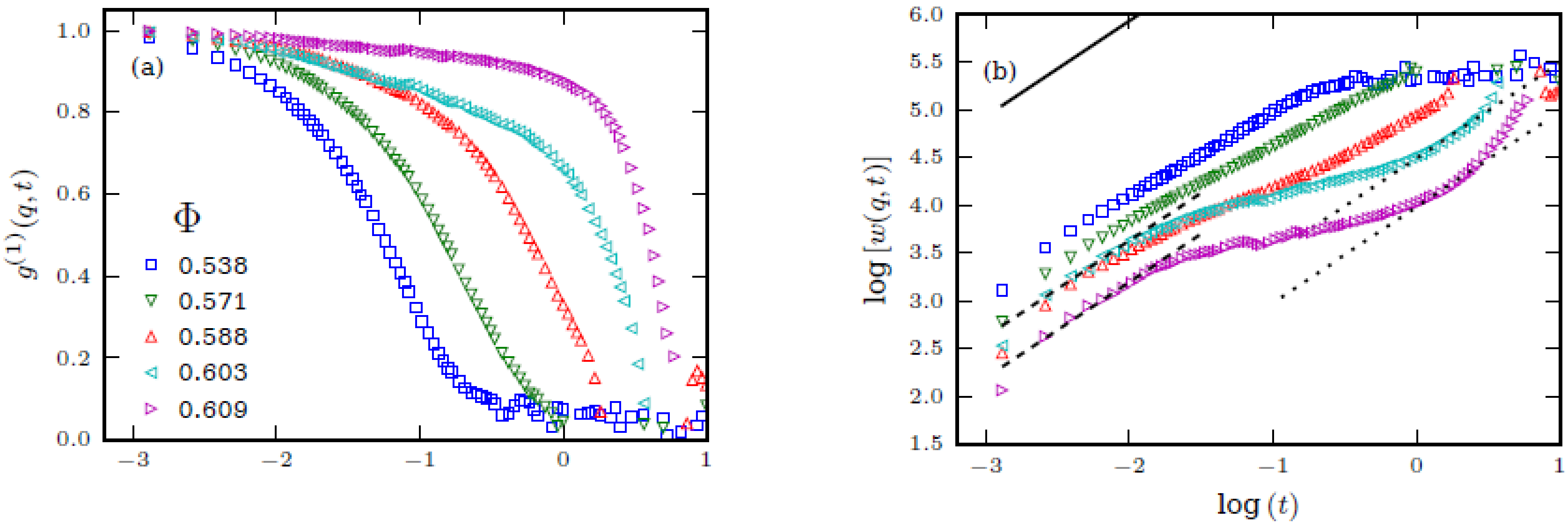
$$\frac{D_0}{D_l(q_m)} = \tau_\infty \exp\left[\frac{F}{(\Phi_0 - \Phi)^\delta}\right]$$

- relaxations follow an unexpected functional (VFT) form suggesting a kinetic arrest near the "random close packing concentration ***Φ_{RCP}~0.67*** (~10% polydispersity)
- Suggests connection with ***Jamming***

P. Kwasniewski, AF, A. Madsen, *Soft Matter*, 2014, 10, 8698-8704
See also; Brambilla, Cipelletti *et al.*, *Phys. Rev. Lett.* 104, 169602 (2010)

Anomalous Dynamics near the Hard-Sphere Glass Transition

- Near the colloidal Glass Transition the dynamics becomes anomalous
  - Compressed exponential relaxations
  - Hyperdiffusive dynamics: $< r^2(t)) >$ *"faster than"* $\sim t$

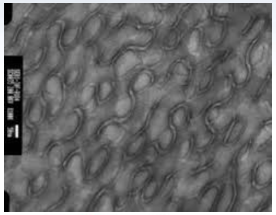


- Is this behavior a signature of *jamming*?

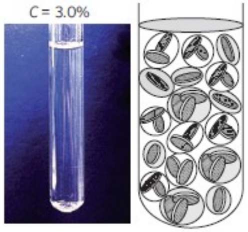
Universal non-diffusive slow dynamics in aging soft matter
L.Cipelletti *et al.*, *Faraday Discuss.*, 2003, **123**, 237

Anomalous Dynamics near the Hard-Sphere Glass Transition

- Polymer-based sponge phases
  P. Falus *et al*. *Phys. Rev. Lett* 2006

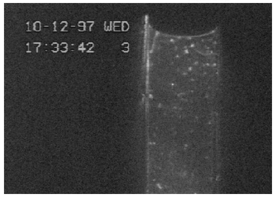


- Aging Clay (Laponite) Gels
  B. Bandyopadhyay et al., Phys. Rev. Lett. 2004;
  R. Angelini et al., Soft Matter 2013

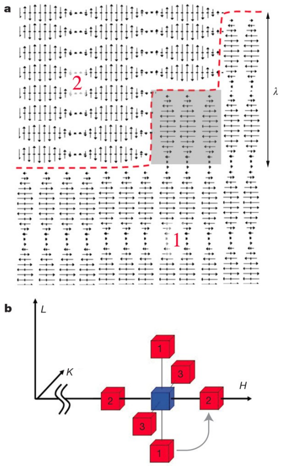


- Antiferromagnetic domain fluctuations (Cr)
  O. Shpyrko et al., Nature 2007

- Aging Ferrofluids
  A. Robert *et al*. Europhys. Lett. 2007



- Aging colloidal gels ("transient gels")
  A. Fluerasu *et al.*, Phys. Rev. E 2007



- Cross-linked Polymer Gels
  R. Hernandez *et al.*, J. Chem Phys 2014
  O. Czakkel, *Europhys. Lett.* 2011, K. Laszlo *et al., Soft Matter* 2010

- Atomic-scale dynamics & aging in metallic glasses
  B. Rutta et al, *Phys. Rev. Lett.* 2012

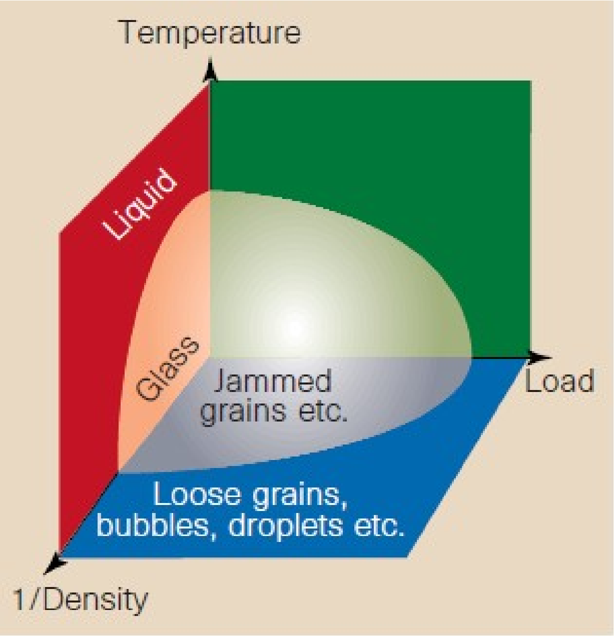
- Etc. etc. etc. ...

Jamming?

- Is this behavior a “universal” ?
- Common behavior in seemingly different systems: hyperdiffusive & faster-than-exponential relaxations associated with *Jamming*

  L.Cipelletti *et al.*, *Faraday Discuss.*, 2003, **123**, 237

- Jamming – heterogeneities & response to flow/shear



A. Liu *et al.* Nature 1998

Anomalous Dynamics near the Hard-Sphere Glass Transition

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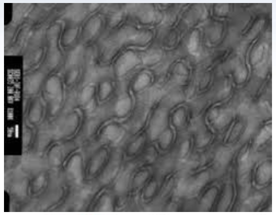
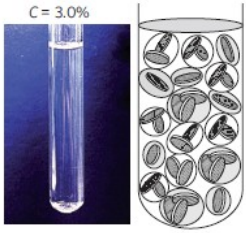
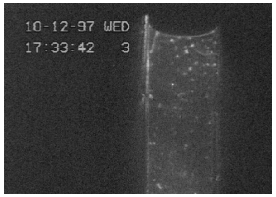
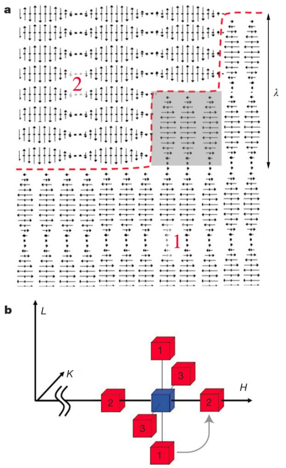




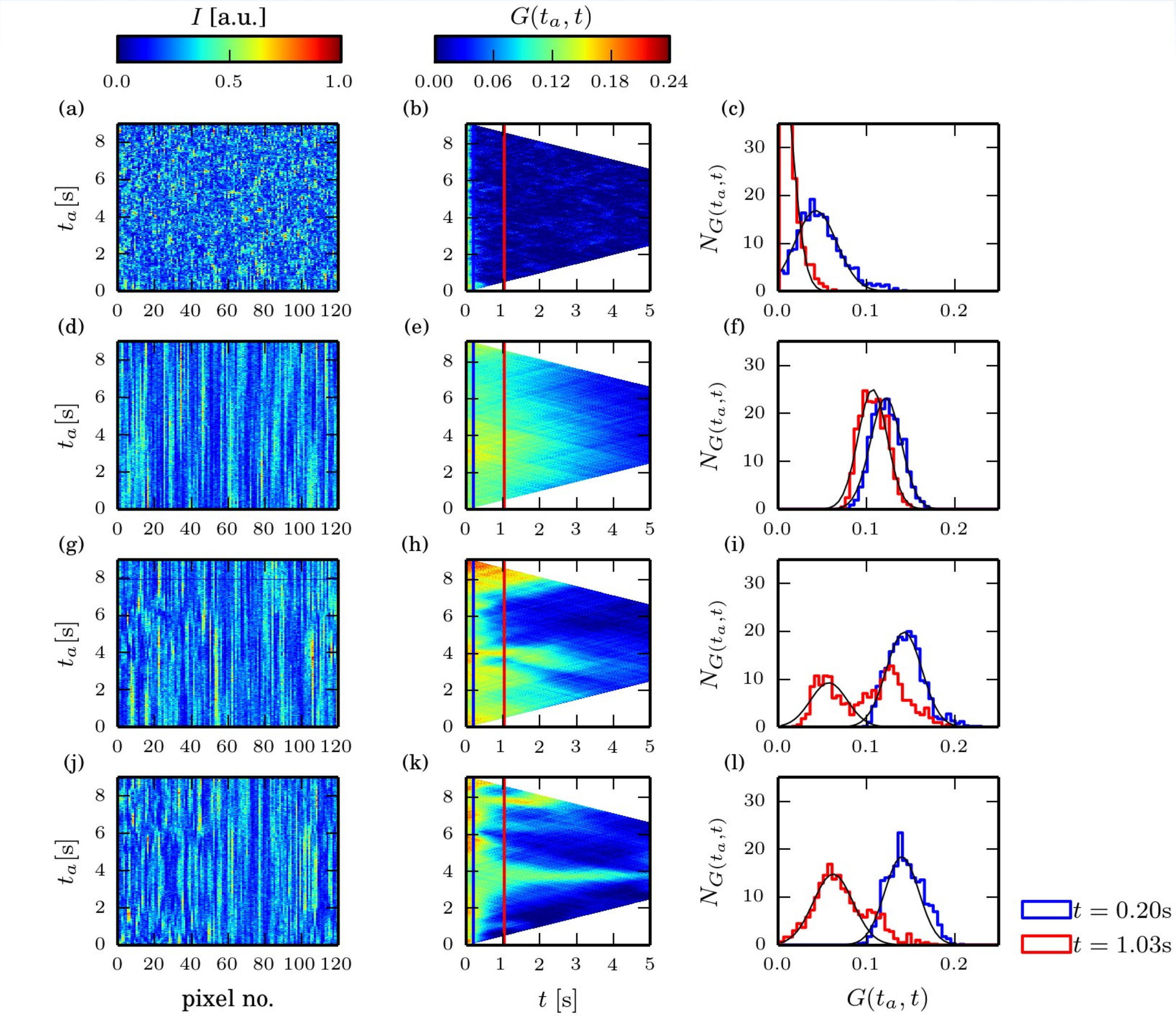




Dynamical Heterogeneities

Φ~0.57

Φ~0.61



Age ~30min

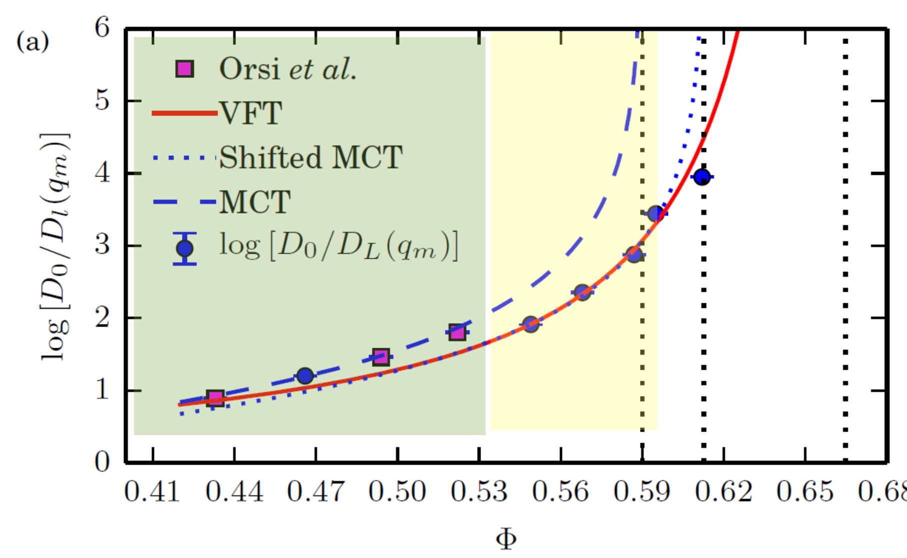
Age ~2h30

Age ~9h

Pawel Kwasniewski *et al.*

Colloidal Glasses: Conclusions

- Low-Φ: Dynamics of colloids well explained by existing many-body theories (MCT)
- Φ ≥ 0.57-0.59 Stress in the networ and stress-induced (nonthermal) fluctuations become dominant and hinder the expected glass transitio
- Non-equilibrium, complex dynamics determined by "rough" energy landscape (heterogeneities) *Hyperdiffusive relaxations →jamming* (common also in other systems)
- Response to perturbations?
  → *flow, shear*



Acknowledgements

Colloids ***Pawel Kwasniewski*** (ESRF), *Davide Orsi* (U. Parma)
A. Madsen (XFEL)

Proteins ***Luxi Li***, V. Stojanoff, L. Wiegart (BNL), S. Mochrie (Yale)

CHX ***Lutz Wiegart, Yugang Zhang***,
M. Carlucci-Dayton, S. Antonelli, R. Greene,
D. Chabot, W. Lewis,

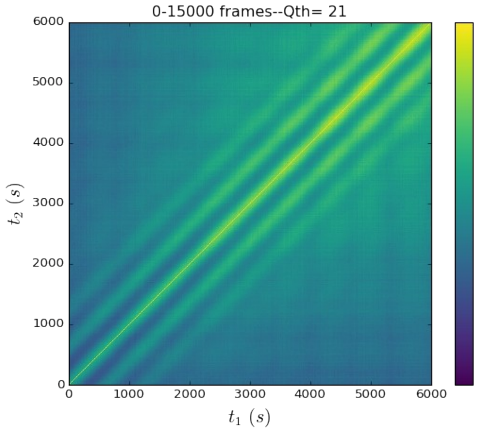
Beamlines ID 10 ESRF - Y. Chushkin, 34-ID APS - R. Harder
8-ID APS - A. Sandy, S. Narayanan

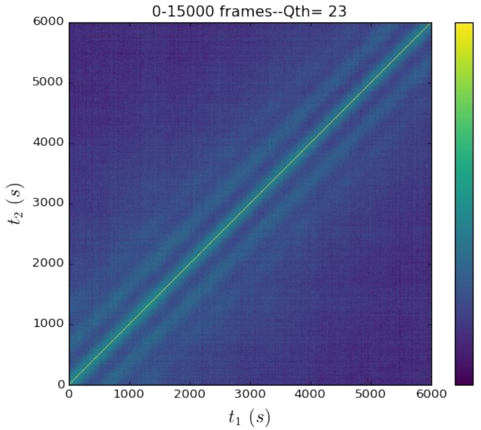
NSLS-II Ron Pindack, Qun Shen, P. Zschack, J. Hill, A. Broadbent
O. Chubar, K. Evans-Lutterodt, P. Siddons ...

Funding NSLS-II project: DOE# E-AC02-98CH10886
BNL SC0012704
BNL LDRD 11-025

CHX user-assisted commissioning

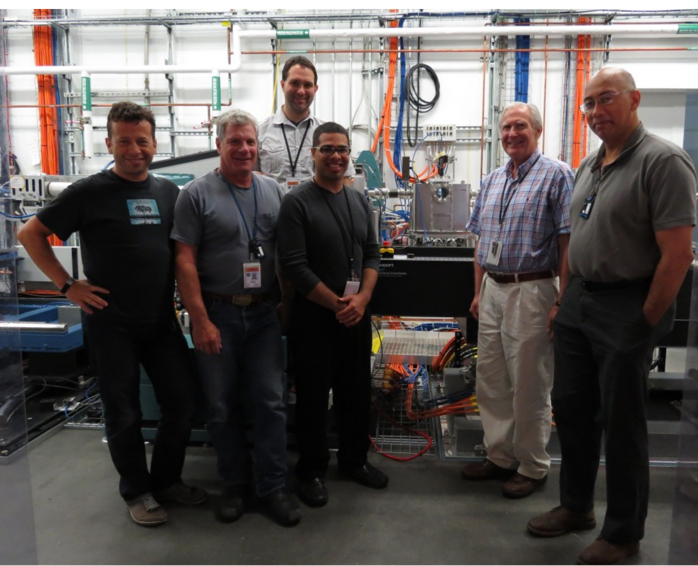
"c-GISAXS Studies of Nanoscale Surface Dynamics during Film Growth and Ion Bombardment", R. Headrick, K. Ludwig *et al.*

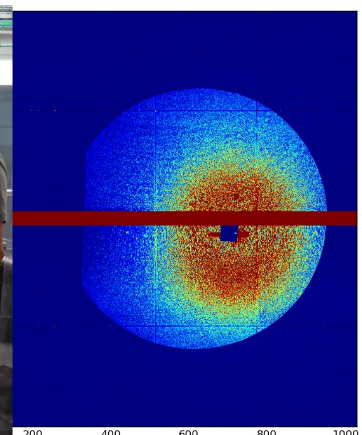




Two-time correlation measured during in-situ sputtering showing evidence of heterodyne mixing

- Performed coherent Grazing Incidence SAXS (c-GISAXS) measurements with Eiger 4M detector during in-situ sputtering with WSi_2 on Si substrates
- *Results:*
  - *Increased time resolution during the early stages of the process over previous measurements performed at APS*
  - *Improved the scattering background by commissioning and using the newly installed SAXS in-vacuum detector system (see previous slide)*
  - *Established an effective data analysis pipeline which is now used by the users for off-line analysis of the experimental data an analysis pipeline for c-GISAXS including two-time correlation analysis*
  - *Measured time-dependent dynamics during the early stages of the deposition process (see attached two-time correlation function)*
  - *Confirmed the presence of heterodyne mixing between the (static) scattering from the bulk film and the (dynamics) signal from the growing surface. This effect improves the resolution of measurements of surface velocities (Note: the users recently published similar results with data obtained at APS before their NSLS-II experiments)*

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