X-ray Photon Correlation Spectroscopy

Gerhard Grübel
Workshop on
Coherence at ESRF-EBS
ESRF, Grenoble, France
September 9-13, 2019

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

DESY.

Layout

XPCS Basics

Higher order correlation functions

The benefits of a long beamline

Applications

Glass transition (crystallization)

Complex fluids/ the aqueous environement

Biological systems

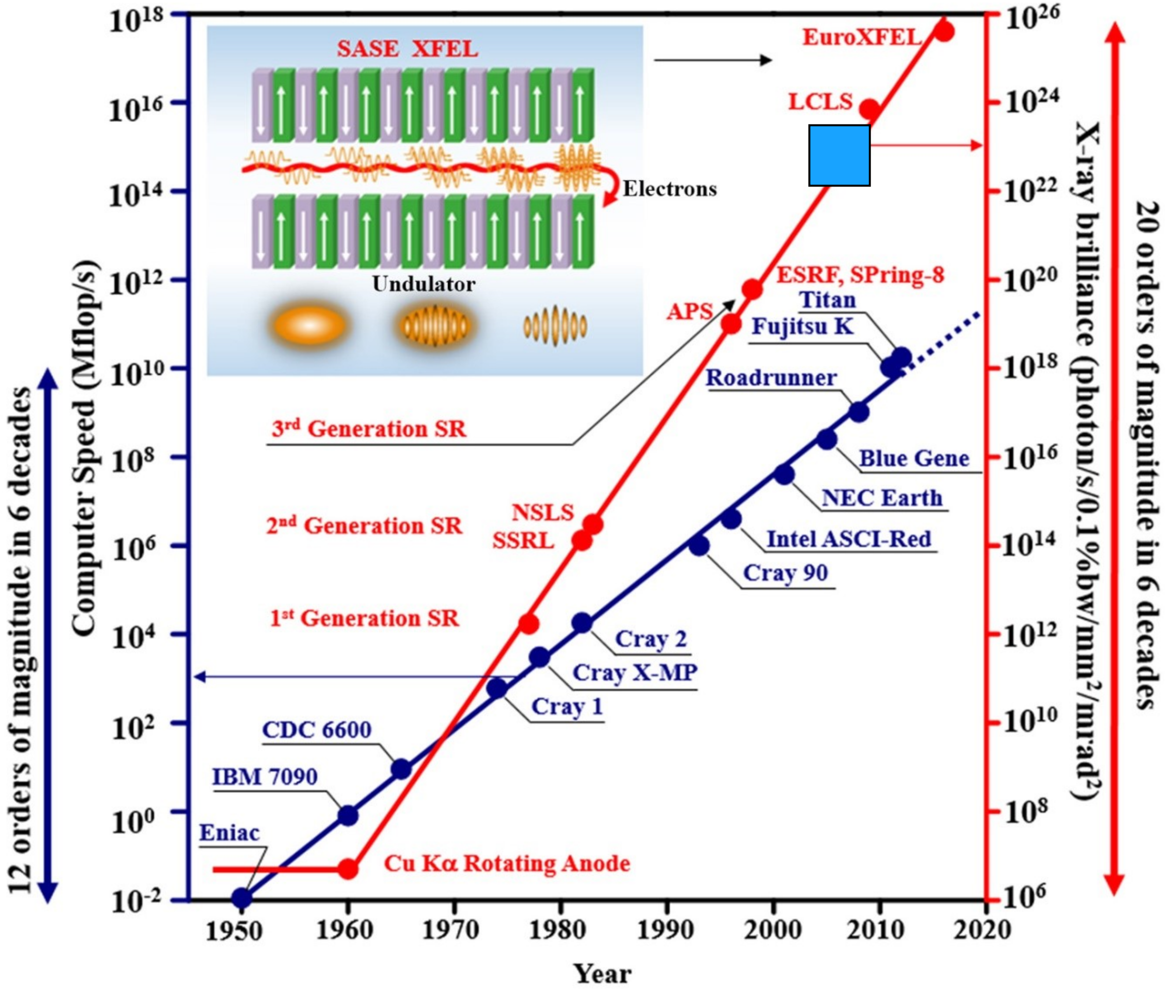
Magnetism

XPCS at higher X-ray energies

Outlook

ESRF needs an XPCS/Coherence beamline

XPCS performance ~ B^2



Science 348, 530-535 (2015)

http://www.physics.ucla.edu/research/imaging/research_CDI.html

Higher Order Correlation Functions

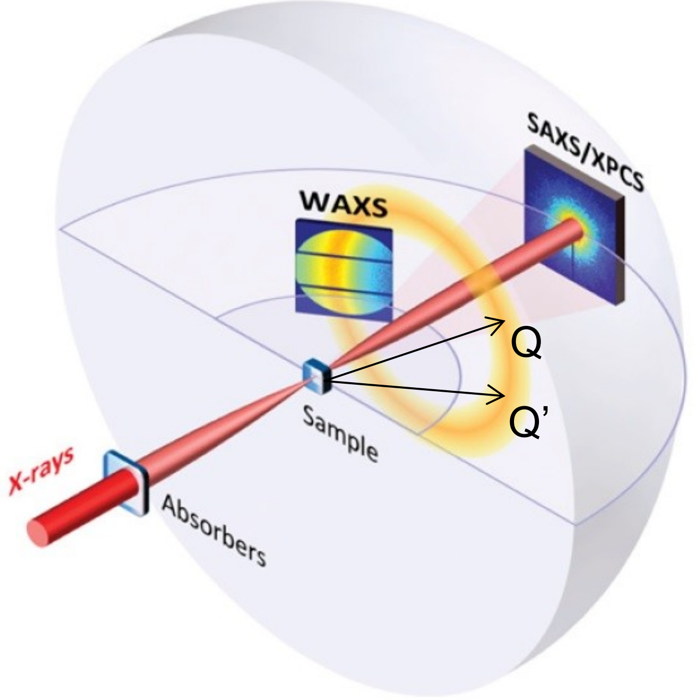
C(Q,Q',t,t')

$$\equiv \langle I(Q,t)I(Q',t')\rangle_{ensemble} \sim \iint \iint e^{-iQ(r-s)-iQ'(r'-s')}\, g_4(r,s,t,r',s',t')$$

with $g_4(r,s,t,r',s',t') \sim \langle \rho(r,t)\rho(s,t)\rho(r',t')\rho(s',t')\rangle$

→ local, transient symmetries — $C \equiv C_{Q,Q'}(\Delta) \sim \langle I(Q,\varphi)I(Q,\varphi+\Delta\rangle\varphi$
(e.g. molecular fluids,…) — *XCCA*

→ fluctuations — $C \equiv C_Q(\tau) \sim \langle I(Q,t)\, I(Q,t+\tau)\rangle$
(accompanying equilibrium and non-equilibrium dynamics) — *XPCS*

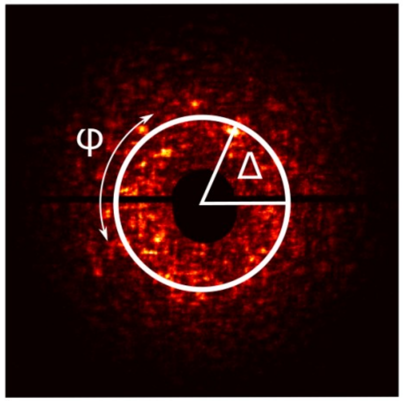


based on coherent X-ray beams

Sci. Rep. 4, 5234 (2014); Opt. Exp. 21, 24647 (2013); Opt. Exp. 20, 9760 (2012); PRL 108, 024801 (2012); Sci. Rep. 5, 17193 (2015)

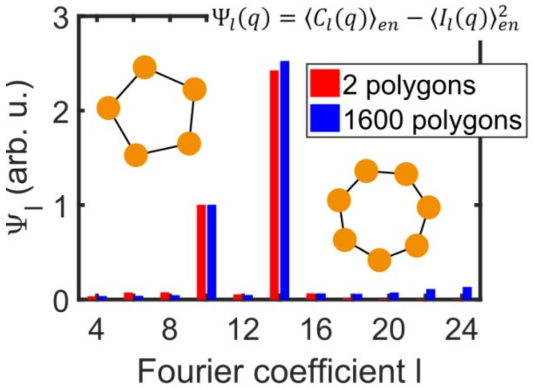
Higher Order Correlation Techniques (XCCA, XPCS)

XCCA
(X-Ray Cross Correlation Analysis)



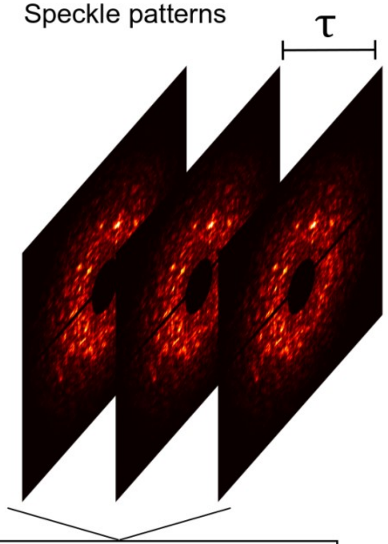
Cross-correlation function

$$C(q,\Delta) = \frac{\langle I(q,\varphi) I(q,\varphi+\Delta)\rangle_\varphi - \langle I(q,\varphi)\rangle_\varphi^2}{\langle I(q,\varphi)\rangle_\varphi^2}$$



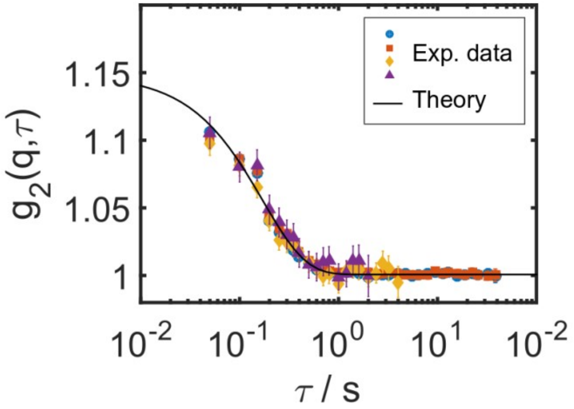
see talk
Felix Lehmkühler

XPCS
(X-Ray Photon Correlation Spectroscopy)

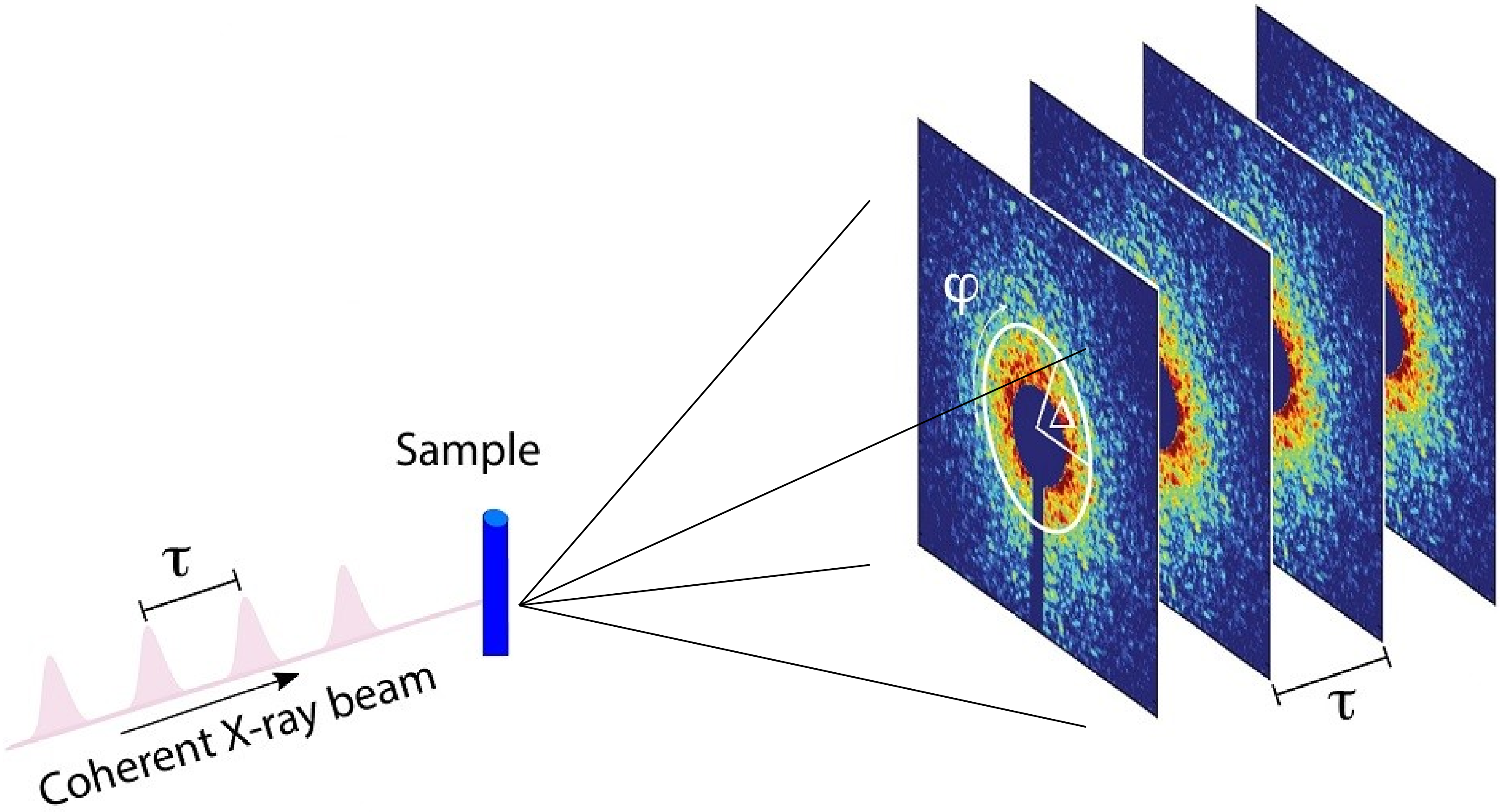


Intensity-intensity time autocorrelation function

$$g_2(q,\tau) = \frac{\langle I(q,t) I(q,t+\tau)\rangle_t}{\langle I(q,t)\rangle_t^2}$$



XPCS (X-ray Photon Correlation Spectroscopy)



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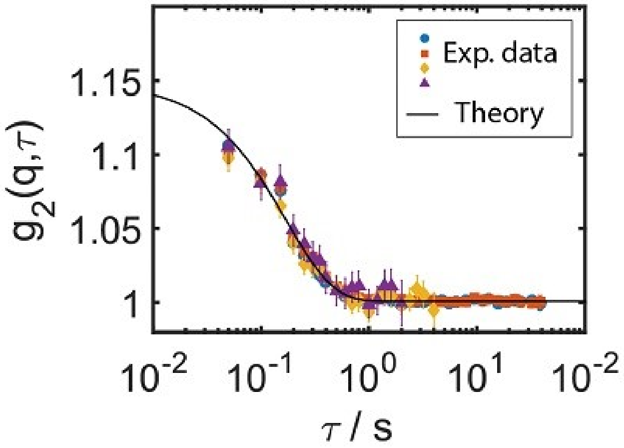


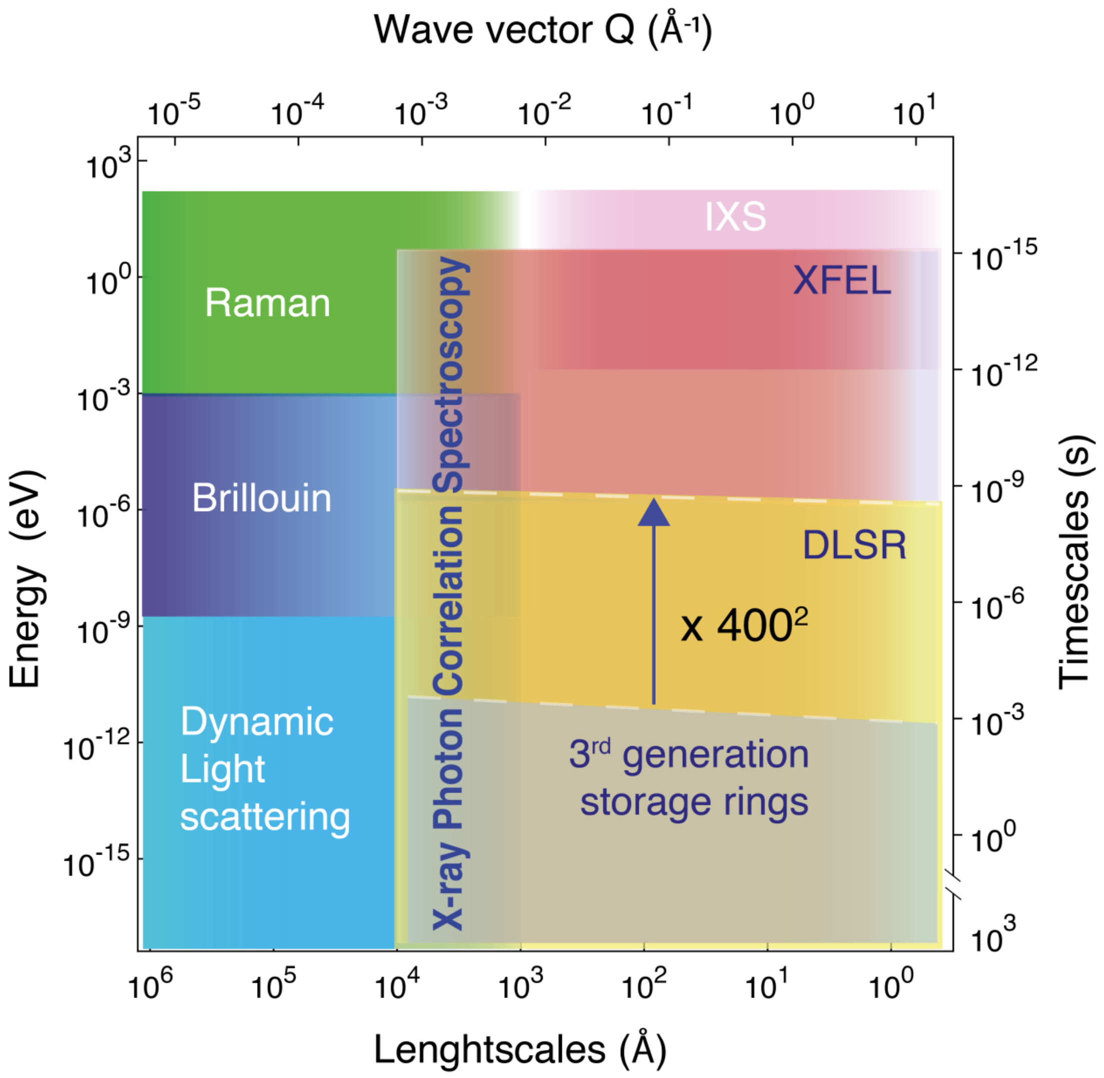
$$g_2(q,\tau) = \beta \exp(-2 [\Gamma(q)\tau]^{\gamma(q)}) + 1$$

$$R_{SN} \sim F_c (\tau_c T n_{pix})^{1/2}$$

$$R_{SN} \text{ constant: } \tau_c^{min} \sim 1/B^2$$

ESRF-EBS: B x 100 → 10000 times faster dynamics

XPCS at ESRF-EBS:



$10^4 – 10^6$

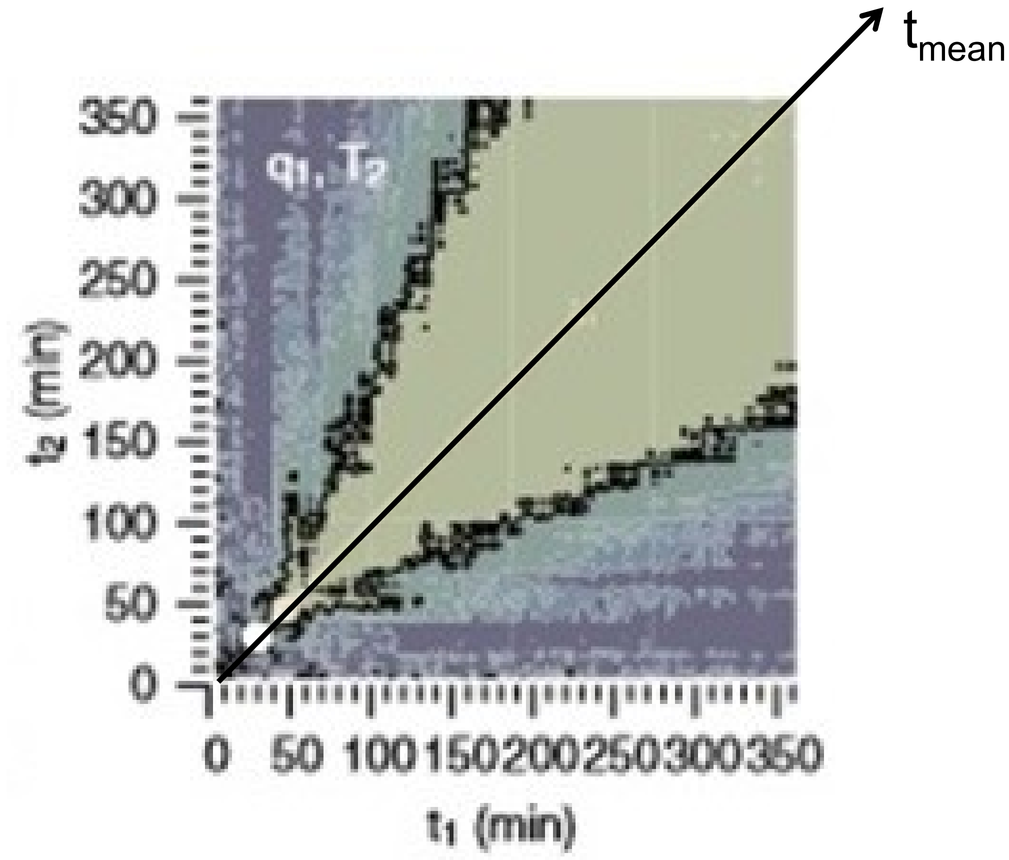
XPCS can access non-equilibrium dynamics

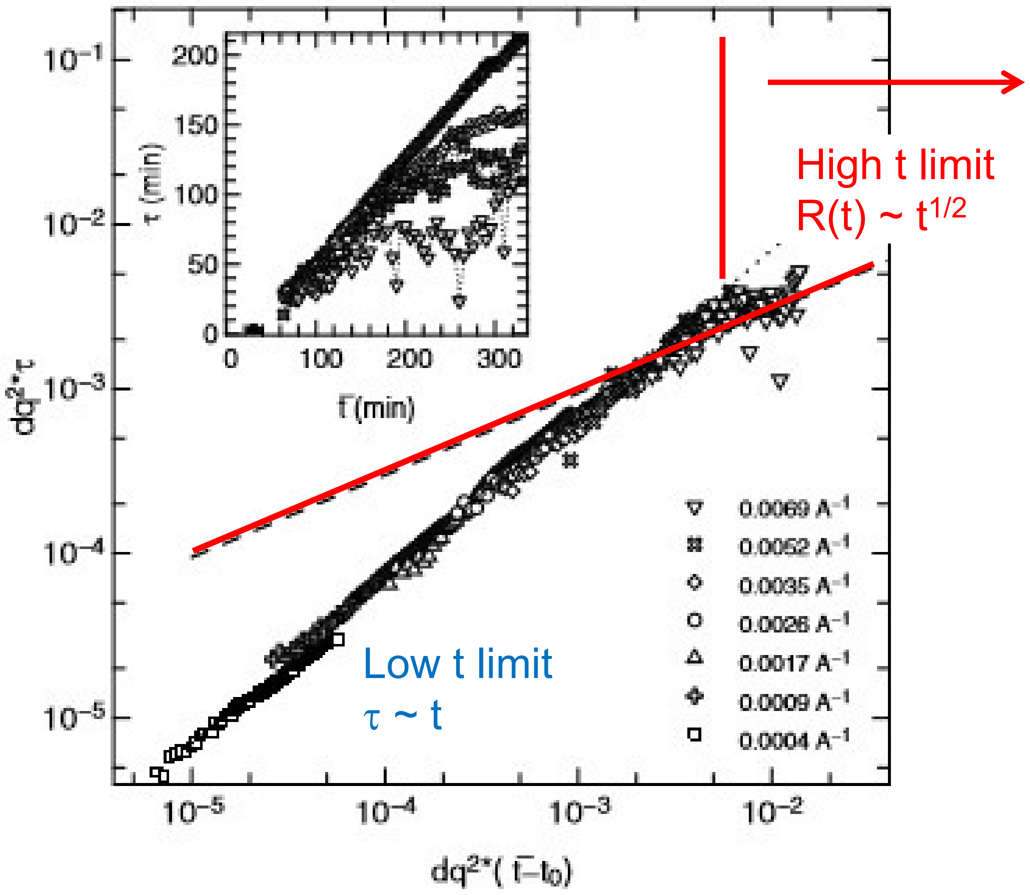
Fluerasu et al. PRL 94,055501,2005

Ordering kinetics in Cu_3Au: after a quench ordering on the fcc lattice occurs (with patches in the four allowed groundstates). At later t domains coarsen with $R(t) \sim t^{1/2}$

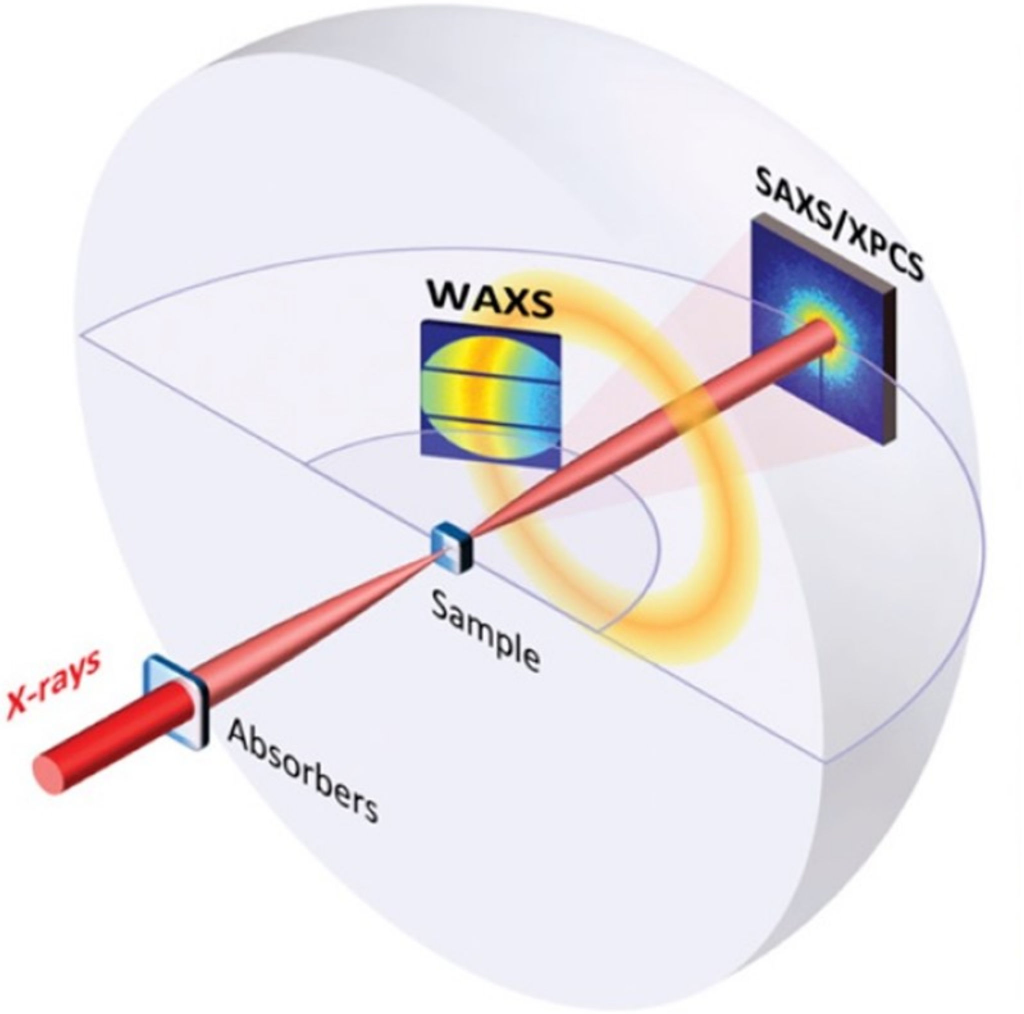
Two-time correlation function: **$C(q, t_1,t_2)$: access to fluctuations about the average behaviour**

up to now only for (very) slow processes: need ESRF-EBS





XPCS: speckle issues



Do not modify sample with XPCS beam
(use as big beam as possible)
Illuminate sample coherently

$\sigma \cong \xi_{x/y}$ = *100 μm* *at 100m*

Resolve speckle on detector

$D_{pixel} \leq D_s = (\lambda/\sigma) \times L$ = *100 μm*

Locate (fast, pixelated) detector at distance L

$L = D_S / (\lambda / \sigma)$ = *(1 Angstrom) =* *100m*

A 200m beamline is an excellent choice.

Obey: PLD $\leq \xi_l = \lambda (\lambda/\Delta\lambda)$

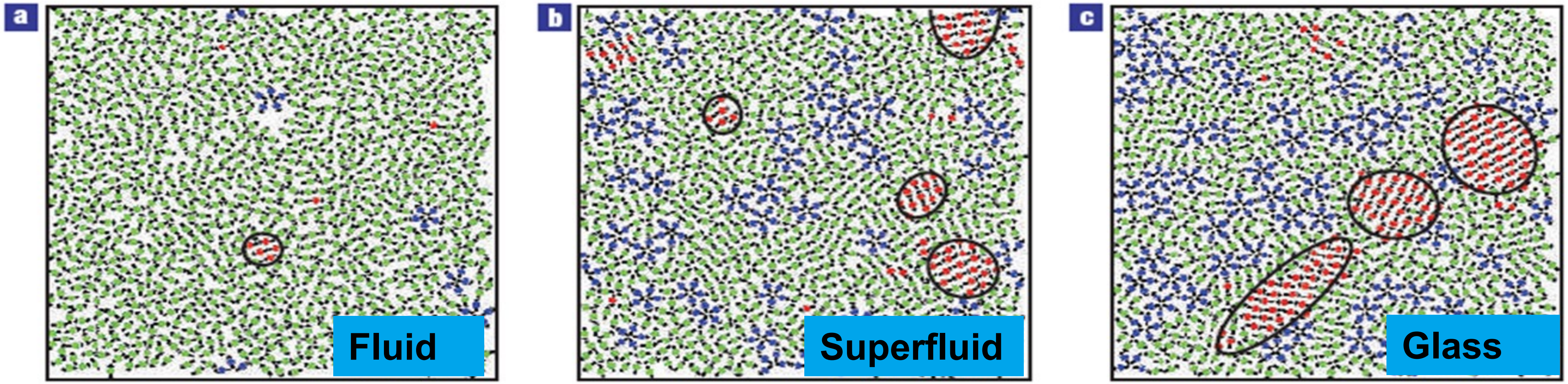
Applications

- Glass Transition
- Complex Fluids / the aqueous environment
- Bio systems (see talk C. Gutt)
- Magnetism
- XPCS at higher energies

Structure of Fluids and Glasses

Some liquids do not crystallize below the melting point but instead enter into a supercooled state and upon cooling eventually become a glass.

Simulations indicate coexistence of local, icosahedral order (LIO) and medium-range crystalline order (MRCO).



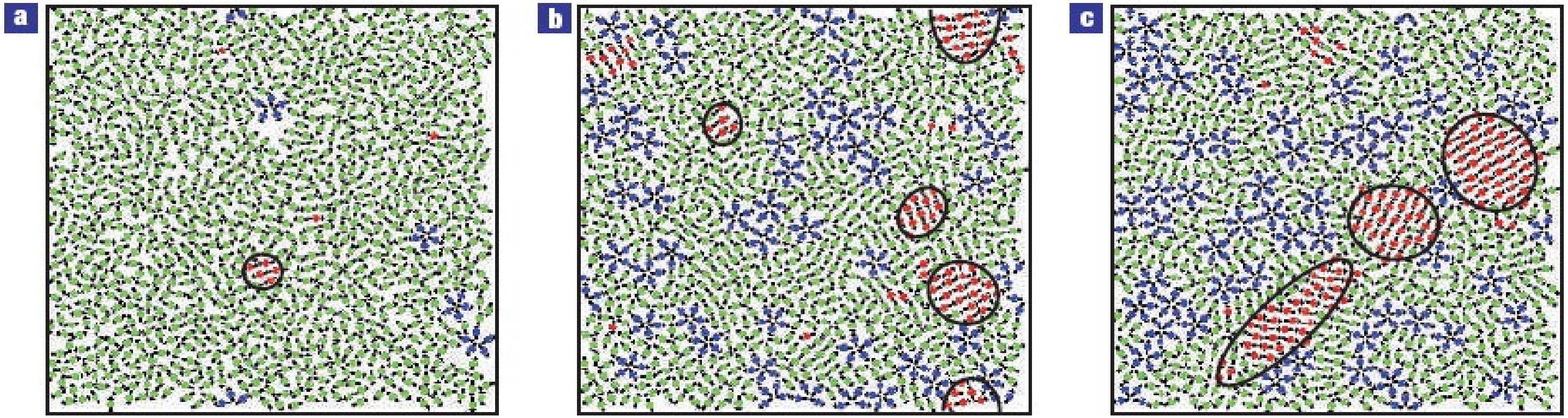
Crystallization is suppressed by geometrical frustration:

- *Tendency towards global, icosahedral order with geometrical frustration since space cannot be filled.*
- *Tendency towards crystallization suppressed by local order.*

Shintani & Tanaka *Nature Physics* 2, 200 (2006)

Dynamics of Fluids and Glasses

Dynamics in liquids slows down dramatically and becomes progressively more (temporally) heterogeneous.
Simulations *(Tanaka et al., Nature Mat. 9(2010)324)* indicate that heterogeneous dynamics is the result of critical-like fluctuations of (static) **structural order** (*glass transition* ⇔ *critical phenomena*): *Slower regions have higher order.*
Characteristic lengths ξ and lifetimes τ of temporally ordered regions increase upon cooling in a correlated manner.



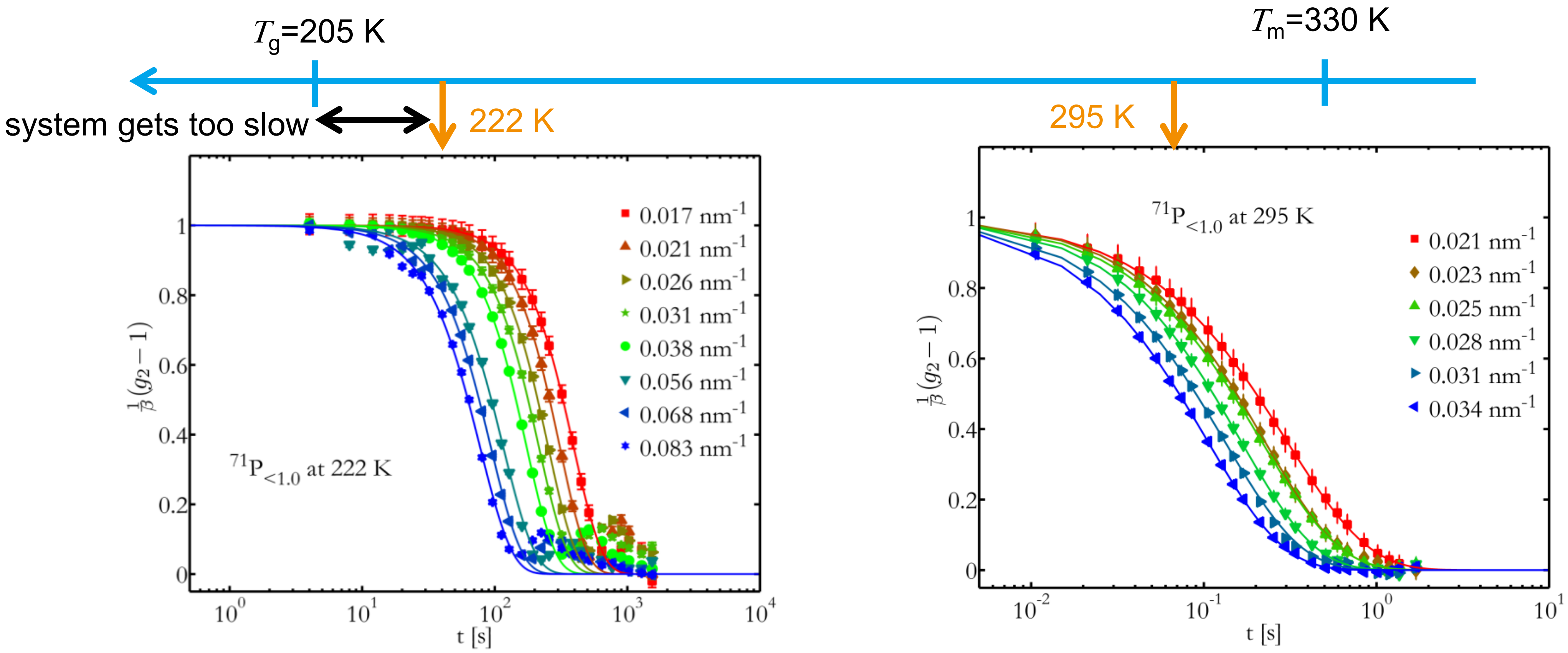
<u>Claim:</u> structural order $\equiv$ **medium-range** <u>bond orientational order</u>

(without traces in S(Q))

Glassforming fluids: The tracer issue

Conrad et al., PRE 91, 042309, 2015

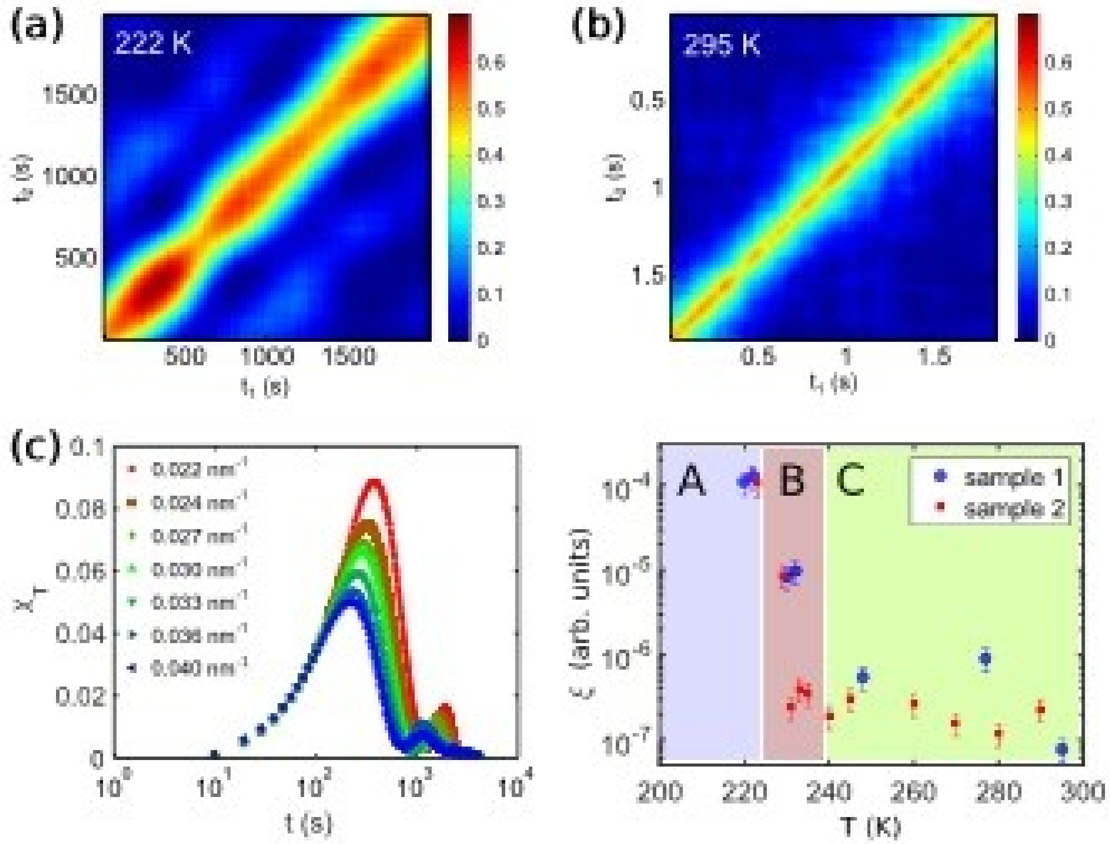
Tracer silica (71 nm, c=1%) in glass-forming PPG: increase scattering and slow down dynamics ($\Gamma = D q^2$; $D = k_B T / 6\pi\eta R$)



compressed exponential (γ =2), $\Gamma \propto q$

exponential (γ =1), $\Gamma \propto q^2$

Dynamical Heterogeneities



χ_T normalized variance of the instantaneous correlation function

Strong dynamical heterogeneities at 222K
(17 degs above the glass transition)
but can't reach Tg (timescale/damage)

Want to get closer to T_g to study the regions with correlated dynamics: ESRF-EBS

See also talk: M. Reiser

Metallic glasses during aging

Giordano & Ruta Nat. Comms 7, 10334, 2016

Aging (or relaxation) regimes in out-of-equilibrium systems (rapidly quenched metallic glass) goverened by two processes:

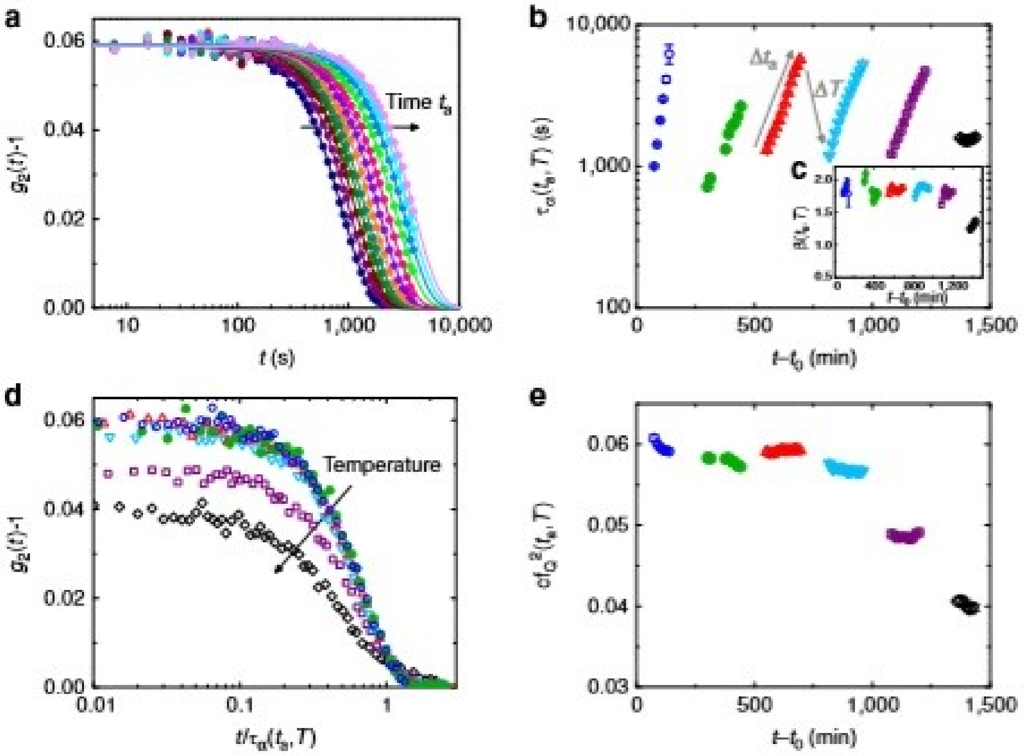
> Rearrangements that release residual stresses

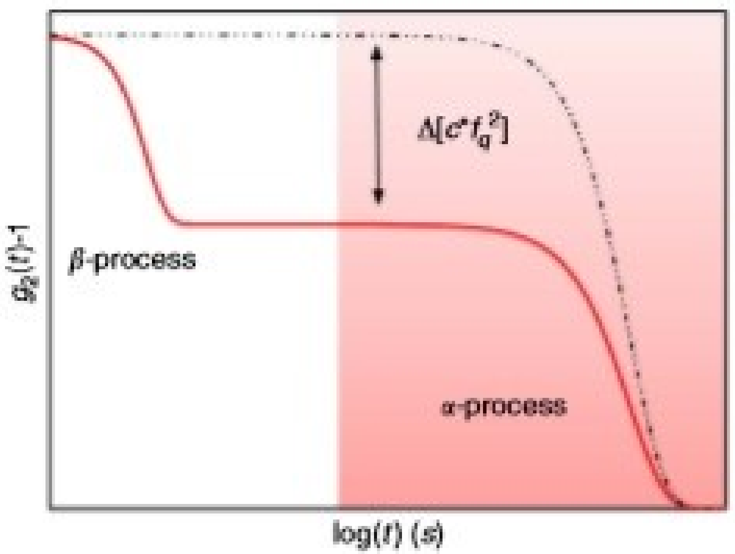
> Medium range ordering process

Metallic glass ($Pd_{77}Si_{16.5}Cu_{6.5}$) T_G = 625K

T=453 K

T = 393K
433K
453K
473K
513K





Second fast (β-) relaxation process at high T (513K):
Onset of medium range ordering (MRO) (crystallization)

Too fast to be detected: ESRF-EBS

MRO accessible to XCCA

Aqueous environements

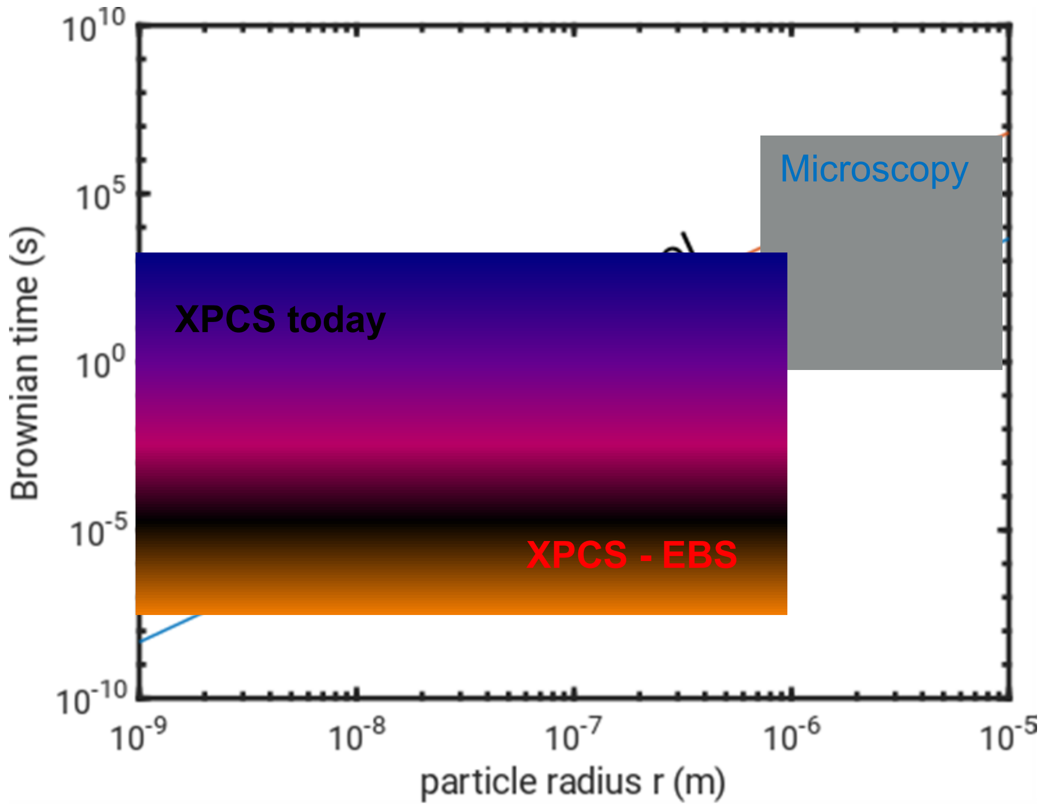
Stokes-Einstein diffusion

Understand dynamics of particles in liquids → complex fluids

- Stokes-Einstein diffusion
  - $D = \frac{k_B T}{6\pi\eta r}$, with viscosity η and particle radius r
  - Brownian time $\tau_B = r^2/D$

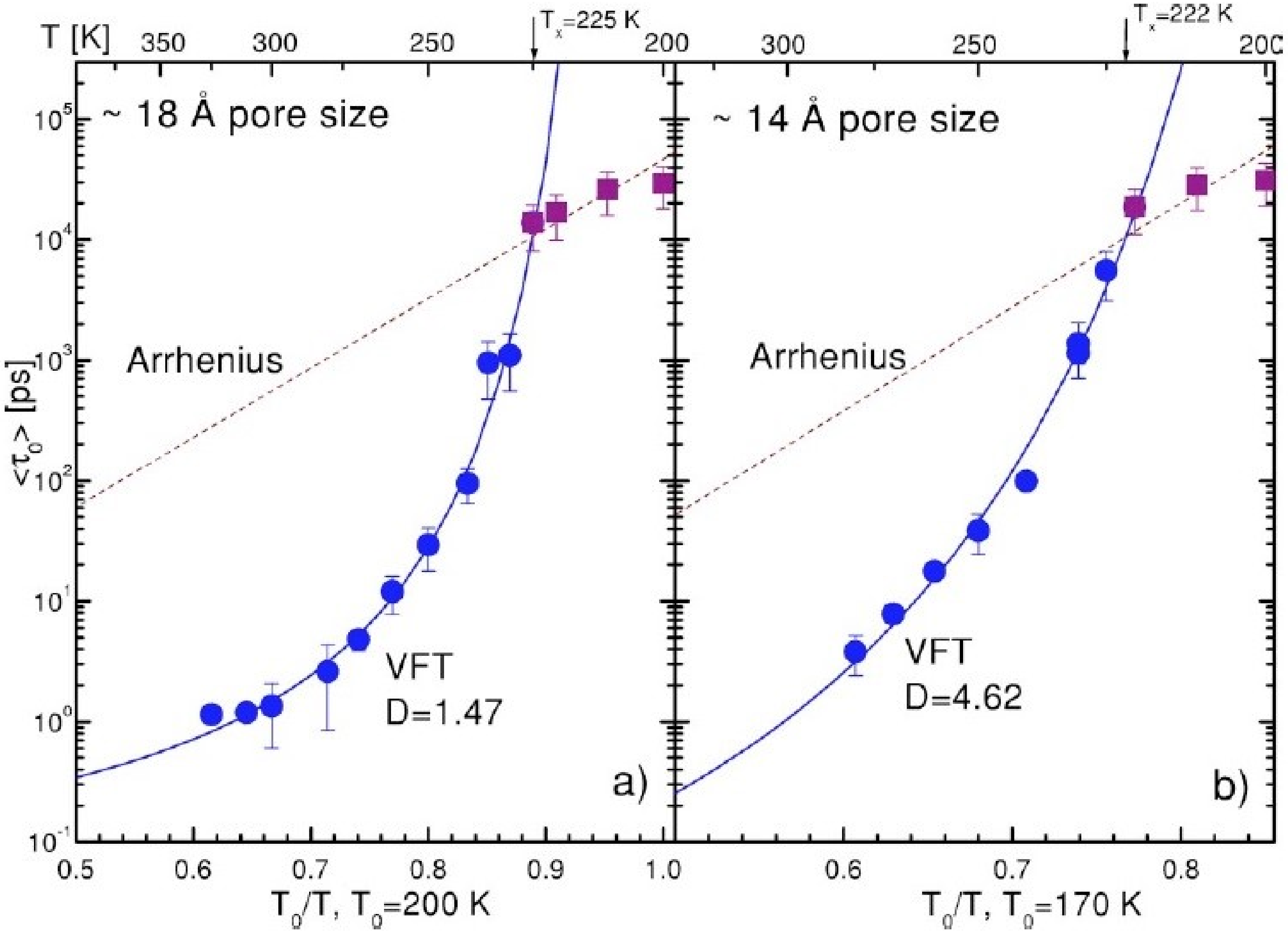
ESRF-EBS will give acces to the majority of waterbased systems

(transport in pores, under confinement…)



Confined liquids

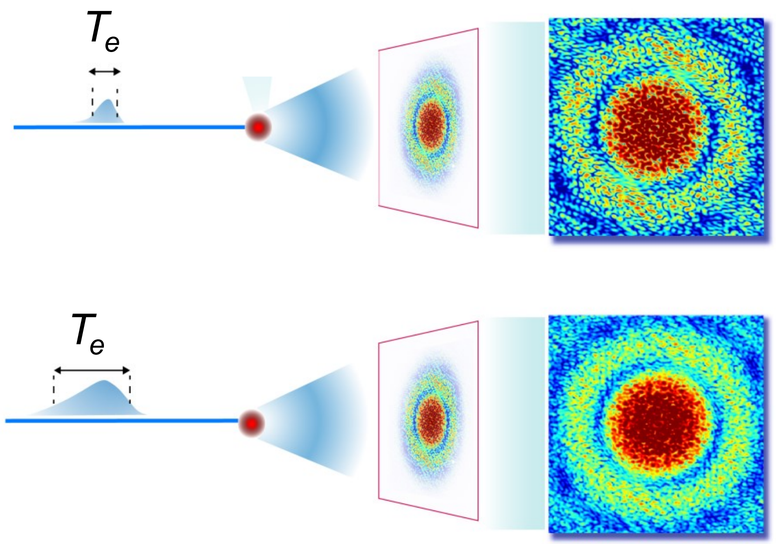
- **Water in confinement (fragile to strong transition)**



ESRF-EBS

Speckle Visibility Technique: Bio-XPCS

Enables access to radiation sensitive samples: Biology (see Gutt et al.)



record contrast as a function of bunch length T_e

$$visibility(Q,T_e) = \beta_0/T_e \int_0^{Te} 2(1-\tau/Te)\, |f(Q,t)|^2\, dt$$

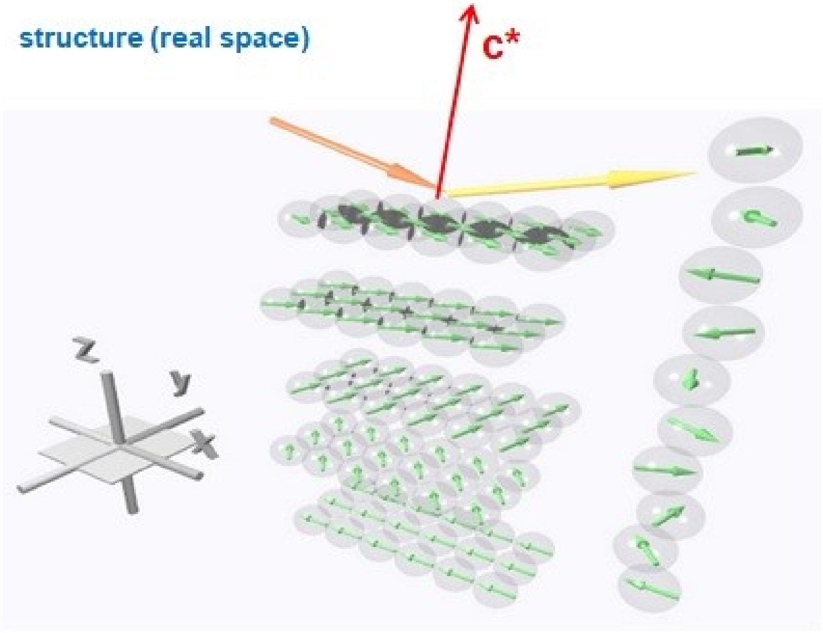
in the limit of very low intensities given by the ratio of zeros to one or double to single events:

$$v(Q,T_e) = P(0,T_e)/P(1,T_e) - 1/\langle k \rangle$$

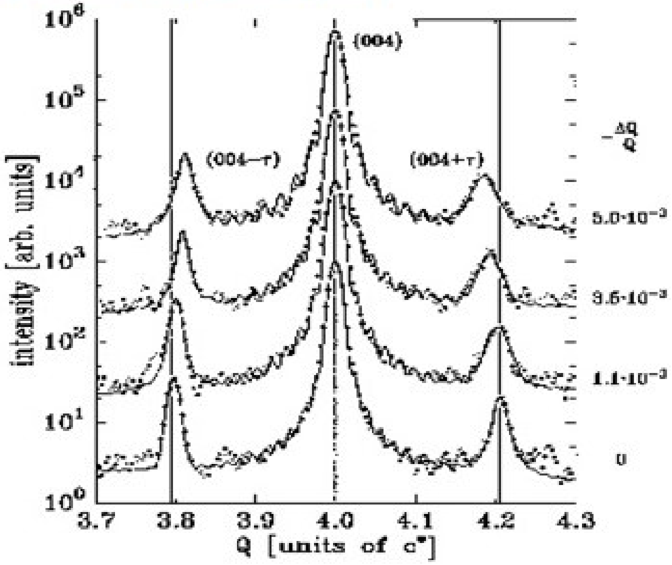
Bandyopadhyay et al., Rev.Sci.Instr. 76 (2005) 093110
deCaro et al., JSR 20 (2013) 332
Verwohlt et al., PRL 120 (2018) 168001

Magnetic structures: The spiral antiferromagnet holmium

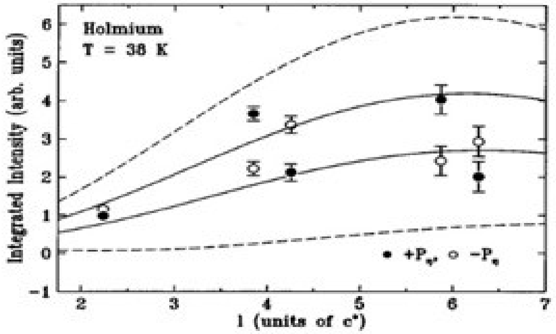
structure (real space)

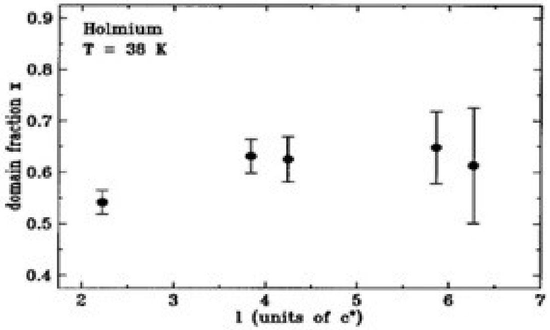


structure (reciprocal space)

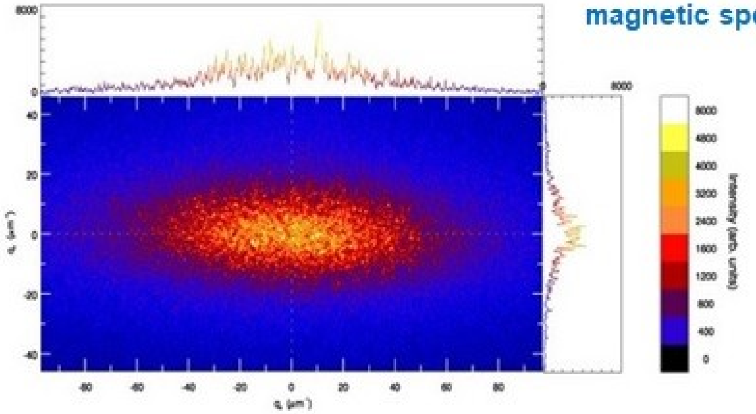


chirality





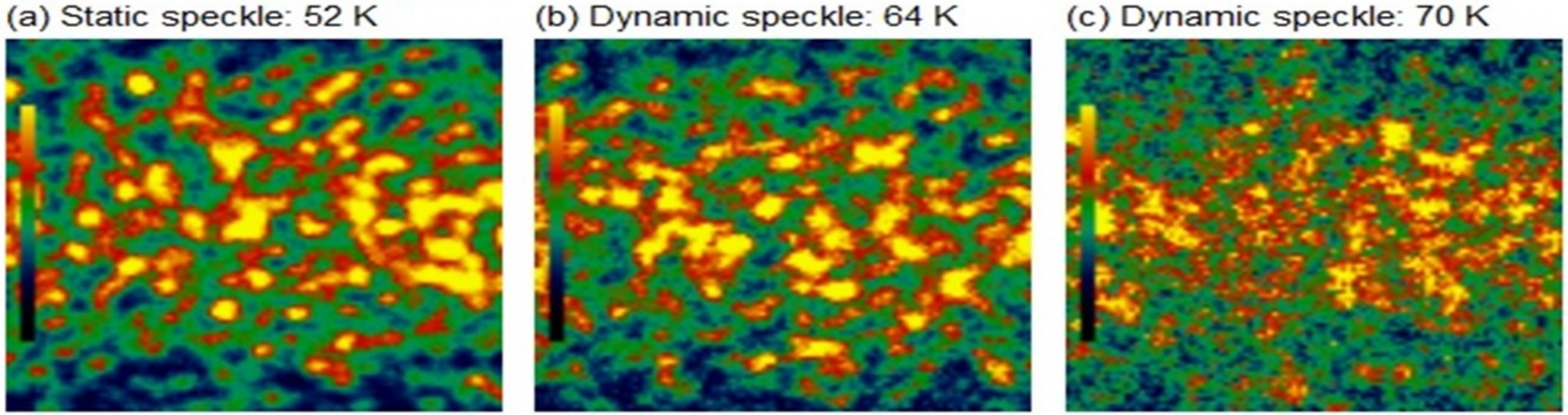
magnetic speckle



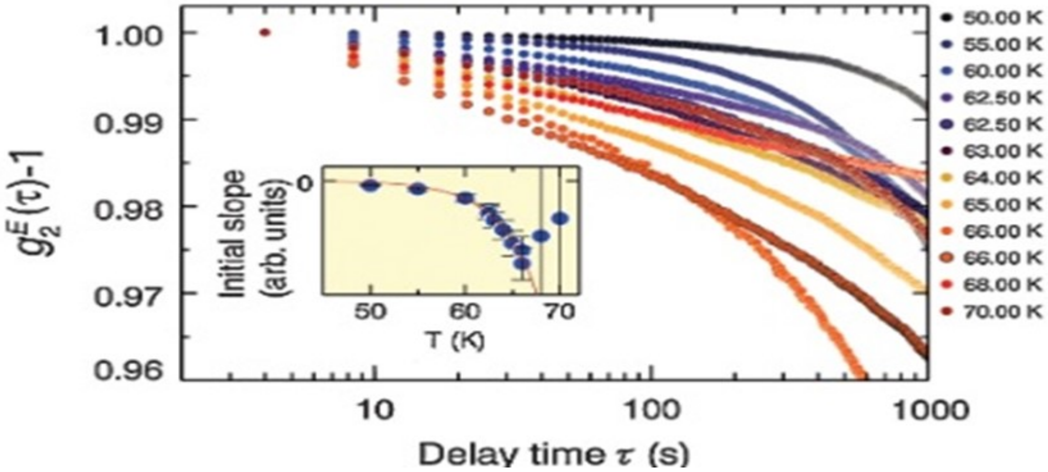
Konings et al., PRL 106,077402(2011)
Sutter et al., PRB55,954 (1997)
Gibbs et al., Phys. Rev. B43, 5663 (1991)

Magnetisation Dynamics

Figure 1 | Magnetic speckle movies



Thin holmium film
(0,0,0+τ)
measured at the M edges



ESRF-EBS will allow to look into the fluctuations of a single (≈100 nm) domain (at Ho L-edge)

S. Konings, C. Schüßler-Langeheine, H. Ott,
E. Weschke, E. Schierle, H. Zabel, and J.B. Goedkoop
Phys. Rev. Lett. 106, 077402 (2011)

XPCS at higher X-ray energies

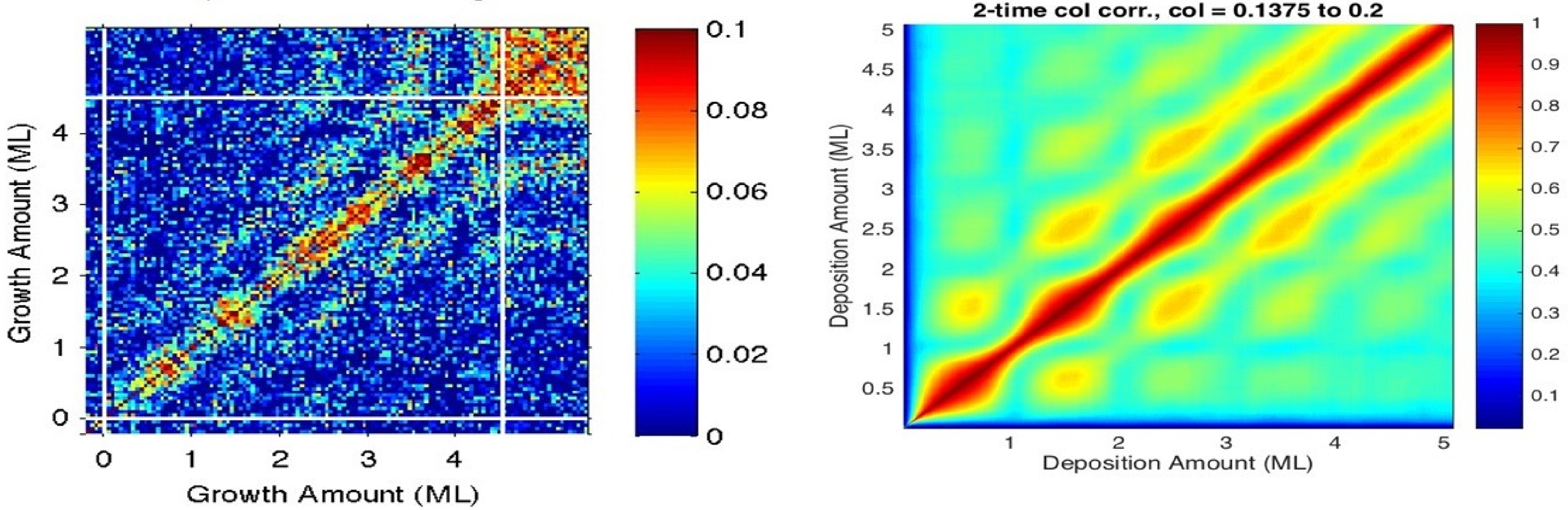
Stephenson et al.

Two-Time Correlations During Layer-By-Layer Growth

Preliminary results on m-plane GaN
(coherent pink beam, 26 keV)

- Initial analysis compares well with simulations of LBL growth on miscut surface

Growth of 4.5 ML; correlations at half-integer ML



Speckles getting smaller with increasing E: need larger sample to detector distance: ESRF-EBS

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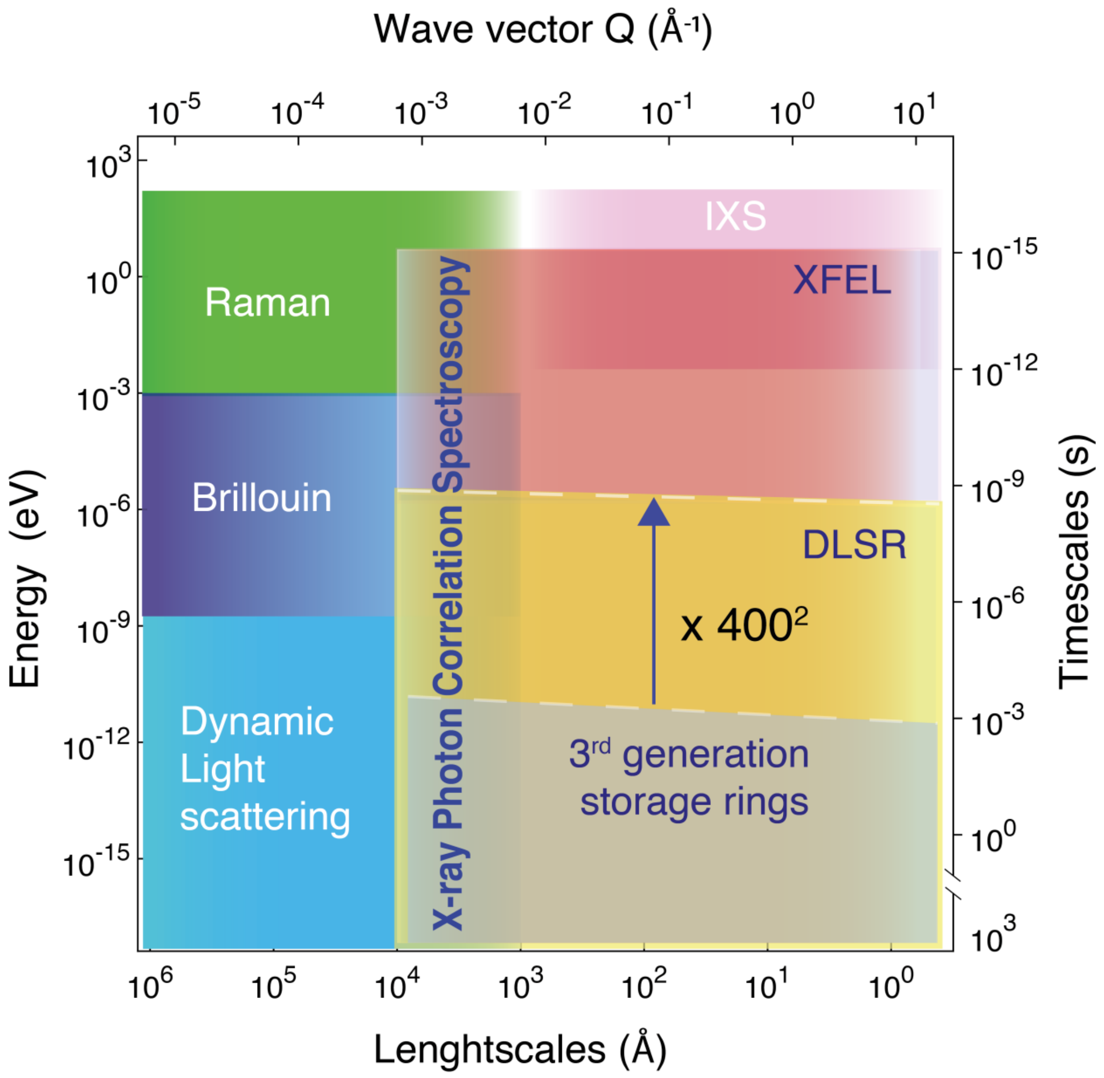
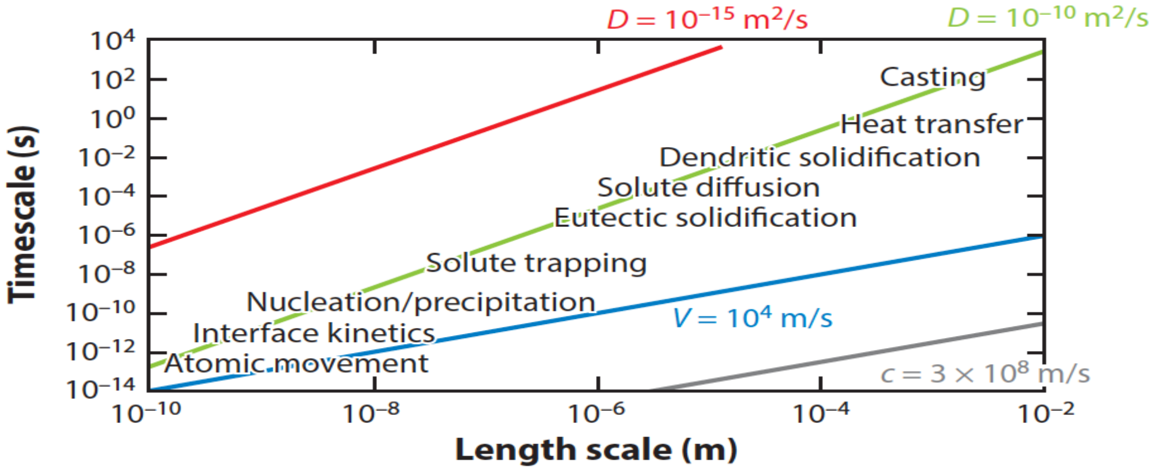
Summary



10^4 -10^6

Outlook

- DLSR based XPCS gives acces to the relevant fast dynamics
- Perspective to tackle relevent issues in glasses, soft matter, liquids, biology, ……
- Many questions related to materials research will be within reach



Sandy et. al, Annual Review of Materials Research

- 2D detection gives access to higher order correlation functions $C(q_1, q_2, t_1, t_2)$.
  Need theory support to identify the appropriate correlator C

Acknowledgement

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Colleagues from ID10/ESRF

Colleagues from ANL, McGill and SLAC

MID gang at E-XFEL

The End