Application of XCCA for nanoparticle self-assembly and colloidal phase transitions

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Fluctuation X-Ray Scattering Workshop
June 2021

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

DESY.

Correlation studies with coherent X-ray scattering

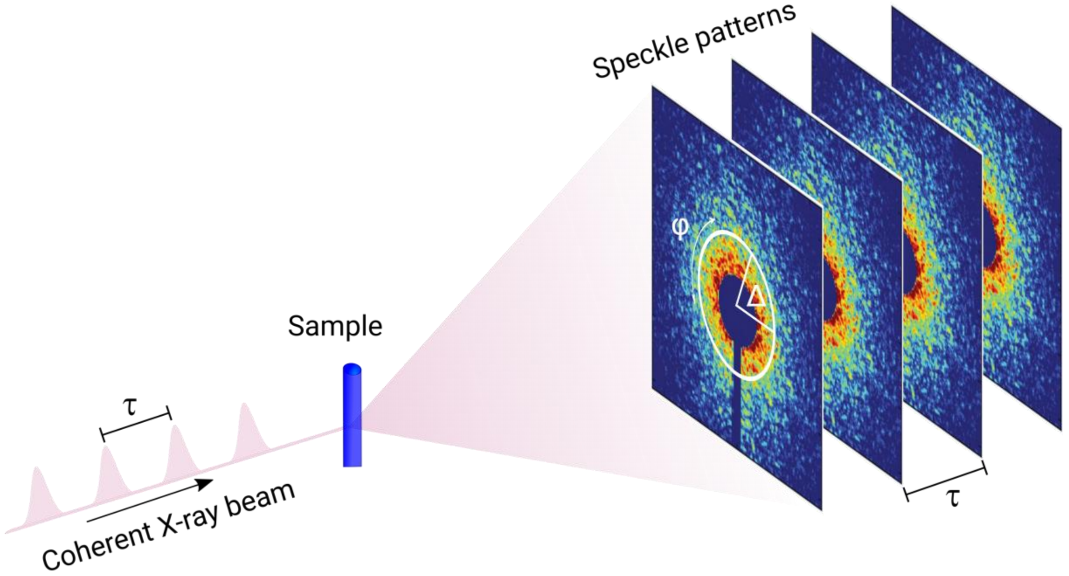
Spatial correlations: X-ray Cross Correlation Analysis (XCCA)

- Orientational structure beyond pair correlation functions
- Angular correlations $C(\Delta) = \langle I(\varphi) I(\varphi + \Delta) \rangle_\varphi$

Time correlations: X-ray photon correlation spectroscopy (XPCS)

- Analogue to dynamic light scattering (DLS)
- Temporal correlations $C(\tau) = \langle I(t) I(t + \tau) \rangle_t$

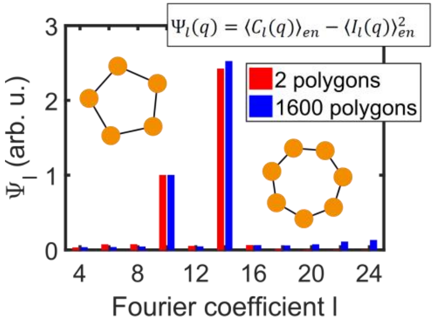
Nanoscale: SAXS



XCCA

Cross-correlation function

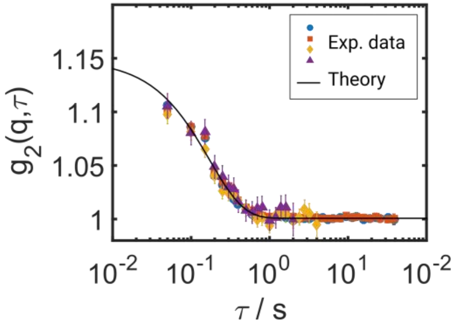
$$C(q,\Delta) = \frac{\langle I(q,\varphi) I(q,\varphi+\Delta)\rangle_\varphi - \langle I(q,\varphi)\rangle_\varphi^2}{\langle I(q,\varphi)\rangle_\varphi^2}$$



XPCS

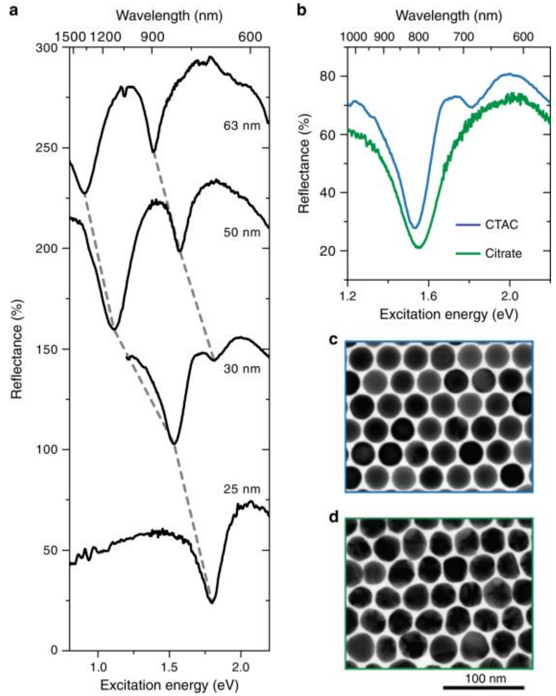
Intensity-intensity time autocorrelation function

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



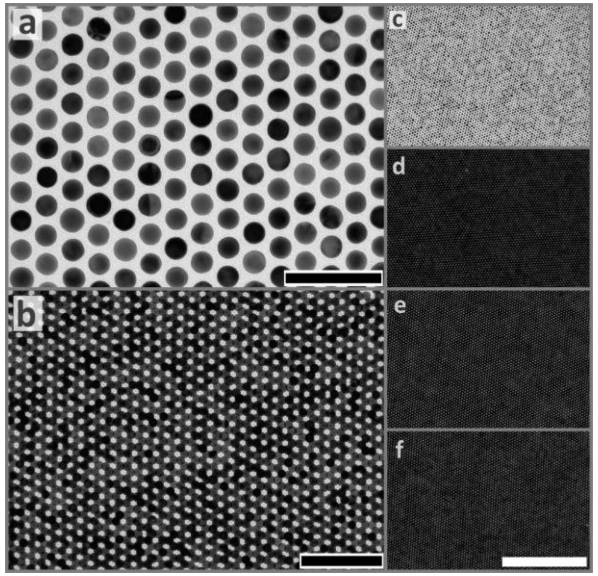
Example 1: Structure of self-assembled films

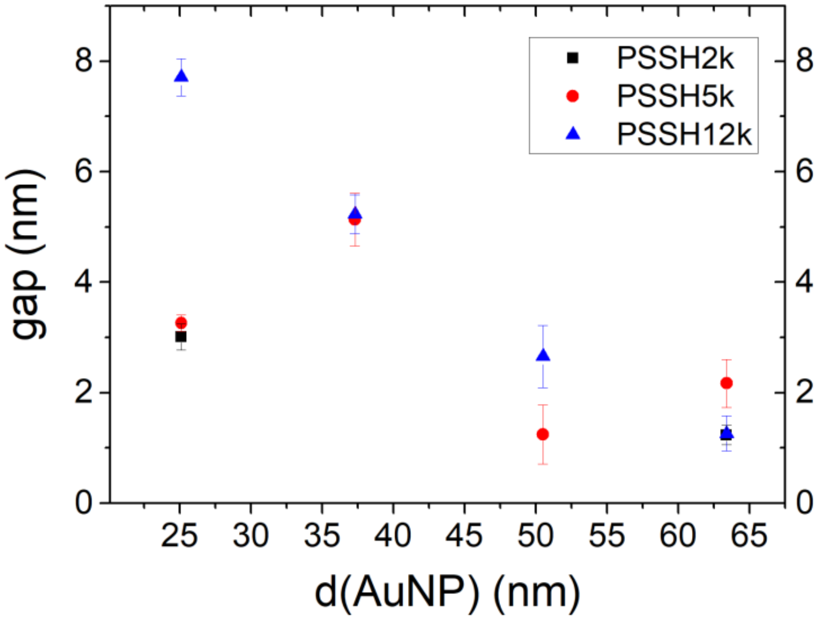
- Plasmonic NP: structure of assemblies correlates with emergence of coupled plasmon modes
- Deep strong coupling under ambient conditions



- Reflectance and polaritonic modes

- Particles dried on TEM grids
- Polystyrene-coated Au particles
  - Gold core of 12 nm radius
  - Tune distance by ligand length

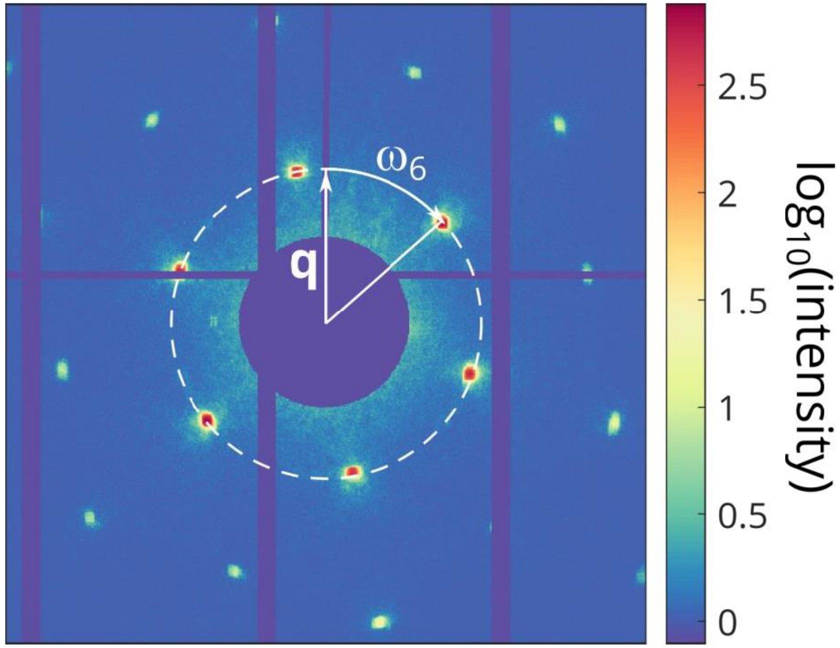




Nature Commun. 11, 3821 (2020), Nature 583, 780 (2020)

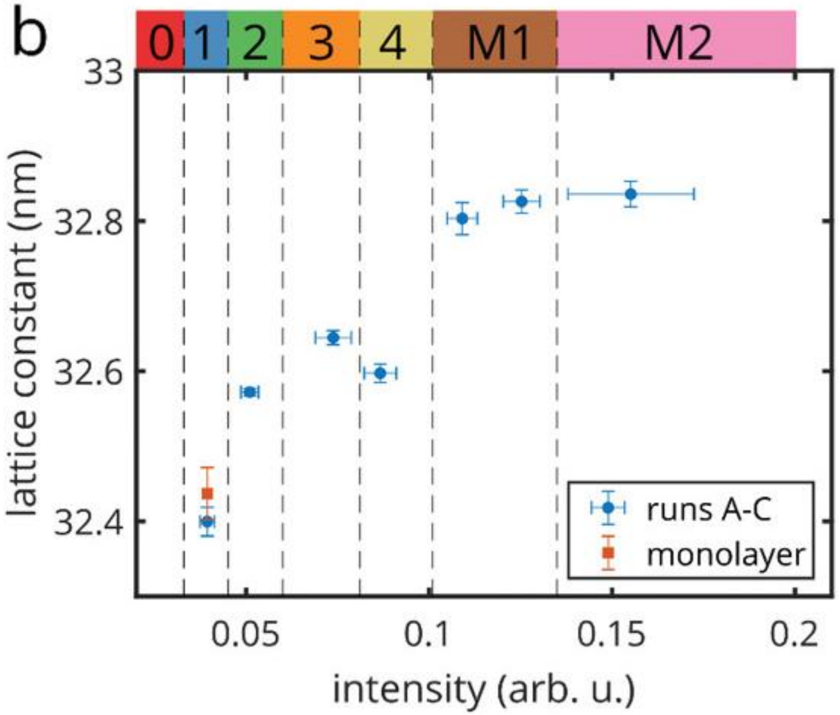
Example 1: Structure of self-assembled films

- Scanning SAXS approach at P10 (PETRA III)
- Beamsize about 1 µm = scan step size
- Intensity + order maps
- Fourier coefficients $I_\ell(q) = |I_\ell(q)| \exp(i\Omega_\ell(q))$



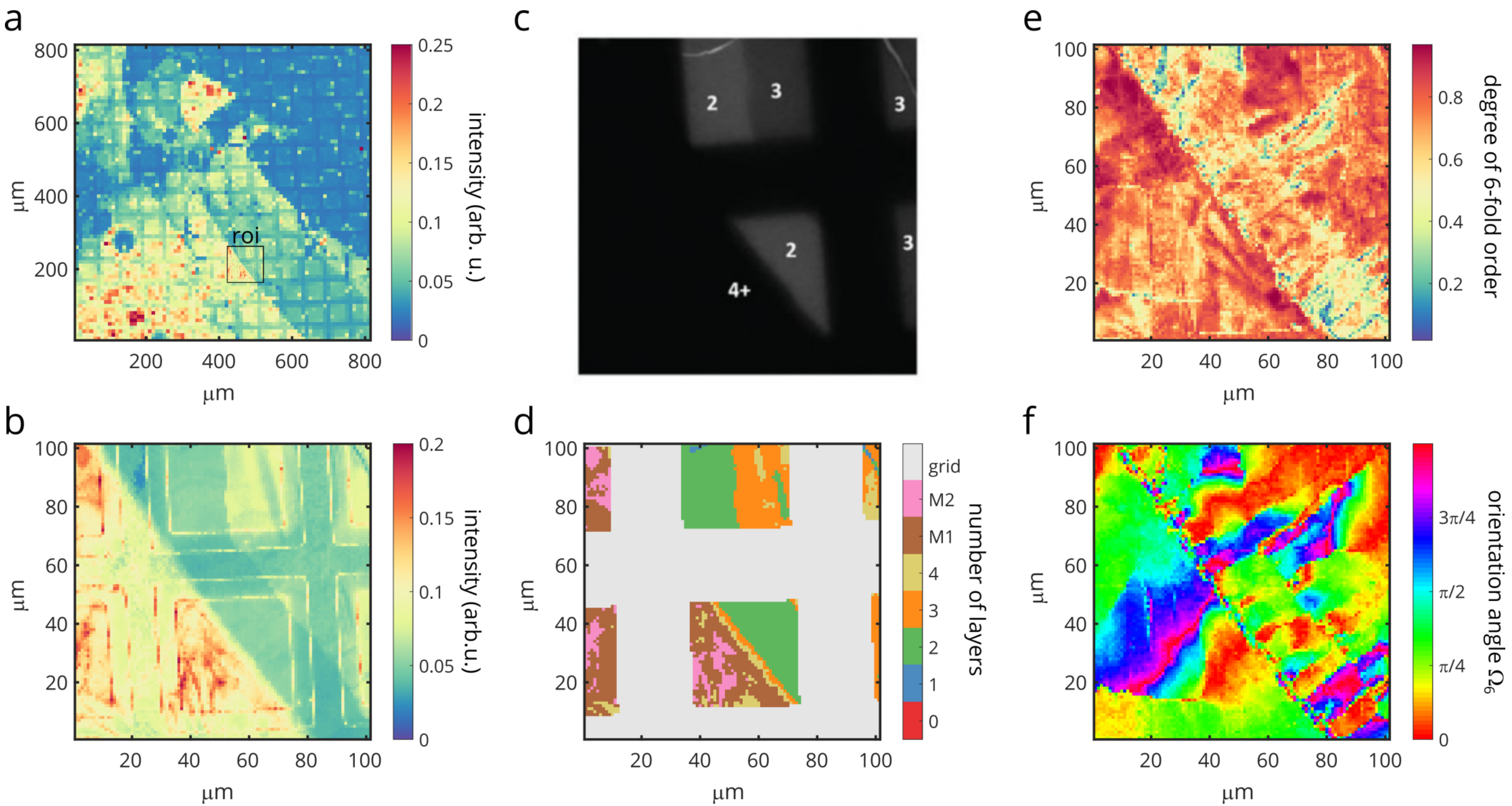
Conventional SAXS analysis

- Identify number of layers by scattering intensity
- Lattice constant



Adv. Mater. Inferf. 7, 2000919 (2020)

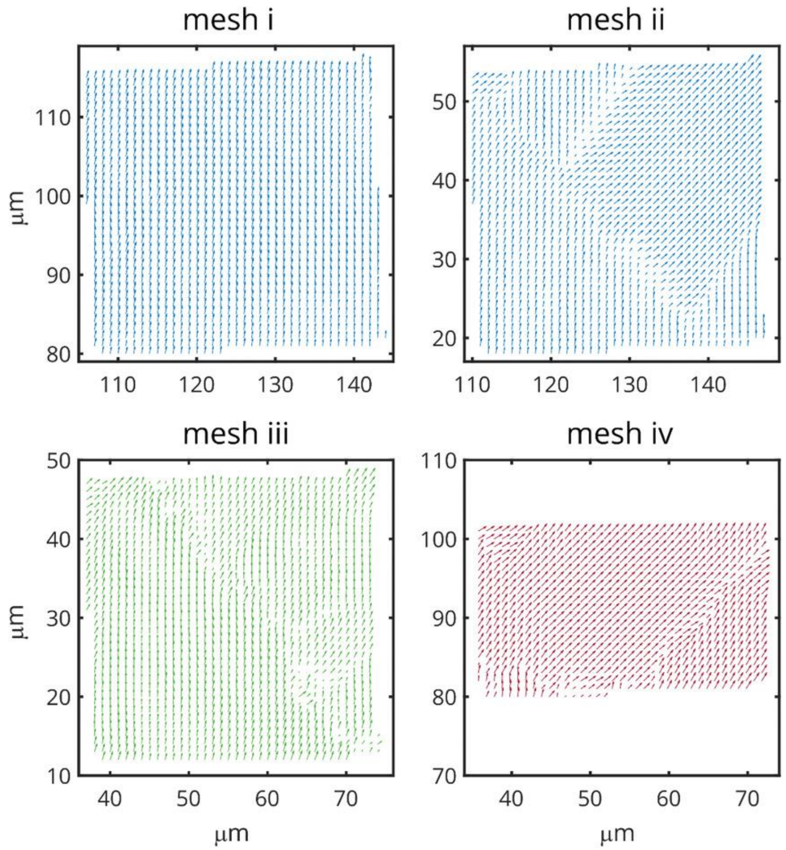
Example 1: Structure of self-assembled films

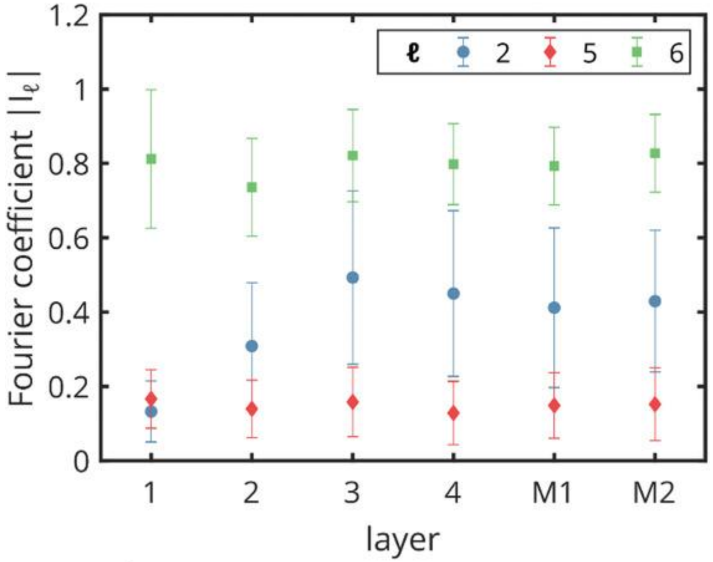


Adv. Mater. Inferf. 7, 2000919 (2020)

Example 1: Structure of self-assembled films

- Domain sizes from phase Ω_ℓ
- Exceeding mesh sizes of 40 µm x 40 µm





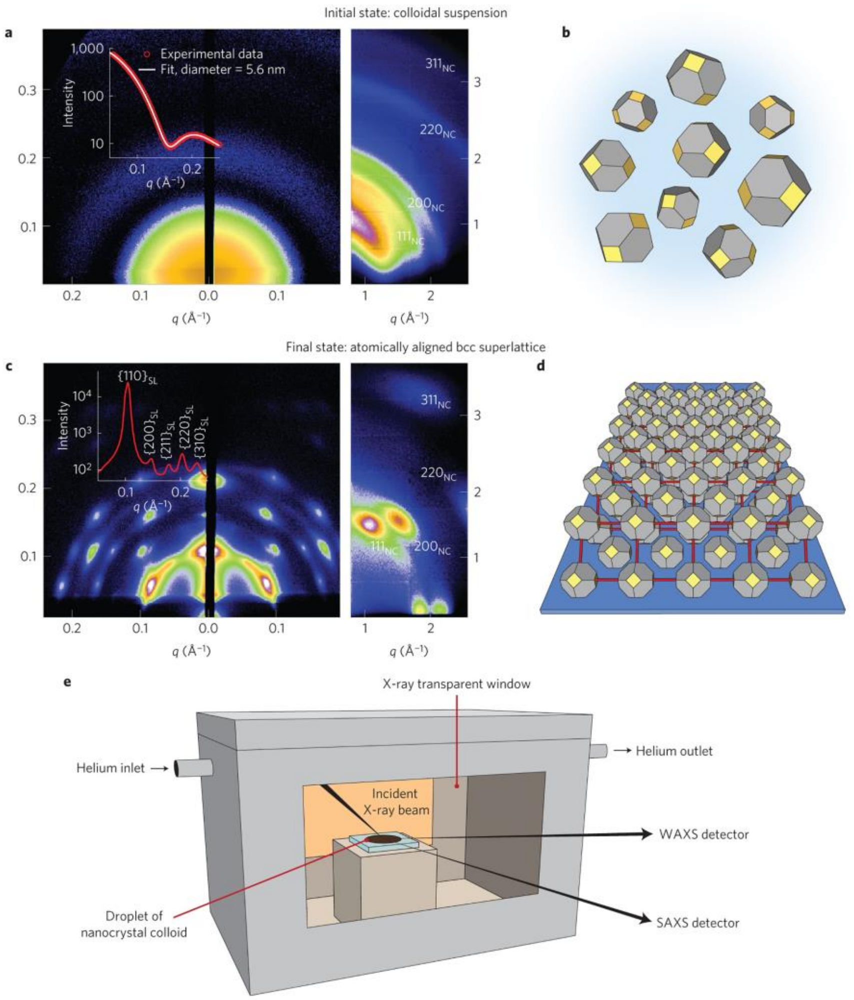
- Degree of six-fold symmetry does not depend on number of layers
- Two-fold symmetry: Friedel‘s law
- Five-fold: measure of background

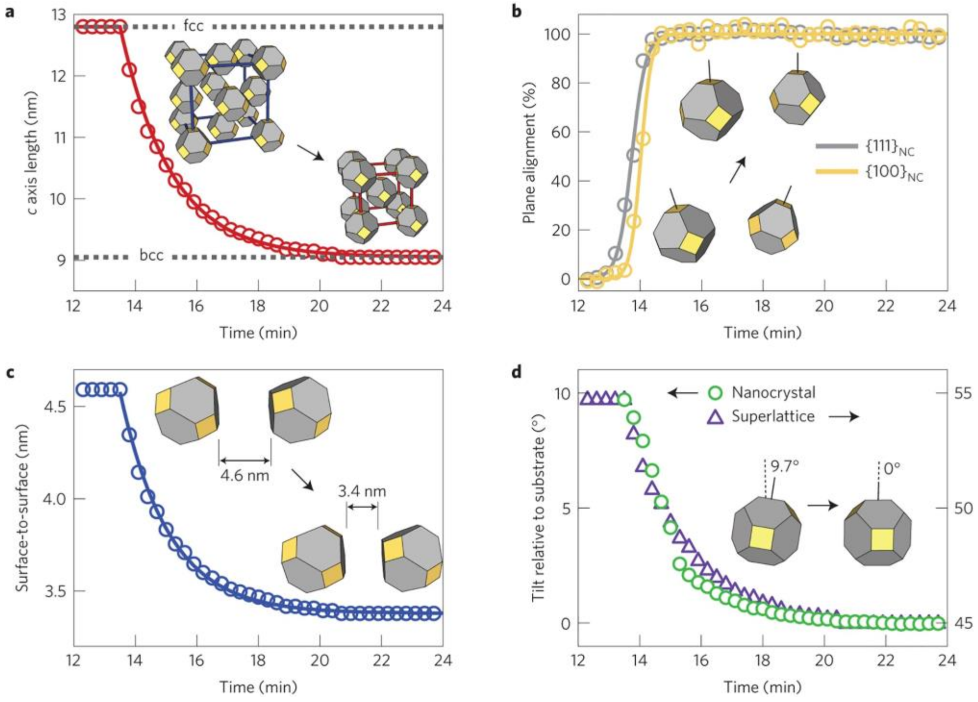
Adv. Mater. Inferf. 7, 2000919 (2020)

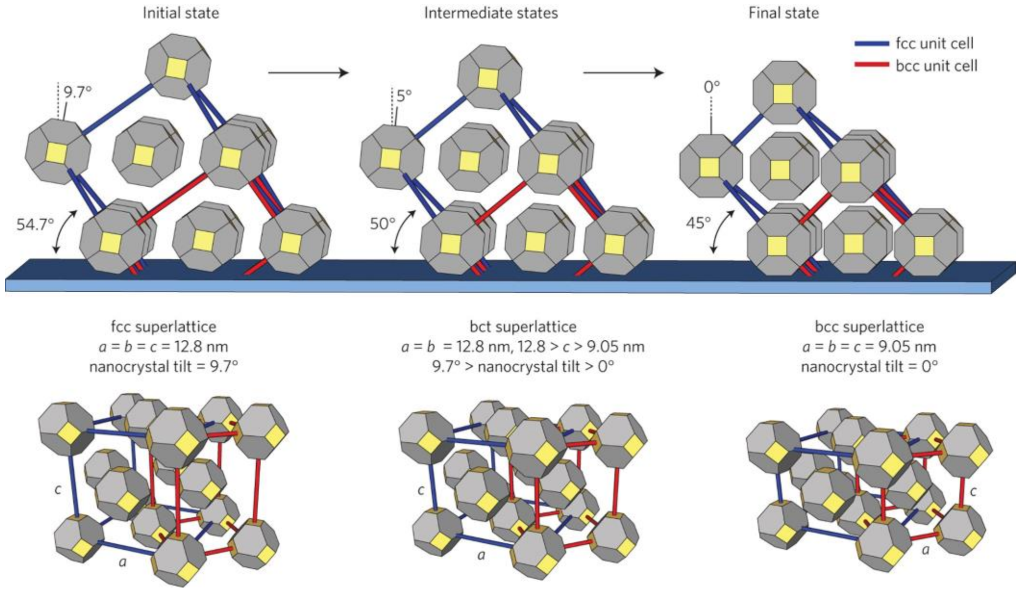
Soft matter 11, 5465 (2015); J. Appl. Cryst. 49, 2046 (2016); IUCrJ 5, 354 (2018); J. Appl. Cryst. 52, 777 (2019)

Example 2: In-situ self-assembly

GISAXS studies



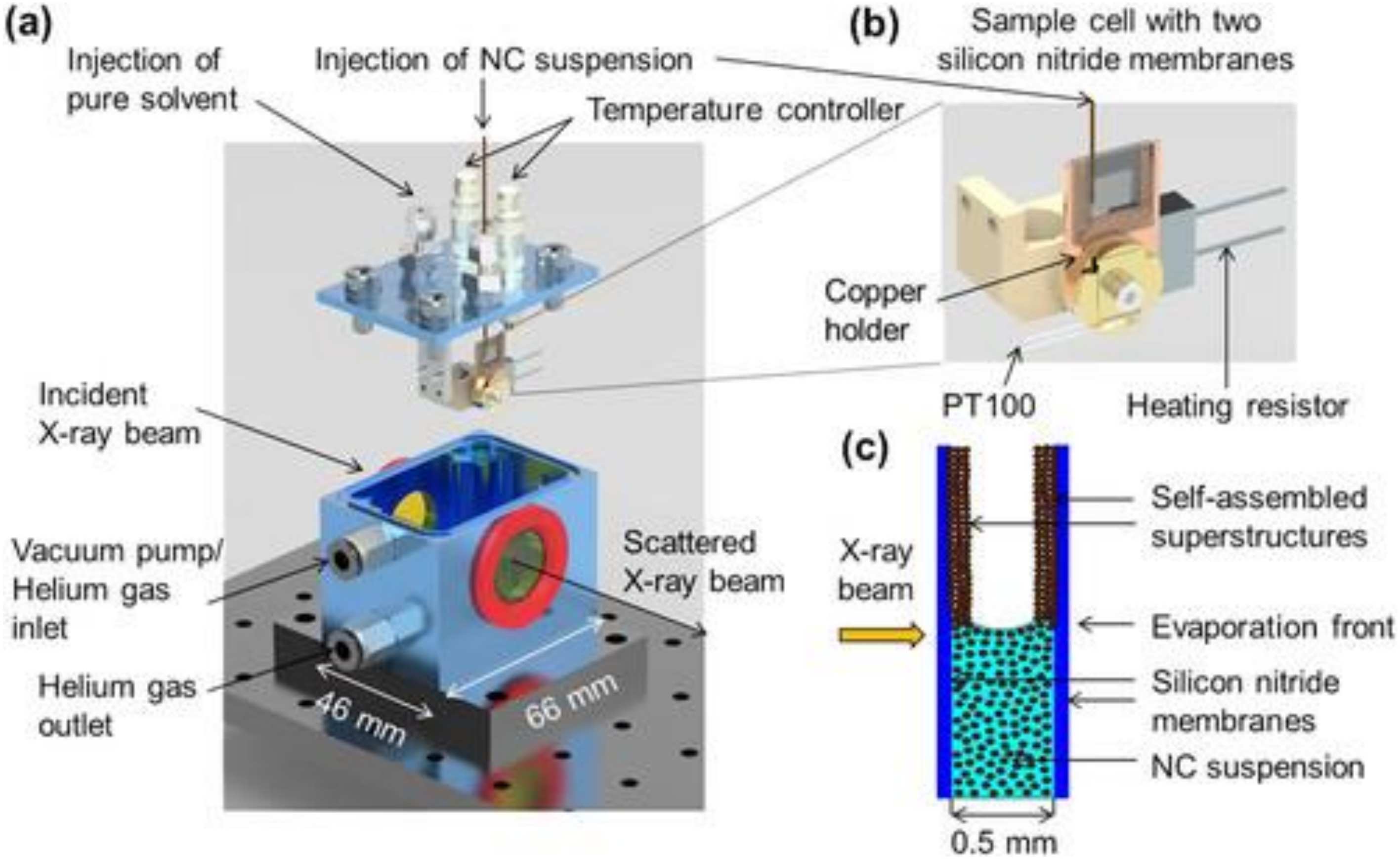




Weidman et al. Nat. Mater. 15, 775 (2016)

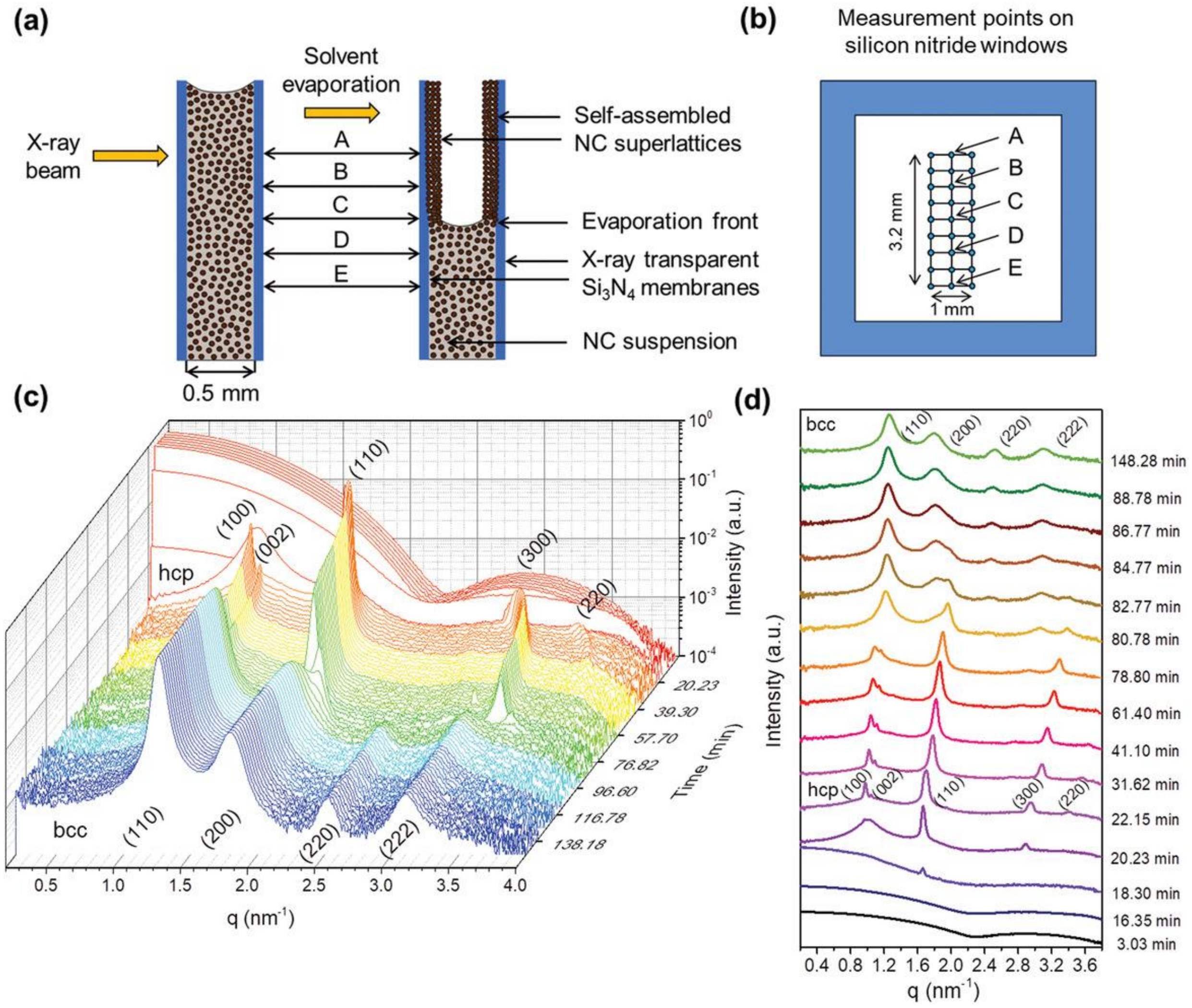
Example 2: In-situ self-assembly

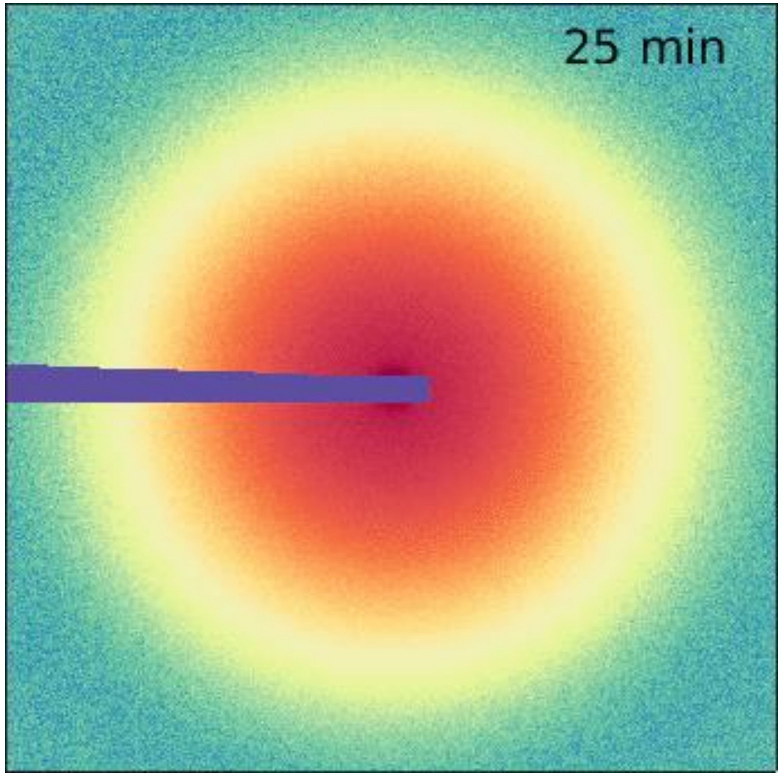
- Obtain information of the structure formation by self-assembly in-situ
- Bulk assembly: Time-resolved SAXS at ID02 (ESRF)
- PbS particles
  - radii between 3 nm to 8 nm
  - Stabilized by oleic acid
  - Dispersed in heptane (hexane, toluene, …)
- About 25 µl sample volume
- Evaporation rate in the range of 0.25 µl/min by helium flusing



Rev. Sci. Instrum. 90, 036103 (2019)

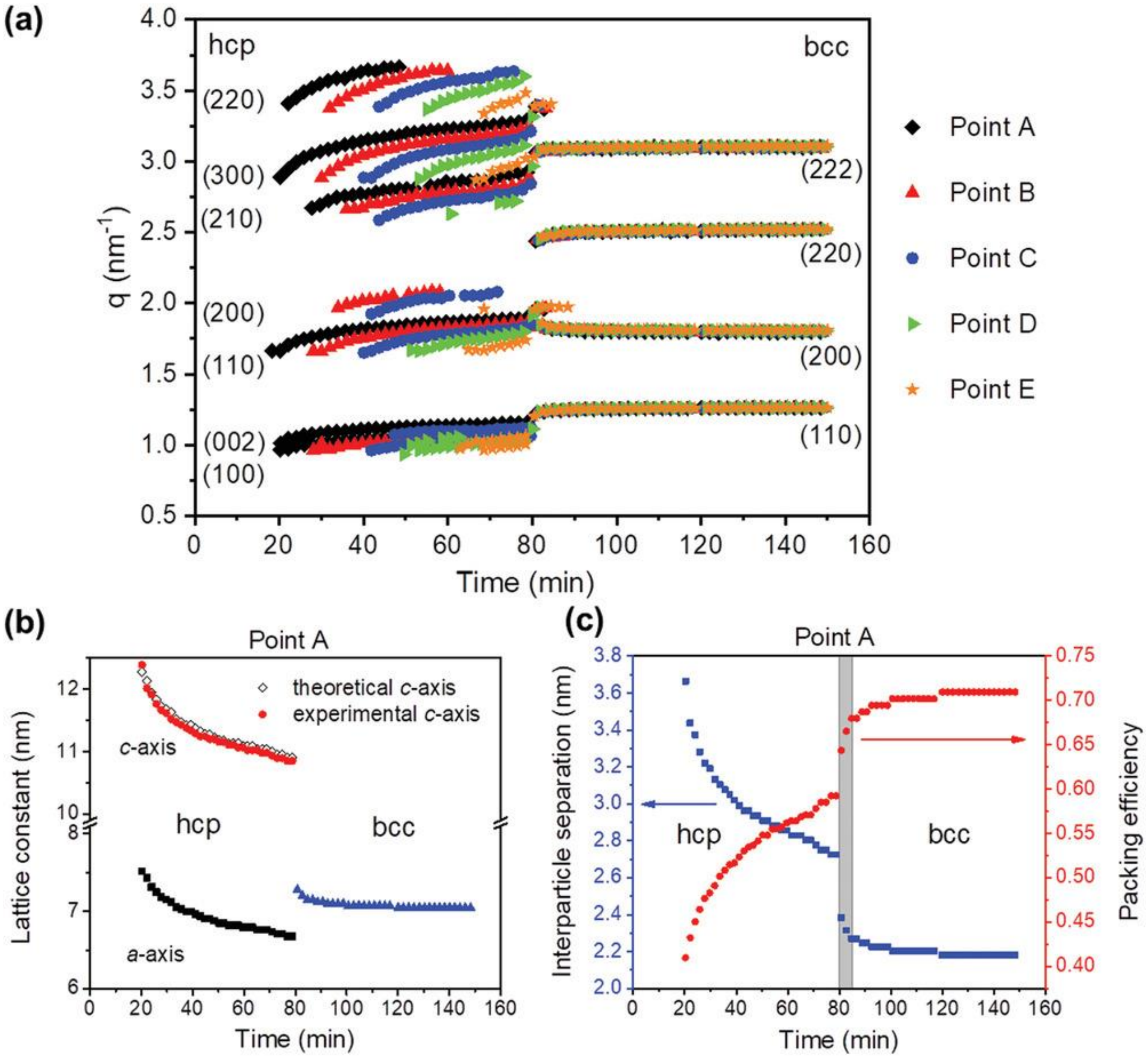
Example 2: In-situ self-assembly





Small 15, 1900438 (2019)

Example 2: In-situ self-assembly



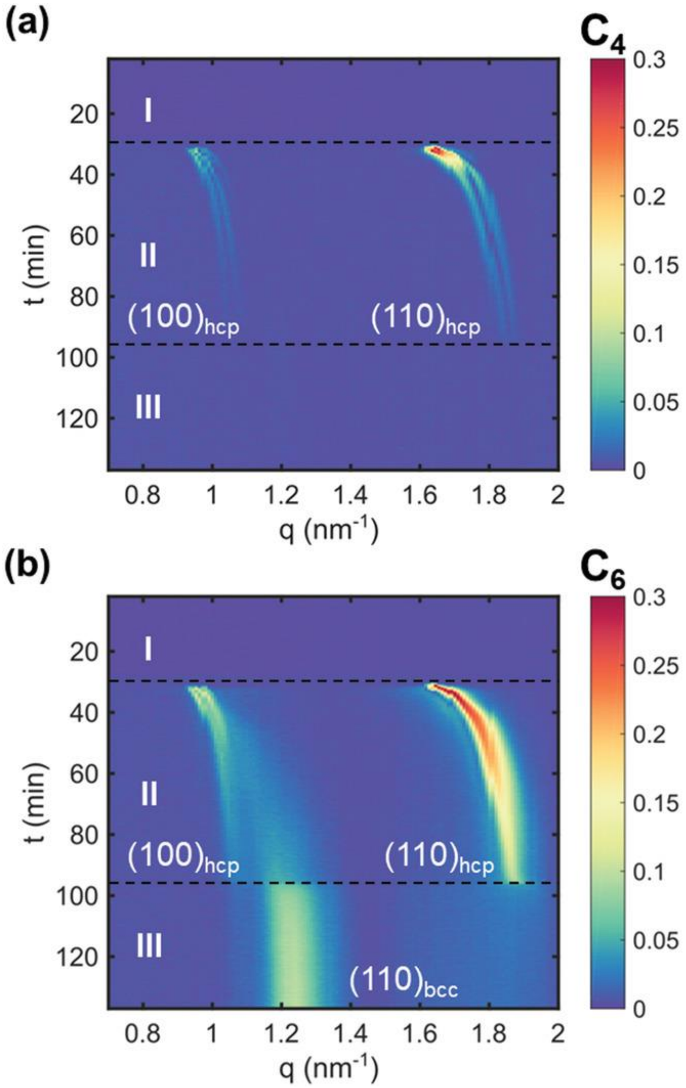
Two-step assembly

- hcp crystal form once the evaporation front passes the exposed spot → swollen state
- Densification
- Transition to bcc when solvent has completely evaporated
- High packing efficency of soft particles

Small 15, 1900438 (2019)

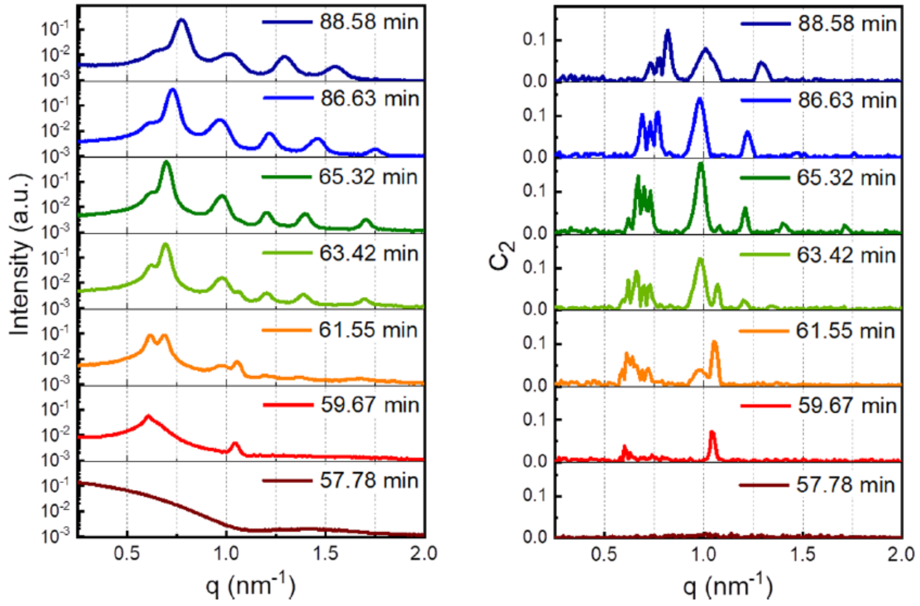
Example 2: In-situ self-assembly

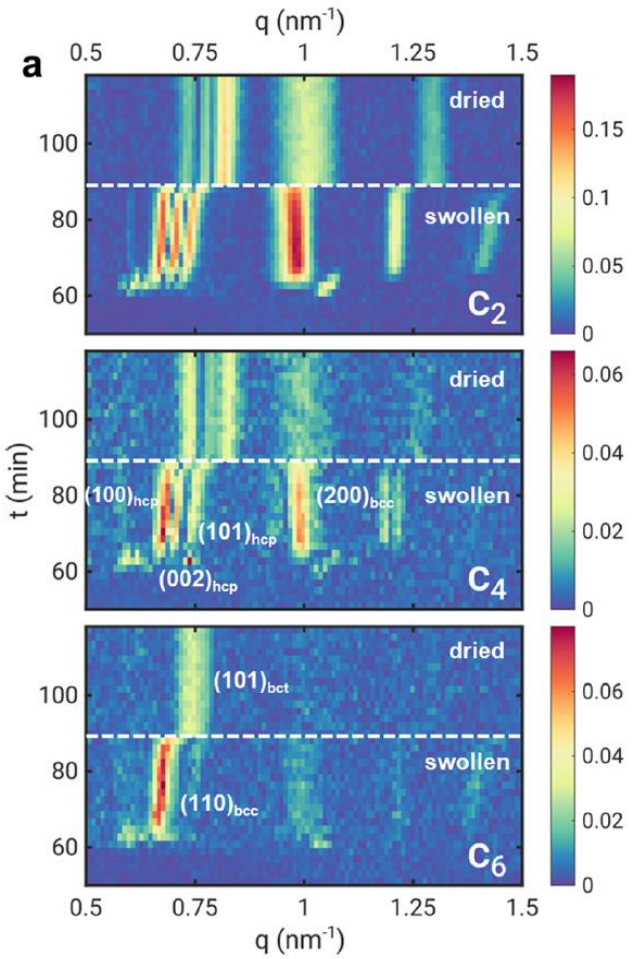
Impact from XCCA



Symmetry of Bragg peaks

- Detection of „hidden peaks“
- Coexistence of different phases



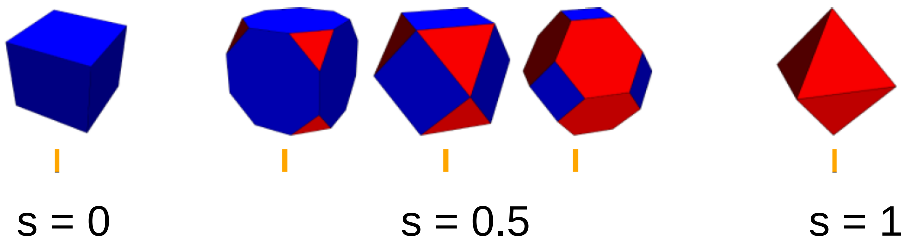


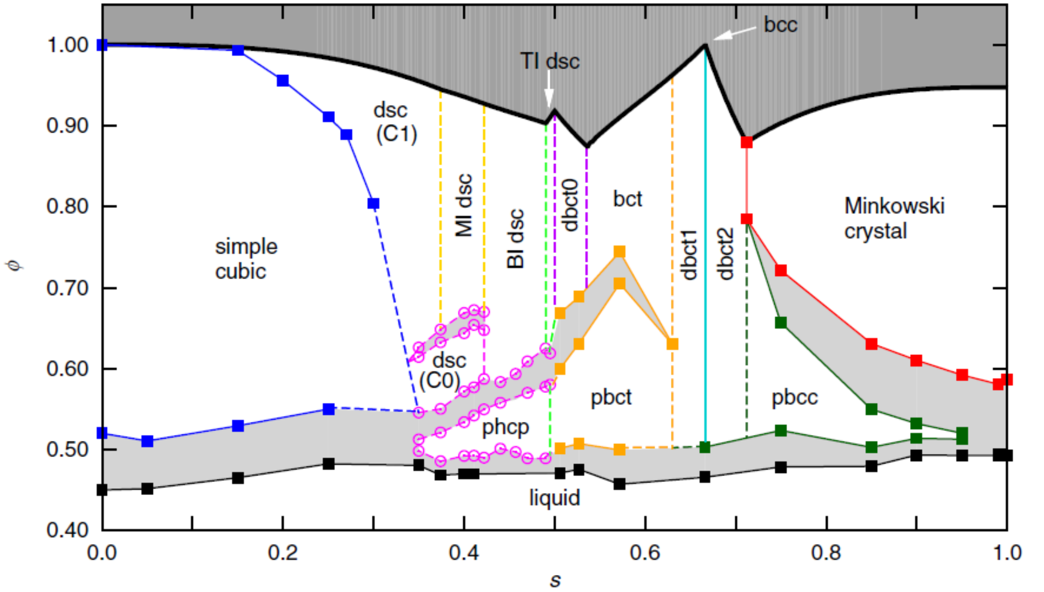
Small 15, 1900438 (2019), J. Phys. Chem. Lett. 10, 6331 (2019)

Example 2: In-situ self-assembly

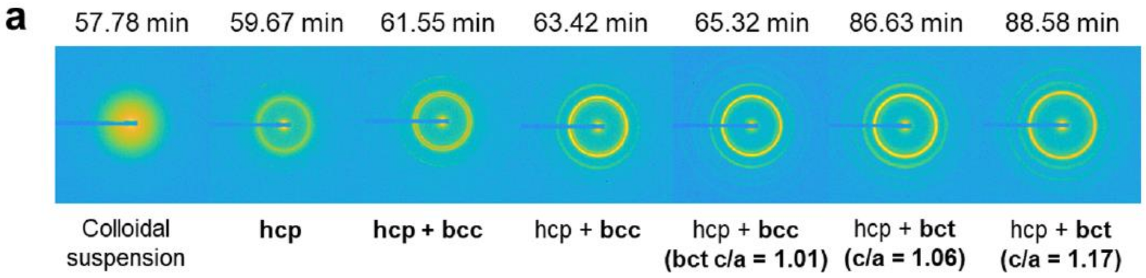
Impact from XCCA

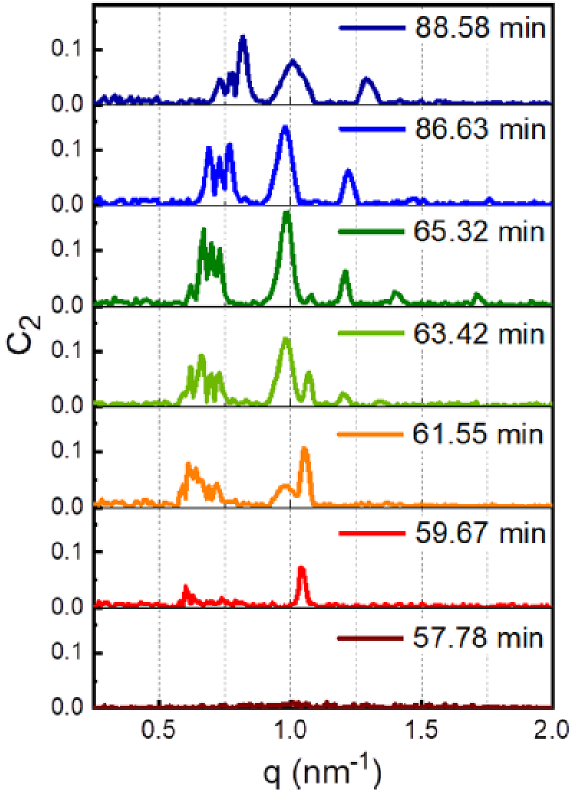
PbS particles as cubocahedron
(truncated cubes with s = 0.5)





Gantapara et al. PRL 111, 015501 (2013)

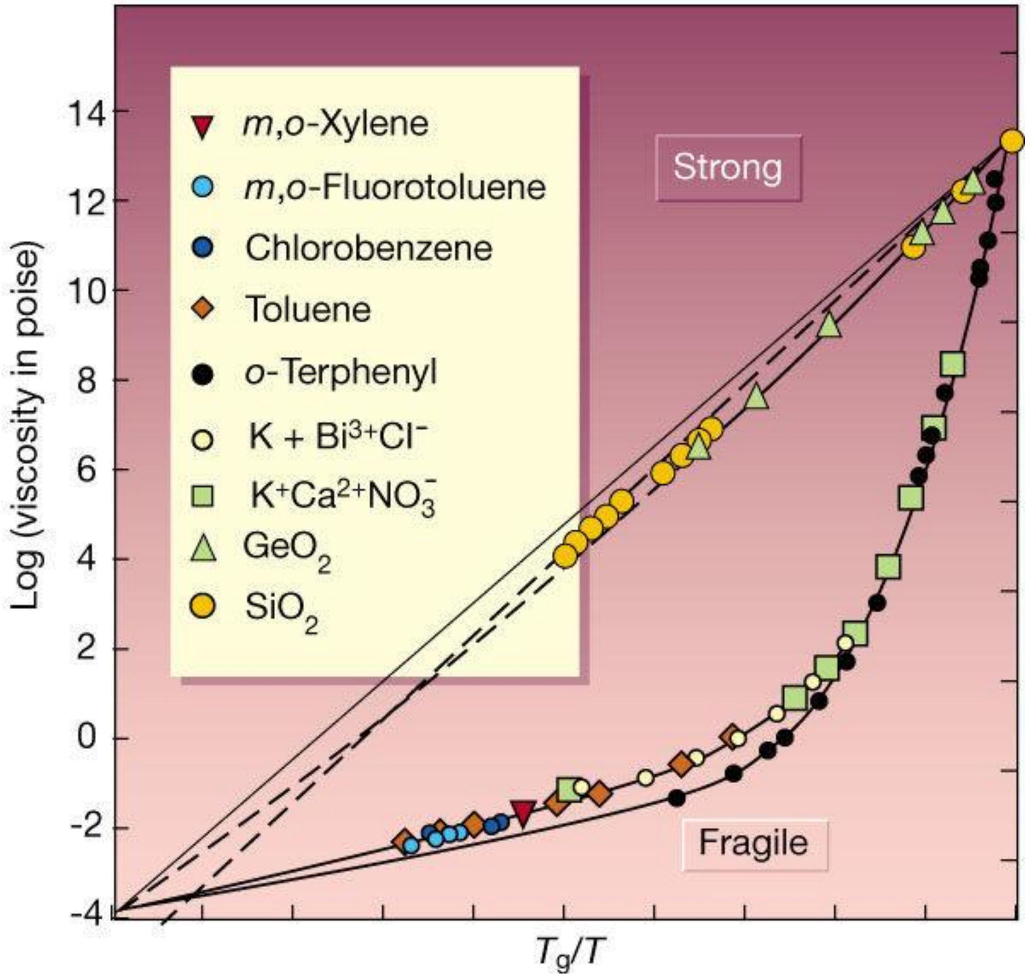




→ Coexistence of plastic bct and hcp found in the final state of the assembly

J. Phys. Chem. Lett. 10, 6331 (2019)

Glass transition

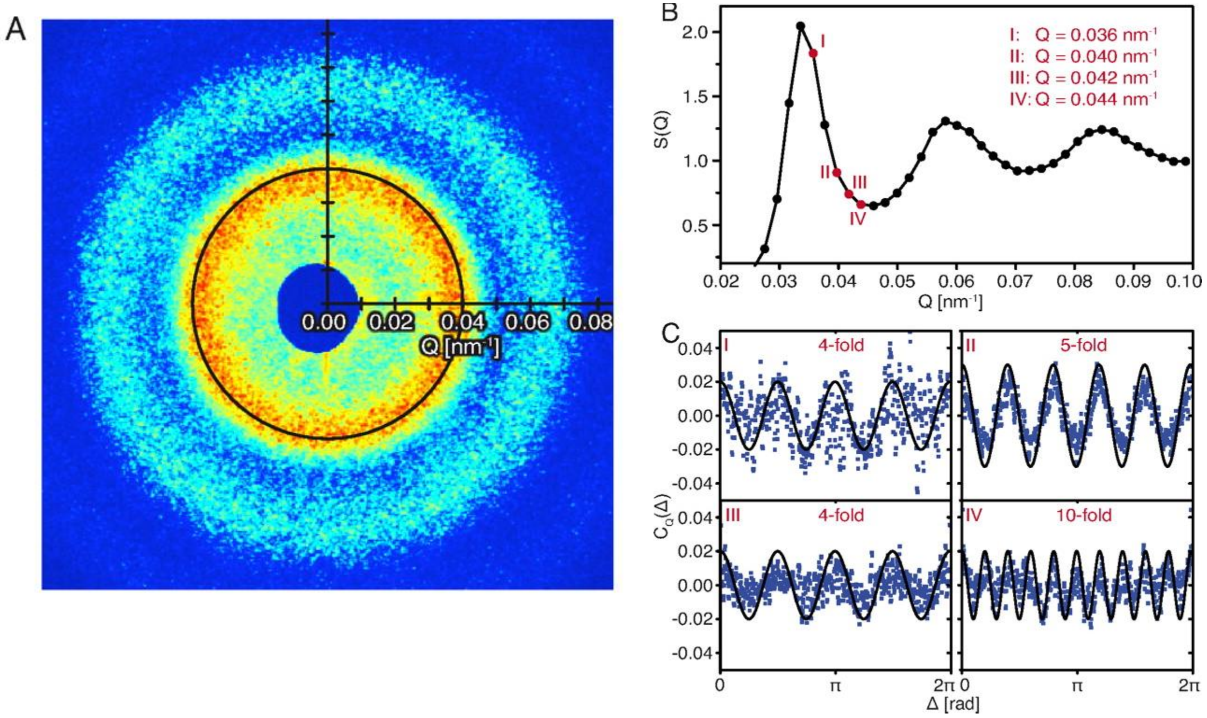


Science 267, 1927 (1995)

Nature 410, 259 (2001)

Approaching the glass transition

- Dynamics slow down by orders of magnitude
- (Average) structure remains unchanged
- Role of local order, e.g. icosahedrons?

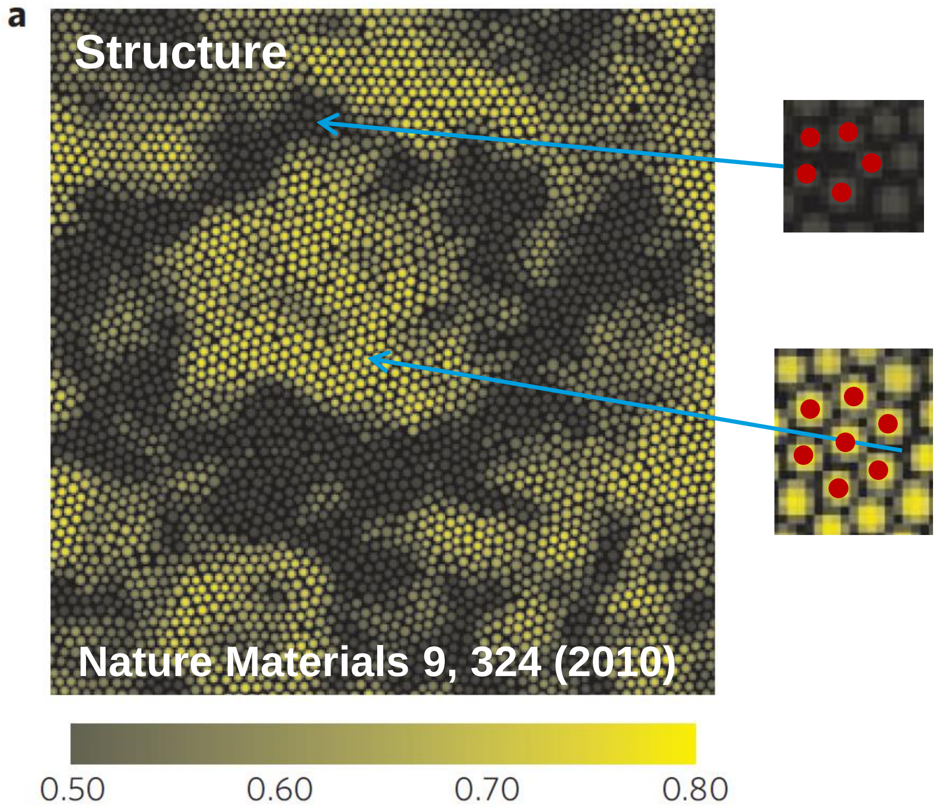


Wochner et al. PNAS 106 11511 (2009)

Glass transition

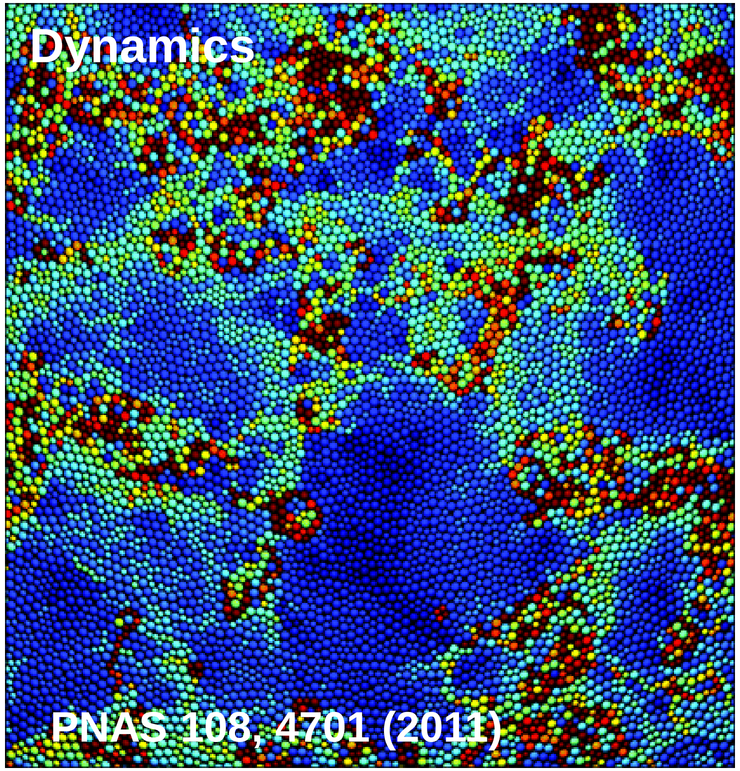
Spatial and dynamics heterogeneities

Spatial and **temporal heterogeneities** in the vicinity of the glass transition and crystallisation of soft matter



Nature Materials 9, 324 (2010)

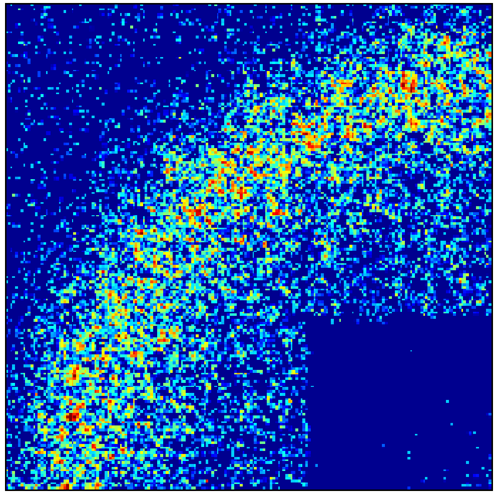
Local bond order parameter



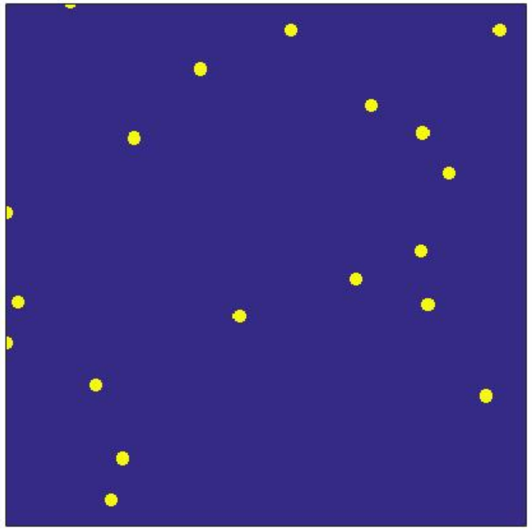
PNAS 108, 4701 (2011)

Access higher-order correlations in time (XPCS) and space (XCCA)

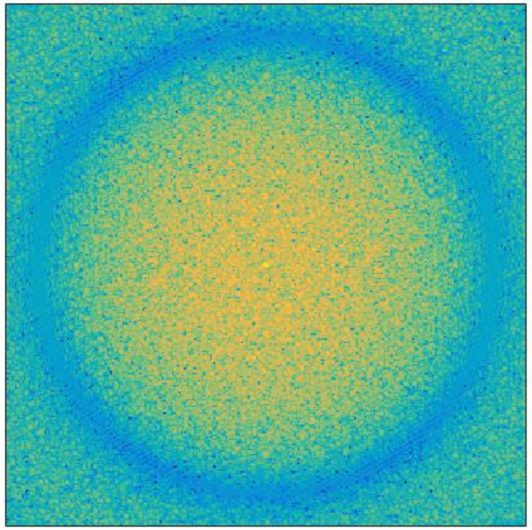
X-ray Photon Correlation Spectroscopy



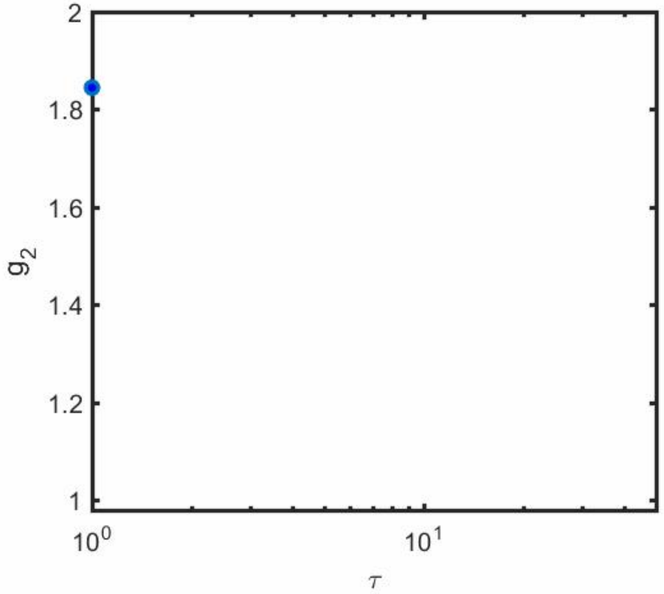
- **Time domain**: changing sample structure → change of speckle pattern
- Access to dynamical properties via $g_2(q,\tau) = \frac{\langle I(q,t)I(q,t+\tau)\rangle_t}{\langle I(q,t)\rangle_t^2} = \beta|f(q,\tau)|^2$
- Intermediate scattering function $f(q,\tau) = S(q,\tau)/S(q,0)$



Diffusing particles



Speckle pattern



g_2 function

Example 3: Structure – dynamics correlations in hard spheres

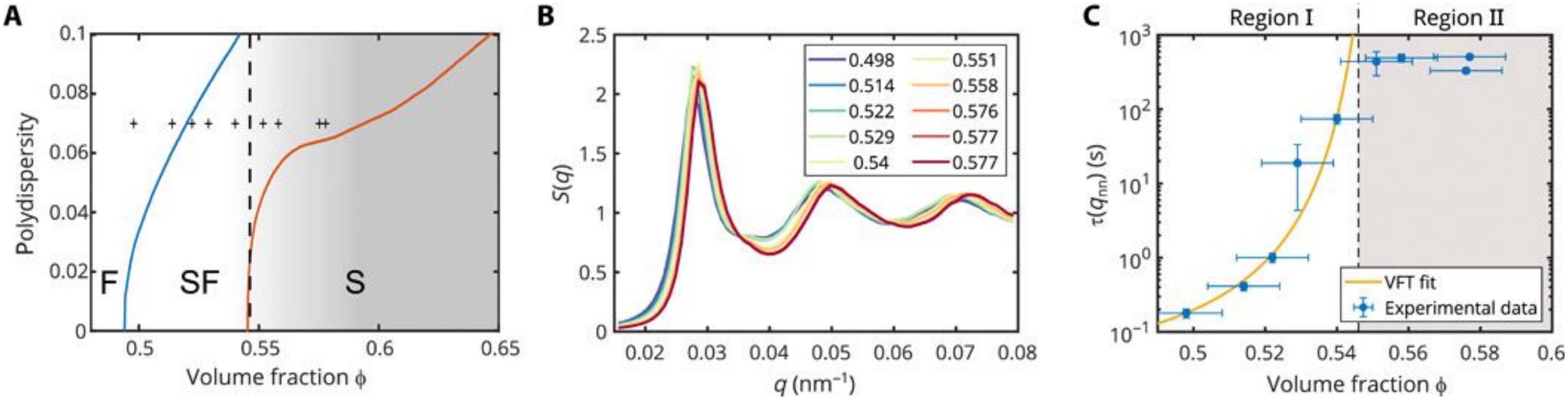
XPCS and XCCA

Hard spheres

- Phase defined by volume fraction
- Fluid, crystal, glass phases (and coexistence regions)
- ID10 experiment on structure and dynamics

Fluid-glass transition

- Structure factor S(q) remains almost unchanged
- Dynamics slows down by orders of magnitude
- Impact from orientational local order → XCCA



FL et al. Sci. Adv. 6, eabc5916 (2020)

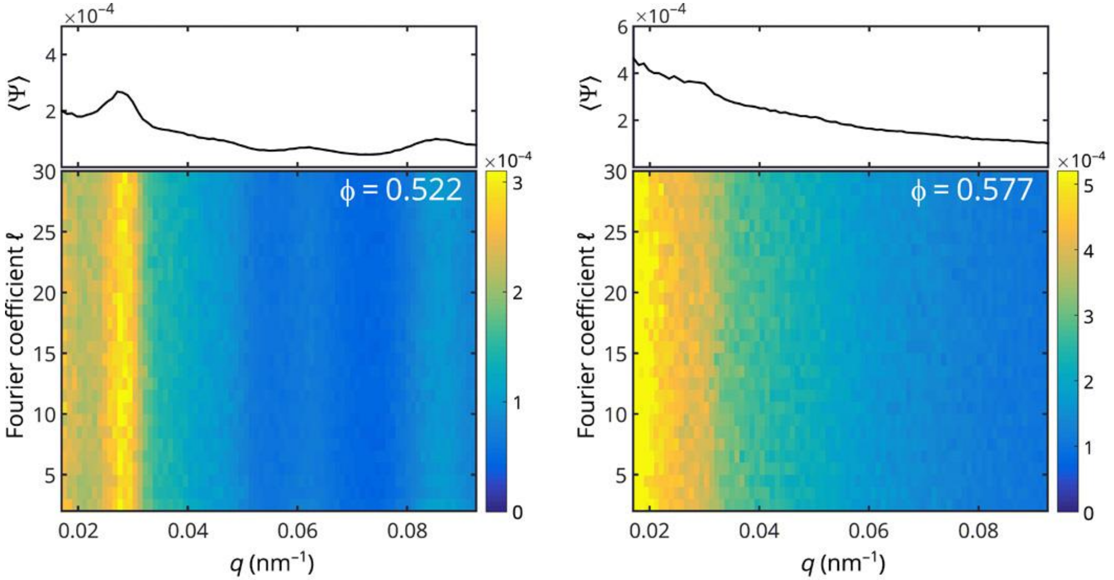
Example 3: Structure – dynamics correlations in hard spheres

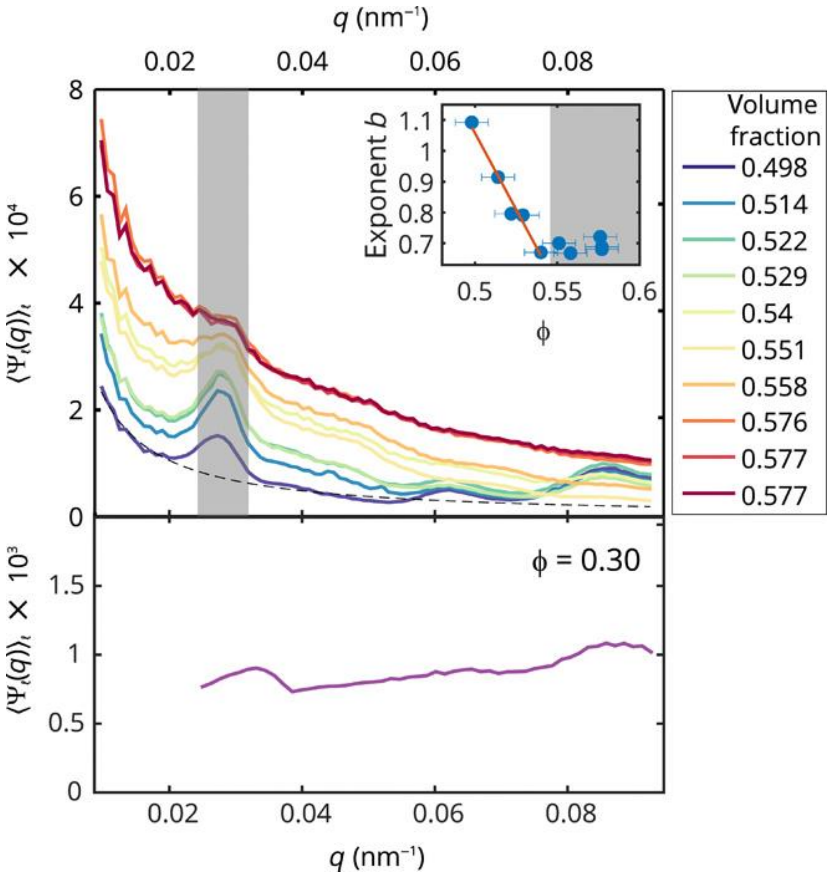
XPCS and XCCA

Map of Fourier coefficients

- Strict q-dependence
- Weak dependence on Fourier coefficient → Use average over all Fourier coefficients

- „Order parameter“ from XCCA analysis
- Combine synchrotron and FEL data





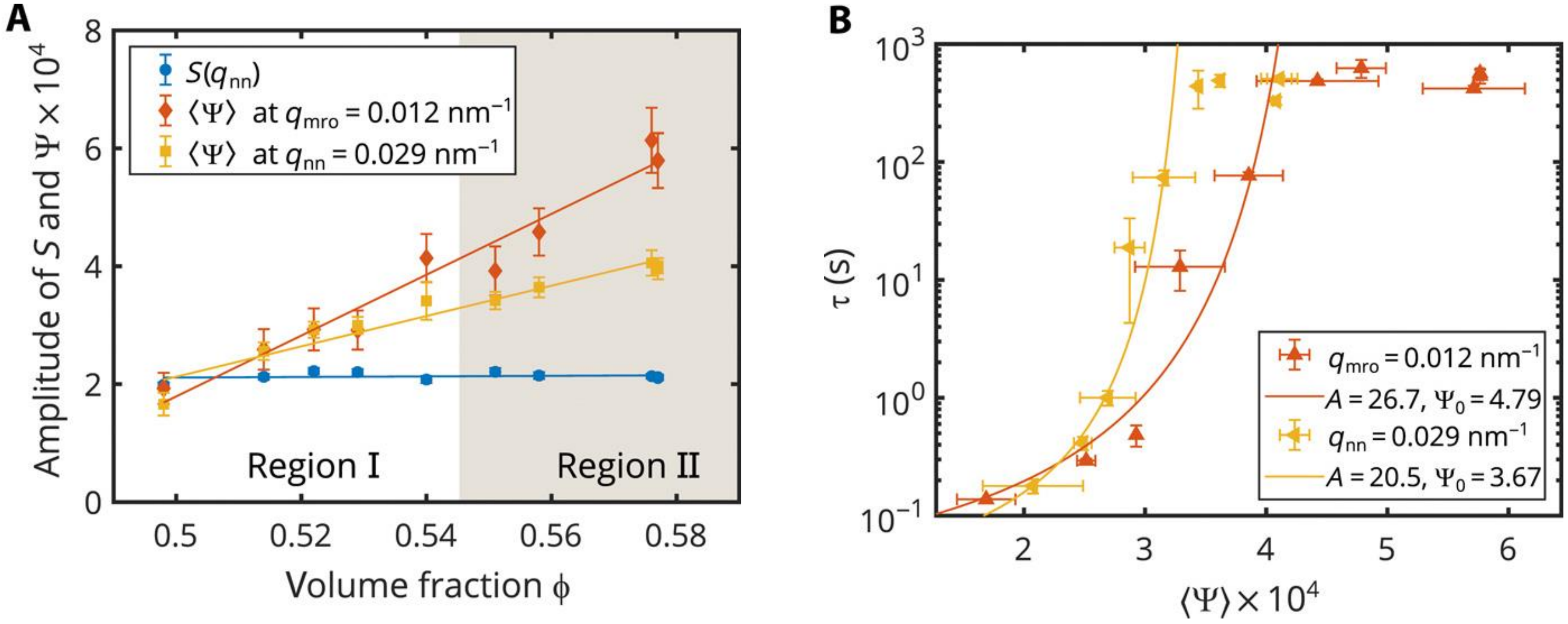
FL et al. Sci. Adv. 6, eabc5916 (2020)

Example 3: Structure – dynamics correlations in hard spheres

XPCS and XCCA

Results

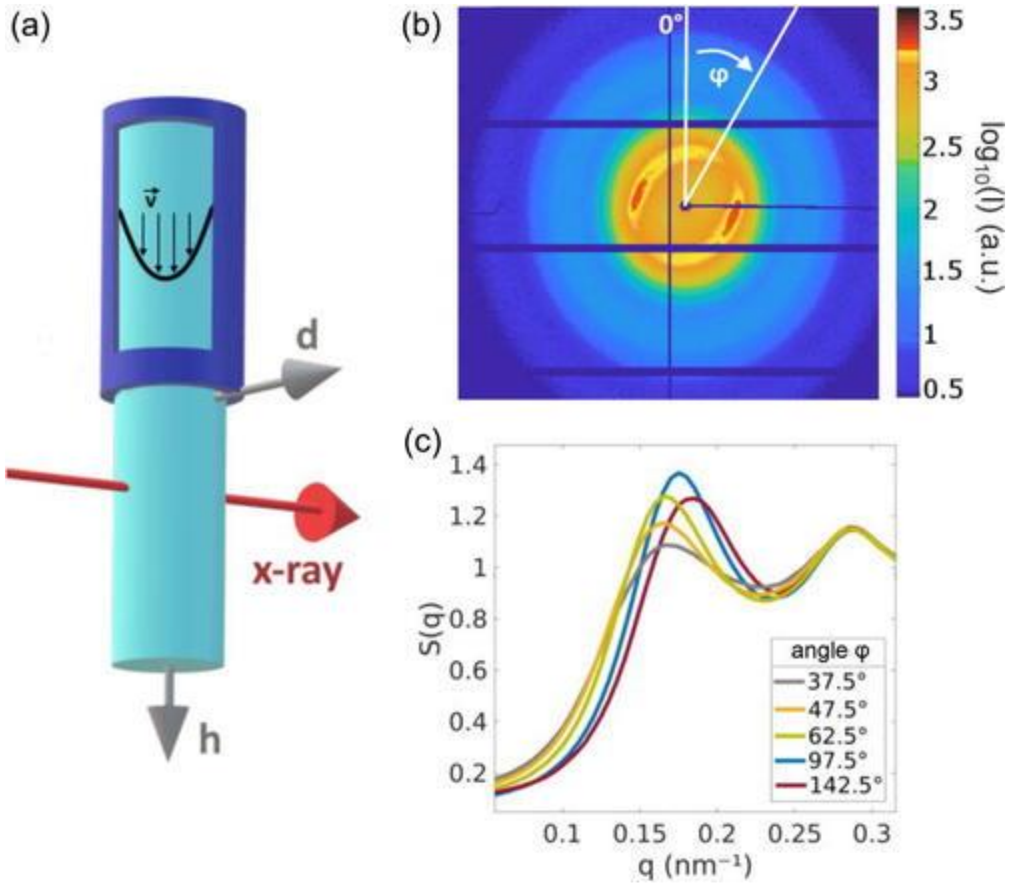
- Broad range of volume fractions: FEL and storage ring studies
- Growth of medium range order
- Ordered precursor at next-neighbour distance
- Correlation of structure and dynamics
- Growth of order inside glass phase

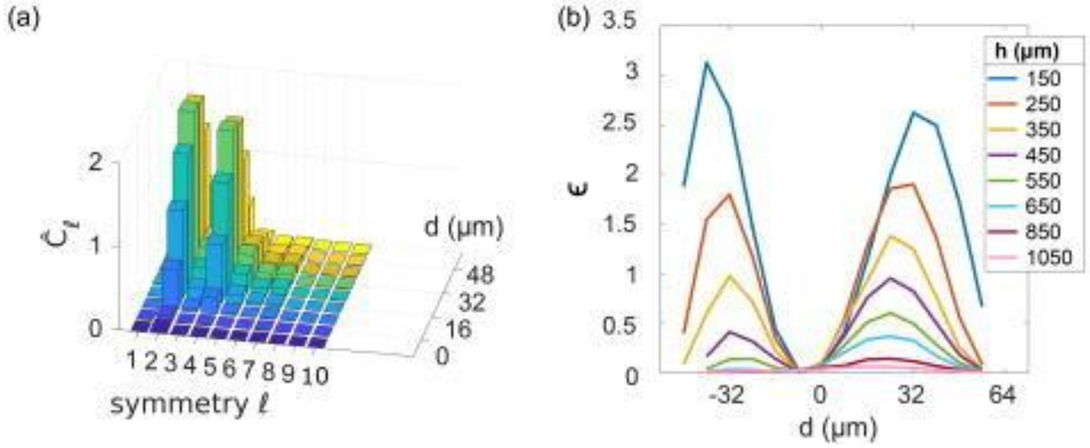


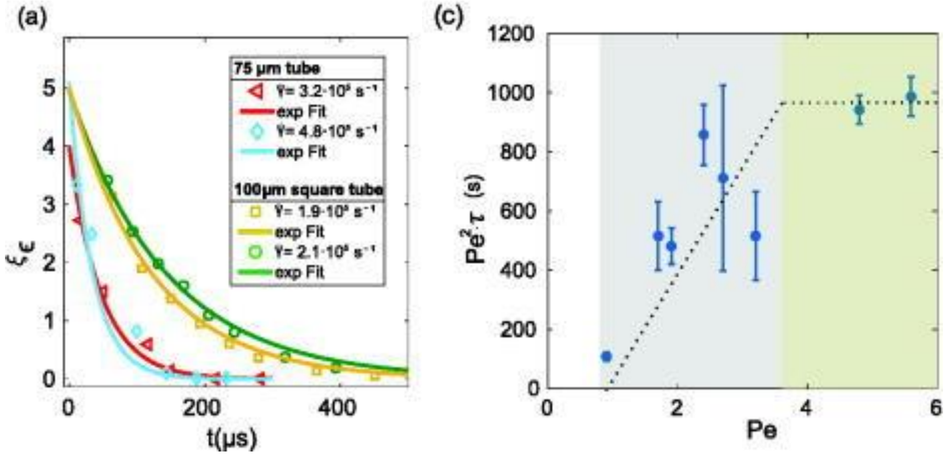
FL et al. Sci. Adv. 6, eabc5916 (2020)

Example 4: Liquid jets

Quantifying non-isotropic structures







V. Markmann et al. Struct. Dyn. 7, 054901 (2020)

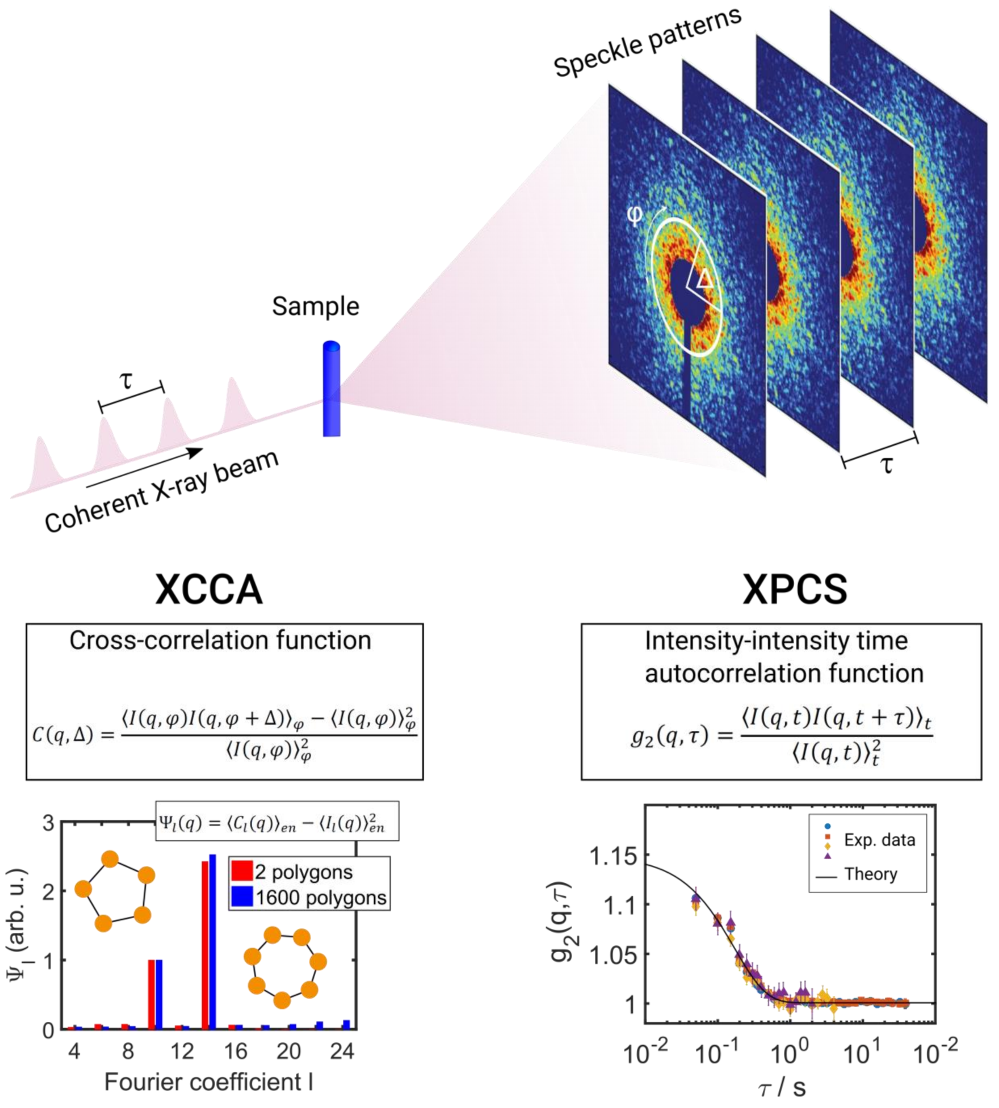
Wrap-up

- Self-assembly of nanoparticles for functional devices
  - Ex-situ characterisation: domain structure, size, orientations
  - In-situ real time assemblies: „hidden“ structures and phase coexistence

- Glass transition in colloidal systems: structure-dynamics correlations

- Characterize non-isotropic structure in liquid jets

- What‘s next → New facilities?



Cross-correlation function

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

Intensity-intensity time autocorrelation function

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

$$\Psi_l(q) = \langle C_l(q)\rangle_{en} - \langle I_l(q)\rangle_{en}^2$$

Example: XPCS – time scales

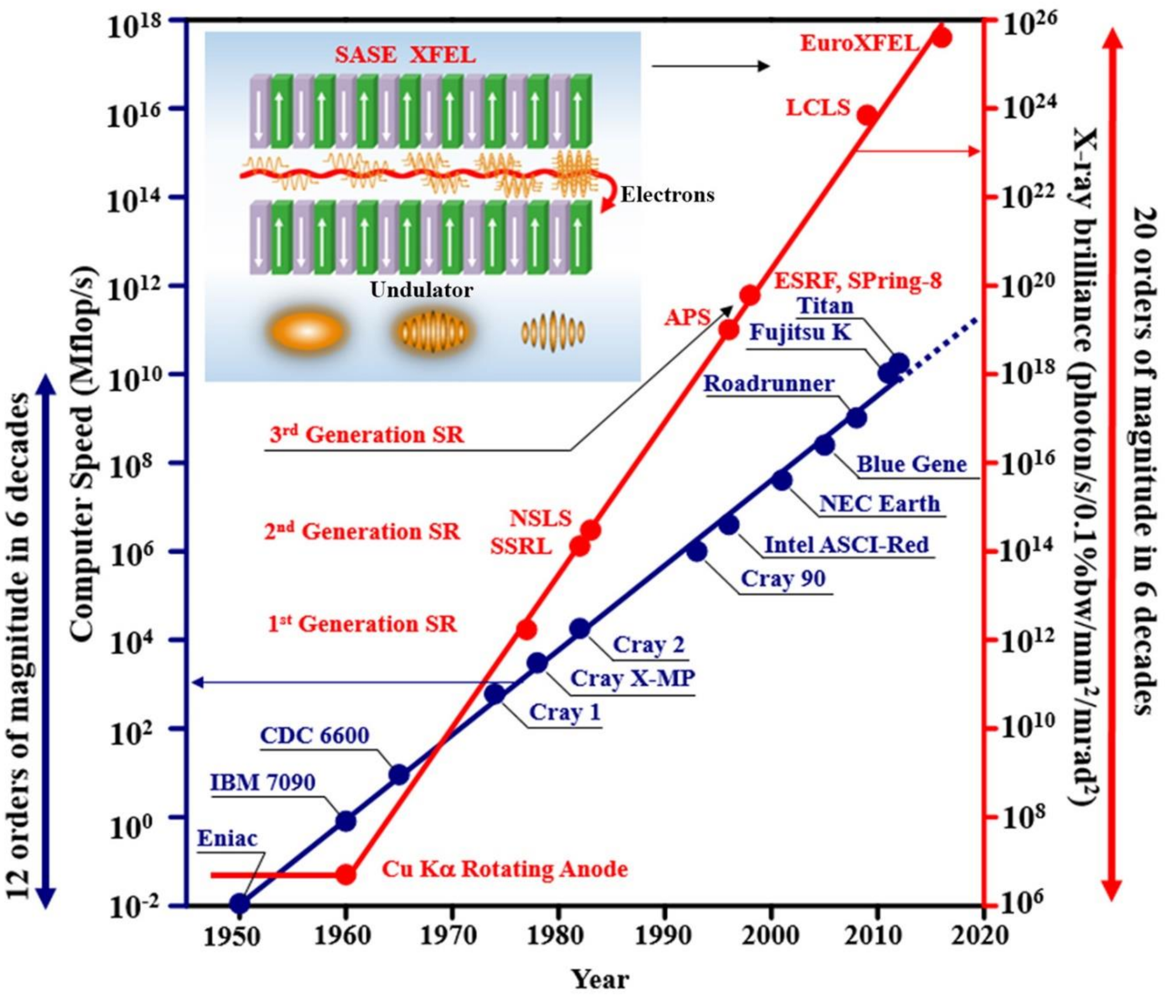
Role of brilliance B

XPCS signal-to-noise ratio

- $R_{SN} \propto I_{coh}\sqrt{\tau_c}$
  - Coherent flux $I_{coh} \propto B$,
  - Shortest correlation time τ_c
- Consequently, $\tau_c \propto 1/I_{coh}^2$
- XPCS performance scales $\sim\boldsymbol{B^2}$
- **Many new possibilities at new facilities!**

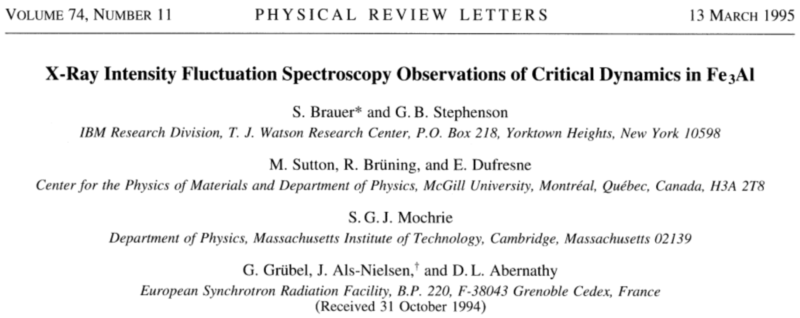
Coherent flux (per s) compared to PETRA III

- PETRA IV: ≥100 x
- European XFEL: 10^5 x



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

XPCS – time scales at storage rings



VOLUME 74, NUMBER 11 PHYSICAL REVIEW LETTERS 13 MARCH 1995

X-Ray Intensity Fluctuation Spectroscopy Observations of Critical Dynamics in Fe_3Al

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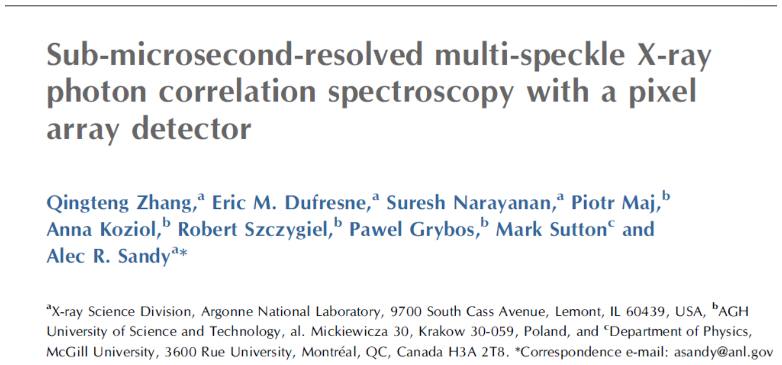
(Received 31 October 1994)



Sub-microsecond-resolved multi-speckle X-ray photon correlation spectroscopy with a pixel array detector

Qingteng Zhang,[a] Eric M. Dufresne,[a] Suresh Narayanan,[a] Piotr Maj,[b] Anna Koziol,[b] Robert Szczygiel,[b] Pawel Grybos,[b] Mark Sutton[c] and Alec R. Sandy[a]*

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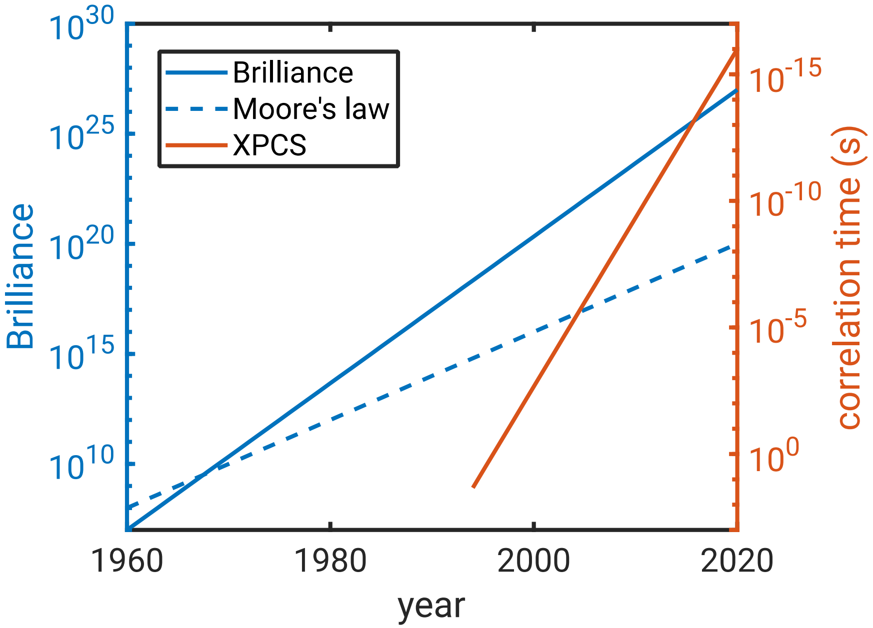
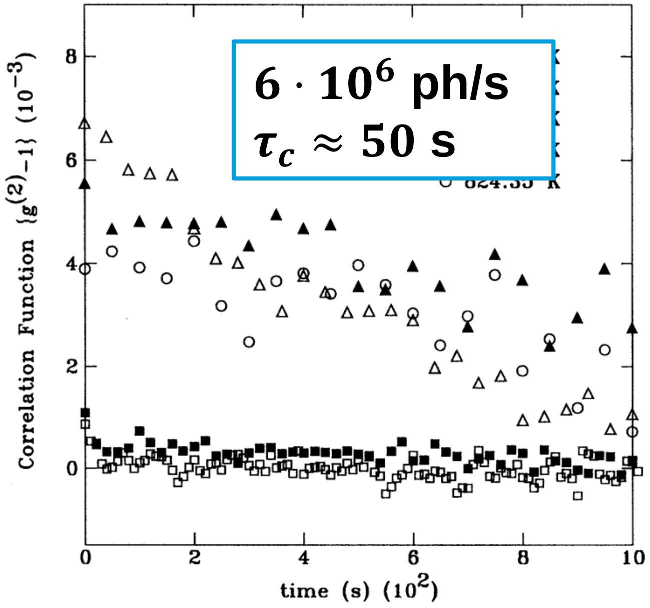
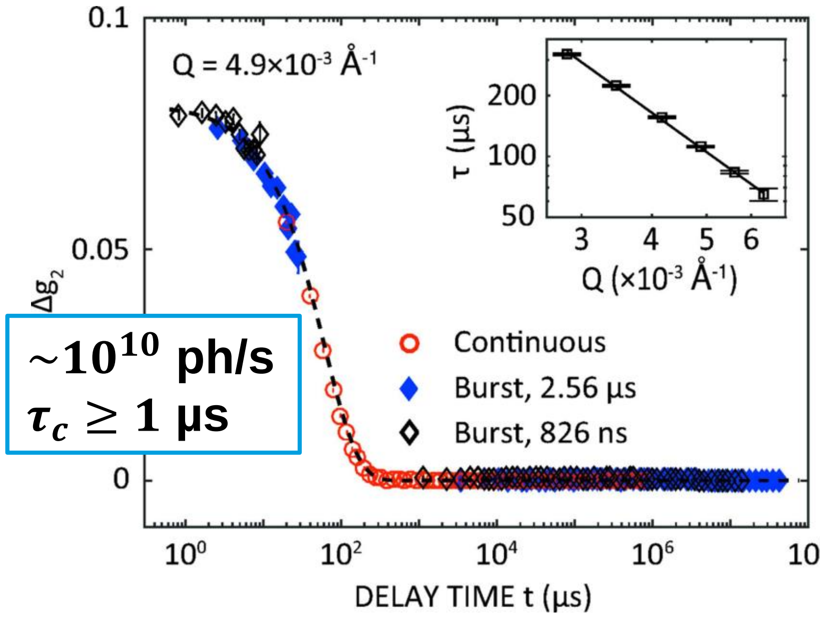




$6 \cdot 10^6$ ph/s
$\tau_c \approx 50$ s

PRL 74, 2010 (1995)



$\sim 10^{10}$ ph/s
$\tau_c \geq 1$ μs

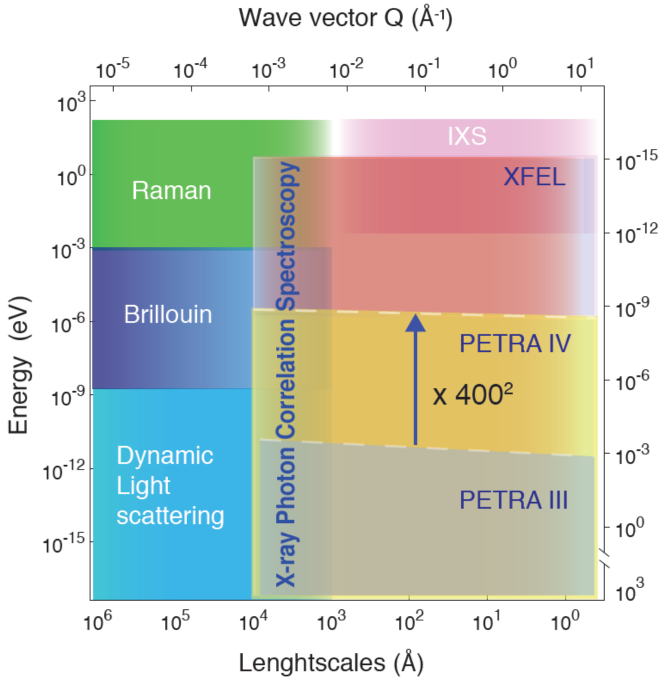
JSR 25, 1408 (2018)

- XPCS: SNR $\propto I_0\sqrt{\tau_c}$
- DLSR: 10^4 gain in $\tau_c \Rightarrow$ $\tau_c \approx$ ns
- European XFEL (avg. Brilliance): 10^{10} gain in $\tau_c \Rightarrow \tau_c \approx$ fs
- Limitations by pulse length and repetition rate

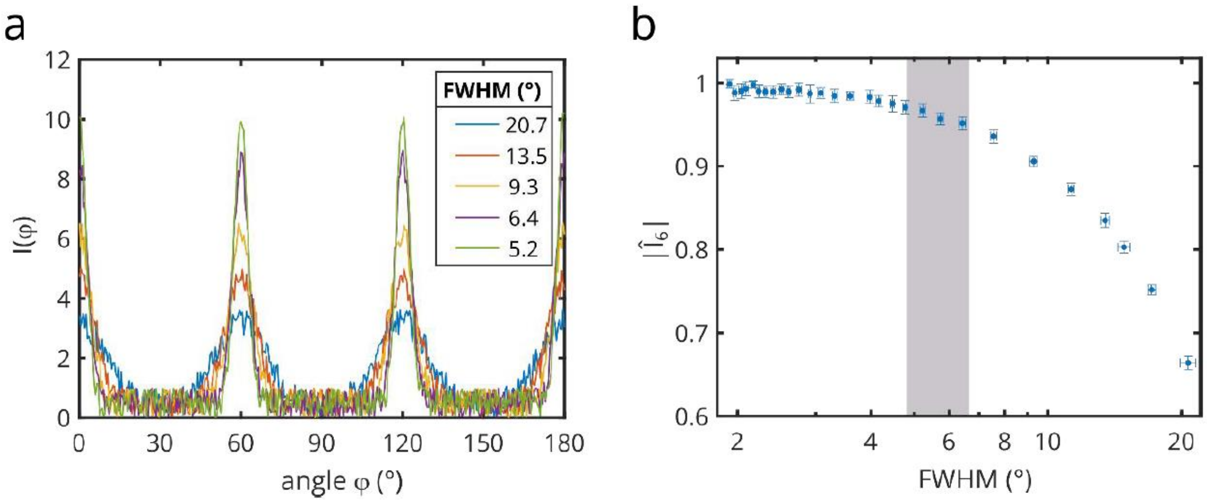
XCCA – outlook

Possibilities at new light sources: towards molecular time and length scales

- Beyond „single shot“ experiments for static structures: FXS / XCCA probed in real-time
- Time limitations → SNR
- Intensity needs → correlation of events within the same pattern → radiation damage
- Detector limitations for studying molecular length scales → (partial) coherent illumination
- Quantitative results: Influences from experimental setup and geometry (e.g. speckle size, Bragg peak widths …) → amplitudes and appearence of Fourier coefficients



XPCS map for new X-ray sources



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