X-ray Photon Correlation Spectroscopy

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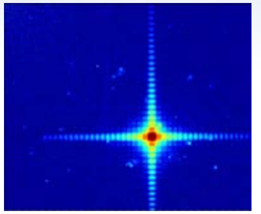
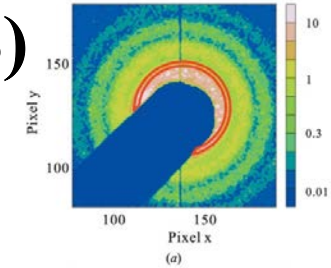
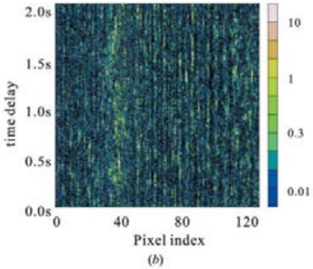
NSLS-II, Brookhaven National Laboratory
National School on Neutron and X-ray Scattering, June 2019

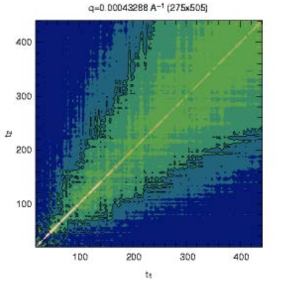
Outline

- **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**



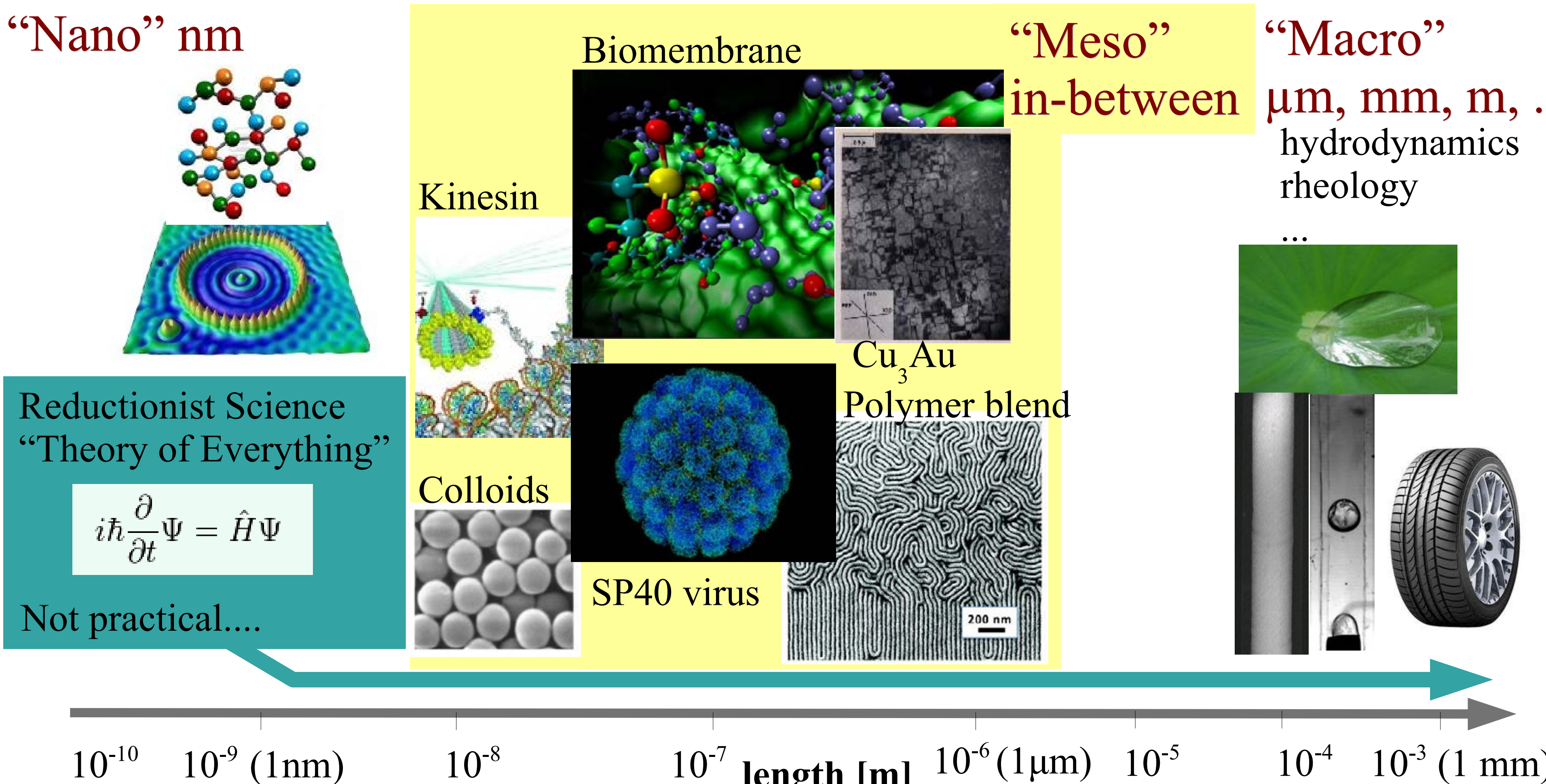






The Next "Big Thing"

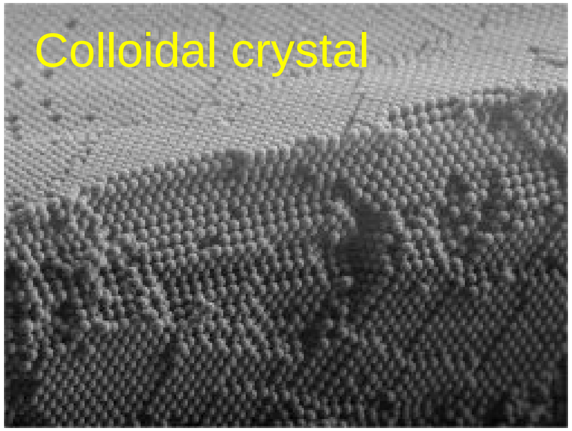
- Opportunities for "Mesoscale Science" DOE BESAC report Sept 2012
  http://www.meso2012.com

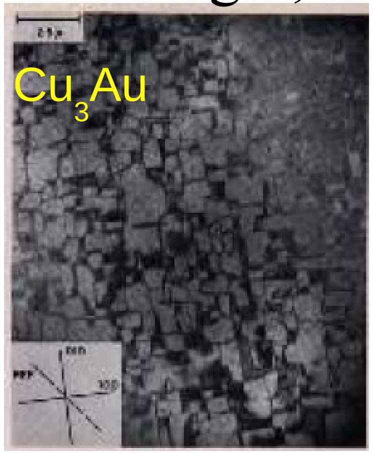


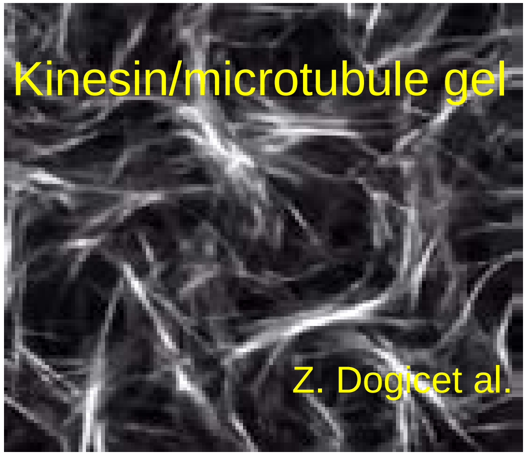
"More is Different"

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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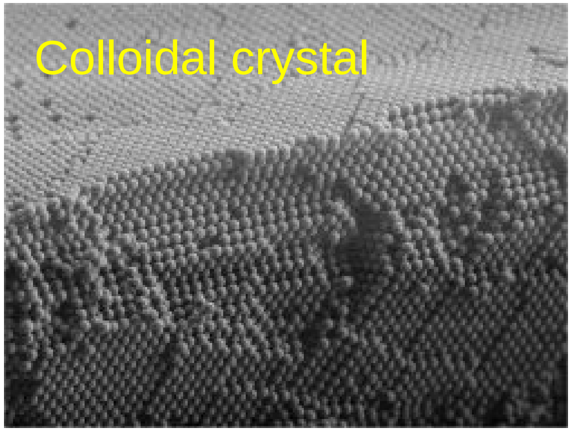
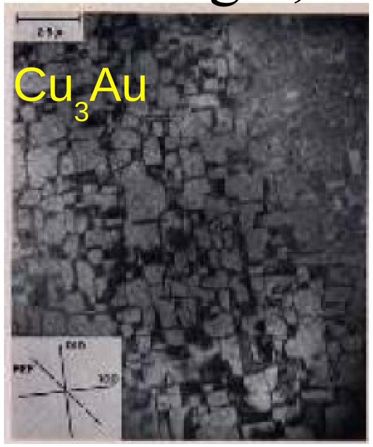
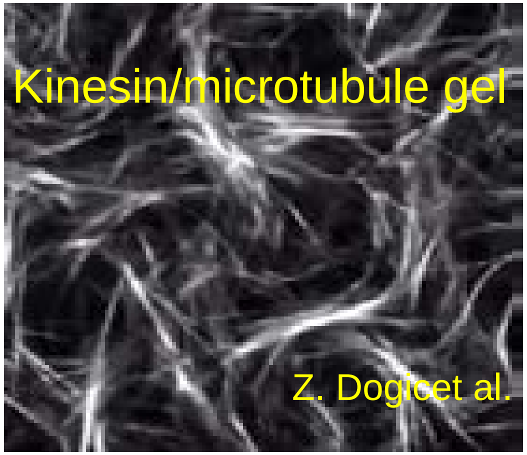




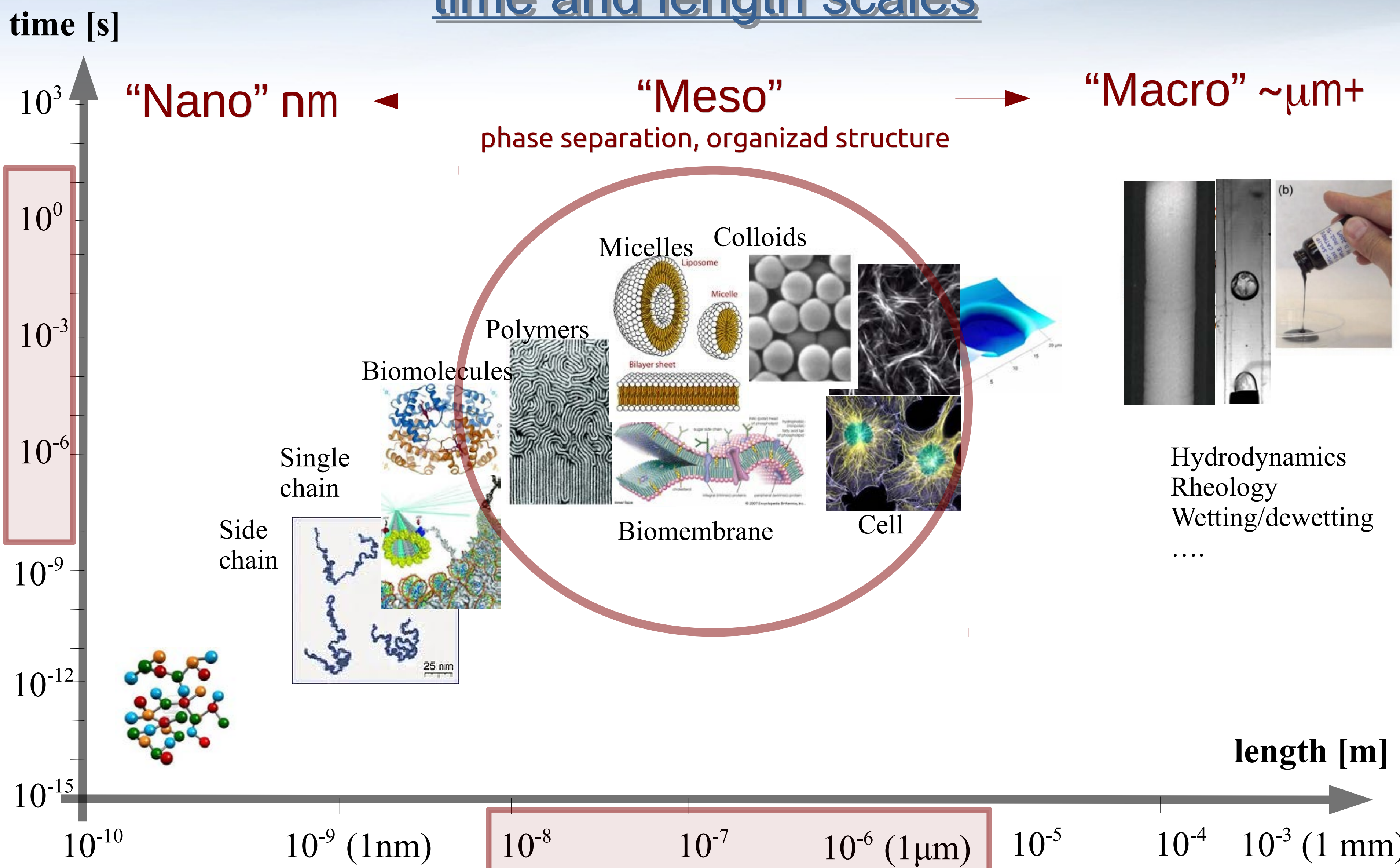


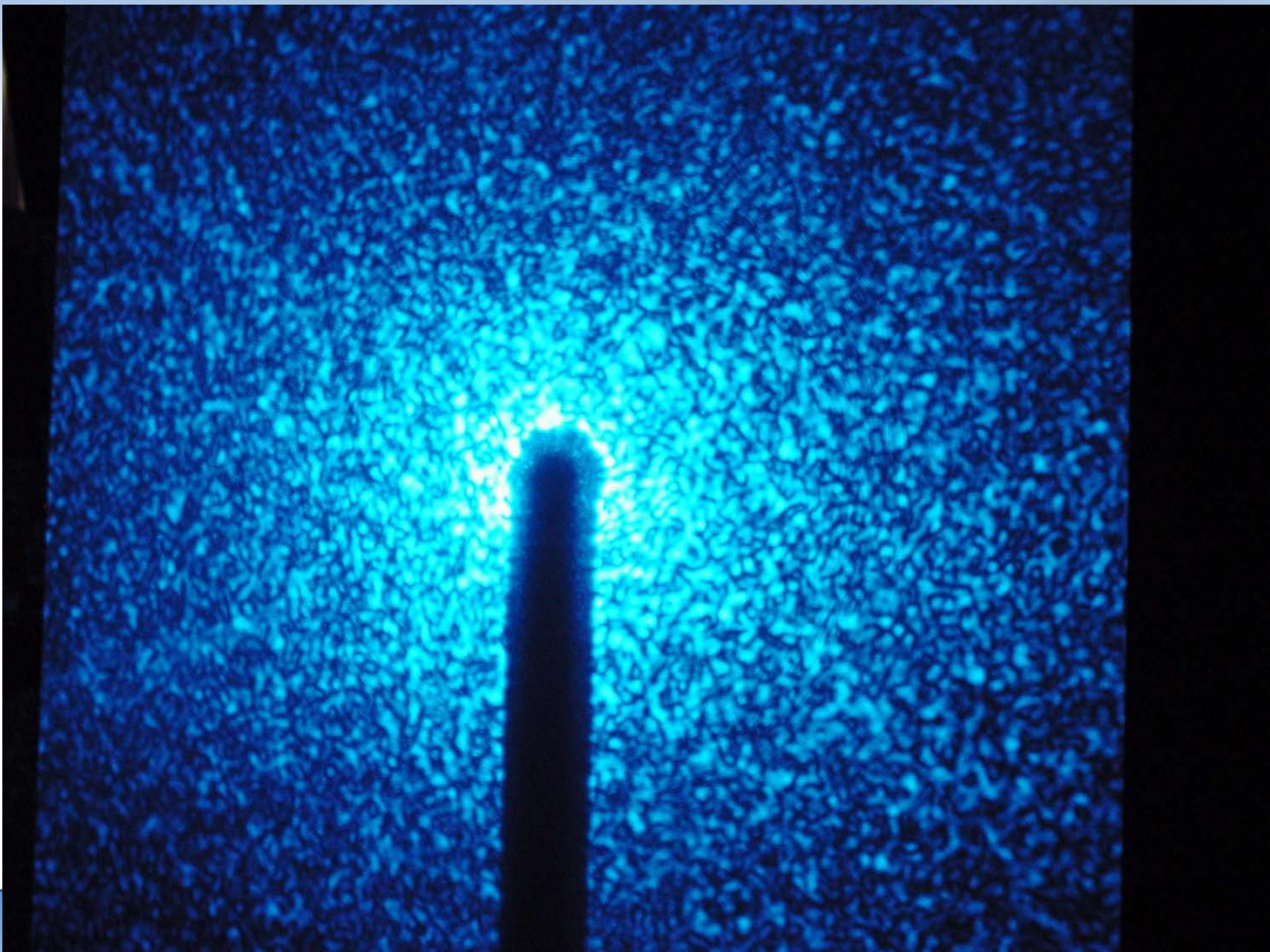
But things are not static !

- Mesoscale Dynamics

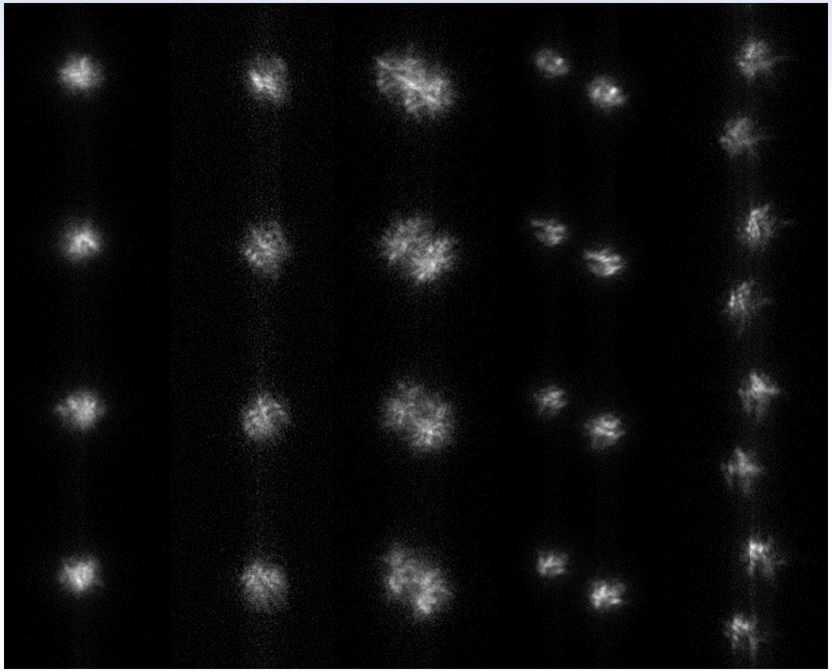
Z. Dogic (Brandeis Univ.)
Dynamics of bundled active networks

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





Speckle



Images of Binary Stars at different degrees

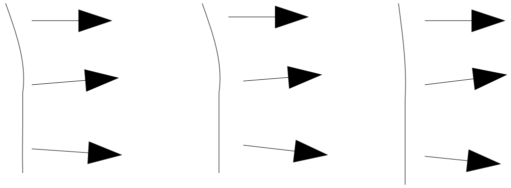
Of separation in the

WIYN Telescope

Matthew F. Hoffmann

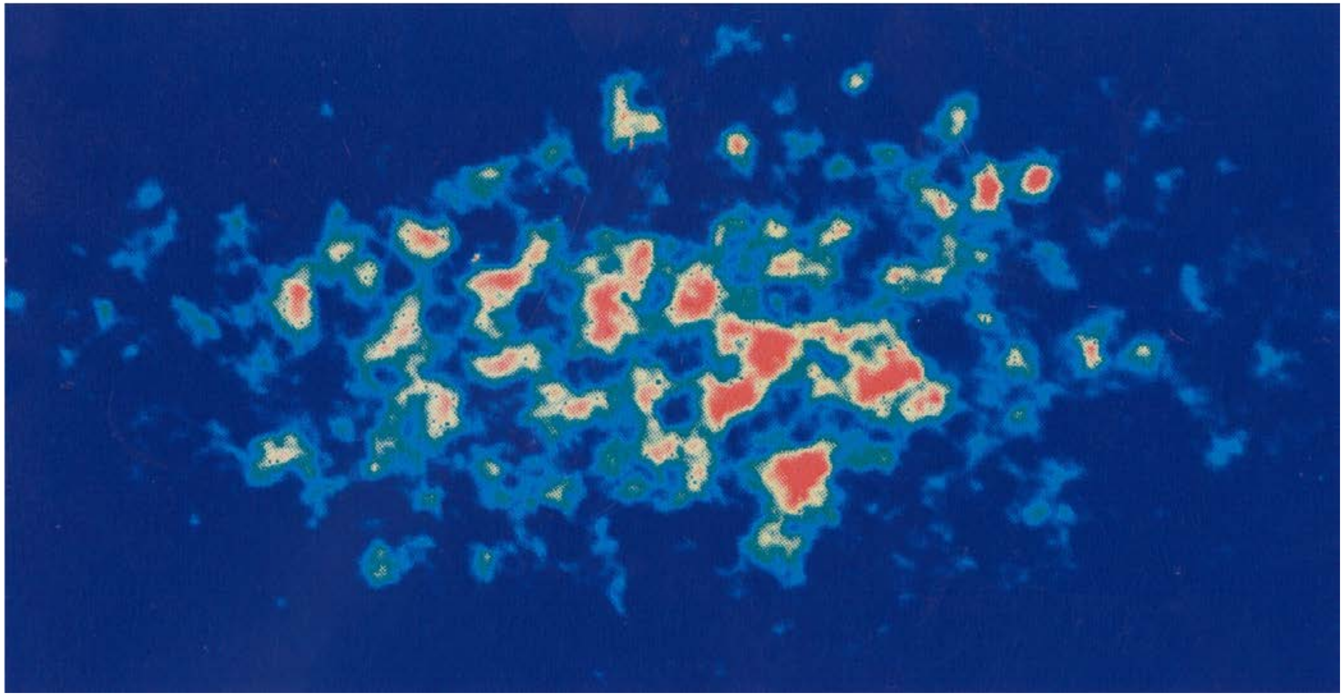
http://www.cis.rit.edu/research/thesis/bs/2000/hoffmann/thesis.html

- Stars (far away) = nearly coherent "point-like" sources
- Fluctuations in the atmosphere create speckle



Speckles with (partially) coherent X-rays

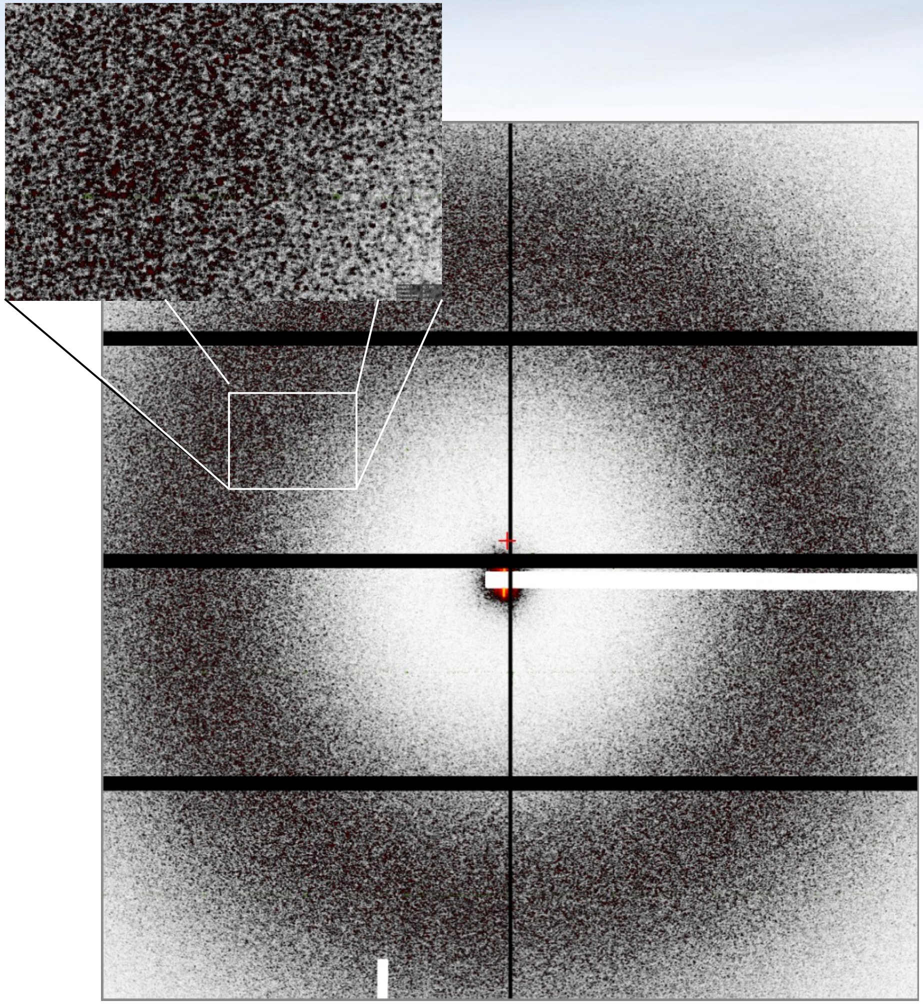
Speckles from Cu_3Au

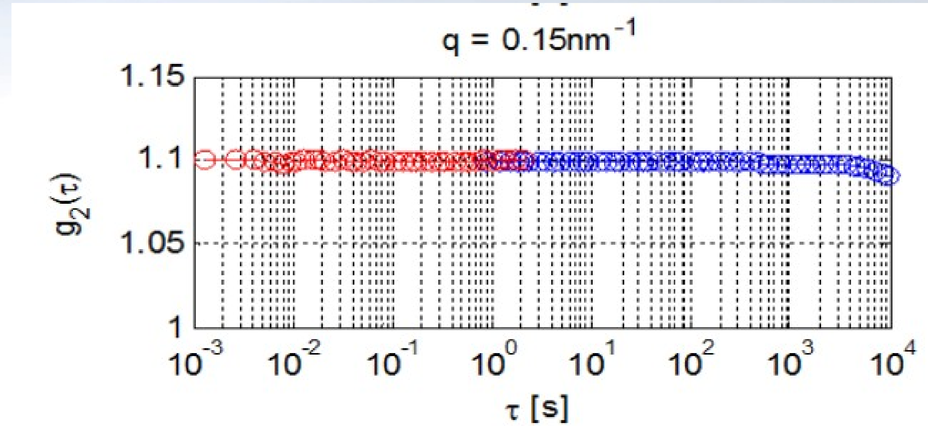


Recorded at X25, NSLS on Kodak film

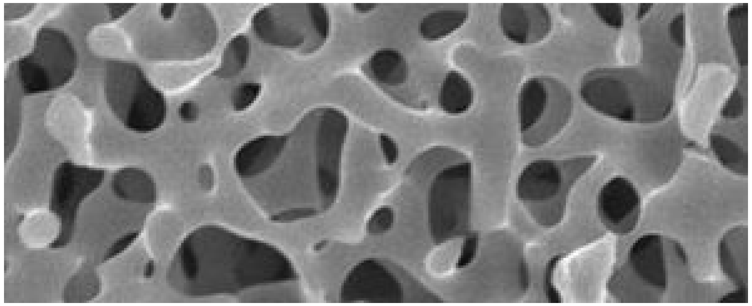
M. Sutton, *et al. Nature* **352**, 608 (1991)

X-ray Speckles (Static!)





Correlation functions $g^{(2)}(q,\tau)$ measured from a CoralPor® static sample show excellent instrument stability.

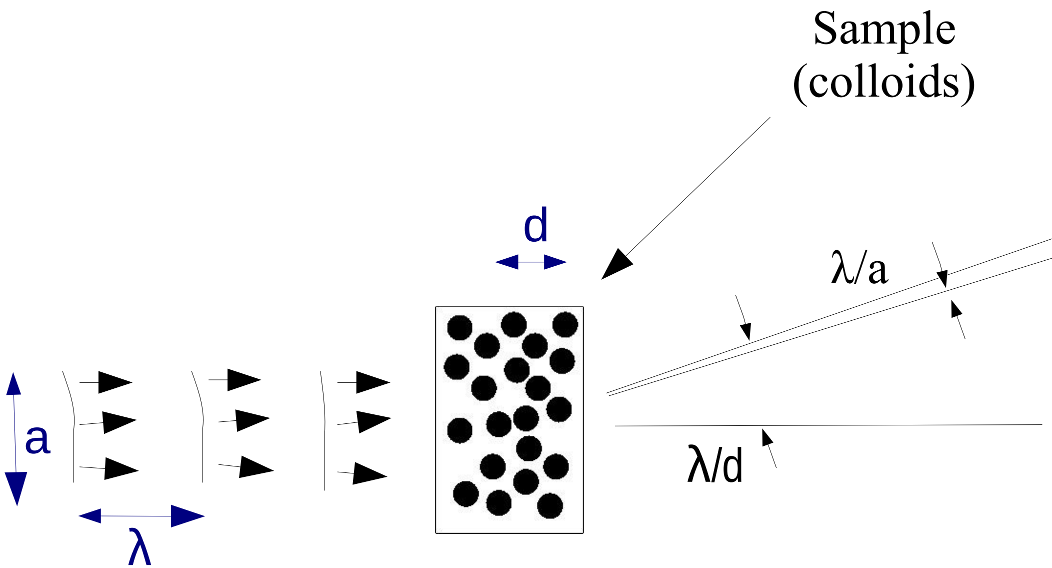


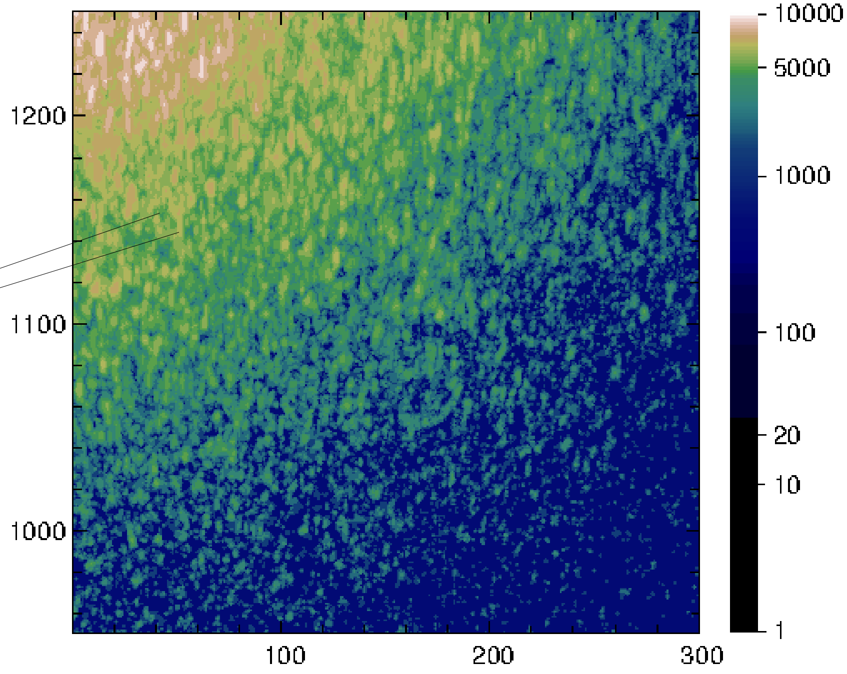
www.schott.com

250mA top-off, 1.5×10^{11} ph/s in $10 \times 10 \mu m^2$; total dose = 101 seconds of "full flux"
Note: decay at ~5×10^3 seconds due to 'beam damage'

Speckles with (partially) coherent X-rays

Speckles from colloidal suspensions



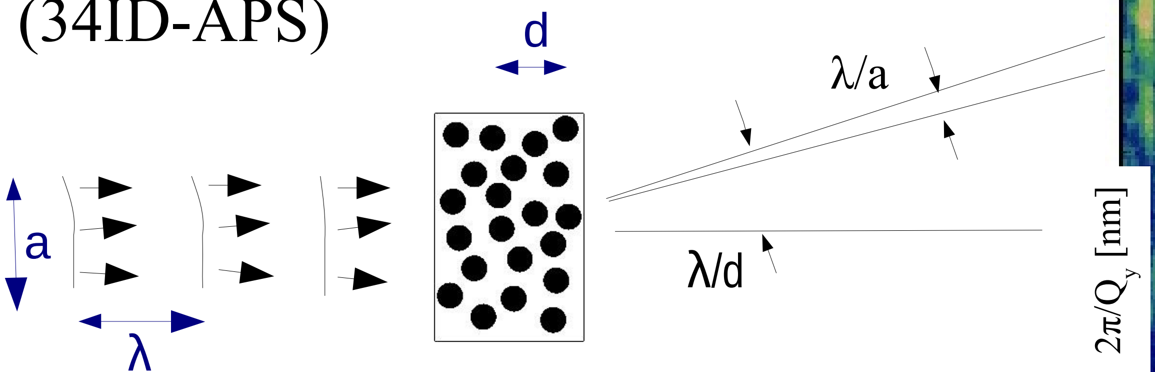


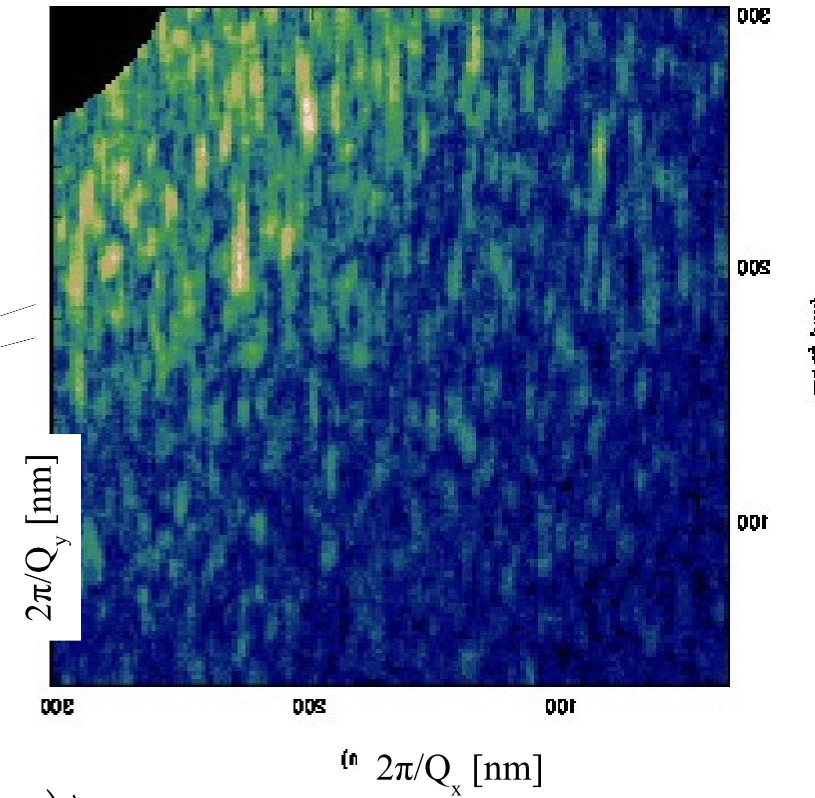
Measured at 34ID with a CCD detector

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)

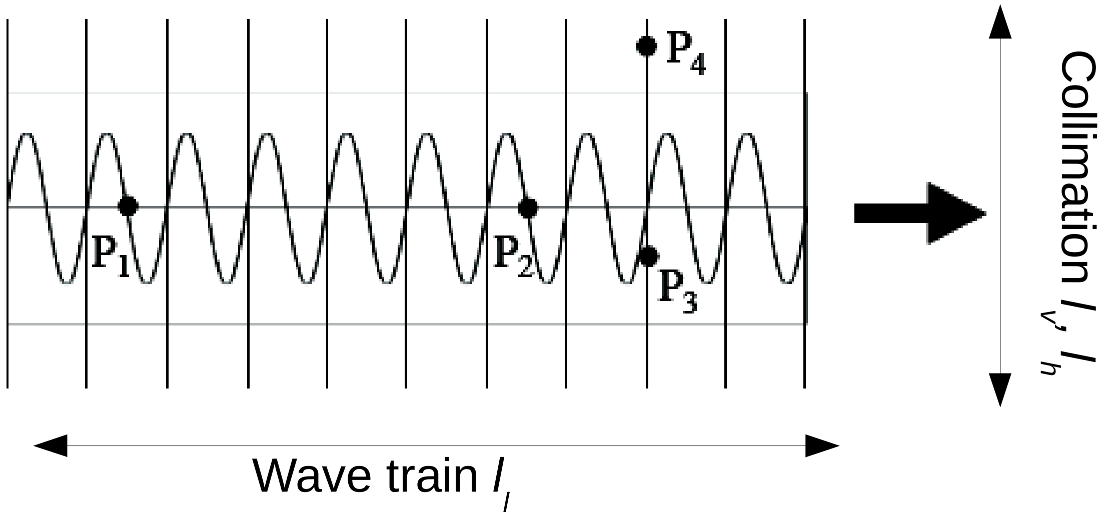




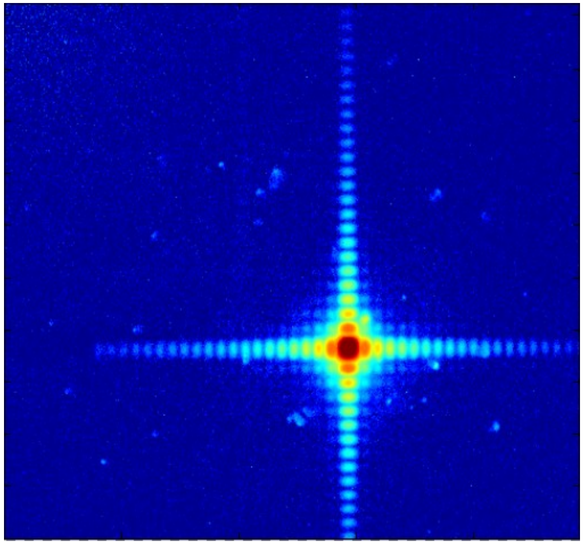
$$g^{(2)}(t) \propto \langle I(t)\, I(0) \rangle$$

Mini-introduction to coherence

- 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: ΔΦ(P3:P4)
  - Longitudinal(temporal) coherence: ΔΦ(P1:P2)



Malcolm Howells, Lecture Notes, ESRF 2007

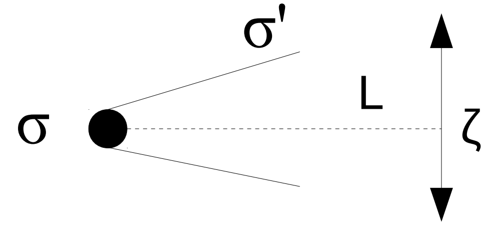


L. Wiegart, CHX, NSLS-II

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:

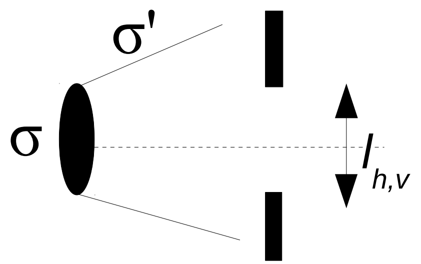
$$l_{h,v} = \frac{\lambda L}{4\pi\sigma_{h,v}}$$

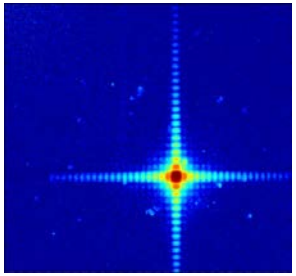
Transverse coherence

- 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)





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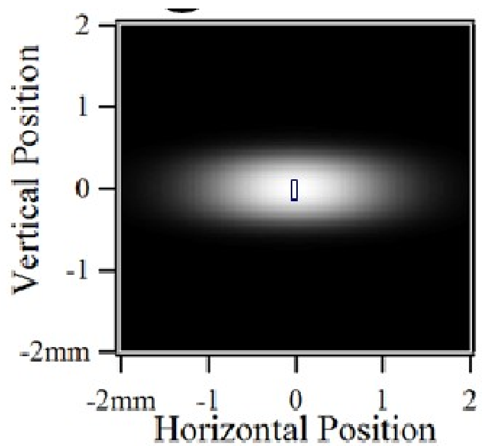
BROOKHAVEN NATIONAL LABORATORY | National Synchrotron Light Source II

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
$\mathbf{M_h}$	38.2	50.7	62.2	75.7	94.6
$\mathbf{M_v}$	4.5	5.3	5.8	7.5	9.0

Longitudinal coherence

- Longitudinal (temporal) coherence:

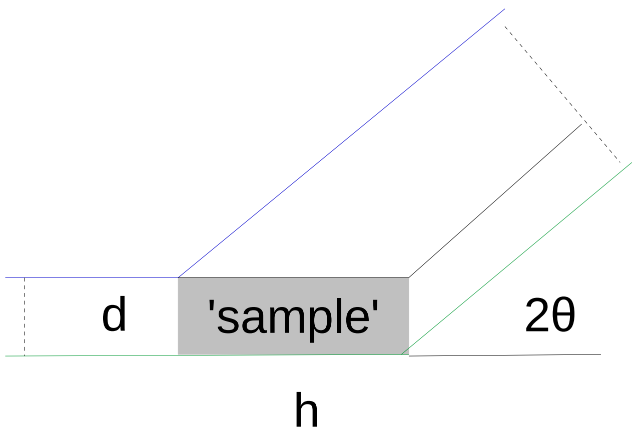
$$\frac{\delta\lambda}{\lambda} \approx \frac{1}{N}, l_l = \lambda N \qquad l_l \approx \frac{\lambda^2}{\delta\lambda}$$

- Experimental requirement:

  max optical path diff. $< l_l$

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

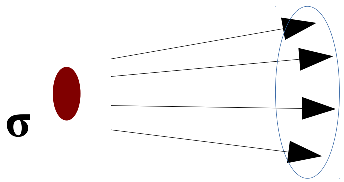
$$h \sin^2(2\theta) + d \sin(\theta) \leqslant l_l$$



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

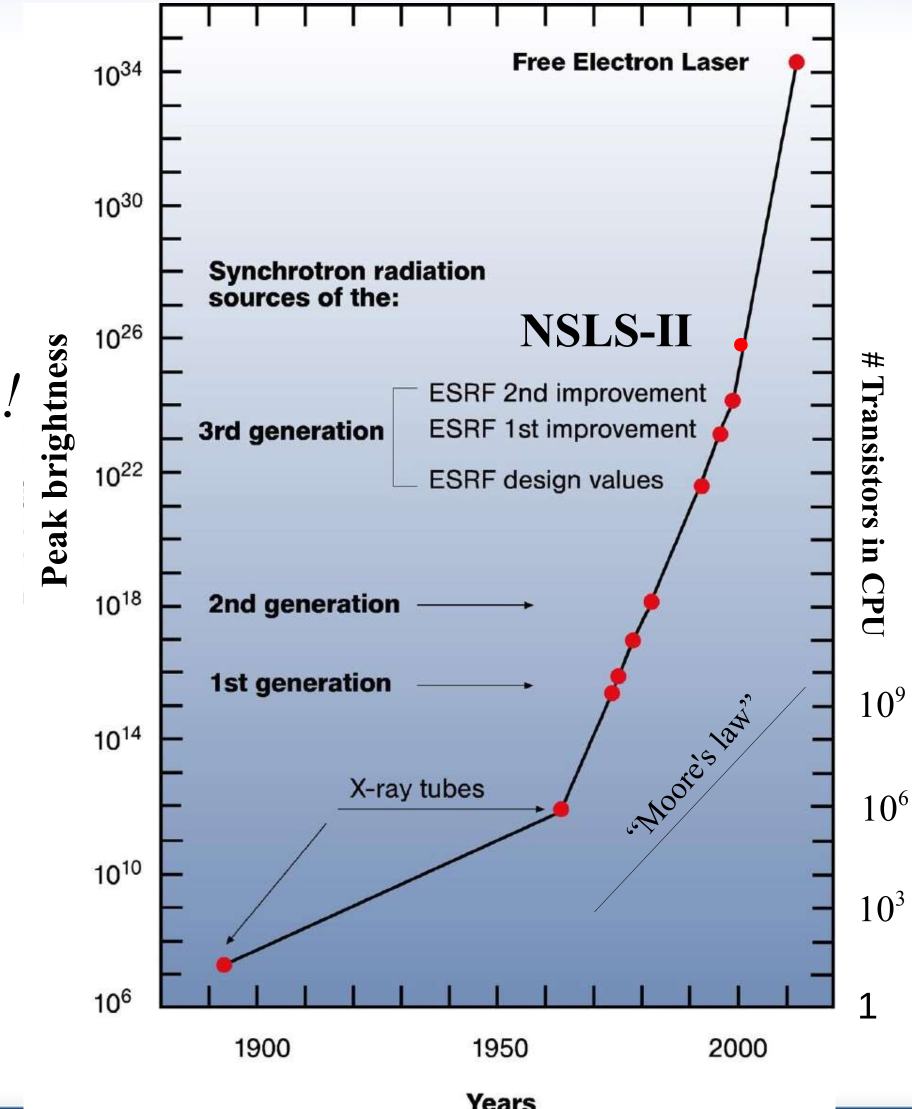
Synchrotron Source Brightness

- 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

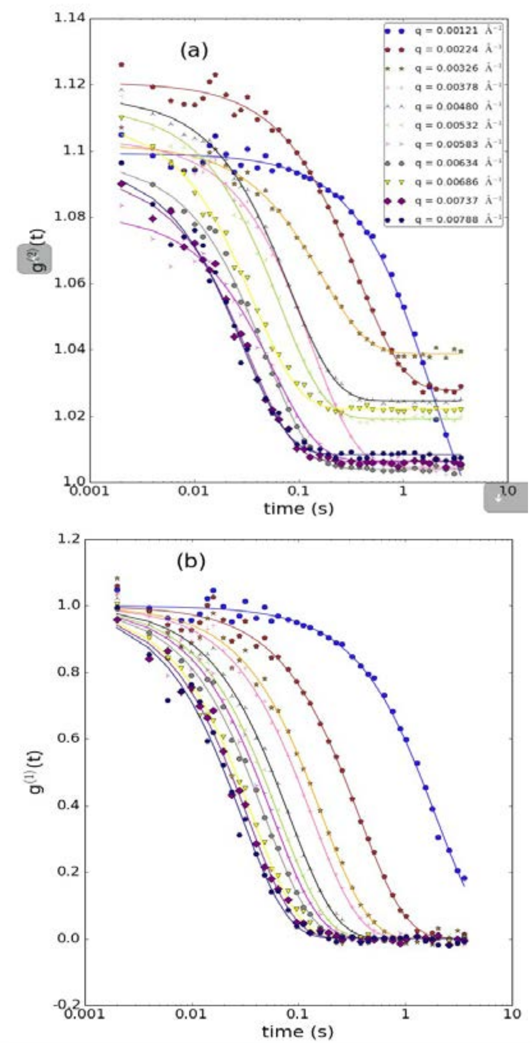
$$\langle I(q,t)I(q,t+\delta t)\rangle = \langle I(q)\rangle^2 + \beta(q)(\ldots)|S(q,t)|^2$$

- 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

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



Correlation Functions

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

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

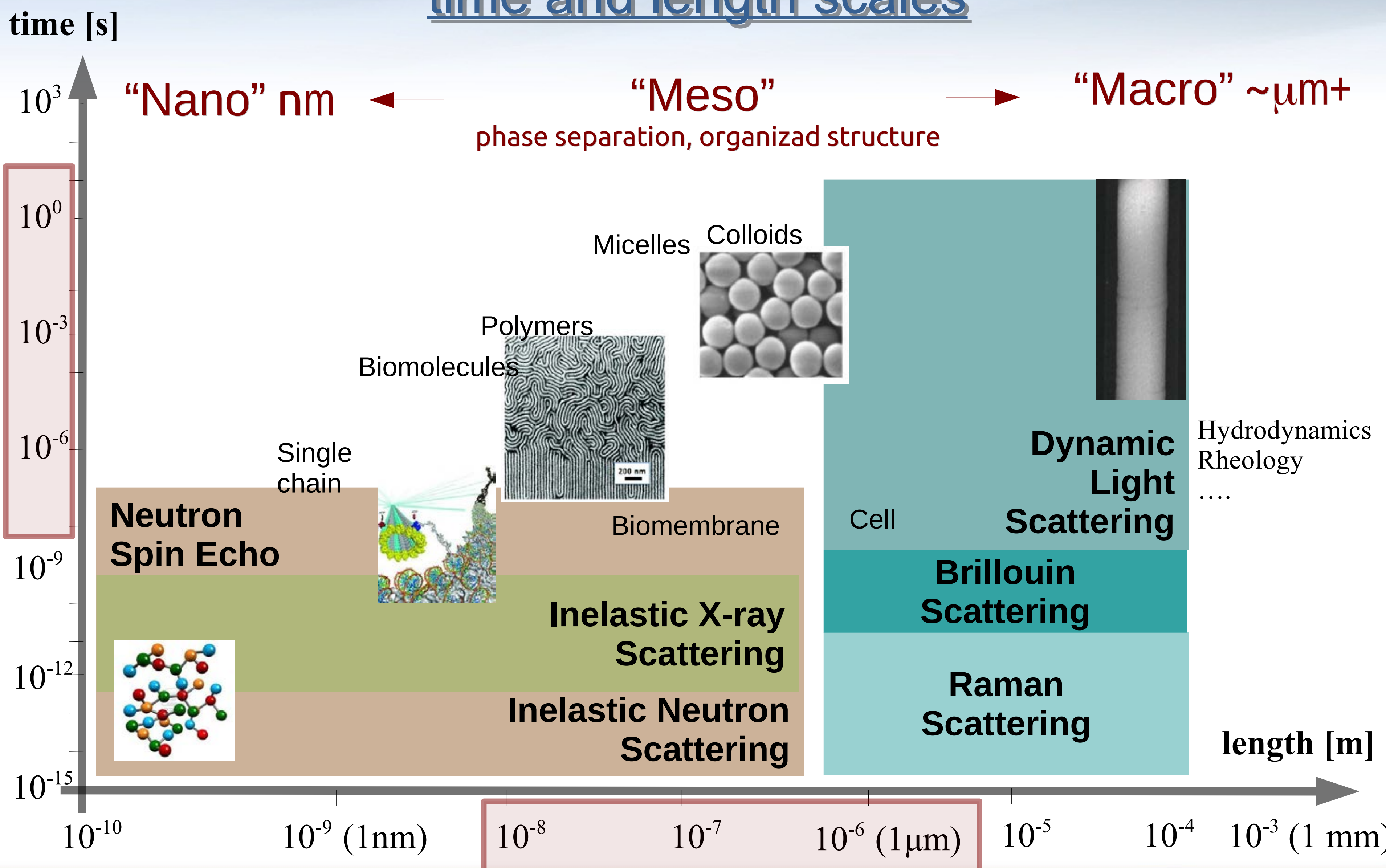
K = detector efficiency
T = total experiment duration
τ = accumulation time
Ω = angle subtended by Q of interest
Σ = scattering cross section per unit volume
W = sample thickness
Λ= 1/attenuation length
B = source brilliance
ΔE/E = normalized energy spread
r = factor depending on source size, pixel size,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



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}

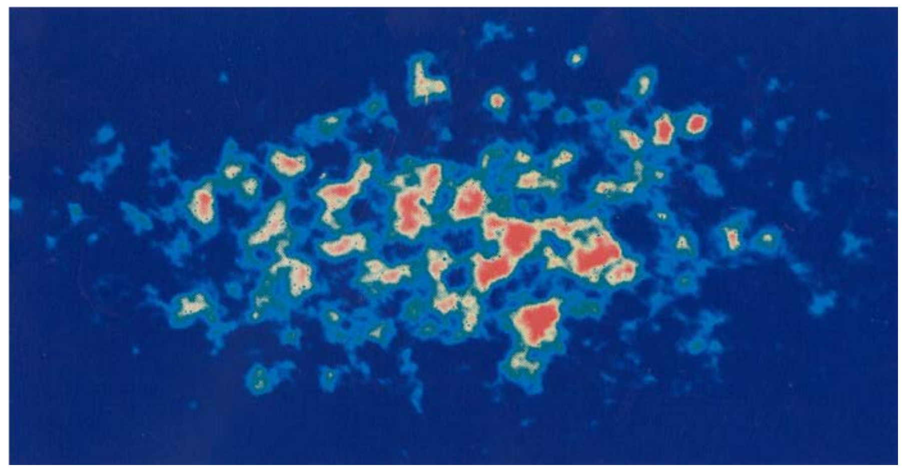
"Nano" nm ← "Meso" → "Macro" ~μm+

phase separation, organizad structure

Speckles from Cu_3Au

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

Cu_3Au



X25 beamline @ NSLS

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

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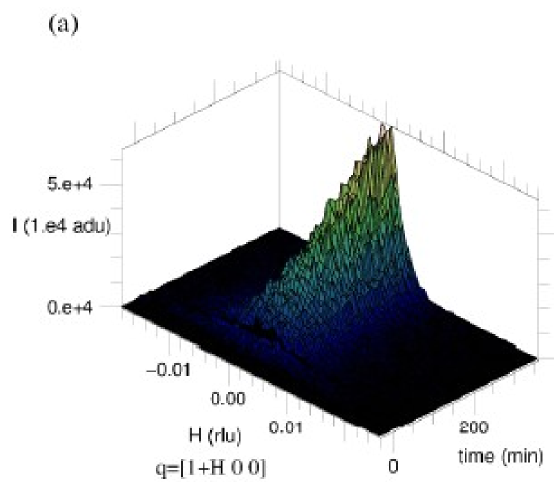
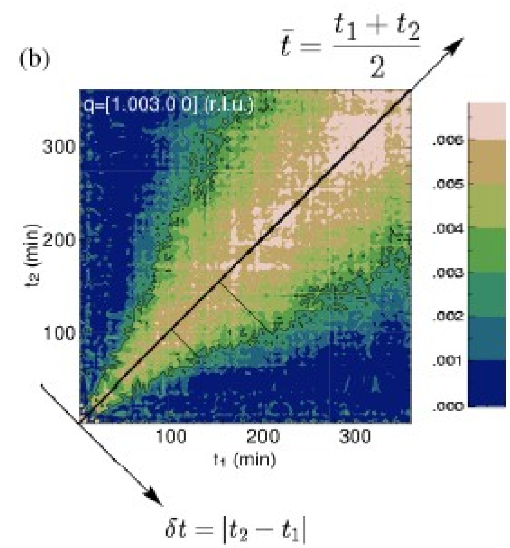
phase separation, organizad structure

Phase-ordering in Cu_3Au

Cu_3Au





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

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

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10^{-3}

10^{-6}

10^{-9}

10^{-12}

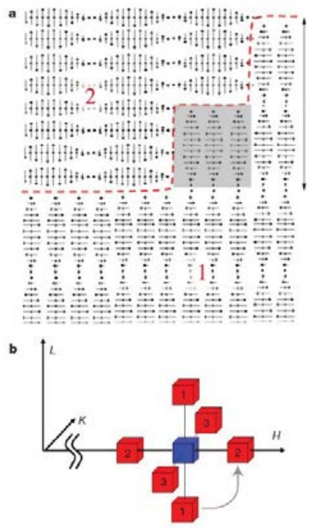
10^{-15}

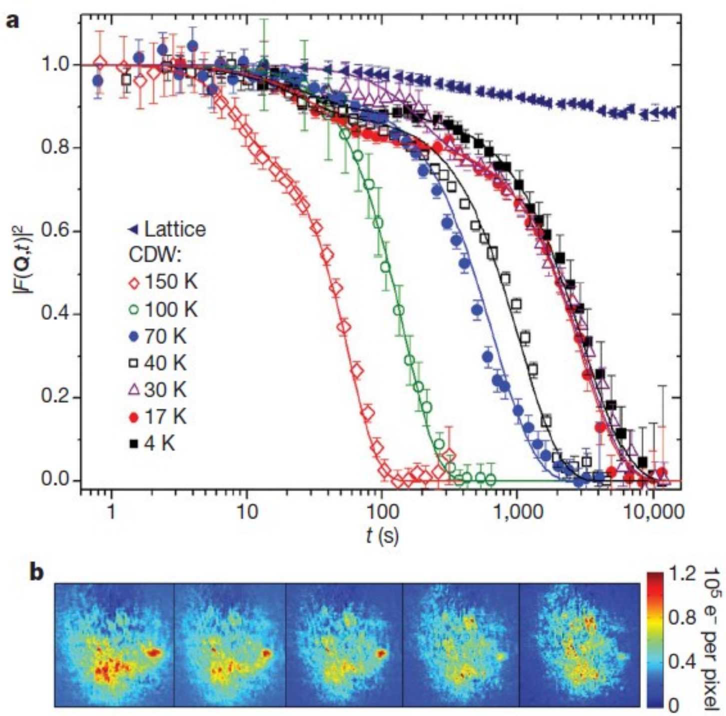
"Nano" nm ← "Meso" → "Macro" ~μm+

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}

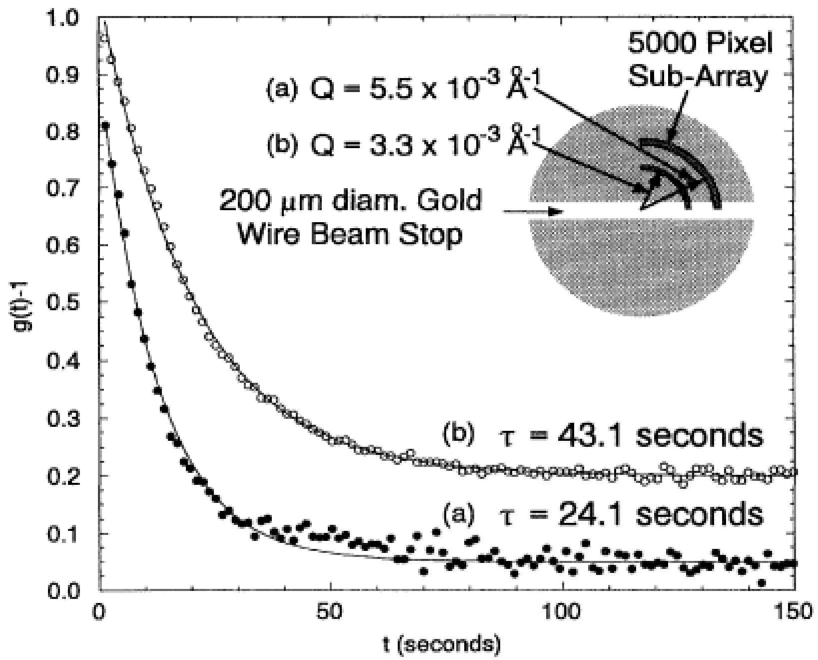
10^{-12}

10^{-15}

Brownian motion: Au colloids in glycerol

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

X25 beamline @ NSLS



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

Micell… Colloids

10^0

10^-3

10^-6

10^-9

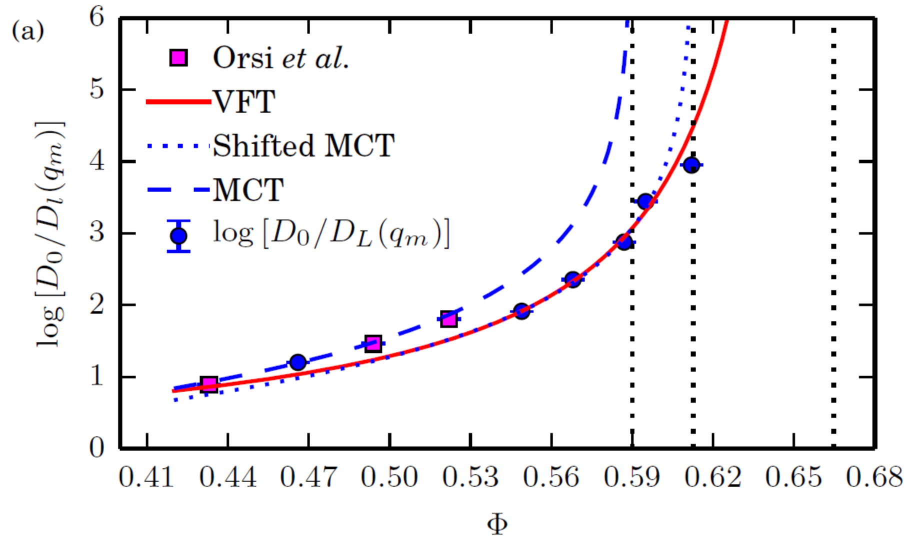
10^-12

10^-15

Brownian motion: high density PMMA colloids

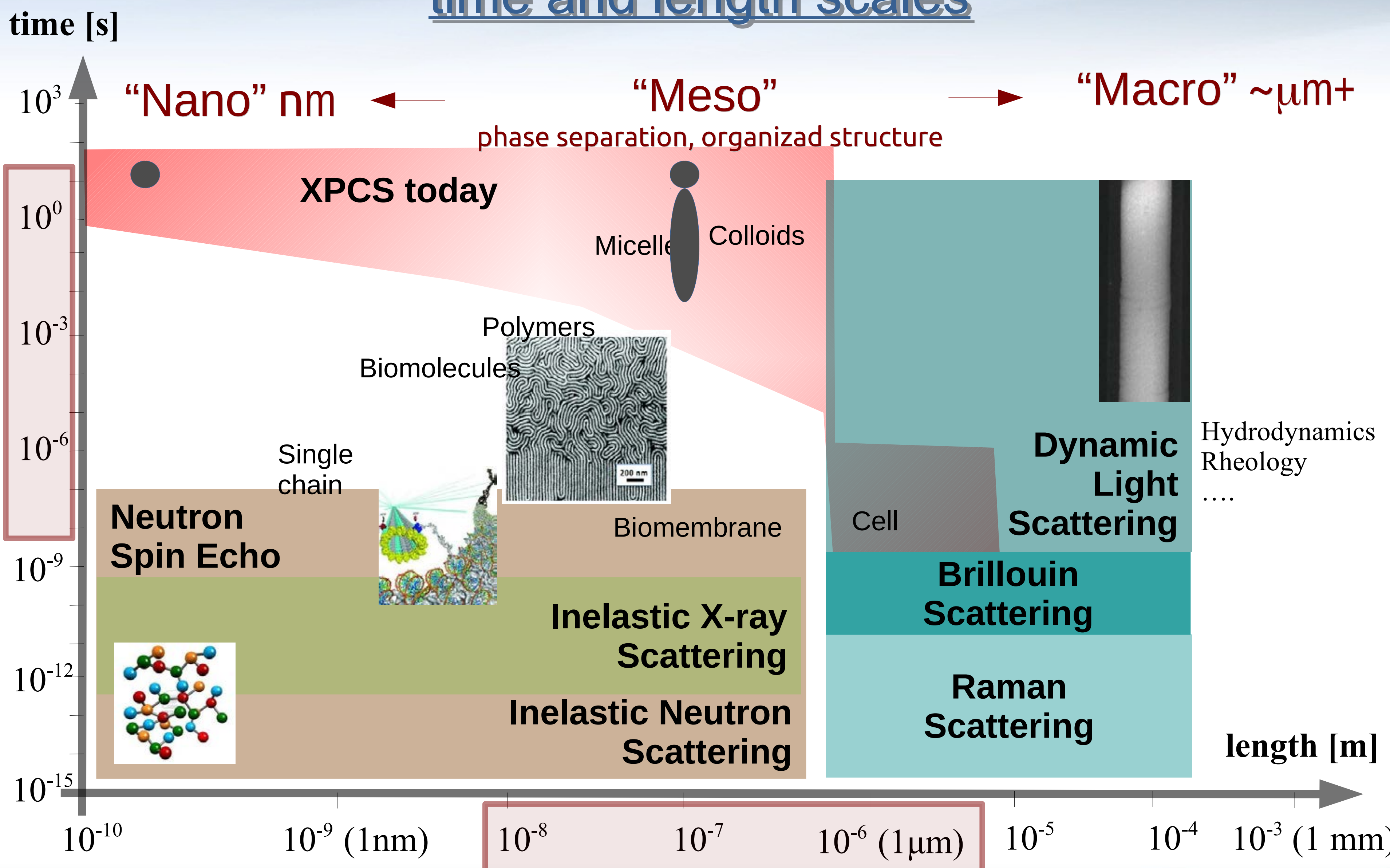
P. Kwasniewski *et al.*
Soft Matter. **10**, 8698 (2014)

ID10 beamline @ ESRF

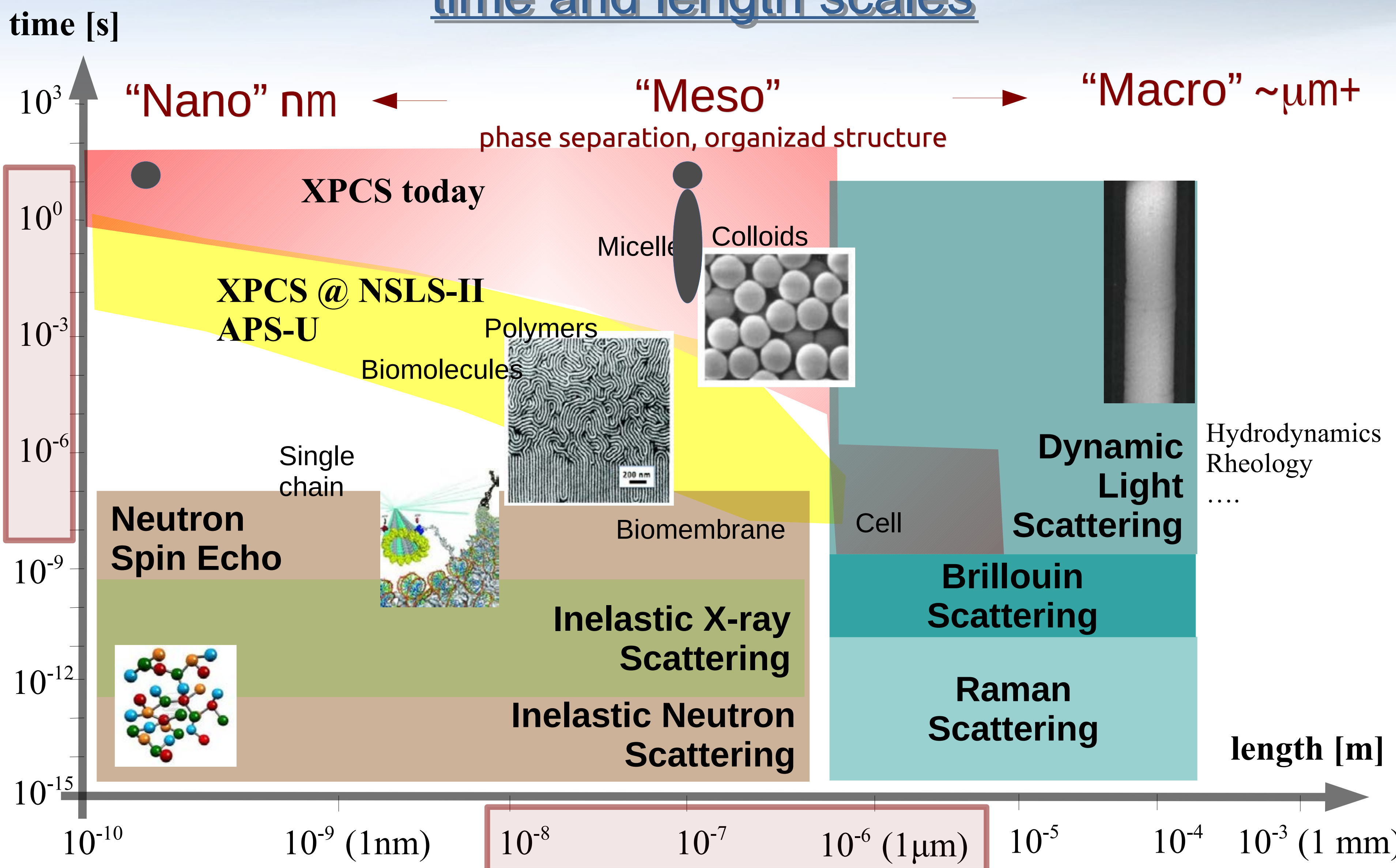


10^-10 10^-9 (1nm) 10^-8 10^-7 10^-6 (1μm) 10^-5 10^-4 10^-3 (1 mm)

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



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

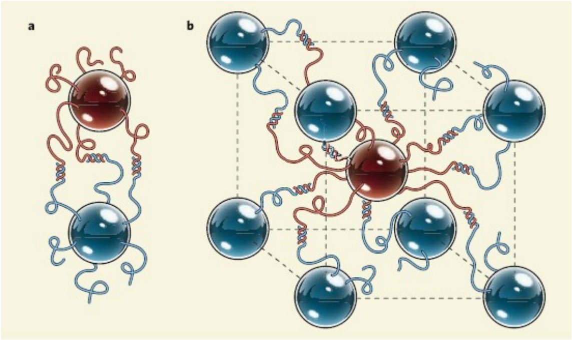


Colloids

- 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

Brownian Motion; Fluctuations

How far does a particle move in a time t due to Brownian motion (diffusion):

This is given by the *mean-squared displacement* $<r^2>$ and it varies linearly with time

$$<r^2> = 6\mathcal{D}\, t$$

Einstein-Smoluchowski equation

$\mathcal{D}$ = diffusivity of the particles

How far the particle moves is dictated, in turn, by its diffusivity $\mathcal{D}$:

$$\mathcal{D} = \frac{k_B T}{6\pi\eta_s R_h}$$

Valid for monodisperse spherical particles

Stokes-Einstein equation

- As absolute temperature T increases, diffusivity increases
- As solvent viscosity η_s increases, diffusivity decreases
- As particle size (hydrodynamic radius, R_h) increases, diffusivity decreases

Intermediate Scattering Function

The intermediate scattering function $f(Q,\tau)$ is related to the static structure factor $S(Q)$ of the sample and

$$f(Q,\tau) = \frac{1}{S(Q)} \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \exp(i\mathbf{Q} \cdot [\mathbf{r_i}(0) - \mathbf{r_j}(\tau)]) \rangle \tag{18}$$

for scattering from N identical particles in the illuminated volume. The simplest possible dynamics is Brownian motion (Stokes-Einstein free diffusion) of such N particles [16, 42]. In the absence of any interactions between particles $S(Q) = 1$ and all the cross terms $(i \neq j)$ in Eq. 18 average out to zero. The mean-square value of the displacement of a free Brownian particle is

$$\langle [\mathbf{r_i}(0) - \mathbf{r_j}(\tau)]^2 \rangle = 6D_0\tau \tag{19}$$

where D_0 denotes the free diffusion coefficient of a particle with radius R_p in a medium with viscosity η and

$$D_0 = \frac{k_B T}{6\pi\eta R_p}. \tag{20}$$

In this case one finds

$$f(Q,\tau) = \exp(-D_0 Q^2 \tau). \tag{21}$$

The *intermediate scattering function* is typically calculated in numerical simulations and can be measured by experimental techniques such as *Dynamics Light Scattering (DLS)*, *X-ray Photon Correlation Spectroscopy (XPCS)*, *Neutron Spin Echo (NSE)*

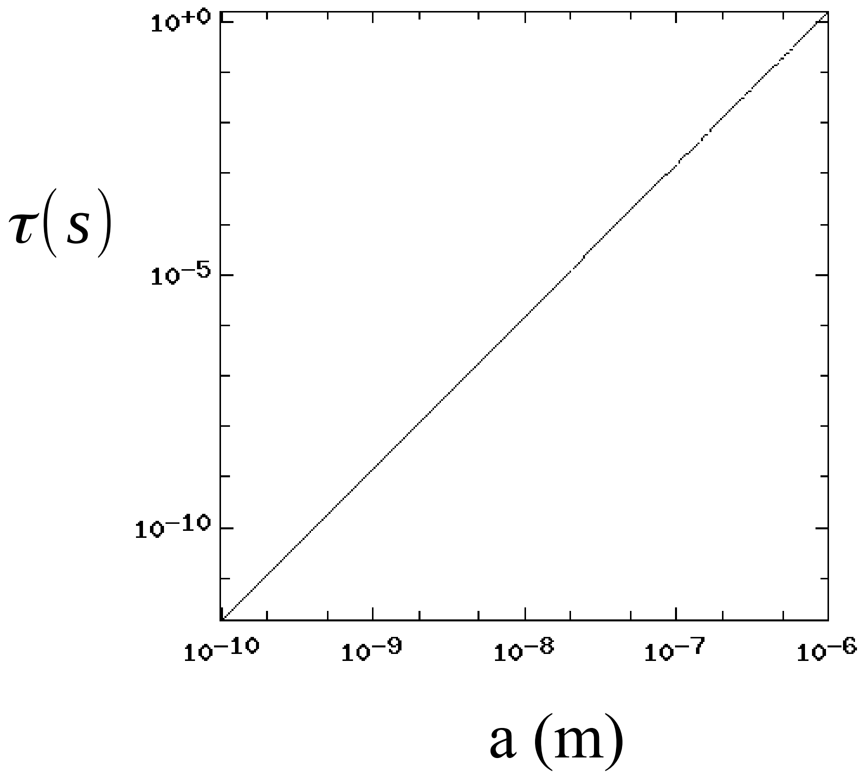
Characteristic timescales

How much time does it take for a particle to travel (diffuse) a distance equal to its diameter a?
This time, from Einstein-Smoluchowski eq. is

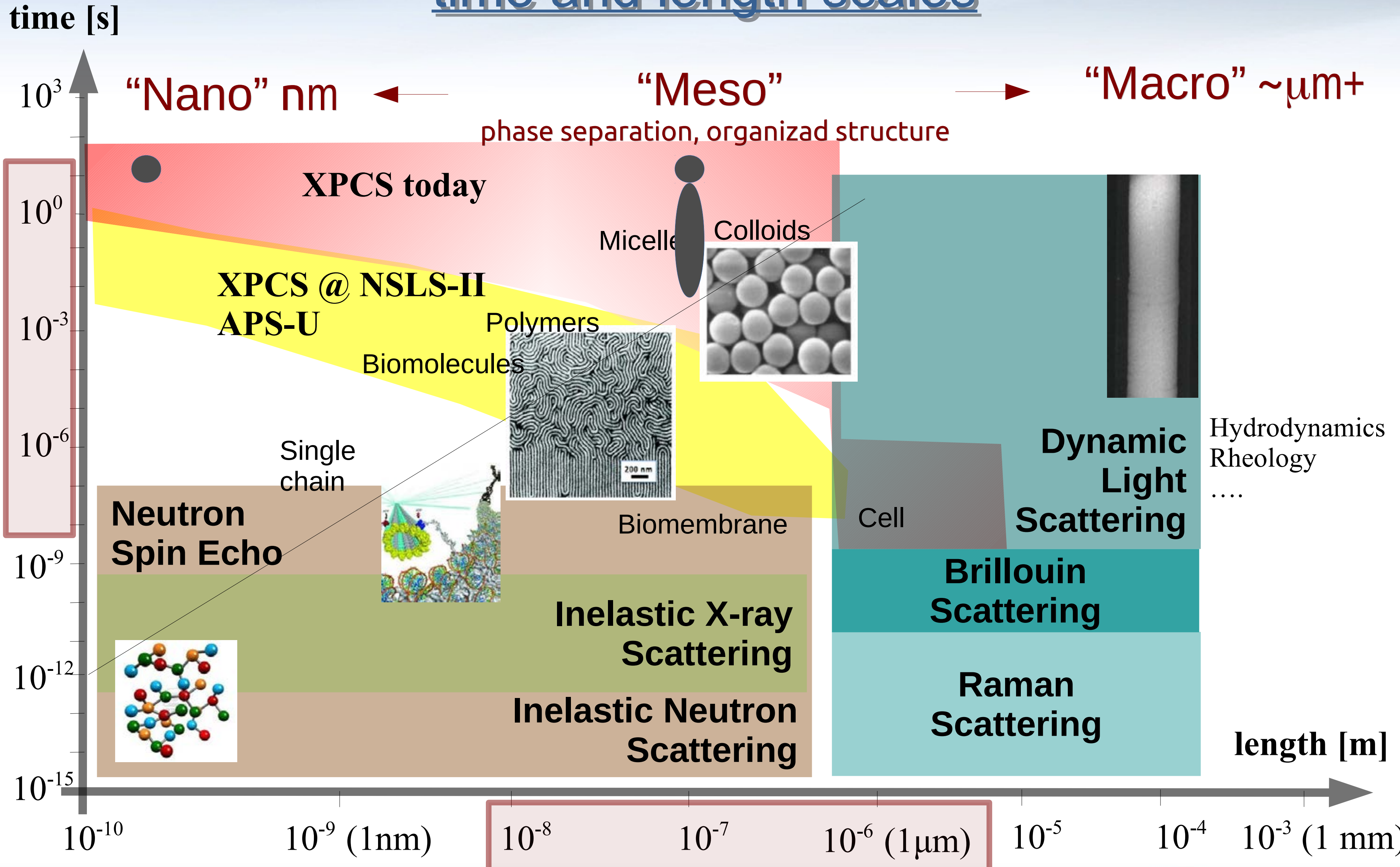
$$\tau = \frac{a^2}{6D}$$

where (Stokes-Einstein)

$$D = \frac{k_B T}{6\pi\eta a}$$

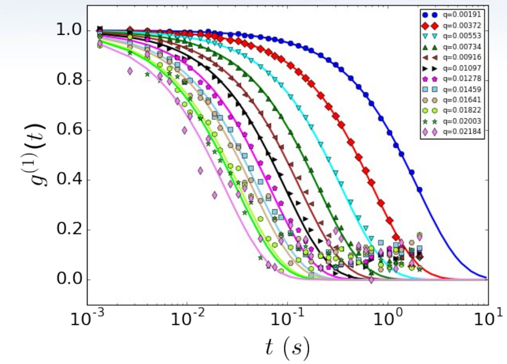


Dynamics of Materials (soft- and bio-): time and length scales



Density-density correlation functions
Dynamic Structure Factor & ISF

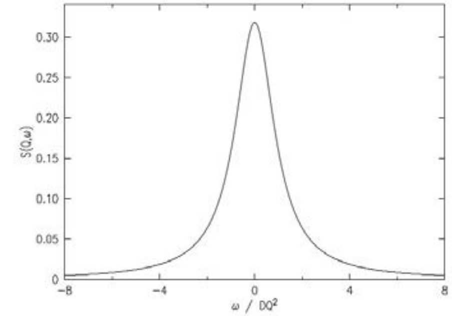
- Intermediate Scattering Function:



$$f(\vec{q},t)=\frac{1}{S(\vec{q})}\int G(\vec{r},t)\exp[-i\vec{q}\vec{r}]d\vec{r}$$

can be measured by experimental techniques such as Neutron Spin Echo (NSE), X-ray Photon Correlation Spectroscopy (XPCS) and Dynamics Light Scattering (DLS)*; ISF is a time-dependent structure factor S(q,t)*
For diffusion, the ISF has an exponential shape

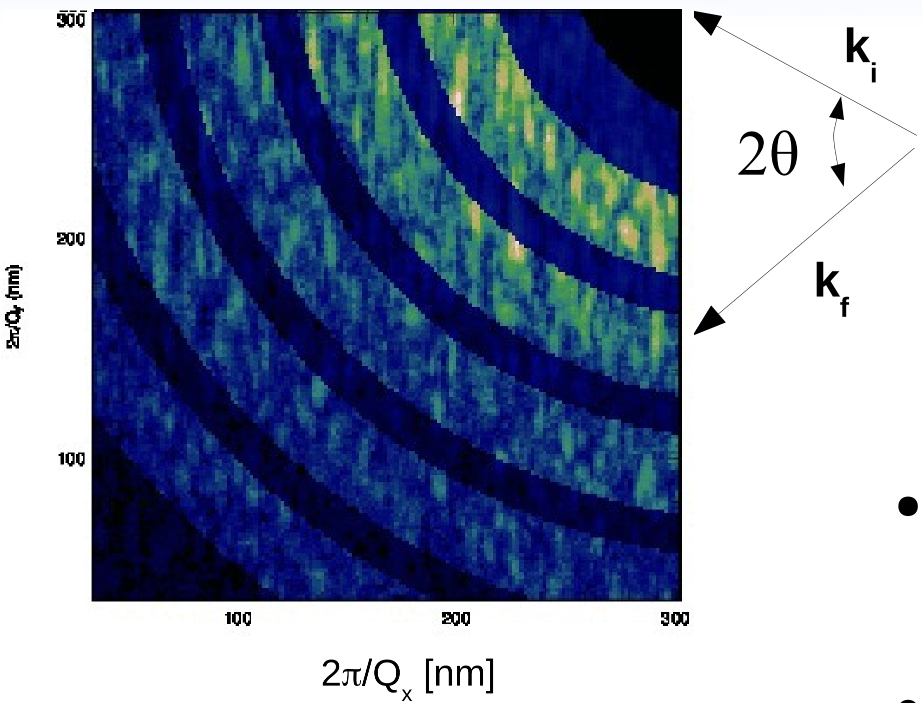
- Dynamic Structure Factor:



$$S(\vec{q},\omega)=\frac{1}{2\pi}\int F(\vec{q},t)\exp[i\omega t]dt$$

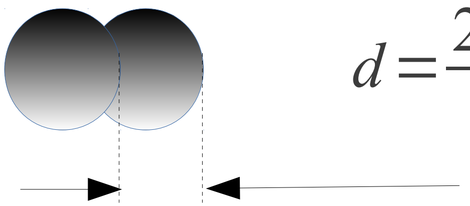
can be measured by experimental techniques such as Inelastic neutron and X-ray scattering. *The dynamic structure factor is a frequency-dependent structure factor*
For diffusion, S(q,ω) has a Lorenzian shape.

Colloidal Dynamics with XPCS



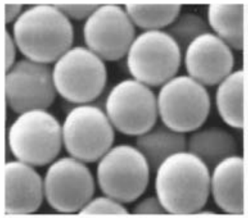
$$q = \frac{4\pi}{\lambda} \sin\left(\frac{2\theta}{2}\right)$$

- Measures time scale associated with displacement of colloids

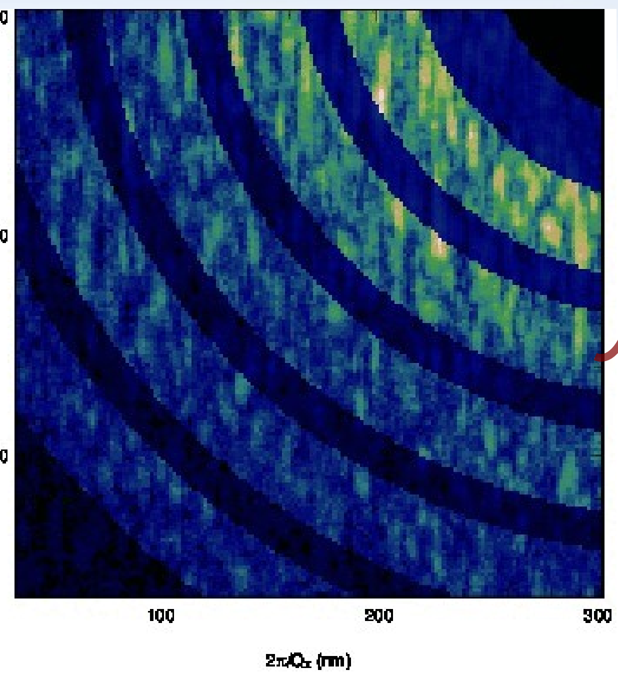


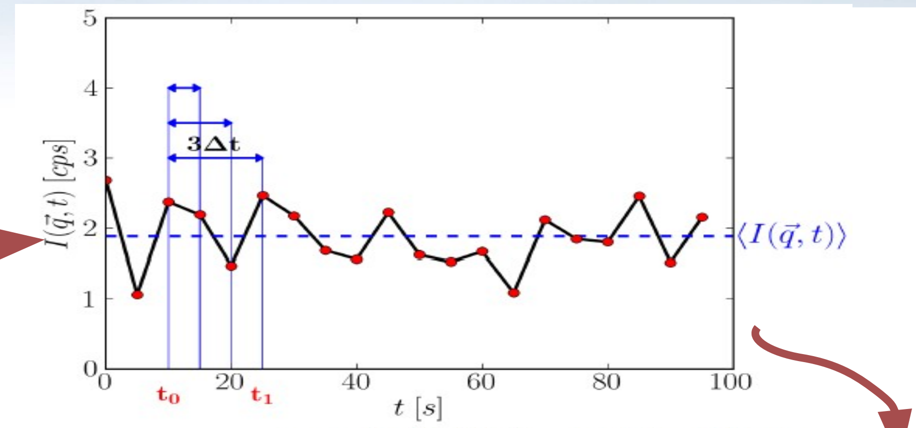
$$d = \frac{2\pi}{q}$$

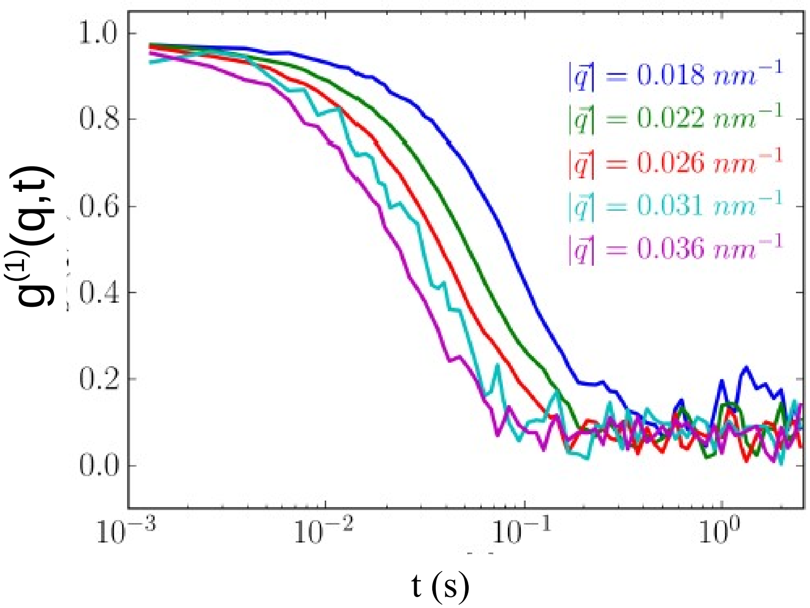
- i.e. measures dynamic structure factor *S(q,t)*
- By averaging over ~10^{11} particles
- For different *q* values



Colloidal Dynamics with XPCS







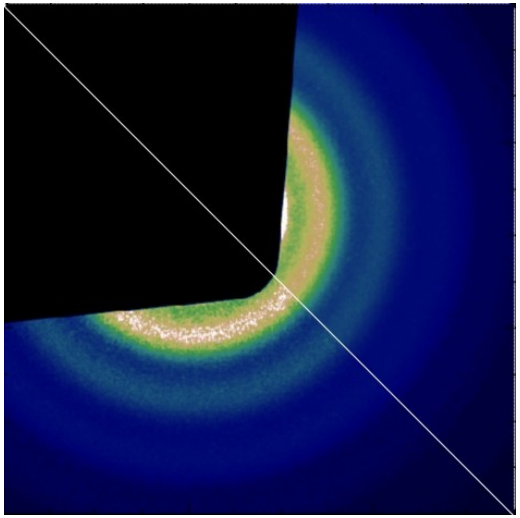
$$g^{(2)}(q,t)=\frac{\langle I(q,t)I(q,t+\delta t)\rangle}{\langle I(q)\rangle^2}$$

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

Speckle & Intensity Autocorrelation Functions

- Coherence & Intensity autocorrelation functions of the speckle patterns measure the intermediate scattering function (a.k.a. dynamics)

$$\langle I(q,t)I(q,t+\tau)\rangle = \langle I(q)\rangle^2 [1+\beta(q)(\ldots)|f(q,\tau)|^2]$$



"Incoherent" scattering (from any SAXS experiment/instrument)

Coherent Scattering / Speckle

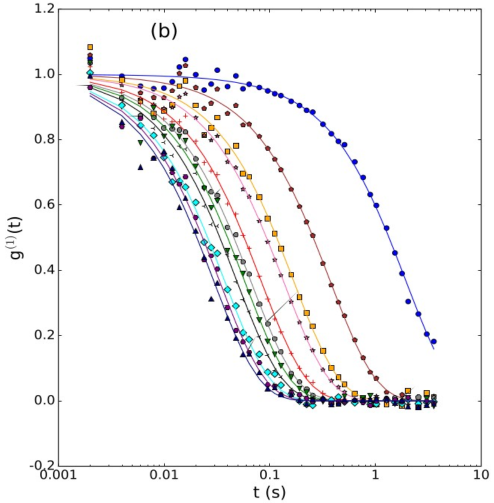
Diffusive Dynamics; Correlation Functions

- Intensity autocorrelation functions, ISF and the Siegert relationship:

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

- Intermediate Scattering Function

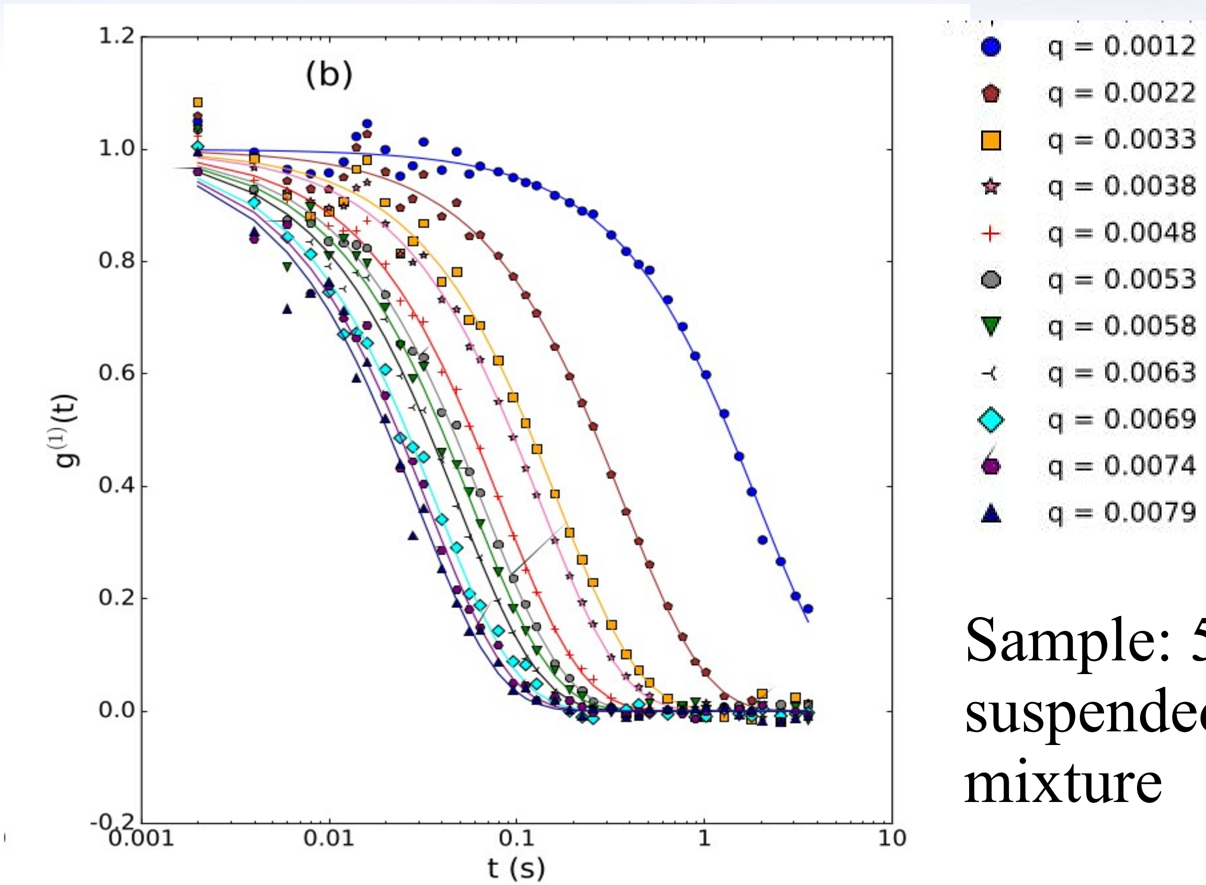
$$g^{(1)}(q,t) = f(q,t) = \exp(-D_0 q^2 t)$$

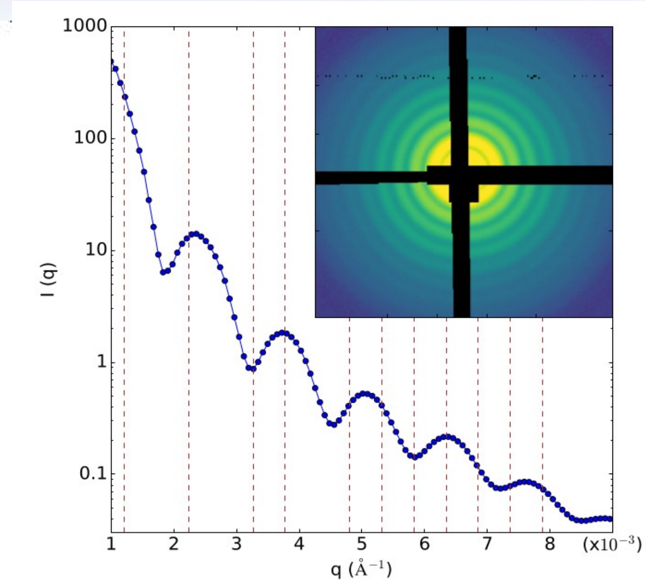


- Mean square displacement

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

Diffusive Dynamics; Correlation Functions



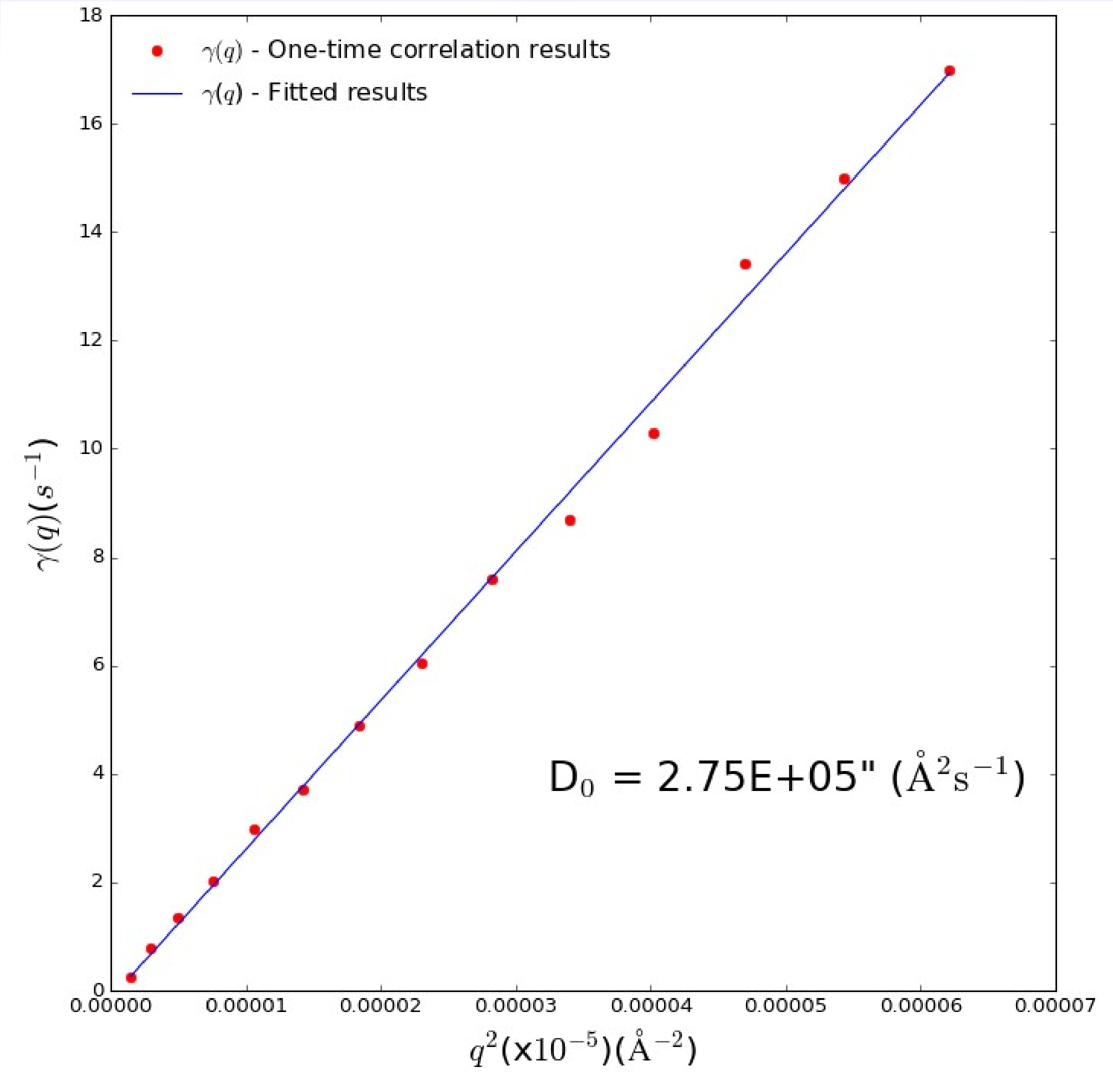


Sample: 500 nm Silica spheres suspended in a water/glycerol mixture

Length scales: $$d = \frac{2\pi}{q}$$

Length scales: ~80 nm – 500 nm

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:

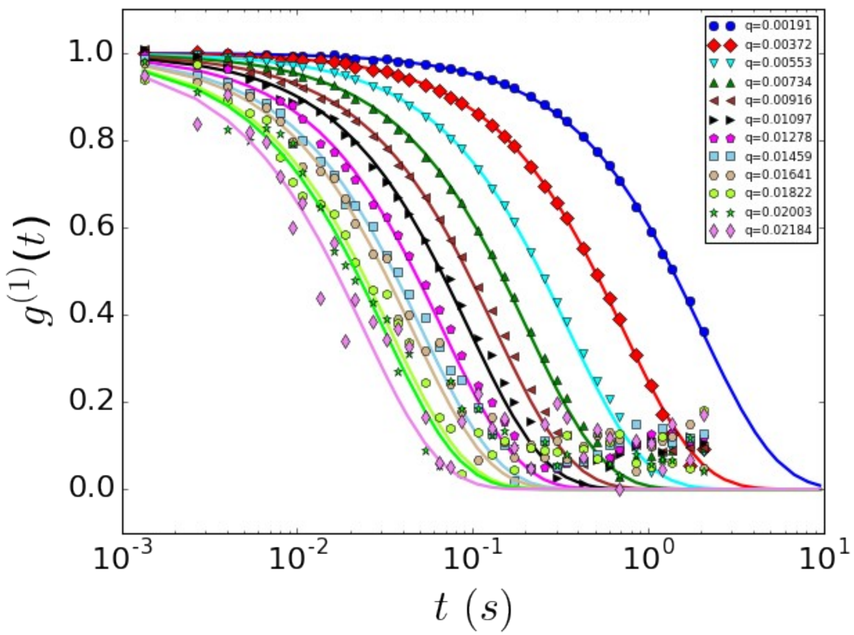
$$\gamma = Dq^2$$

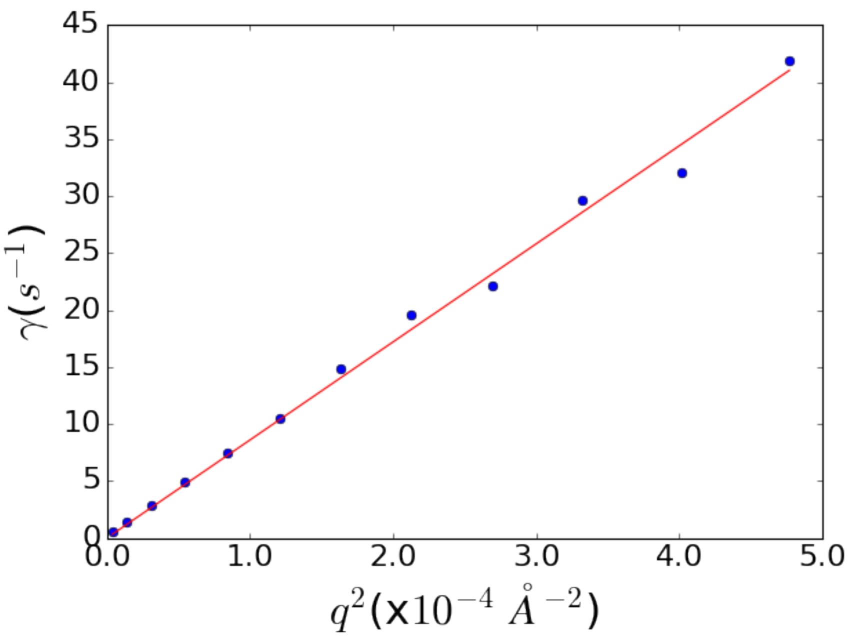
CHX Analysis Pipeline!

Colloidal Dynamics with XPCS

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

Relaxation rate: $\gamma = Dq^2$

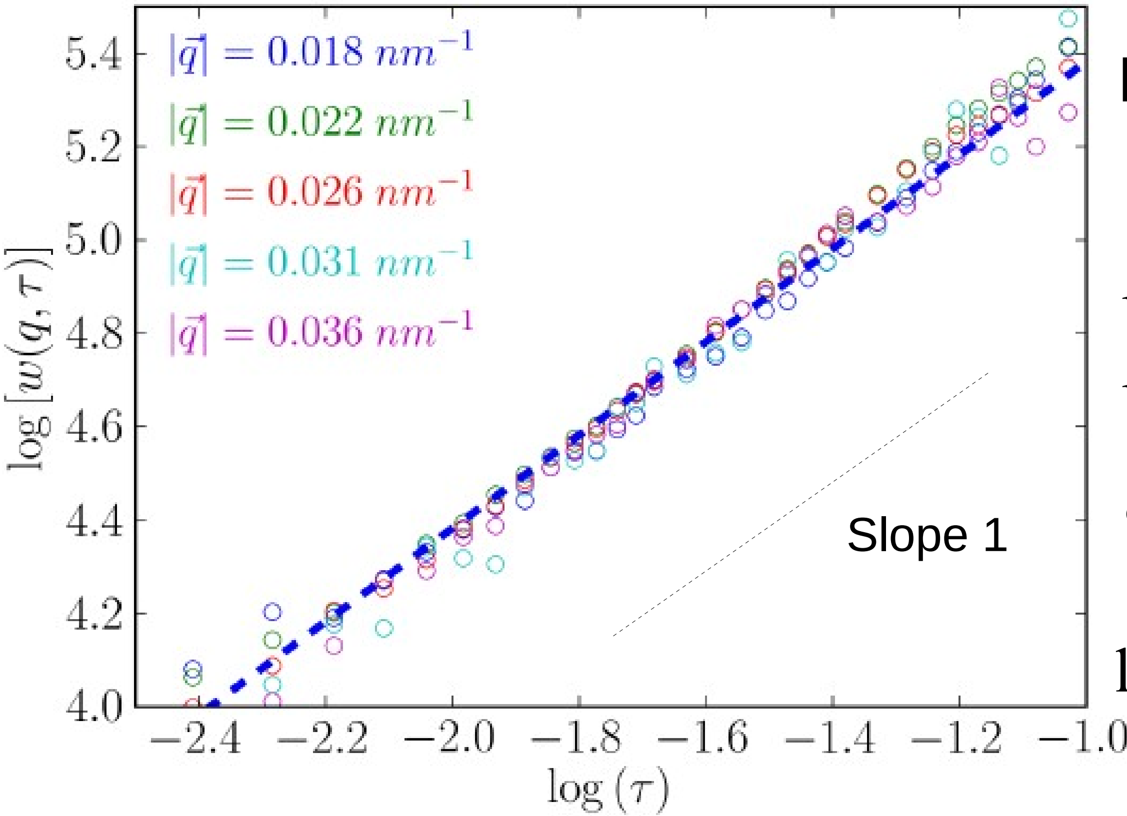




Sample: 15 nm Au nanoparticles stabilized (citric acid) and suspended in a polymer liquid 2.7K PEG

Colloidal Dynamics with XPCS

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



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

MSD: $MSD \propto D\,t$

hence:

$$w(q,t) = -\log[g^{(1)}(q,t)/q^2]$$
$$w(q,t) = D\,t$$

a.k.a. "width function" is like MSD and

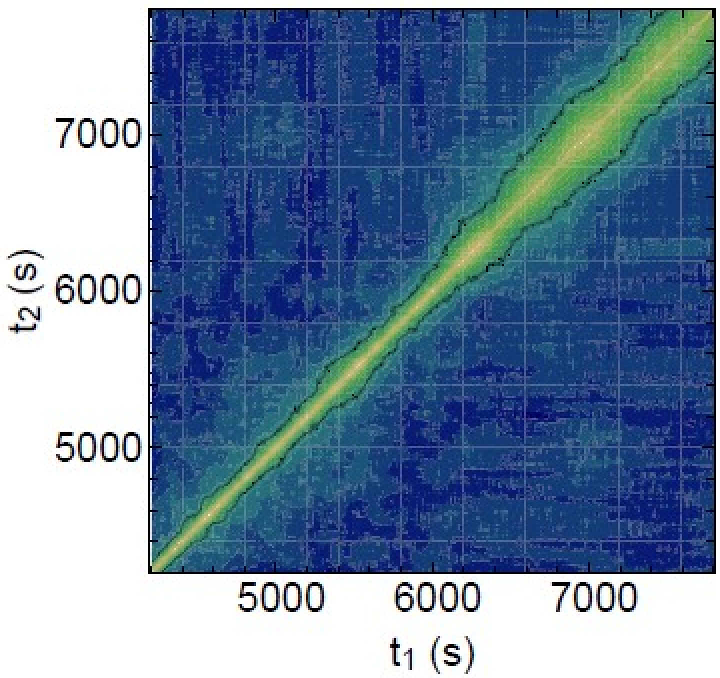
$$\log[w(q,t)] = \log[D] + \log[t]$$

Sample here: PMMA 103 nm particles in cis-decalin

Two-time analysis

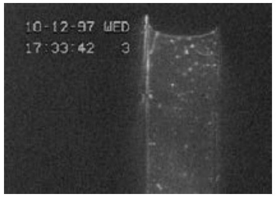
Non-equlibrium dynamics in colloidal depletion gels (colloid/polymer mixtures):

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

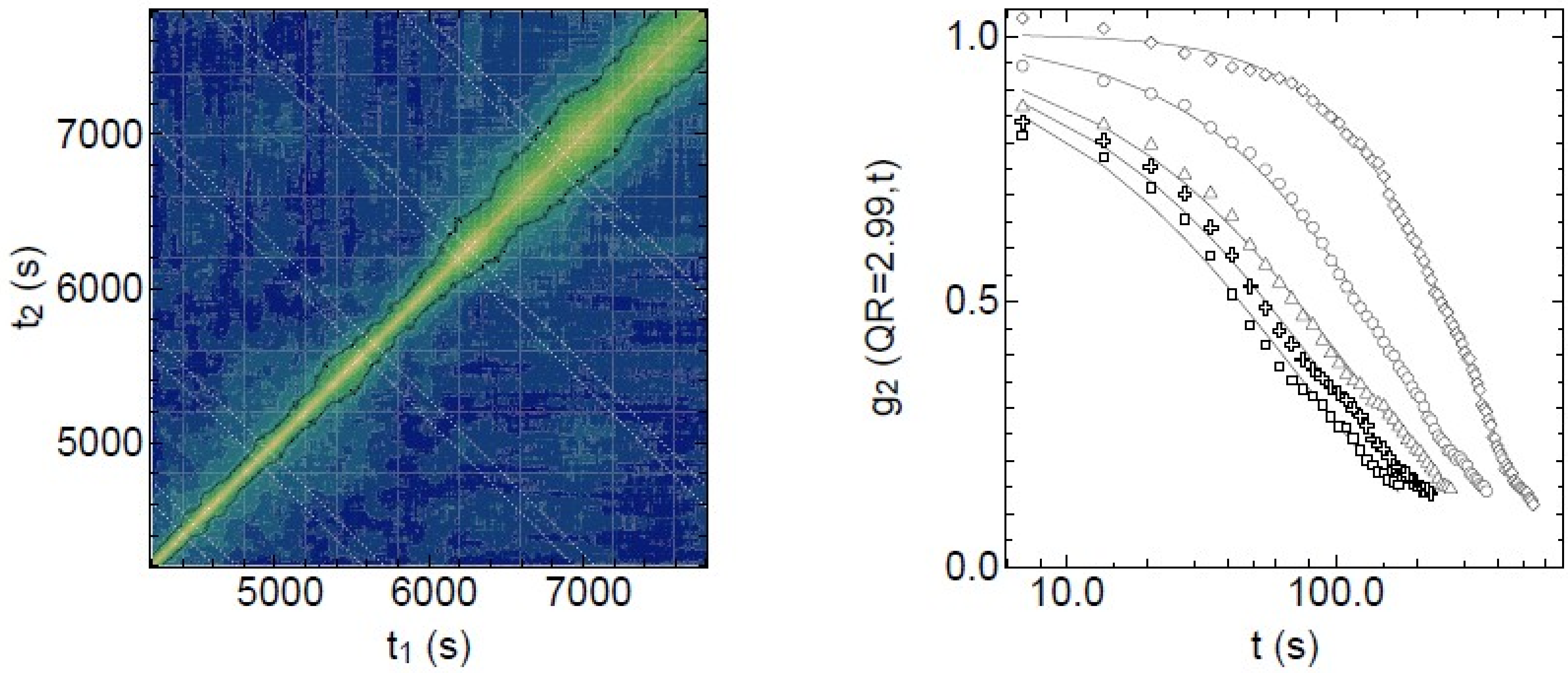


* M.Sutton et al., Optics Express **11**, 2268 (2003).

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

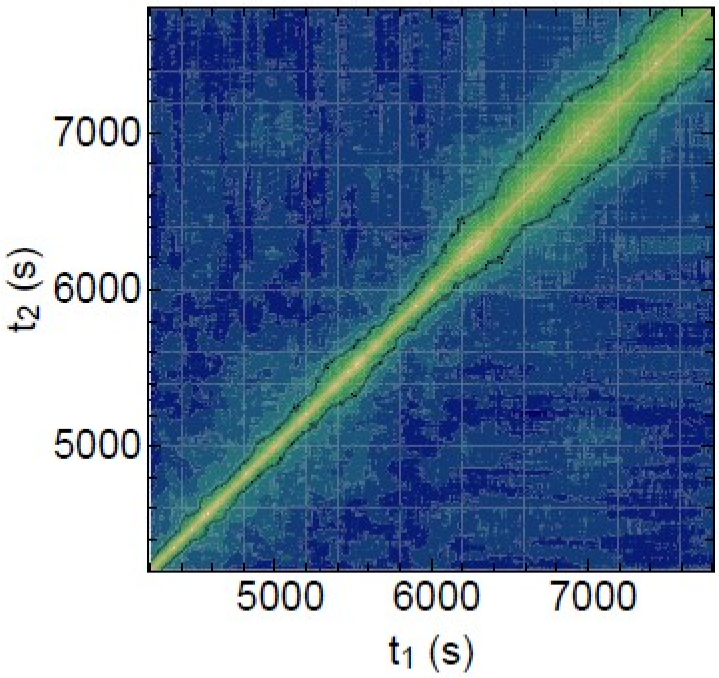
Two-time analysis

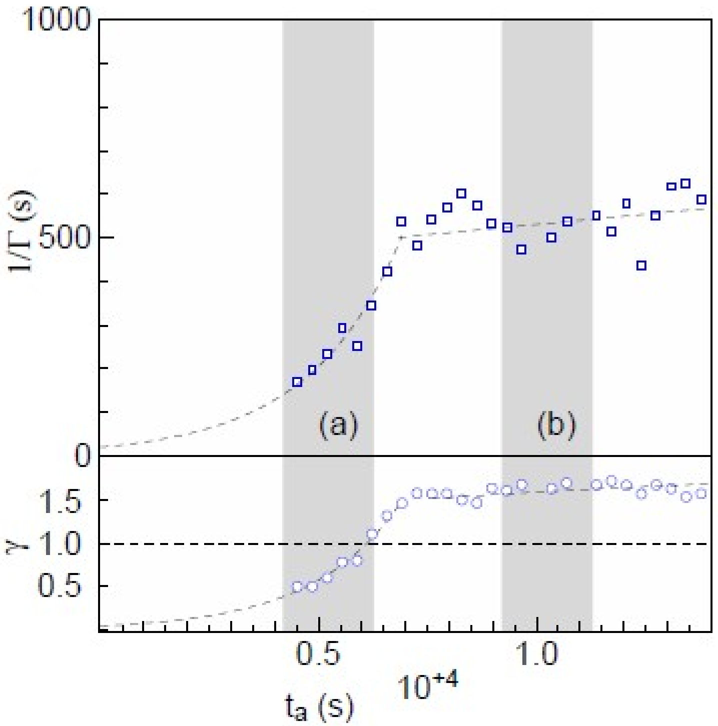
Two-time correlation functions: $C(Q,t_1,t_1) = \frac{\langle I(Q,t_1) I(Q,t_2)\rangle_{pix}}{\langle I(Q,t_1)\rangle_{pix} \langle I(Q,t_2)\rangle_{pix}}$



Two-time analysis

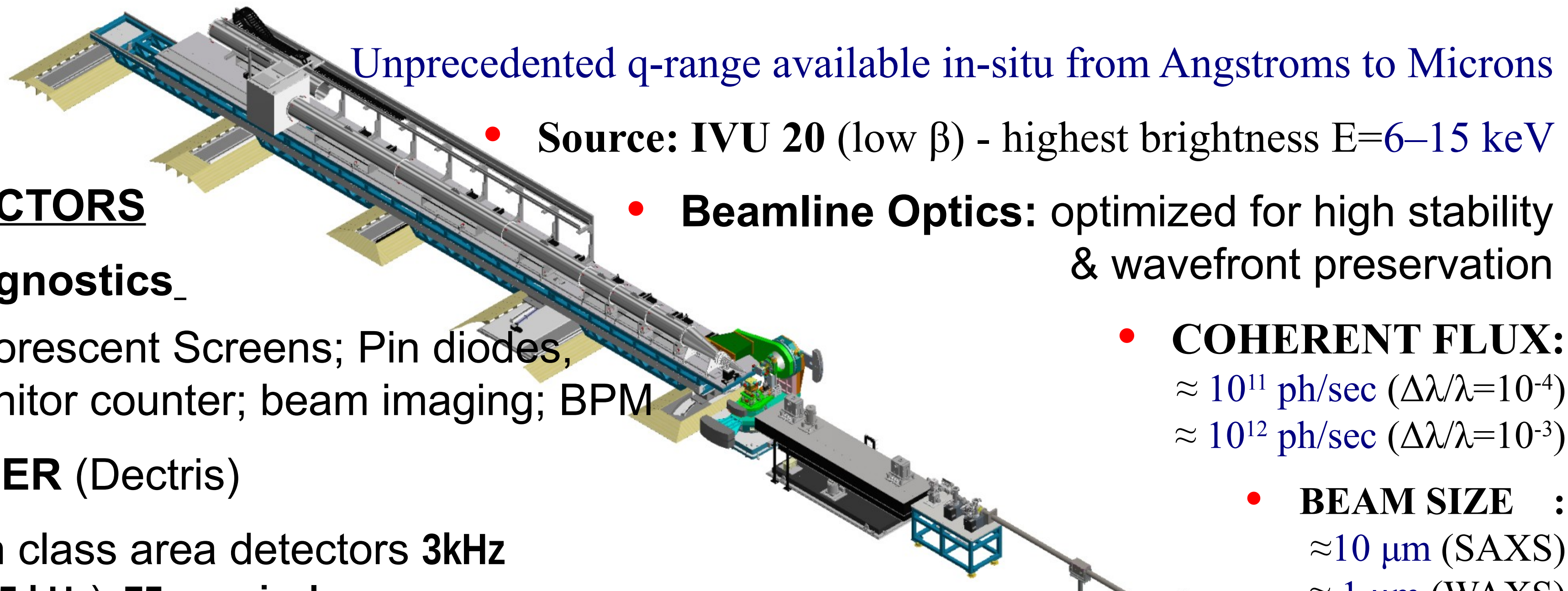
Two-time analysis: $g_2(Q, t_a, t) = \beta exp\left(-(\Gamma t)^{\gamma}\right) + g_{\infty}$





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:**
  ≈ 10^{11} ph/sec ($\Delta\lambda/\lambda=10^{-4}$)
  ≈ 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

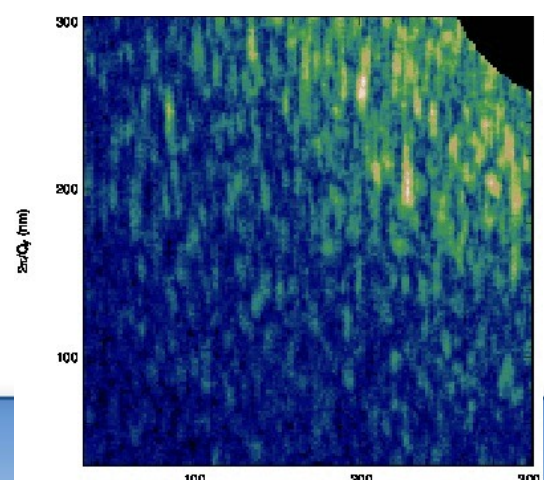
2. EIGER (Dectris)

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

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

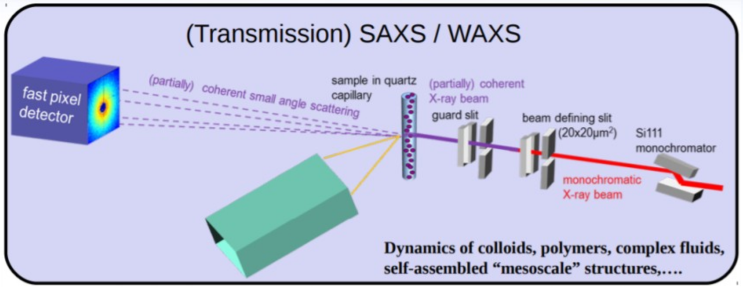
3. Point Detectors (FMB Oxford)

- Scintillator detector systems;
- Avalanche Photodiode (APD)

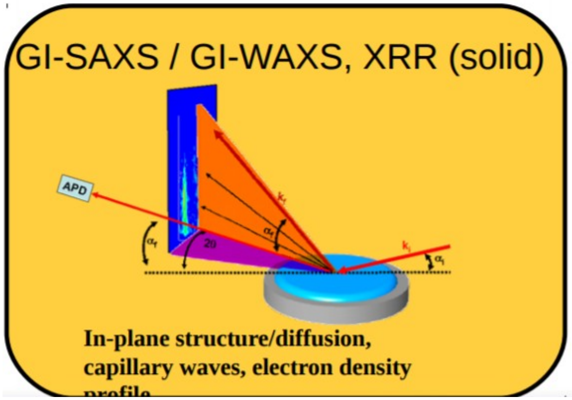


XPCS & different Scattering Geometries

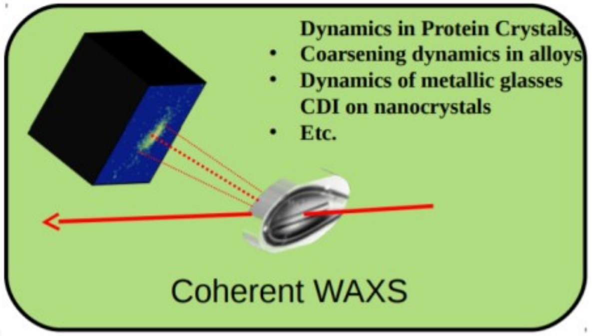
- **SAXS**
  e.g. for studies of the interplay between nanoscale and mesoscale structure, dynamics and macroscopic properties.



- **GI-SAXS**
  e.g. for studies of dynamical phenomena at surfaces and interfaces during thin film growth

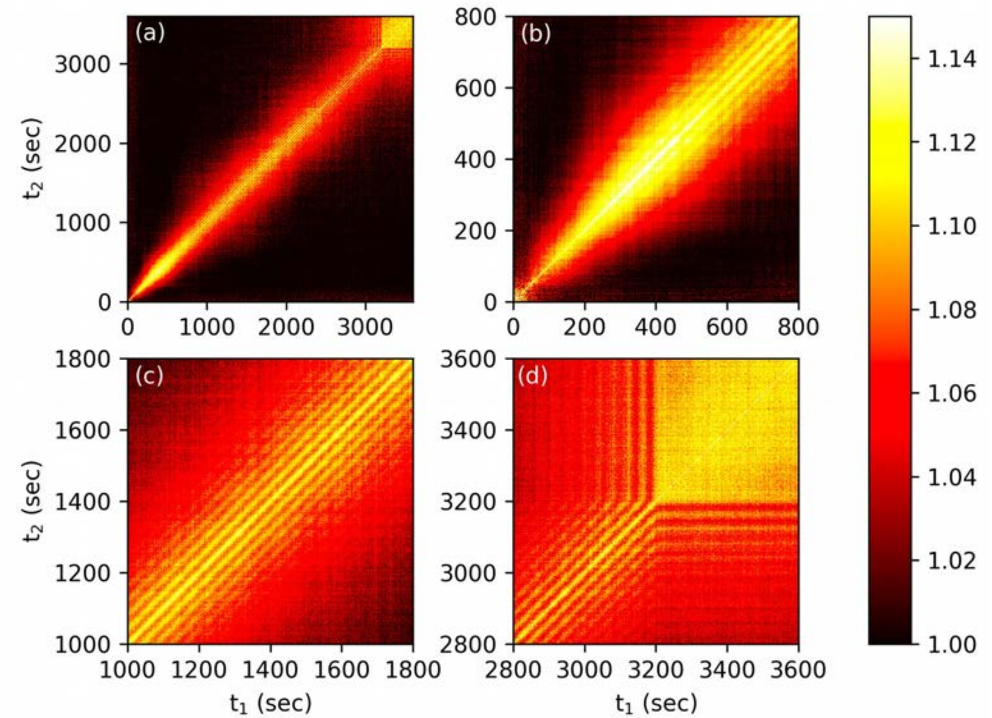


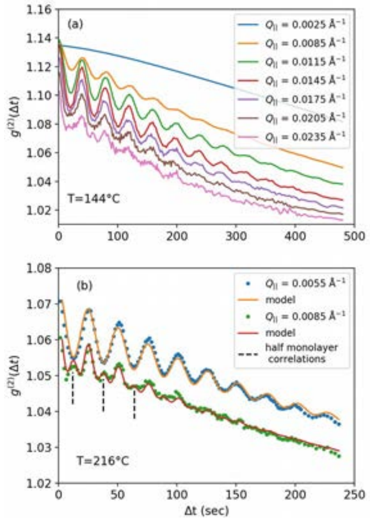
- **WAXS**
  e.g. for studies of dynamics of ferroelectric domains in ferroelectric periodic heterostructures

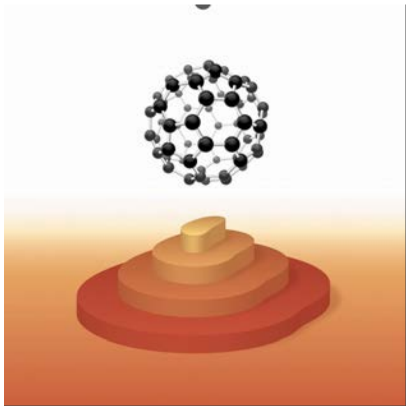


Example: GI-XPCS during in-situ growth

- The research is of a major fundamental and practical importance, providing a better understanding of the properties of artificially grown thin films.
- GI-XPCS -> understanding aspects such as step flow and other out-of-equilibrium fluctuations which are impossible to access with other techniques

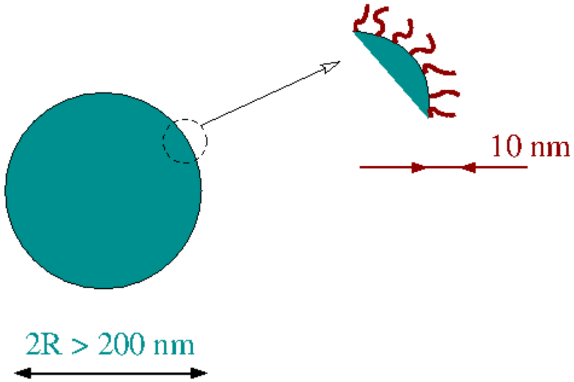


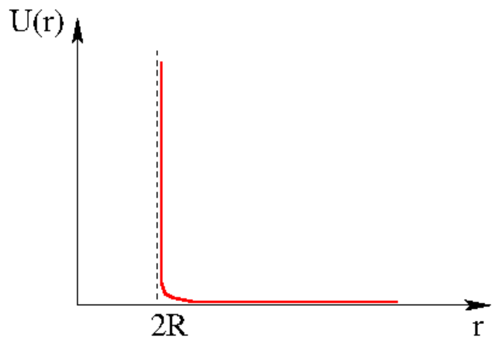




R. Headrick *et al.*, Nature Comm. 2019

A more detailed science example: high density hard-sphere (colloidal) suspensions



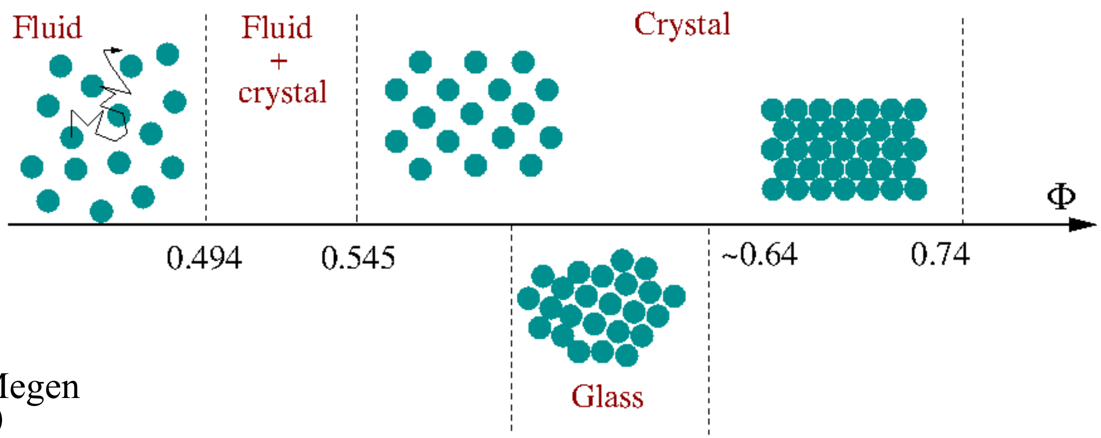


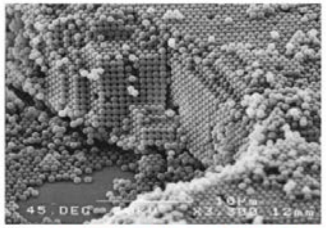
Hard-sphere colloids:

- 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*

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

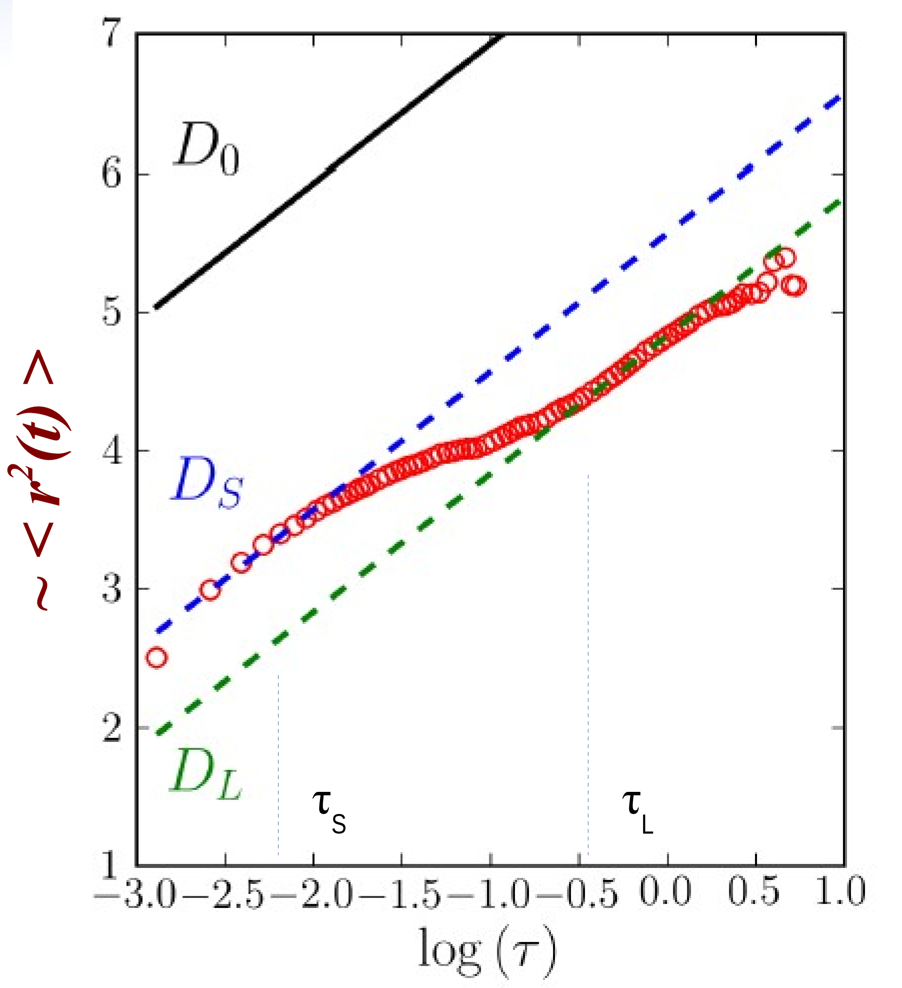




(b) R.M. Amos et al., PRE **61**, 2929 (2000)

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

Dynamics in high density hard-sphere suspensions



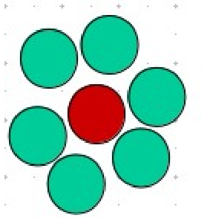
P. Kwasniewski, PhD Thesis 2012

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"

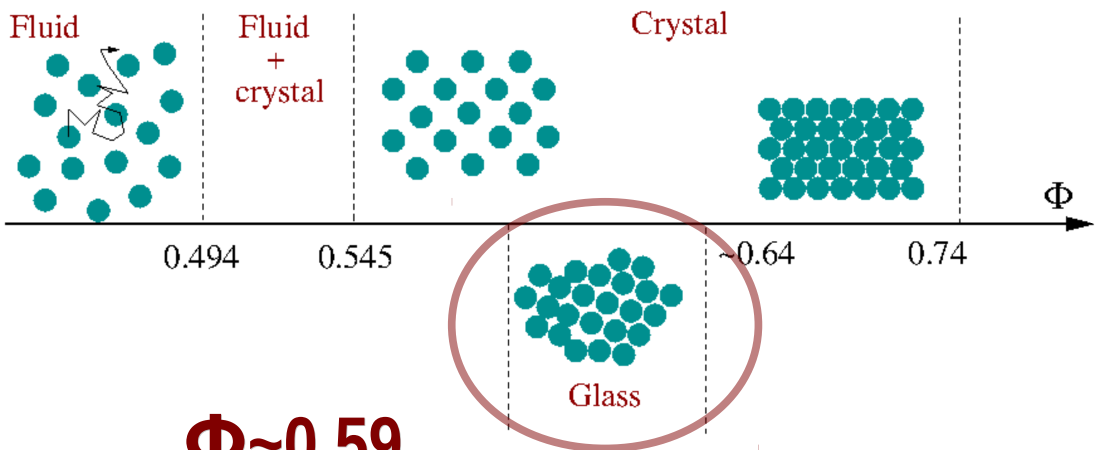
Slowed down (compared to D_S) by *direct interactions*

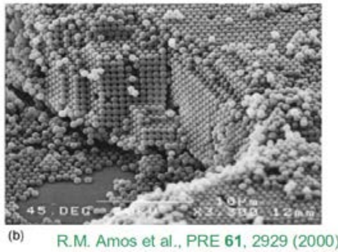
P. Kwasniewski, AF, A. Madsen, Soft Matter, 2014, **10**, 8698-8704

The Colloidal Glass Transition

- What happens here?

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

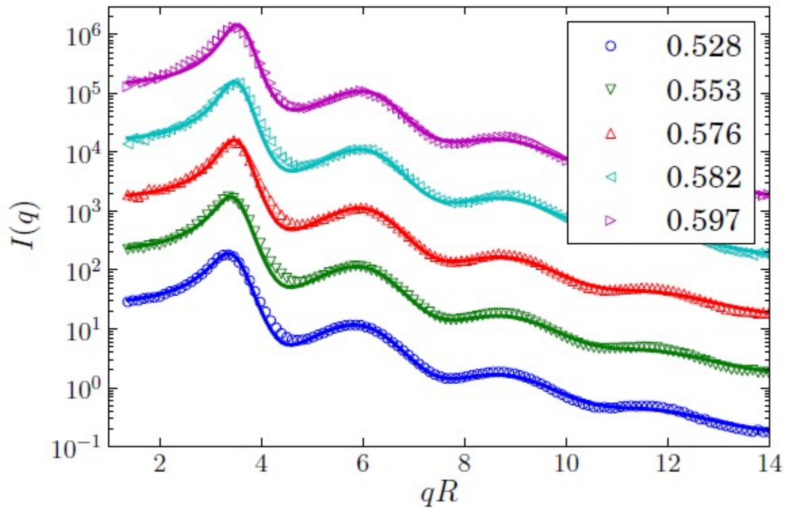




R.M. Amos et al., PRE **61**, 2929 (2000)

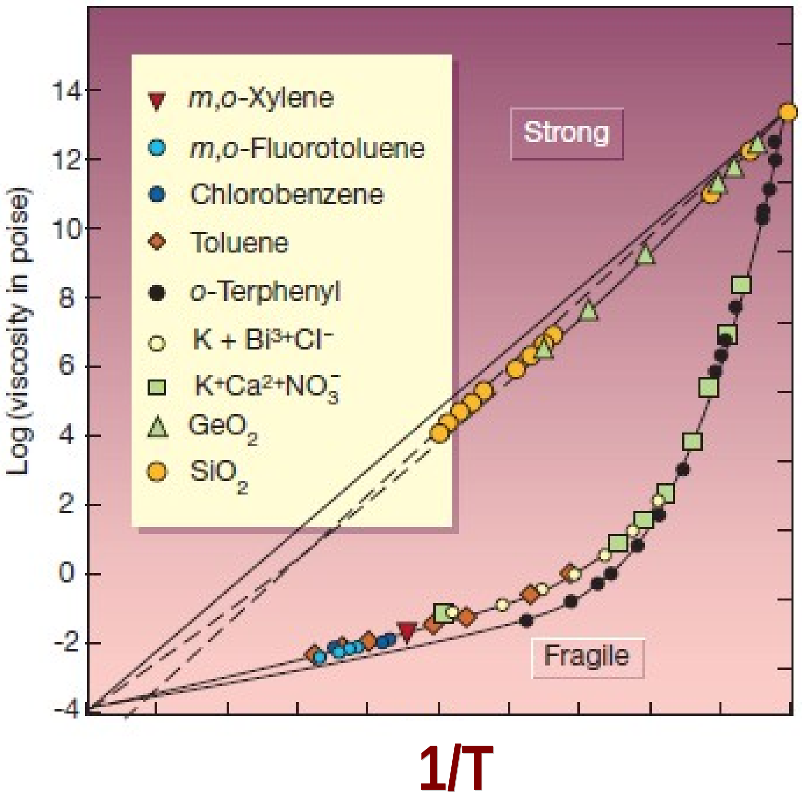
Φ~0.59

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

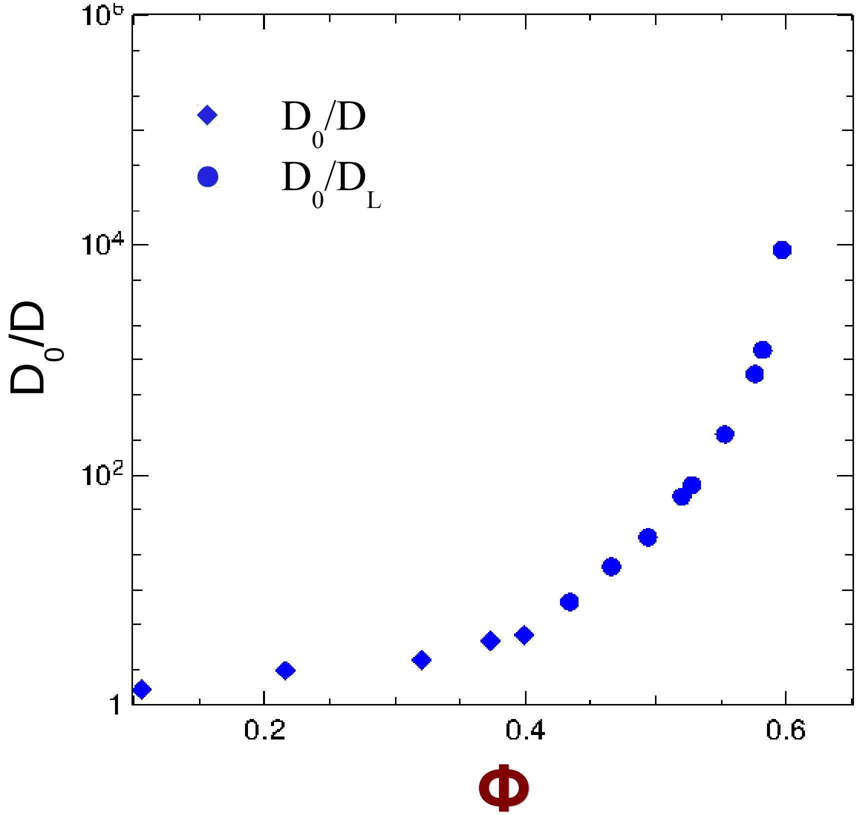


Supercooled Liquids vs. Hard-Sphere Colloids

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

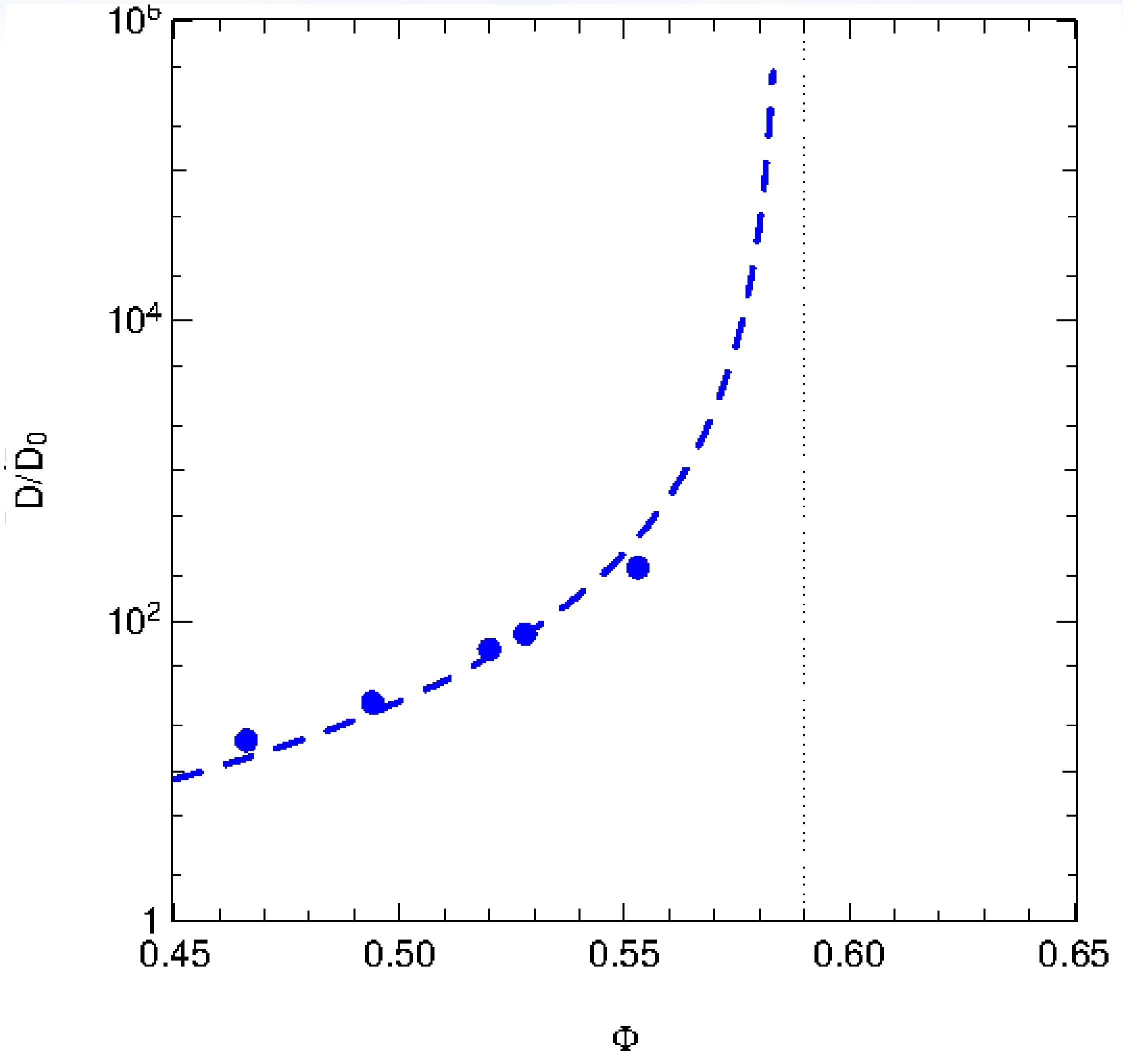


Denenedetti, Stillinger, *Nature* 2001



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

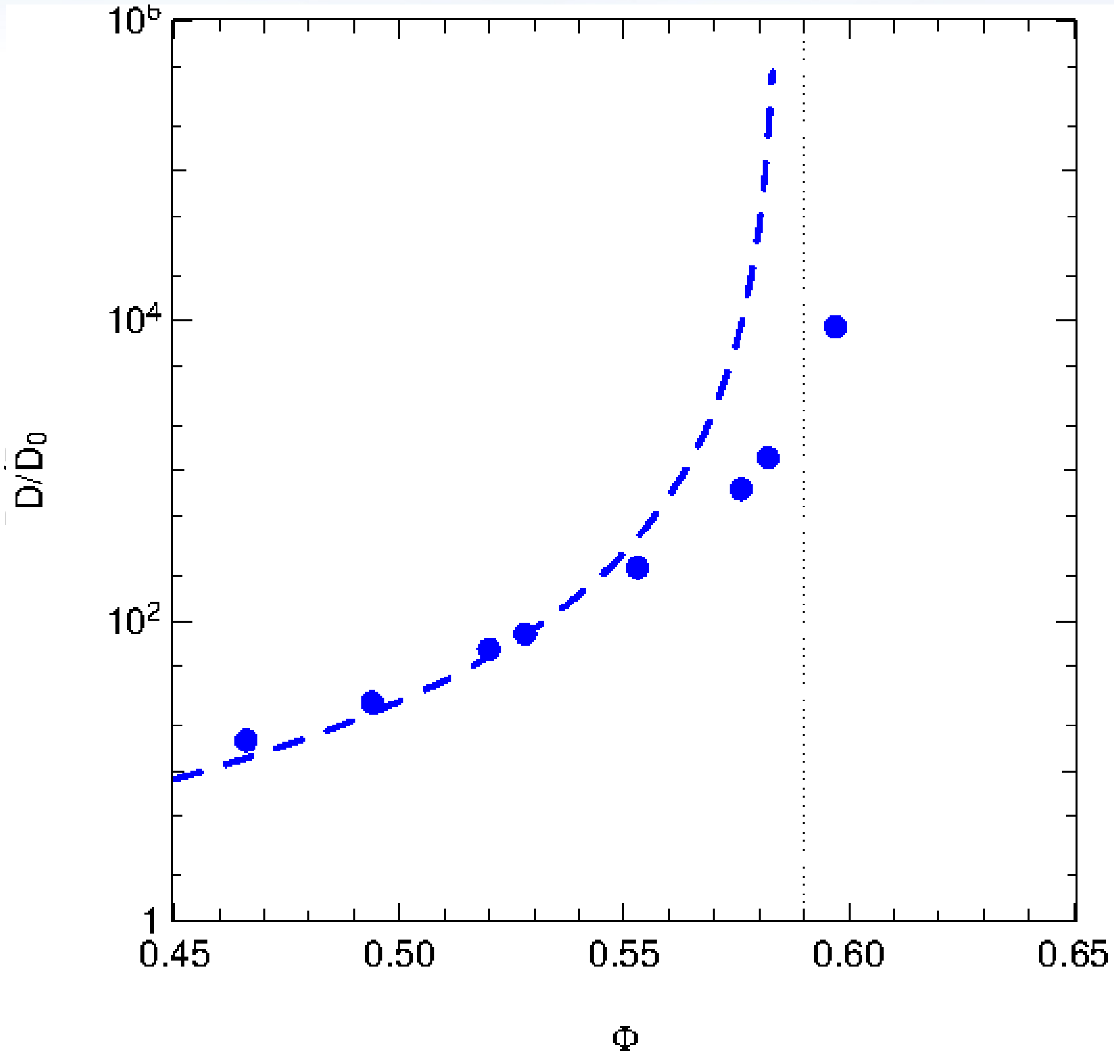


Structural relaxations:

- 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



Structural relaxations:

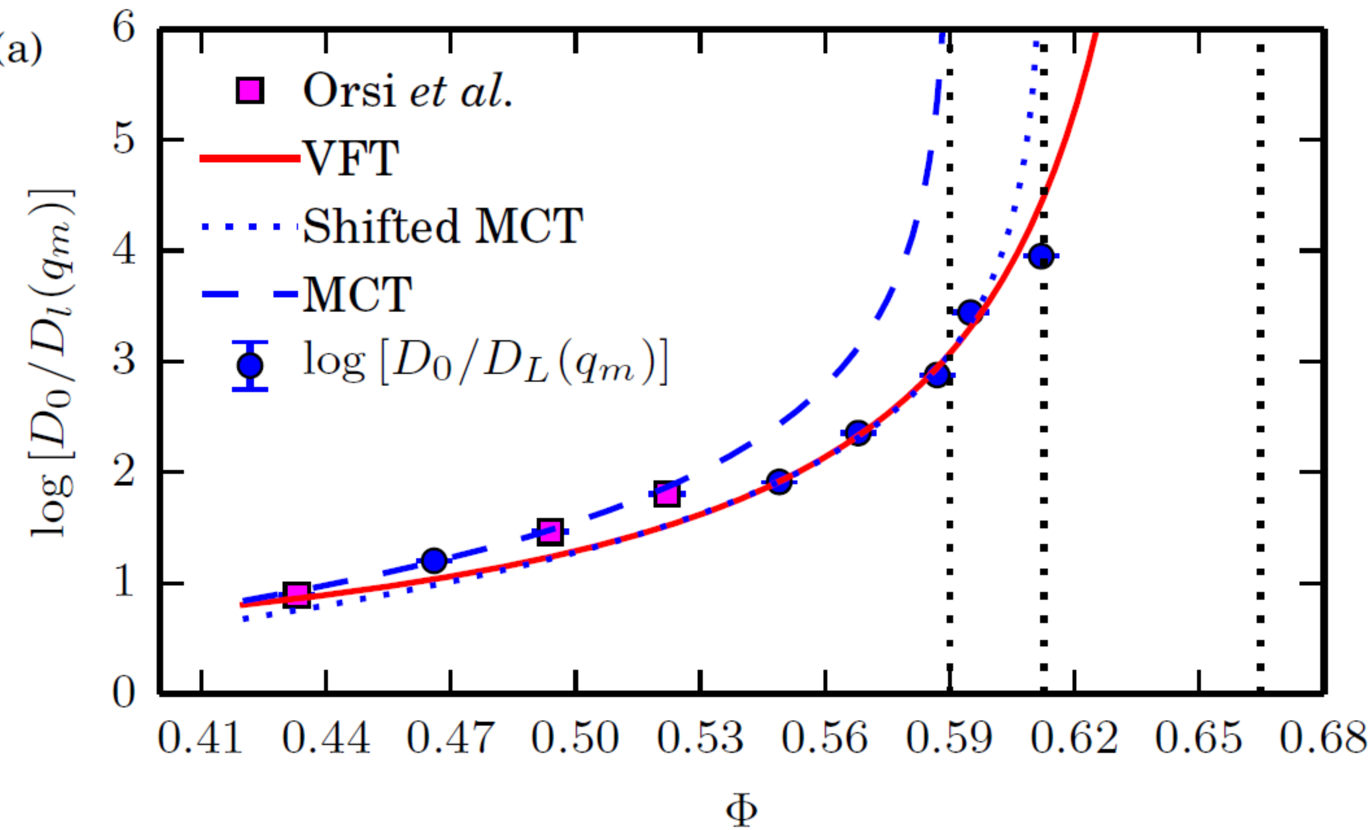
- Structural relaxations slow-down with increasing **Φ**
- And are expected to *diverge* at the colloidal glass transition concentration Φ_g - "Mode Coupling Theory" (MCT)
- $D_0/D_L \rightarrow \infty$ at $\Phi_g \sim 0.59$

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

Not so simple:

- Instead of diverging the relaxations remain finite (but slow!) above Φ_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:

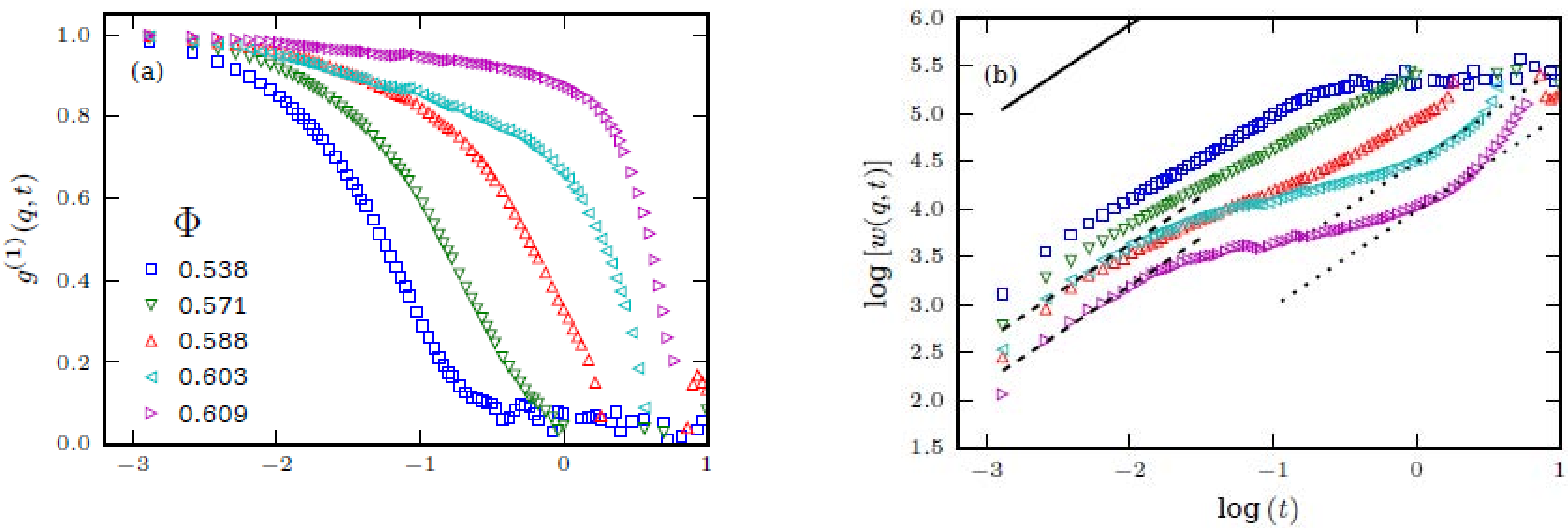
$$\frac{D_0}{D_l(q_m)} = \tau_\infty \exp\left[\frac{F}{(\Phi_0 - \Phi)^\delta}\right]$$

- 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"* **~*t***



- Is this behavior a signature of *jamming*?

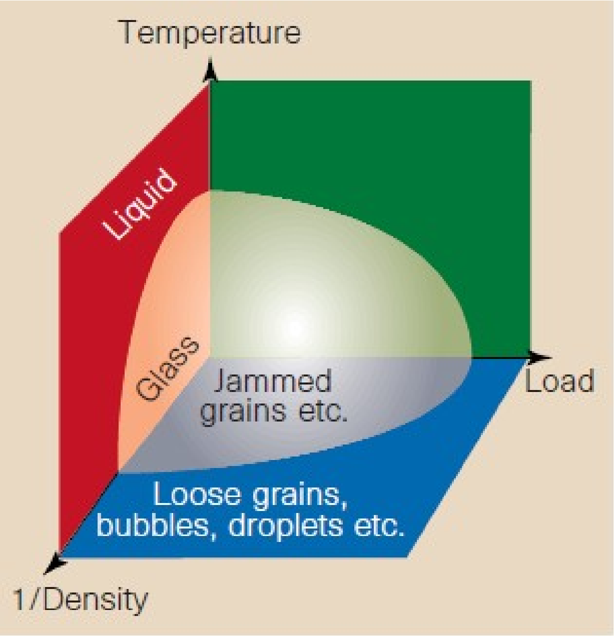
Universal non-diffusive slow dynamics in aging soft matter
L.Cipelletti *et al.*, *Faraday Discuss.*, 2003, **123**, 237

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

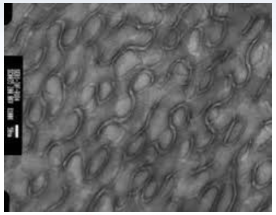


A. Liu *et al.* Nature 1998

Anomalous Dynamics near the Hard-Sphere Glass Transition

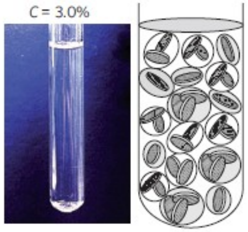
- Polymer-based sponge phases

  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

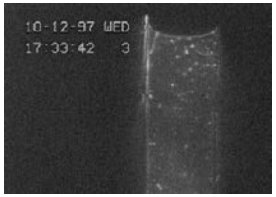


- Antiferromagnetic domain fluctuations (Cr)

  O. Shpyrko et al., Nature 2007

- Aging Ferrofluids

  A. Robert *et al*. Europhys. Lett. 2007



- Aging colloidal gels ("transient gels")

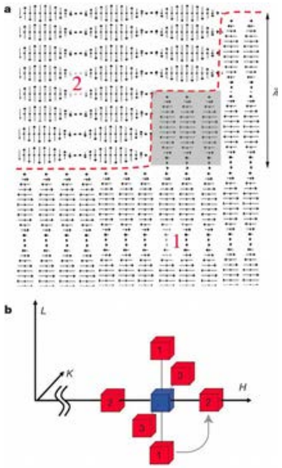
  A. Fluerasu *et al.*, Phys. Rev. E 2007

- 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

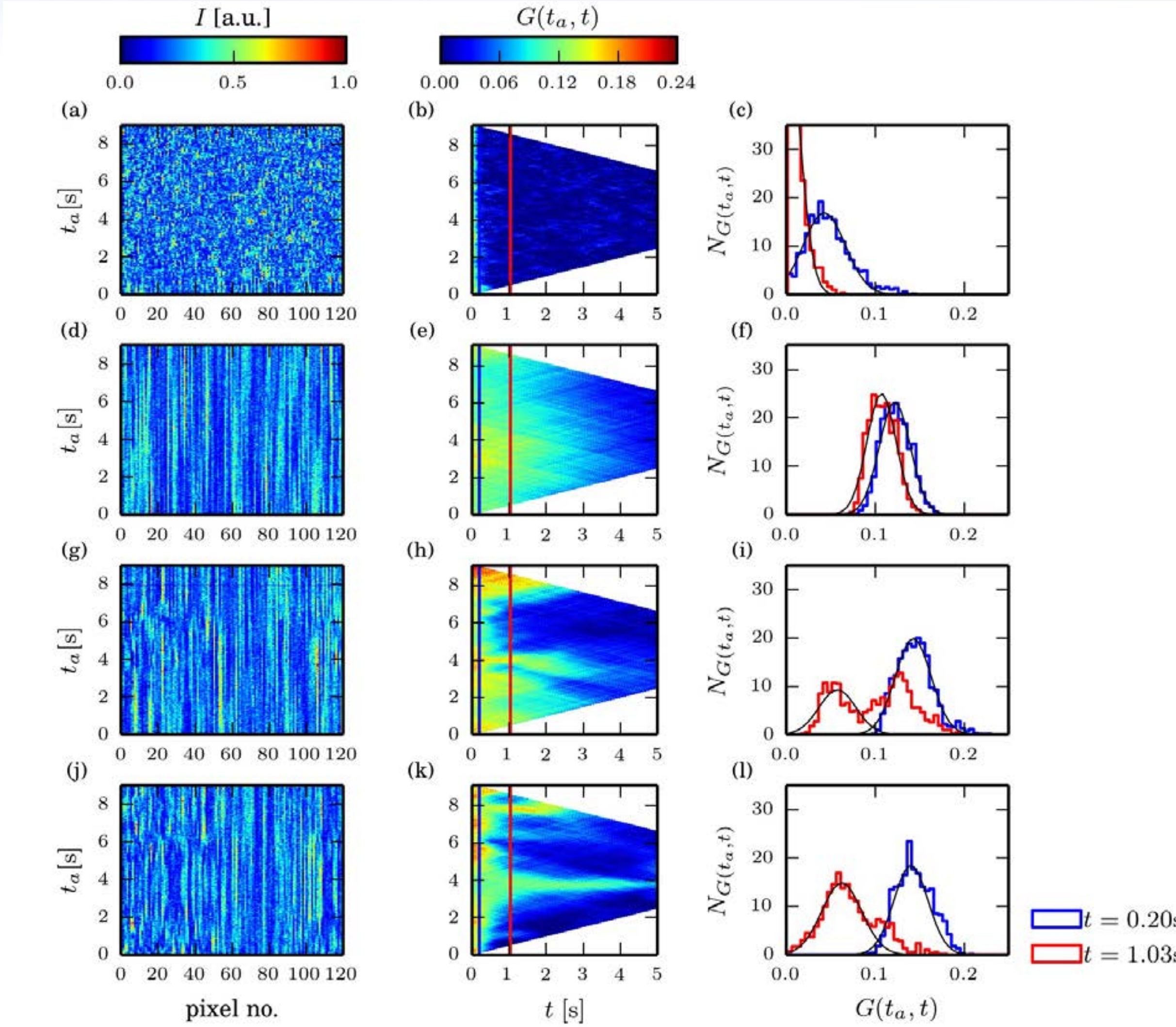


- Etc. etc. etc. ...

Dynamical Heterogeneities

Φ~0.57

Φ~0.61



Age ~30min

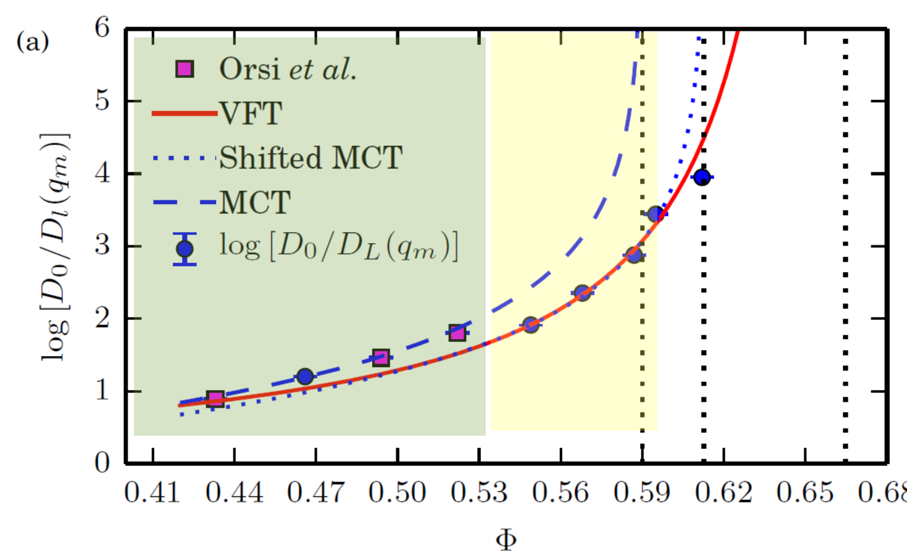
Age ~2h30

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 network and stress-induced (nonthermal) fluctuations become dominant and hinder the expected glass transition
- Non-equilibrium, complex dynamics determined by "rough" energy landscape (heterogeneities) *Hyperdiffusive relaxations →jamming*
  (common also in other systems)
- Response to perturbations?
  → *flow, shear*



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M. Carlucci-Dayton, S. Antonelli, R. Greene,
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O. Chubar, K. Evans-Lutterodt, P. Siddons ...

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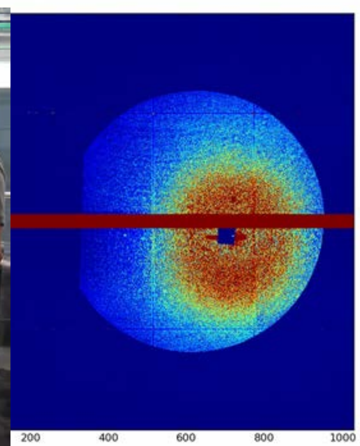
BNL SC0012704
BNL LDRD 11-025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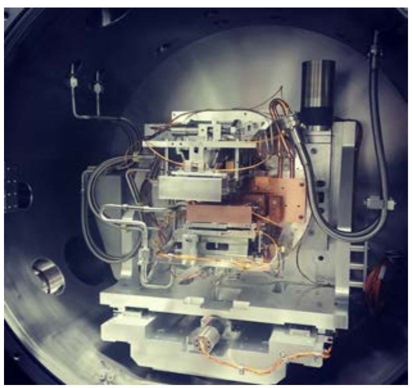
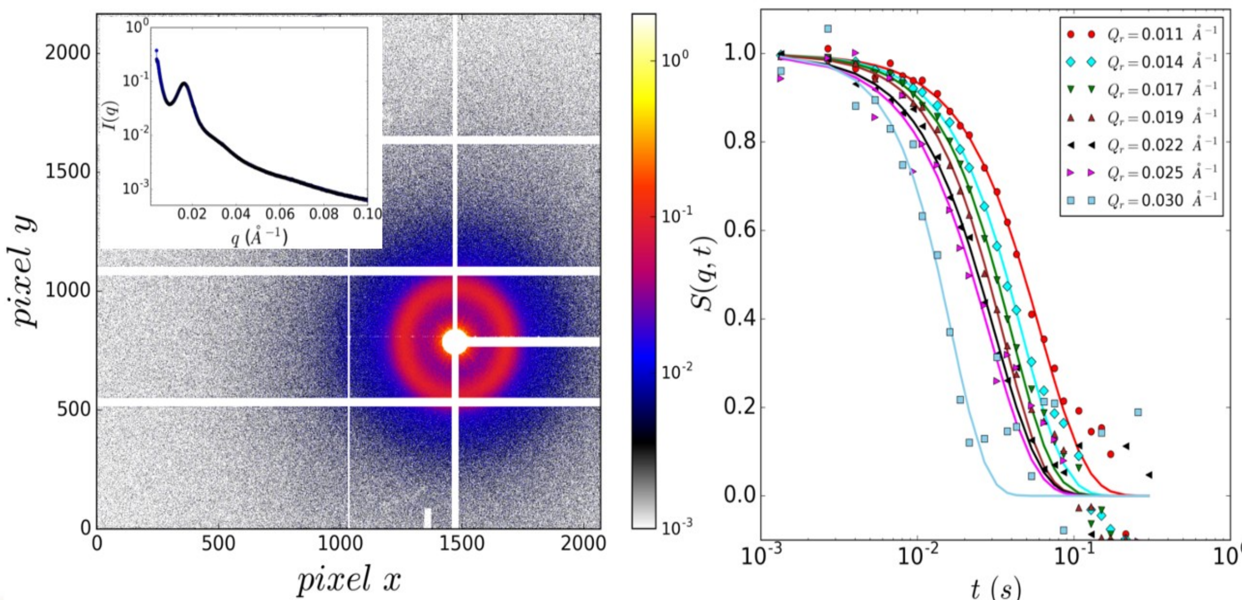


A "Mini User Guide" to XPCS

Questions:

- How much does the sample scatter?
  - we need ~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 different locations?

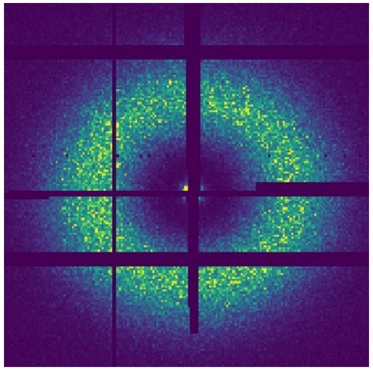


Speckles

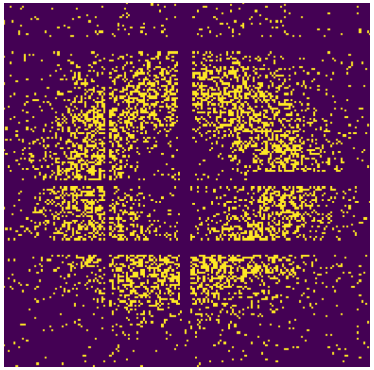
- Speckle statistics is described by the negative binomial distribution with
  - $M=M(q,T)$: # of coherent modes
  - $K=K(q,T)$: avg # of counts at a given q/ring
- Normalized variance becomes:

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

Large K(q,T)



Small K(q,T)

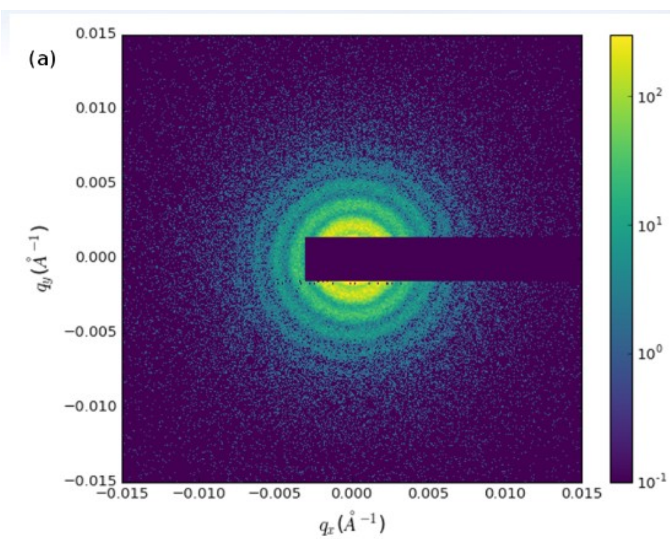


Mandel, L. (1958). *Proc. Phys. Soc.* **72**, 1037.
Mandel, L. (1959). *Proc. Phys. Soc.* **74**, 233.
Goodman, J. W. (2007). *Speckle Phenomena in Optics: Theory and Applications*. Englewood: Roberts and Company.

Speckles & Speckle Visibility Spectroscopy

- 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

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



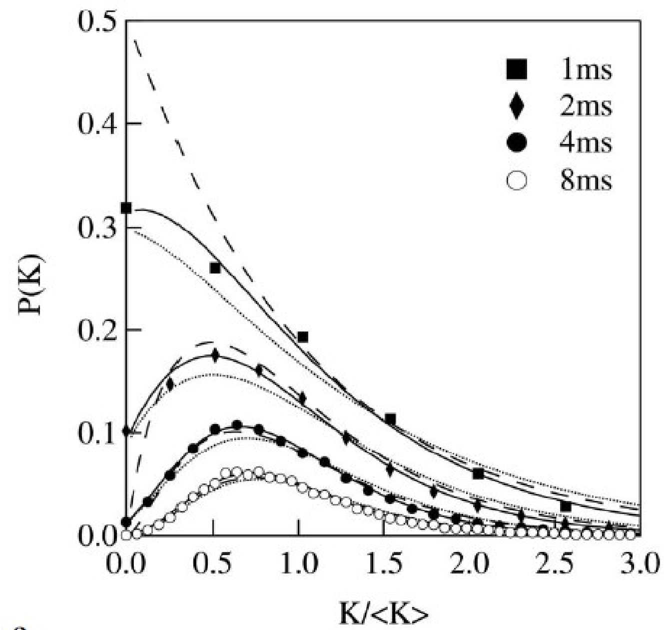
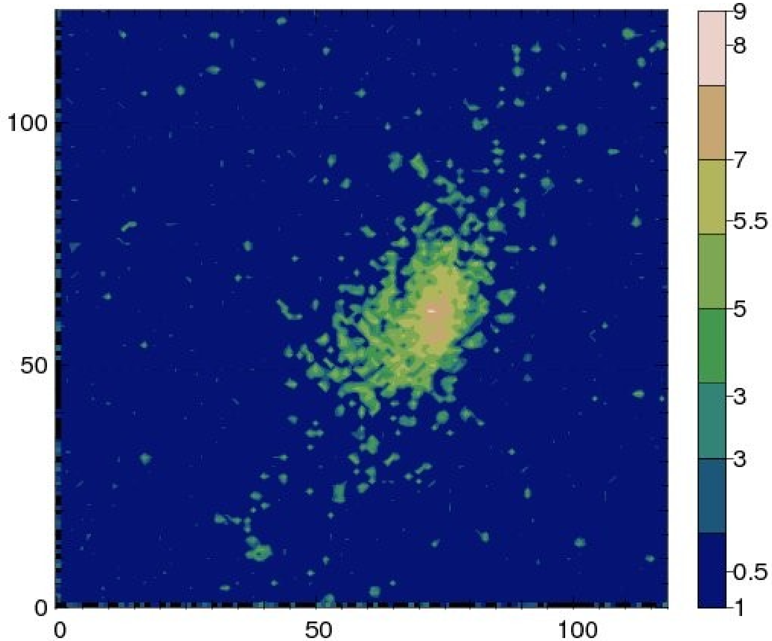


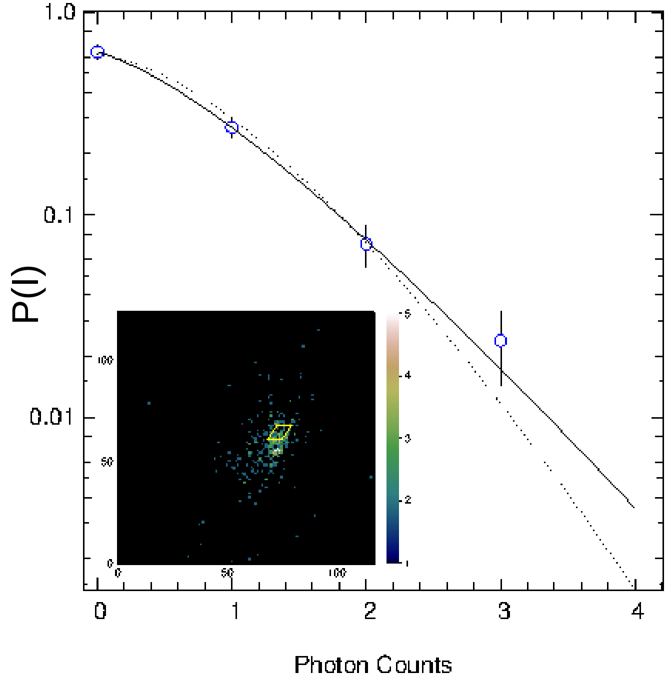
Figure 2
Photon count statistics analysis performed over an ensemble of pixels marked in the circular region in Fig. 1(*a*) for four integration times. Markers represent the photon count probability density $P(K)$ from the experiments, and solid lines are the fitting curves using the negative-binomial 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.

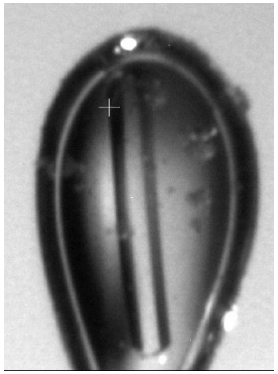
Luxi Li et al. J. Synch. Rad. 2014

X-ray Speckles come to life

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

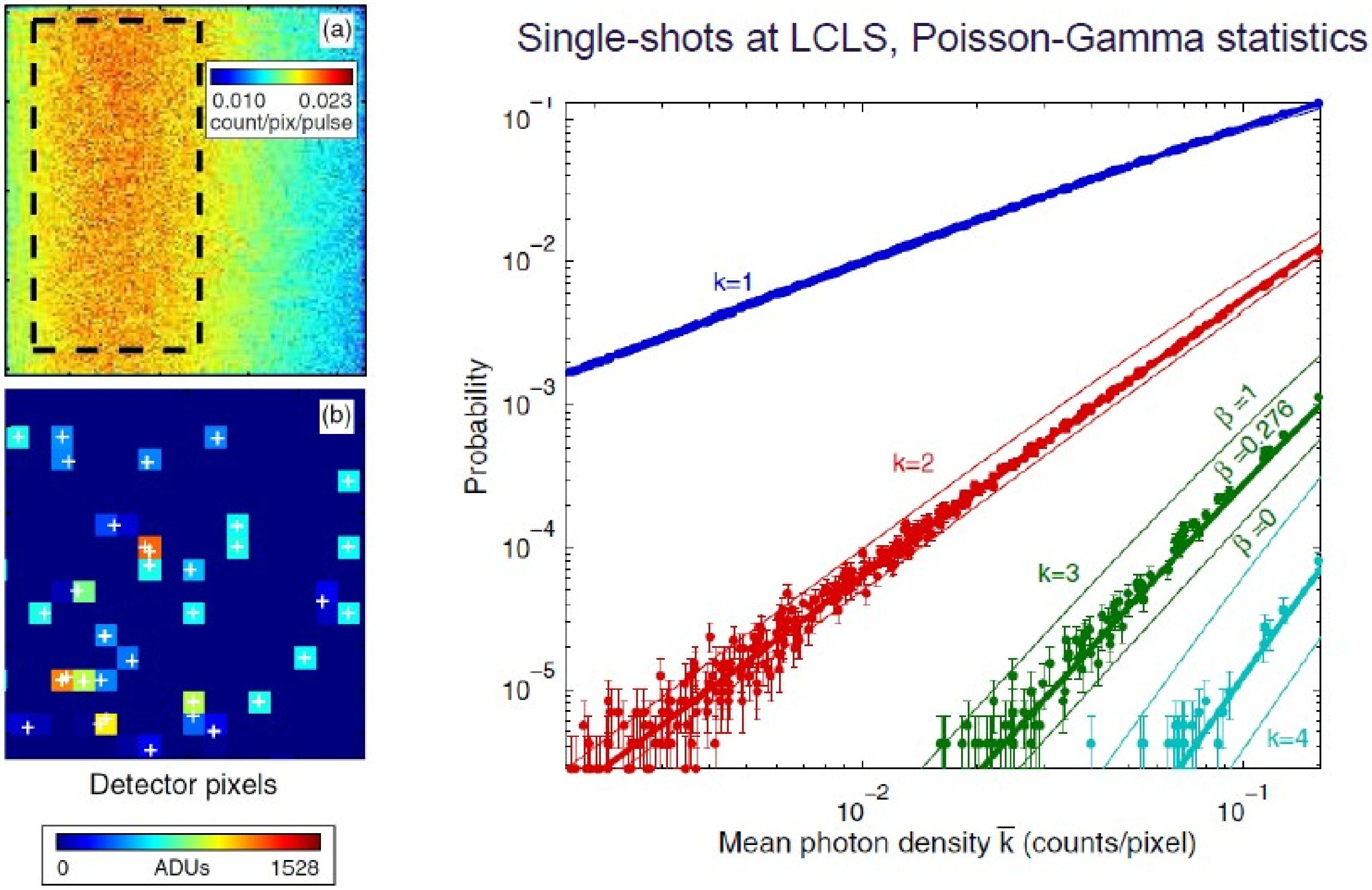






L. Li *et al.*, unpublished

Speckles from single shot LCLS pulses



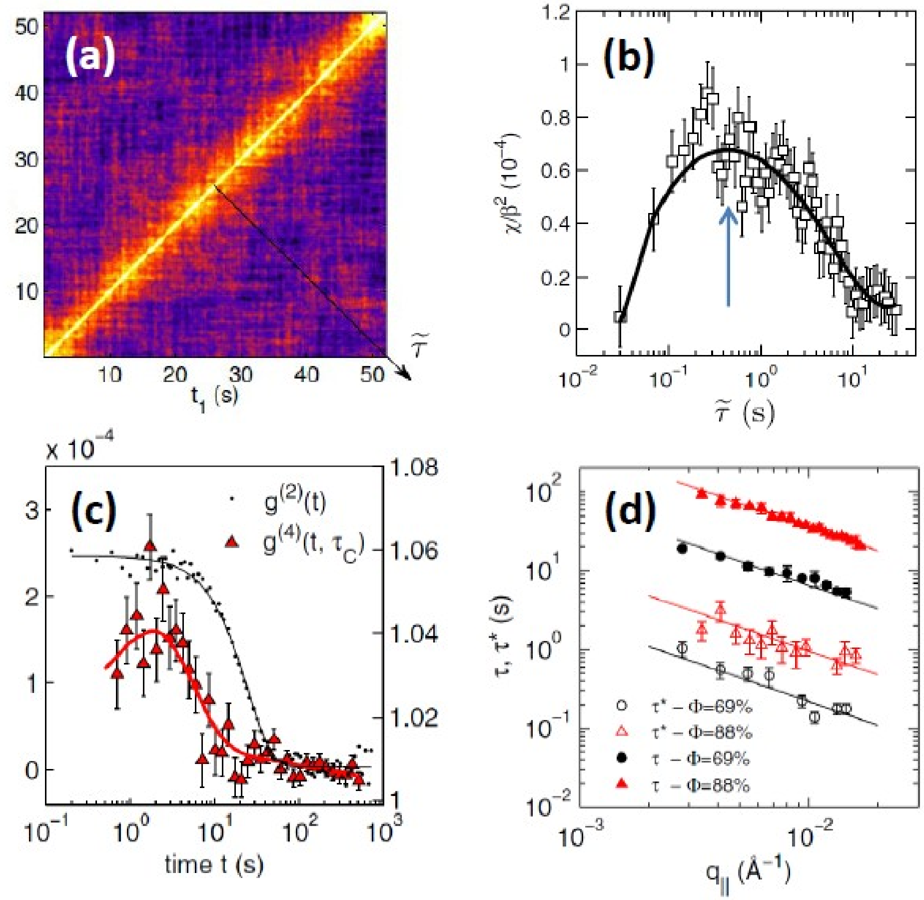
S. O. Hruszkewycz et al., PRL**109**, 185502 (2012)

4th 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)