Methoden moderner Röntgenphysik: Streuung und Abbildung

Lecture 16	Vorlesung zum Haupt- oder Masterstudiengang Physik, SoSe 2021
	G. Grübel, O. Seeck, F. Lehmkühler, A. Philippi-Kobs, V. Markmann, M. Martins
Location	online
Date	Tuesday 12:30 - 14:00 (starting 6.4.)
	Thursday 8:30 - 10:00 (until 8.7.)

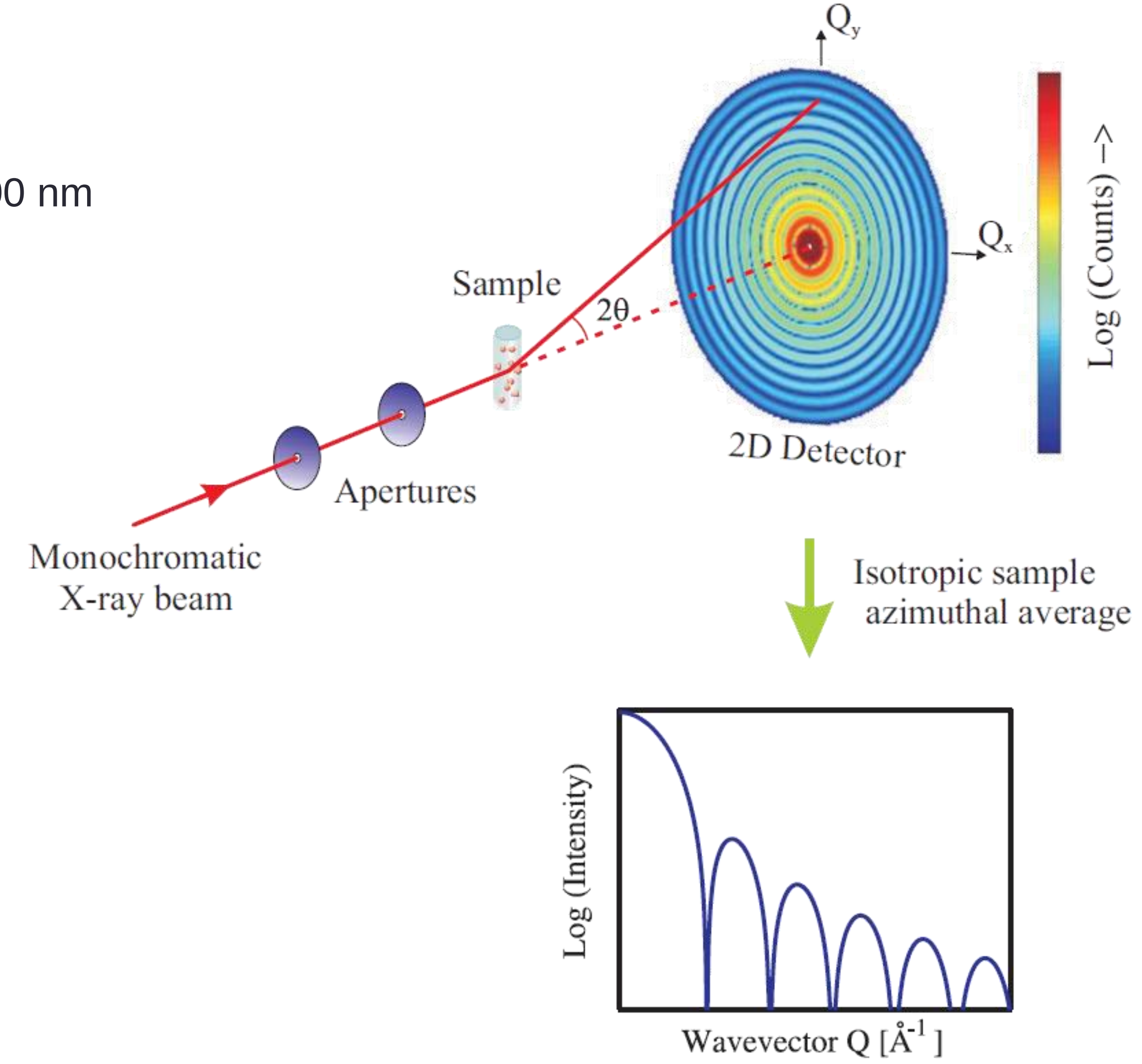
Soft Matter – Timeline

- Do 27.05.2021 Soft Matter studies I: Methods & experiments
  Definitions, complex liquids, colloids, storage ring and FEL experiments, setups, liquid jets, **…**
- Di 01.06.2021 Soft Matter studies II: Structure
  SAXS & WAXS applications, X-ray cross correlations, **…**
- Do 03.06.2021 Soft Matter studies III: Dynamics
  XPCS applications, diffusion, dynamical heterogeneities, …
- Di 08.06.2021 XPCS & XCCA simulations and modelling
- Do 10.06.2021 Case study I: Glass transition
  Supercooled liquids, glasses vs. crystals, glass transition concepts, structure-dynamics relations, …
- Di 15.05.2021 Case study II: Water
  Phase diagram, anomalies, crystalline and glassy forms, FEL studies, …
- Do 17.06.2021 Outlook: Opportunities at new facilities

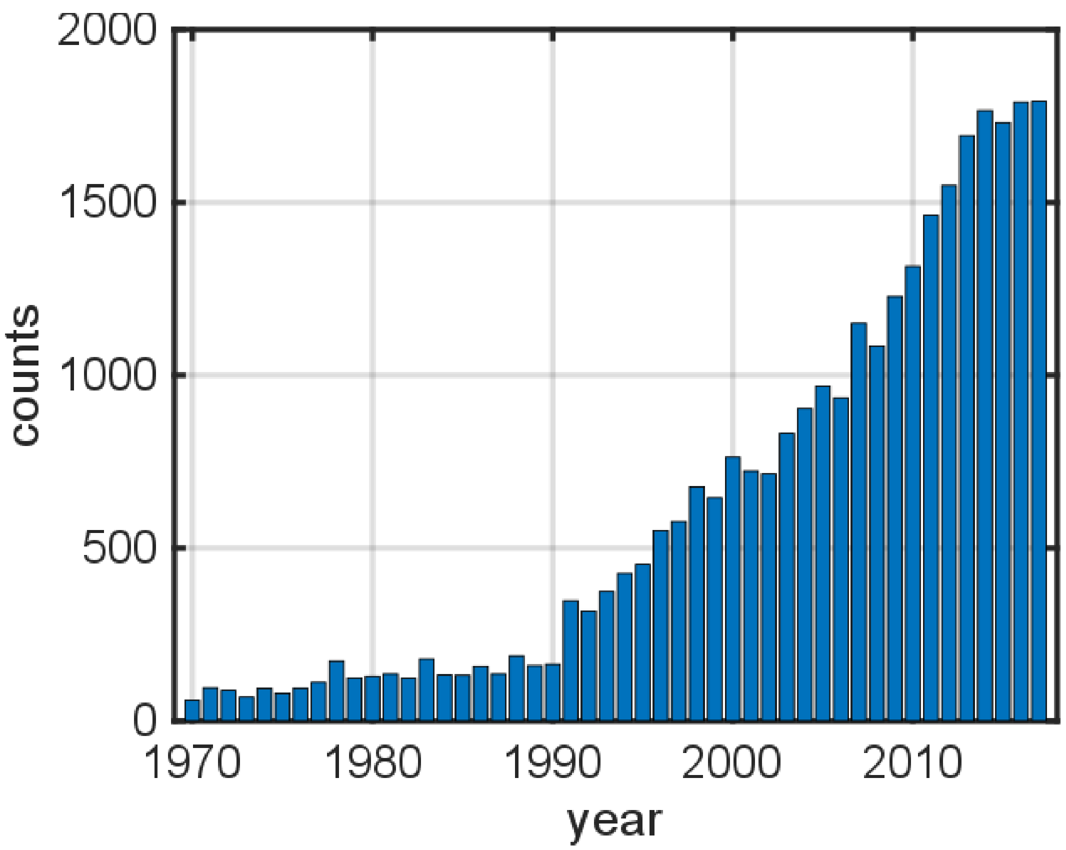
Small-angle X-ray scattering

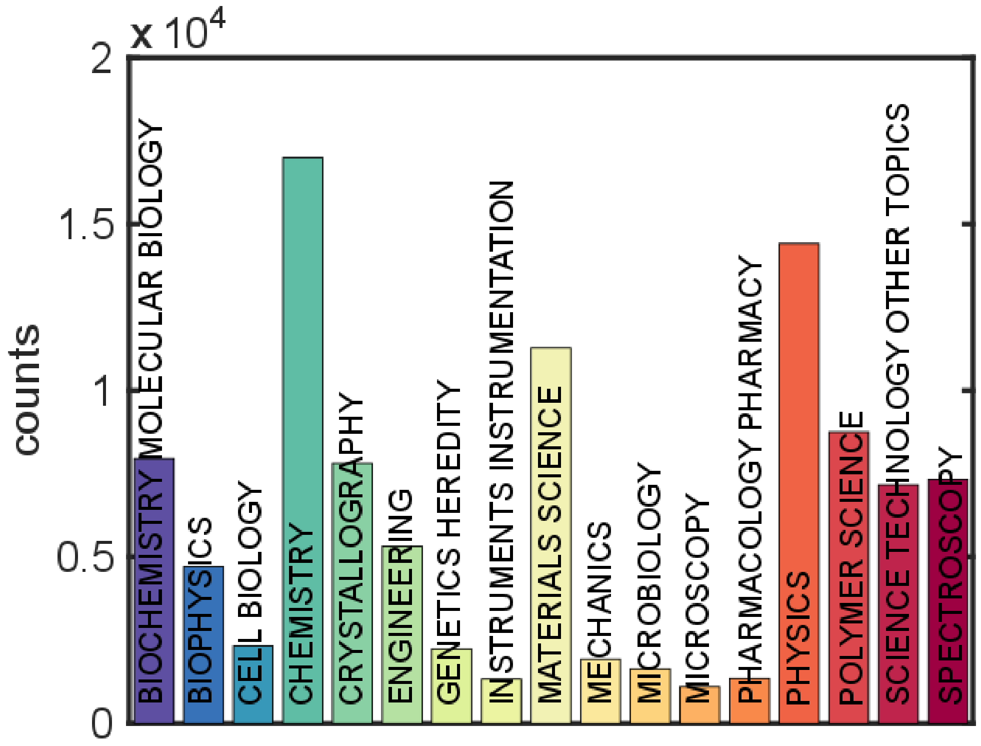
Typical dimensions of soft matter: 1 ~ 1000 nm
→ Small angles using hard X-rays

Soft matter: "particles" and "solvent"



Small-angle X-ray scattering





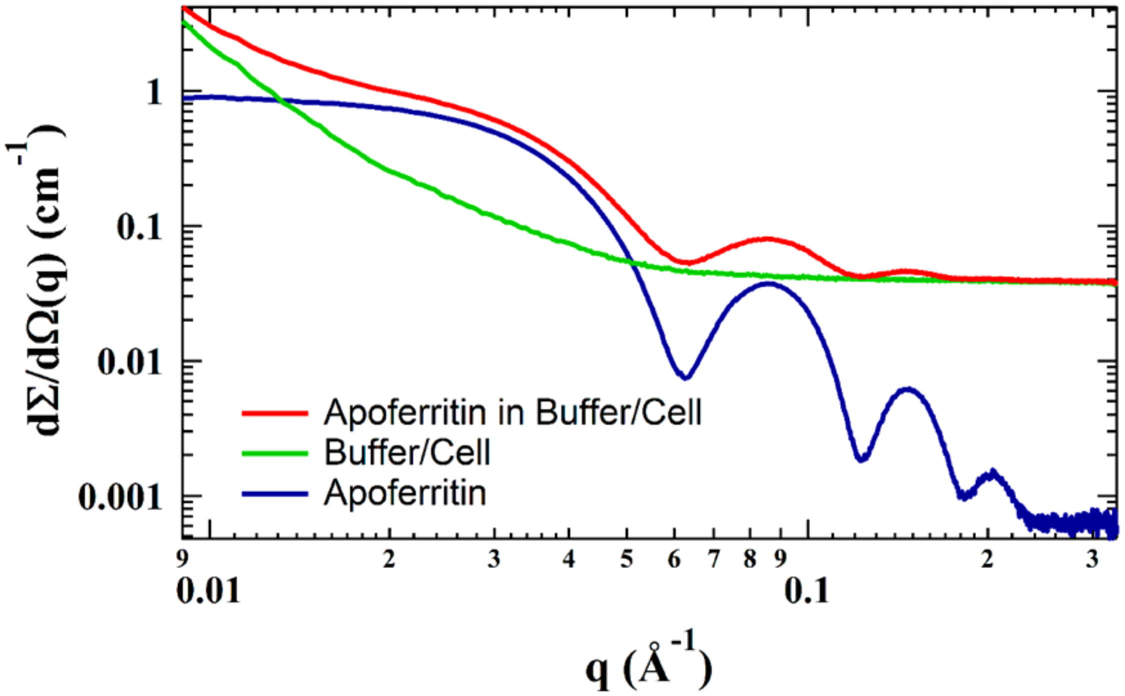
Web of knowledge topic search: "Small angle X-ray scattering"

SAXS – Analysis methods: Formfactor

Lecture 6: $\mathrm{I_{SAXS}(q) = \left(\rho_{sI,p} - \rho_{sI,0}\right)^2 \left|\int_{V_p} e^{iqr} dV_p\right|^2}$ for particle (p) in solvent (0)

Diluted case: Formfactors

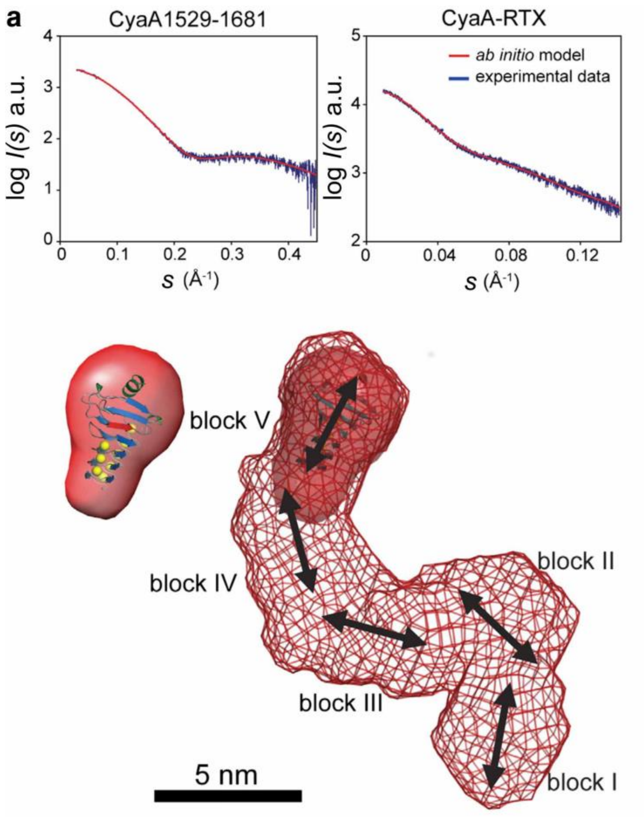
- Spheres: $F(q) = 3\,\frac{\sin(qR) - qR\cos(qR)}{(qR)^3}$
- In general difficult to calculate → numerical approaches
- Soft Matter: Dispersity & (solvent) background
- $I_c = \frac{1}{I_0} \frac{\frac{I_{raw}}{t_e} - \frac{I_{dark}}{t_{dark}}}{I_{qe}} \cdot \frac{D_p^2}{p^2} \cdot \frac{D_p}{D_0} \Rightarrow I_{particle} = \frac{I_{c,s}}{d_s T_s} - \frac{I_{c,b}}{d_b T_b}$



Chem. Rev. 116, 11128 (2016)

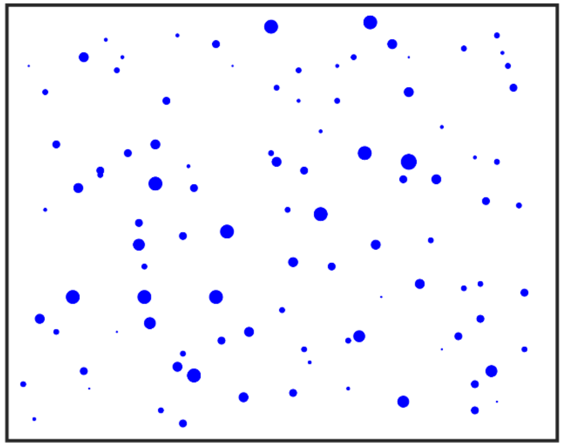
SAXS – Analysis methods: Formfactor

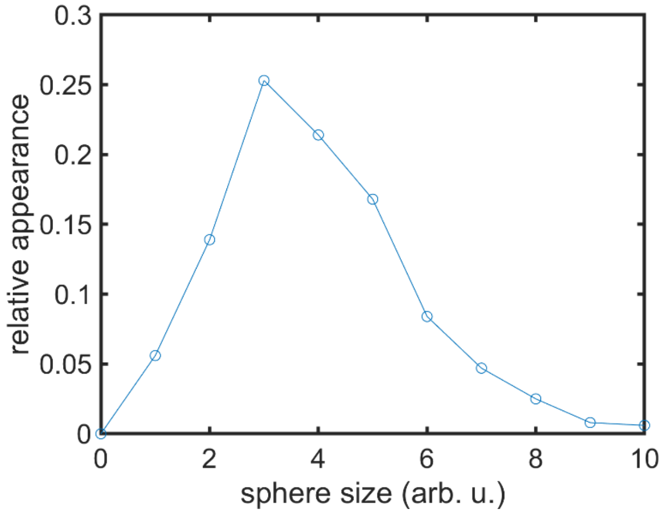
Ab initio methods (use "dummy" bead models) → BioSAXS

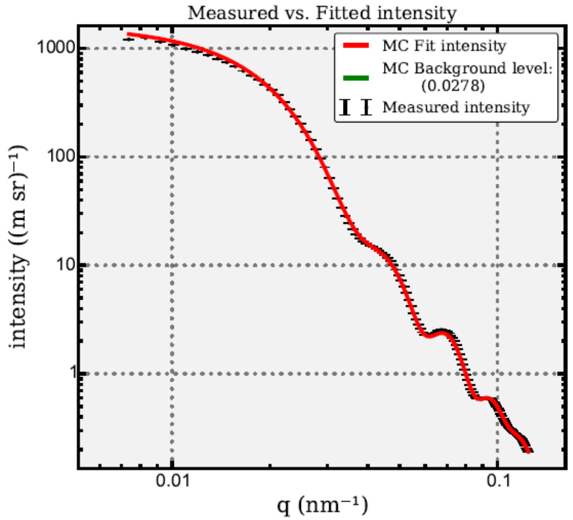


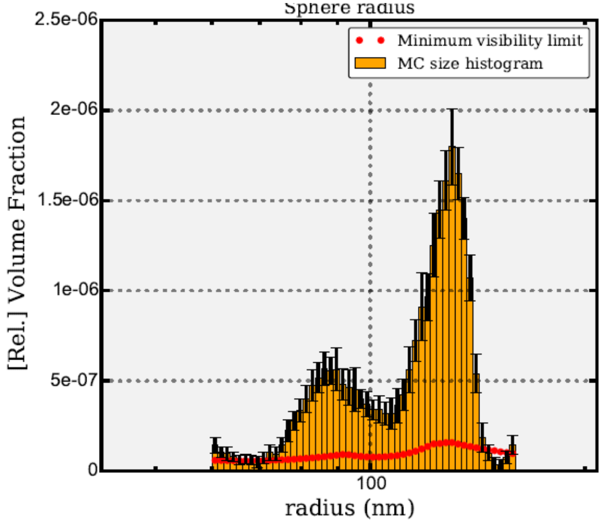
doi:10.1042/ETLS20170138

Monte-Carlo methods (calculate scattering from differently sized spheres)





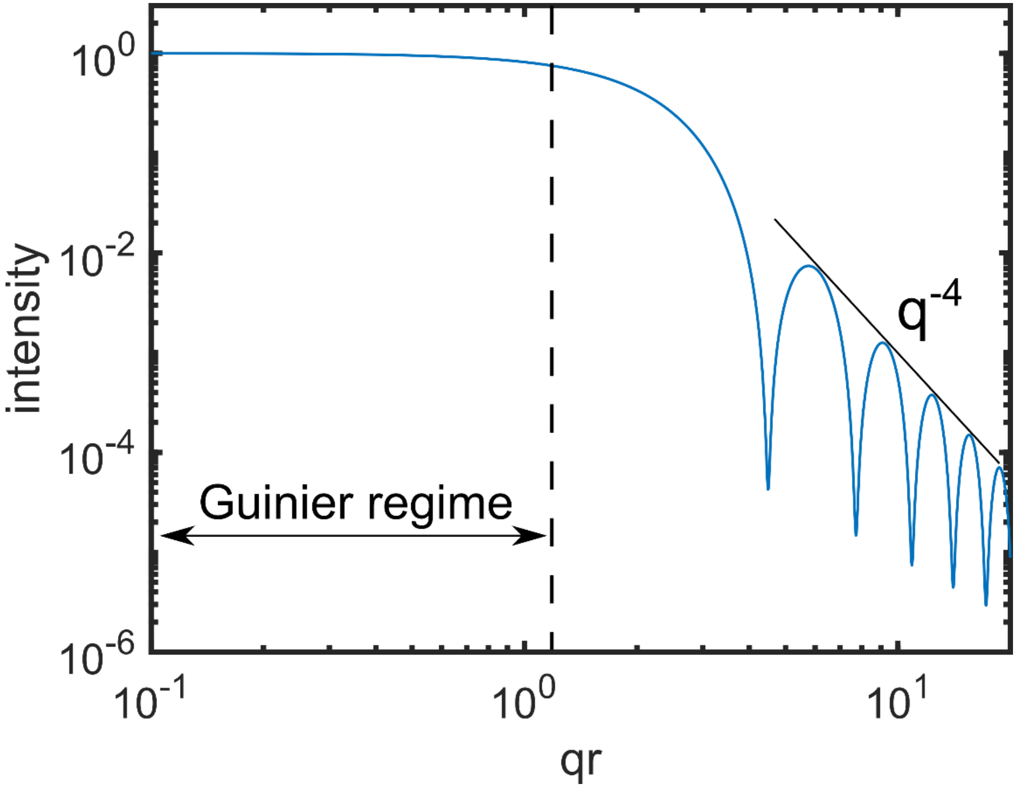




SAXS – Analysis methods: Formfactor

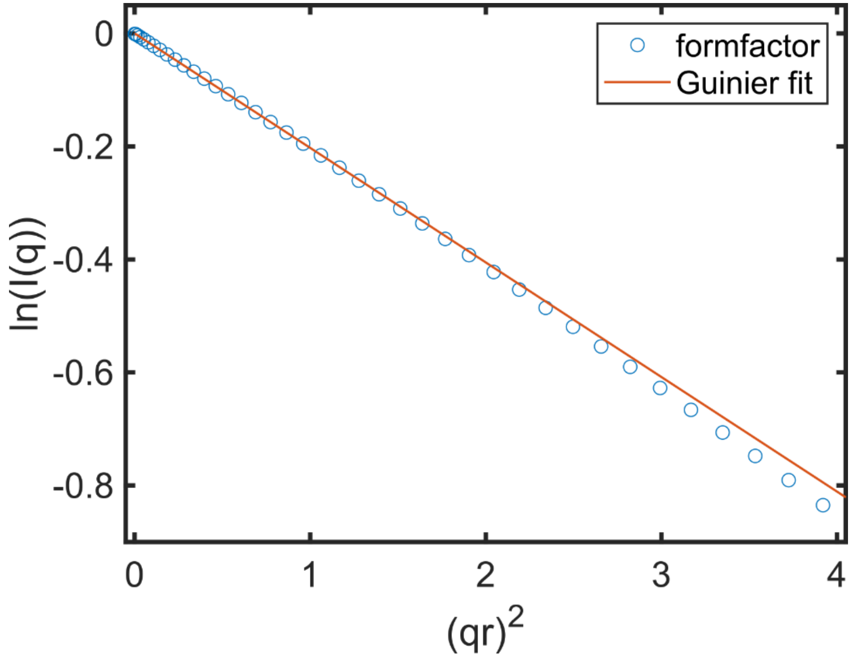
Large-q approximation: Porod‘s law

- Spheres: $I(q) \propto q^{-4}$



Small-q approximation: Guinier regime

- $I(q) \approx I(0)\exp\left(-\frac{q^2 R_g^2}{3}\right)$ for $qR_g < 1$
- Radius of gyration R_g
- Spheres: $R_g = \sqrt{\frac{3}{5}}R$



Slope:
$R_g = 0.780$
→ $R = 1.007$

SAXS – Analysis methods: Formfactors & dispersity

In reality, particle show a certain size distribution

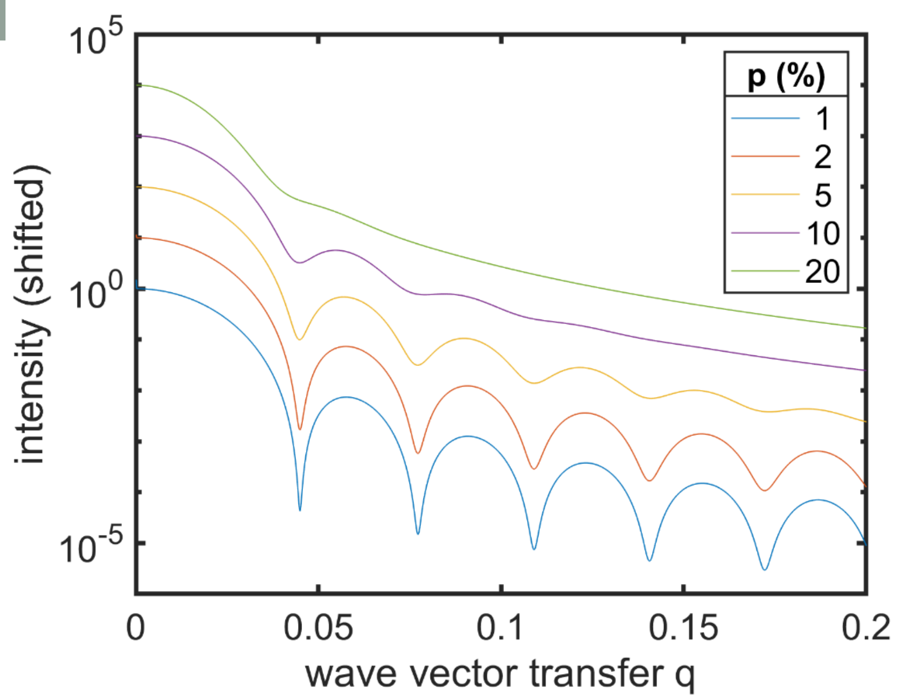
Use distribution function $n(R)$ with $\int n(R)\mathrm{d}R = 1$:

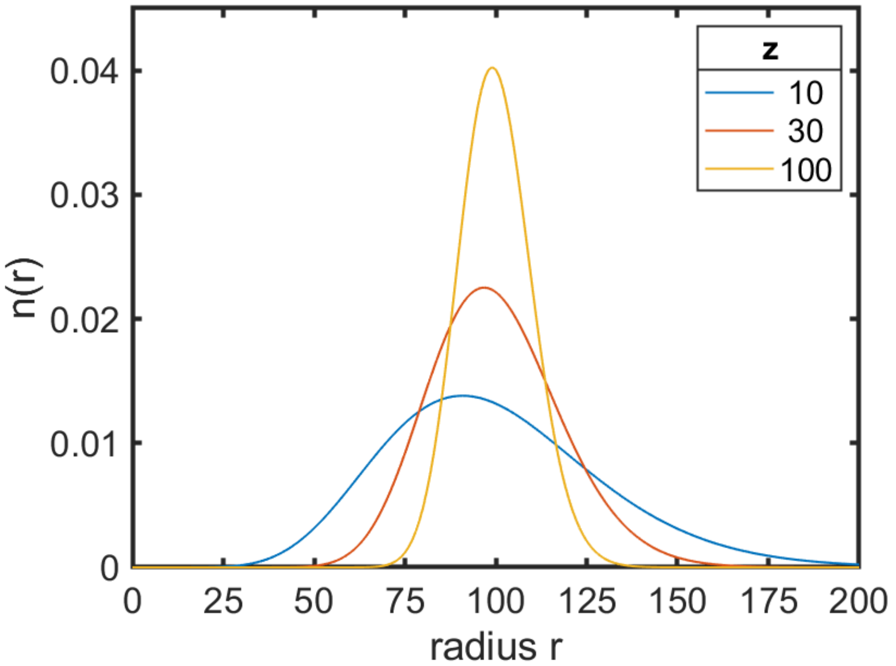
$$\mathrm{I}_{\mathrm{SAXS}}(q) = \int n(R) I_{\mathrm{formfactor}}(q,R)\mathrm{d}R$$

For colloids and polymers, a Schulz-Zimm distribution is frequently used:

$$n(R,R_0,z) = \frac{1}{(z+1)!}\left(\frac{z+1}{R_0}\right)^{z+1} R^z \exp\left(-\frac{z+1}{R_0}R\right)$$

Dispersity: $p = \frac{\Delta R}{R_0} = \sqrt{\frac{1}{z+1}}$, here: 30%, 18%, 10%





SAXS – Analysis methods: Structure factors

From lecture 5 (Kinematical Diffraction I): Structure factor of a liquid (or glass)

$$S(q) = 1 + \rho_0 \int_0^\infty \frac{4\pi r}{q} [g(r) - 1] \sin(qr) \mathrm{d}r$$

With the radial pair correlation function $g(r)$. This relates to the potential of mean force between two particles $U_{MF}(r)$

$$g(r) = \exp\left(-\frac{U_{MF}(r)}{k_B T}\right)$$

For very dilute systems $U_{MF}(r)$ equals the interaction potential $U(r)$.

Relation of $S(q)$ or $g(r)$ and $U(r)$ → **Ornstein-Zernike equation** relating total correlations $h(r) \equiv g(r) - 1$ to direct two-particle correlations $c(r)$ and indirect correlations $c(|\mathbf{r} - \mathbf{r}'|)$ (i.e. via third particles)

$$h(r) = c(r) + \rho_0 \int c(|\mathbf{r} - \mathbf{r}'|) h(|\mathbf{r}'|) \mathrm{d}\mathbf{r}'$$

SAXS – Analysis methods: Structure factors

$$h(r) = c(r) + \rho_0 \int c(|\mathbf{r} - \mathbf{r}'|) h(|\mathbf{r}'|) \mathrm{d}\mathbf{r}'$$

$c(r)$ short range part.

Structure factor → Fourier transform: $\hat{h}(q) = \hat{c}(q) + \rho \hat{h}(q) \hat{c}(q)$

OZ equation (or its Fourier transform) represents an infinitive recursion → can be solved using so-called „closure relations“, taking potential $U(r)$ into account.

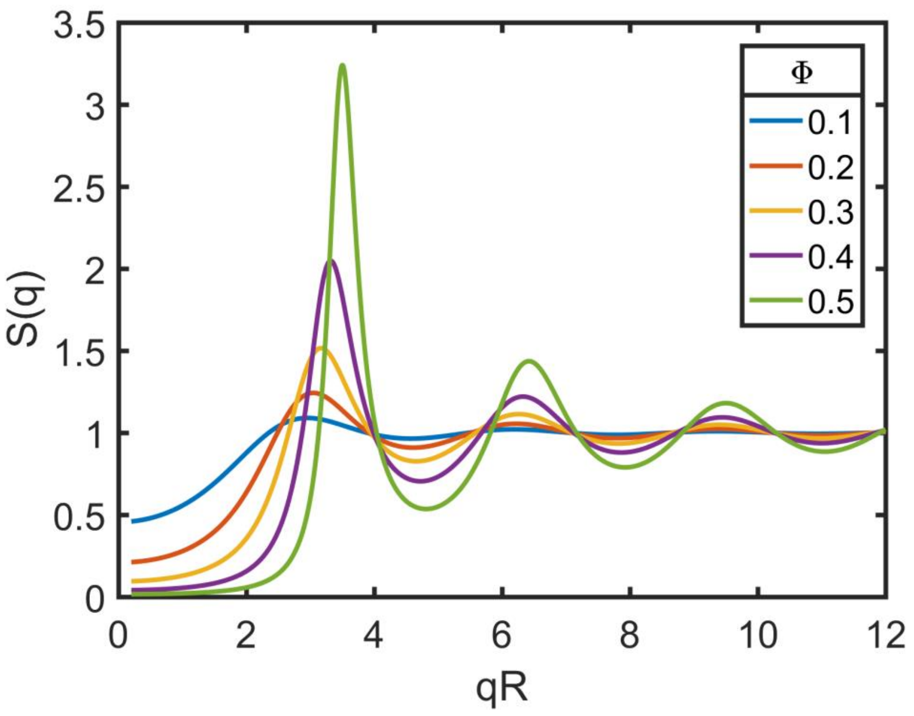
Percus-Yevick closure:

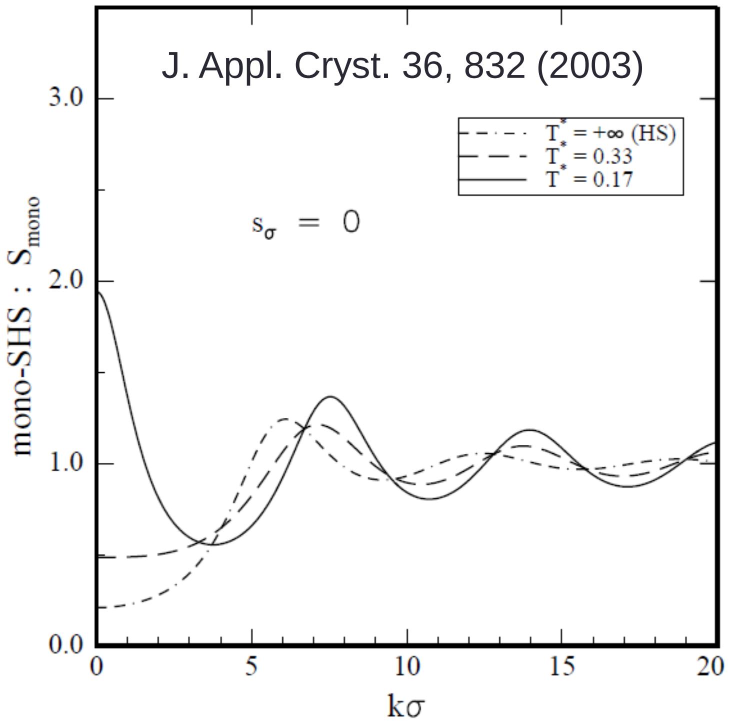
$$c(r) = g(r) \left[1 - \exp\left(\frac{U(r)}{k_B T} \right) \right]$$

→ solves the hard-sphere potential $U_{HS}(r) = \begin{cases} \infty, & r \leq 2R \\ 0, & r > 2R \end{cases}$ analytically.

→ Mean-spherical approximation closure relation $c(r) = -\frac{U_{ES}(r)}{k_B T}$ solves electrostatic interactions (DLVO) [→ Lecture 15]

Structure factors – hard spheres





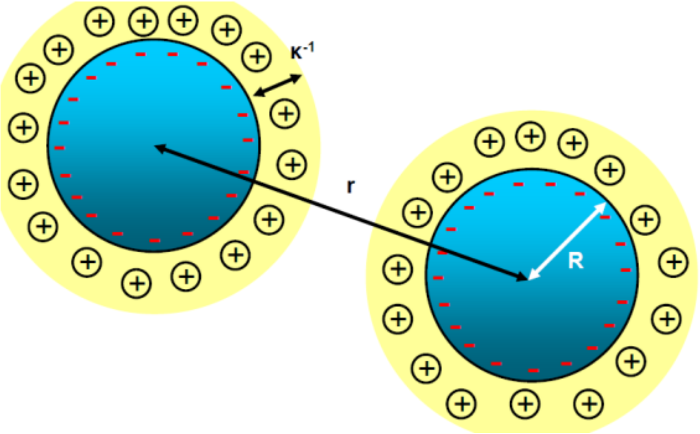
Hard spheres

- Volume fraction as only parameter
- Does not include crystallisation/glass transition!
- I.e. typically breaks down close to $\Phi \approx 0.5$

Sticky hard spheres

$$\frac{U_{SHS}(r)}{k_B T} = \begin{cases} \infty, & r < \sigma \\ \ln\left(\frac{12\tau\Delta}{\sigma + \Delta}\right), & \sigma \leq r \leq \sigma + \Delta \\ 0, & \sigma + \Delta < r \end{cases}$$

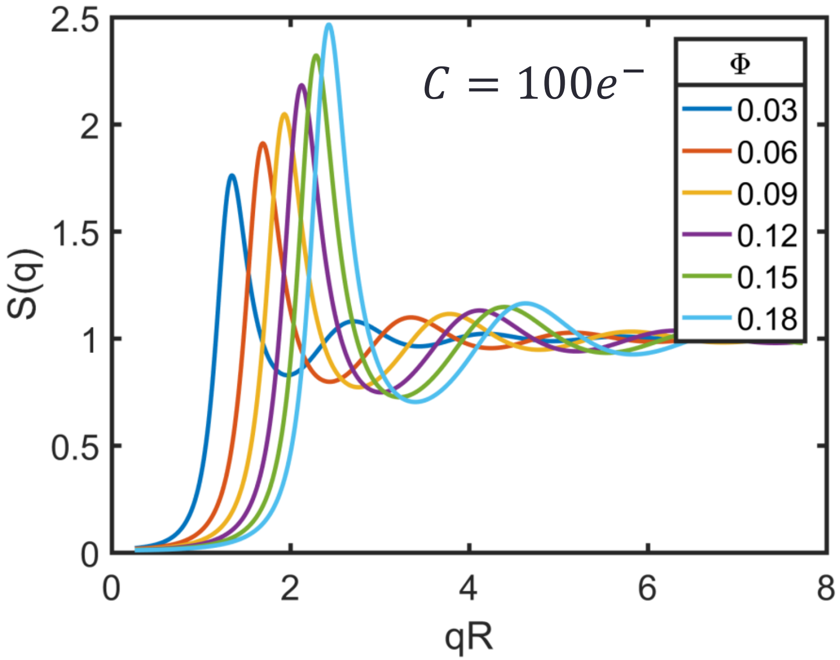
Structure factors – RMSA

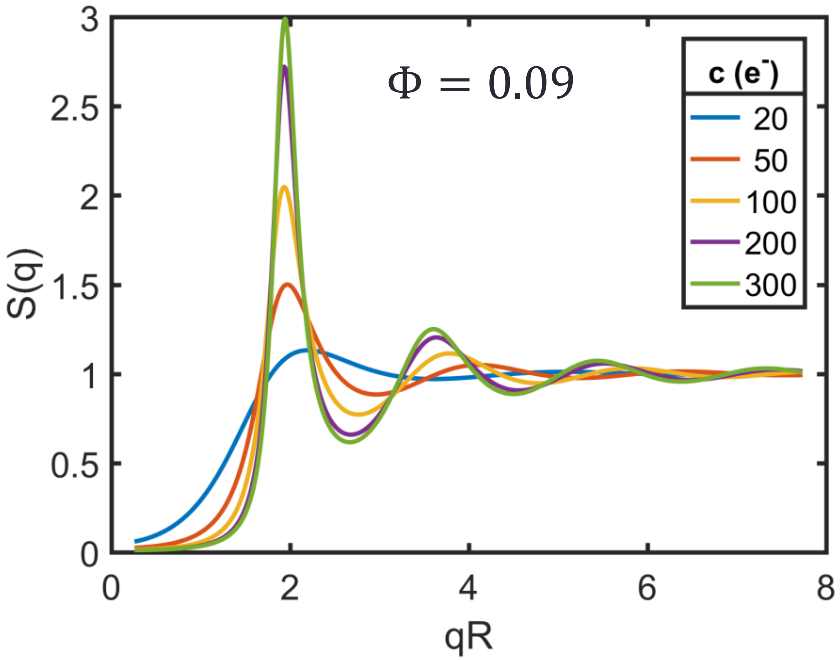


Charge stabilized systems → rescaled mean spherical approximation (RMSA)

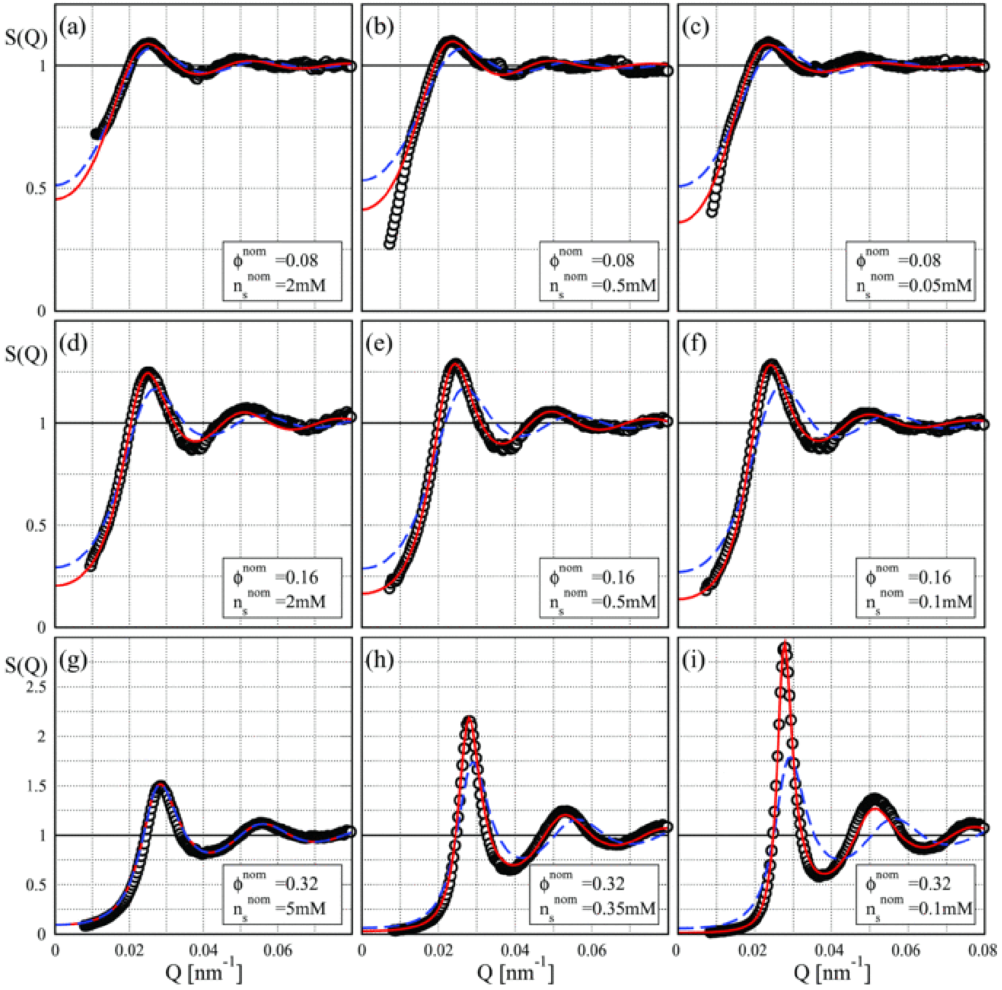
Structure factor as function of Φ, charge, screening

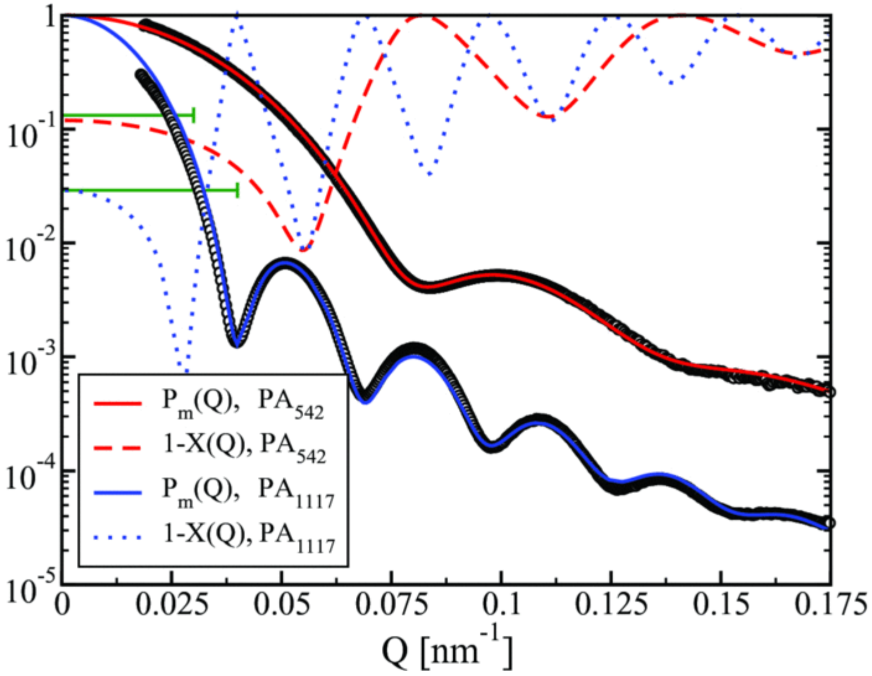
High screening → hard spheres





Example 1: Structure and Formfactors from charge stabilized colloids



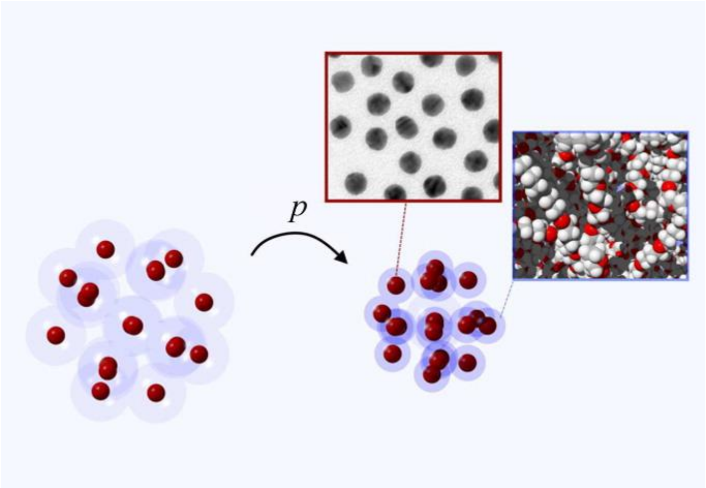


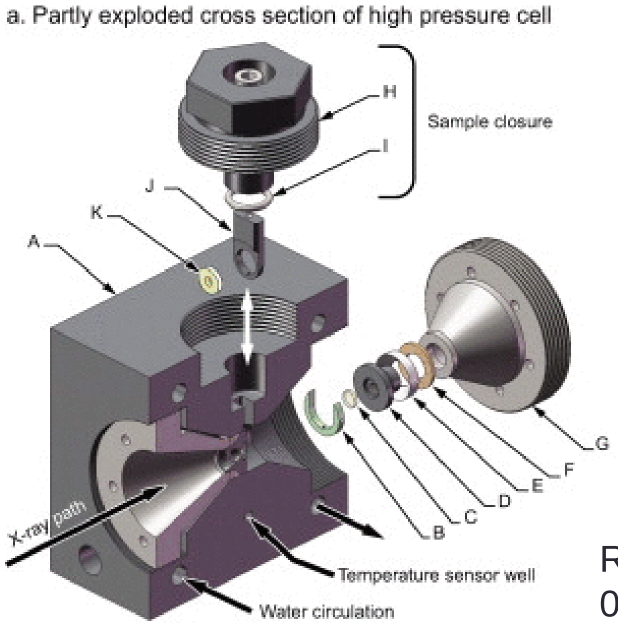
PMMA spheres in water

Westermeier et al. JCP 137, 114504 (2012)

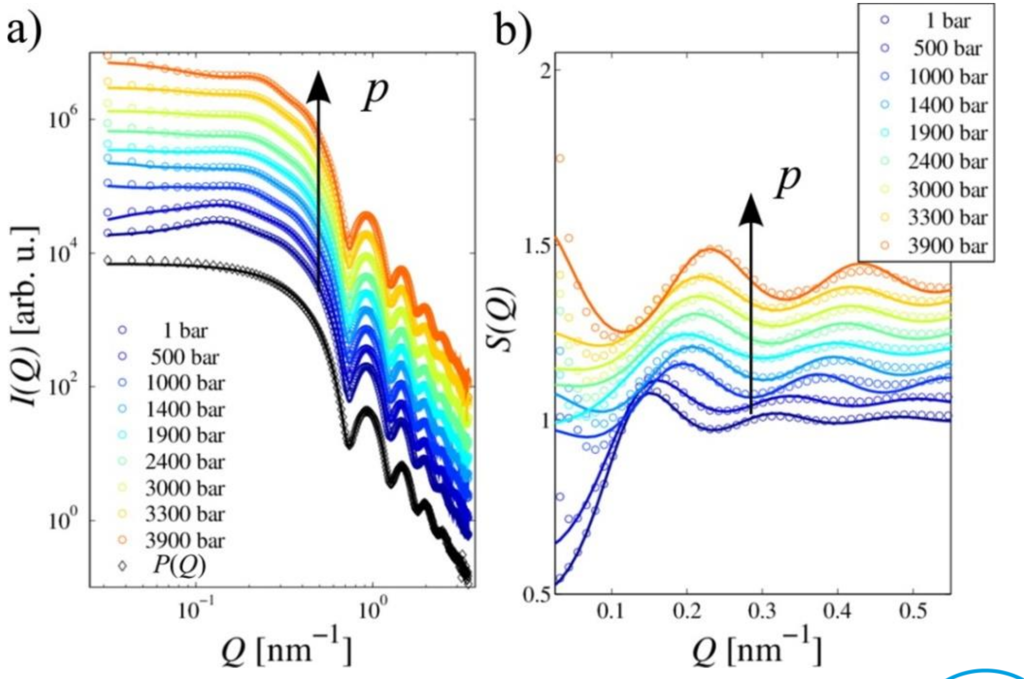
Example 2: High pressure studies

- Structure at high pressures → solid sample chambers (e.g., diamond windows of 500 µm thickness)
- X-rays to penetrate diamond windows (~30-40 % transmission at ~8-10 keV, see http://henke.lbl.gov/optical_constants/)
- Functionalized core-shell particles at pressures <4 kbar: from repulsion to attraction (sticky hard spheres!)





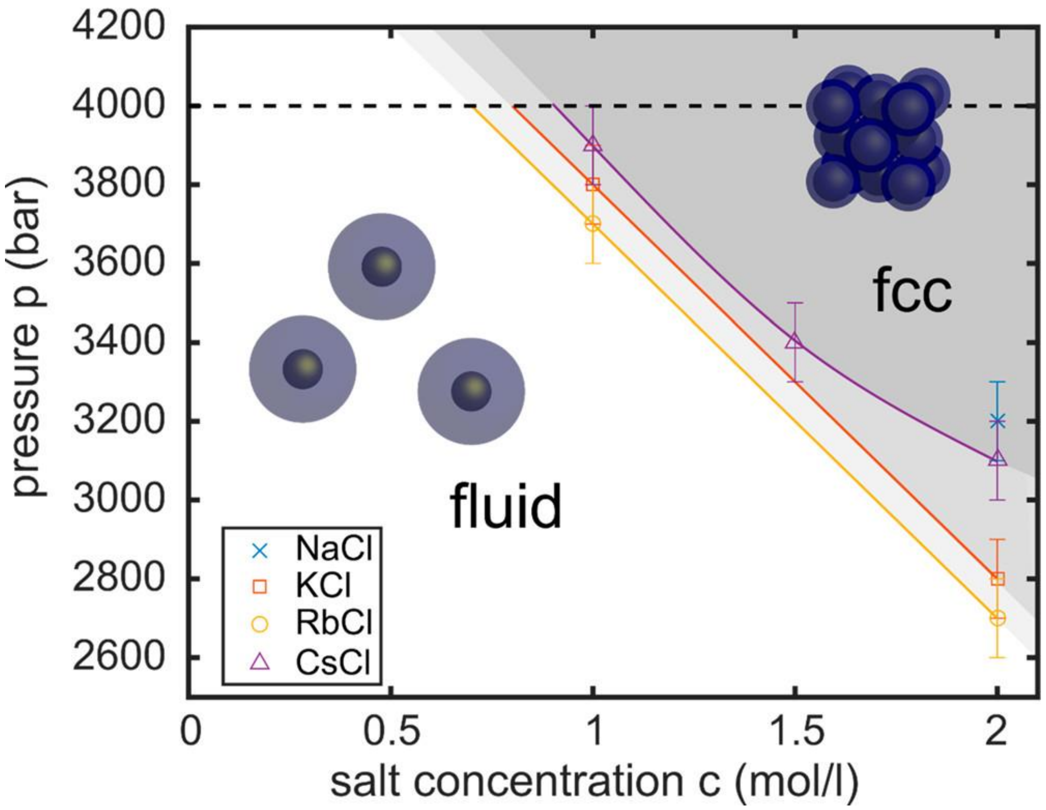
Rev. Sci. Instrum. 81, 064103 (2010).

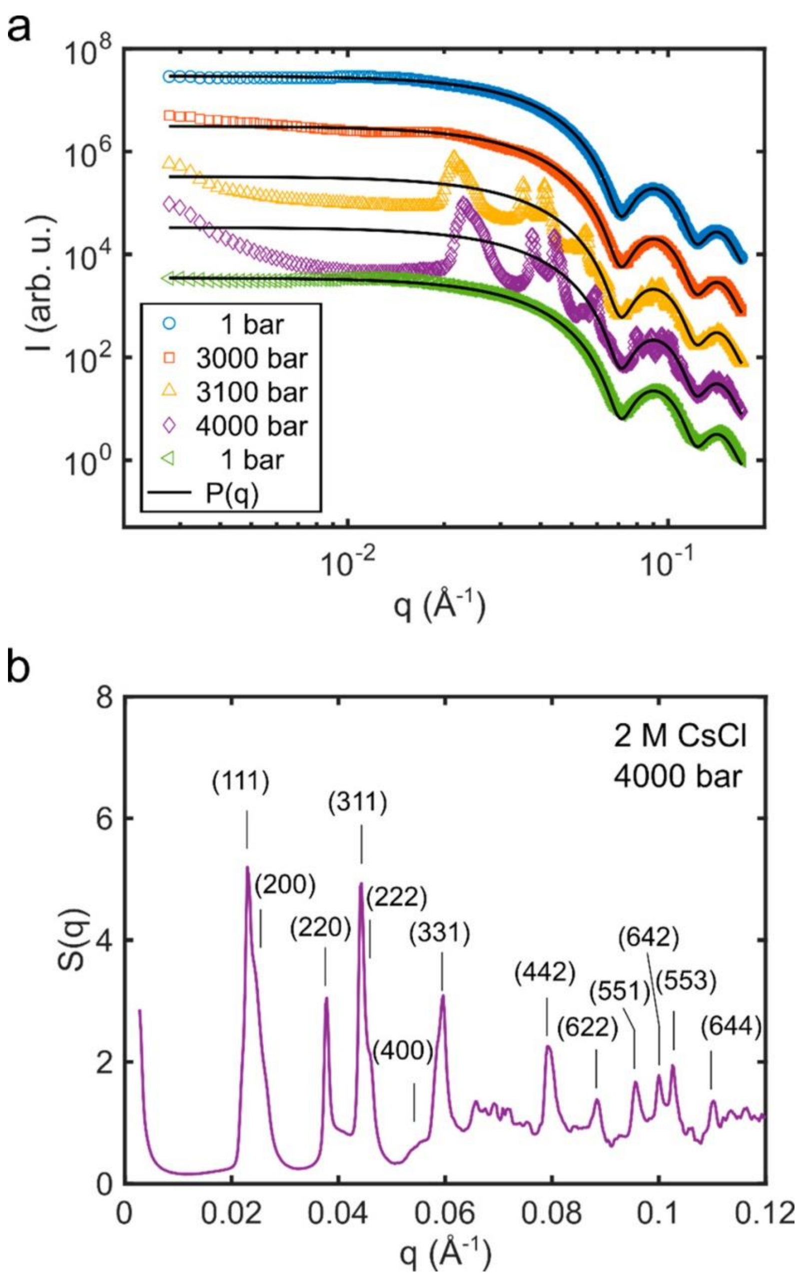


J. Phys. Chem. C 2016, 120, 19856-19861

Example 2: High pressure studies

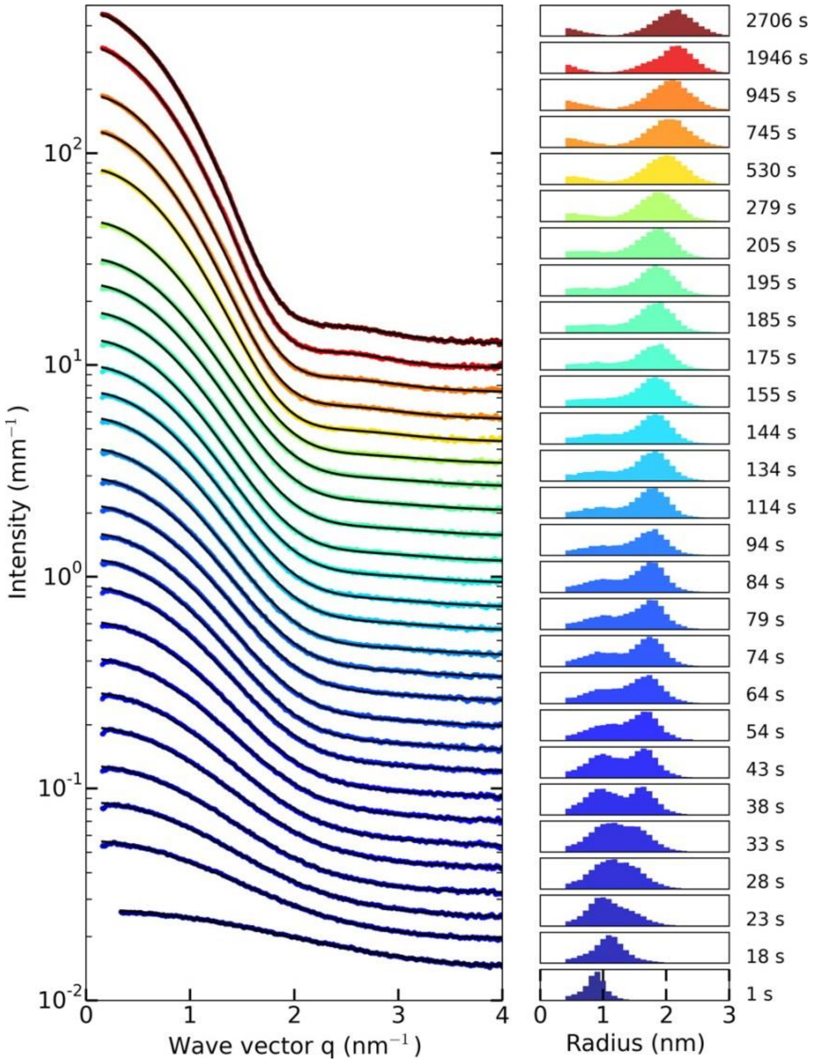
- Addition of salt → crystallisation at high pressure
- Reason: Solubility of PEG shell in water

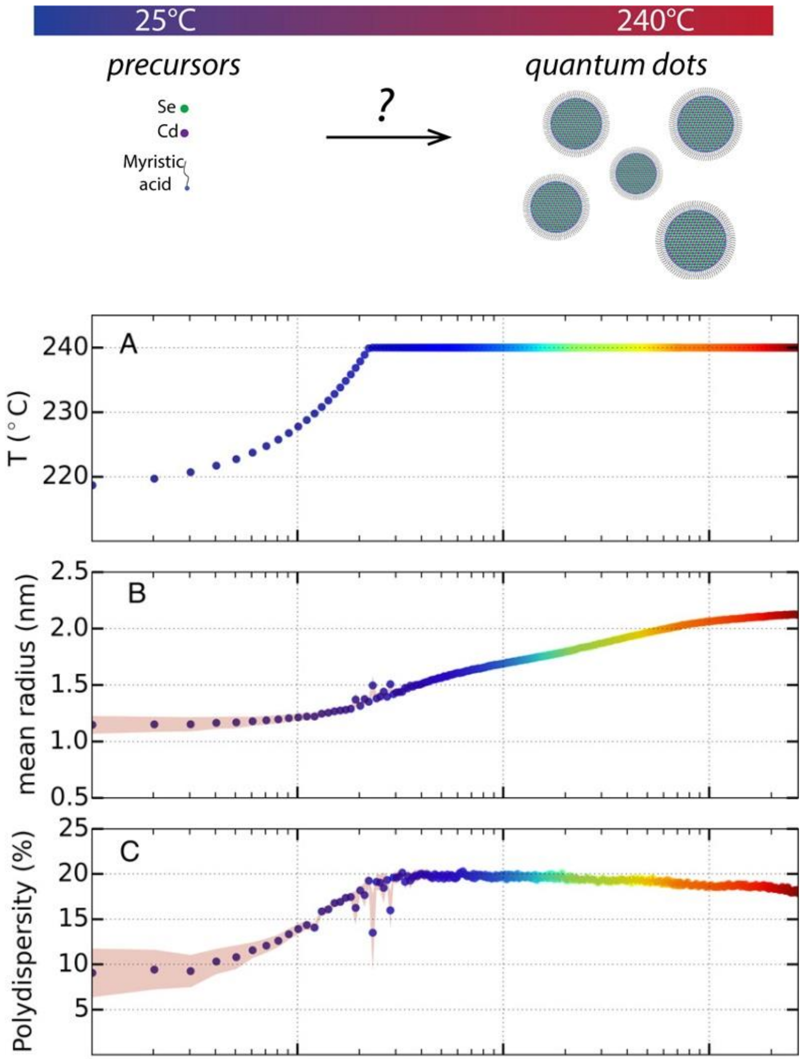




J. Phys. Chem. Lett. 2018, 9, 4720

Example 3: nucleation and growth of quantum dots

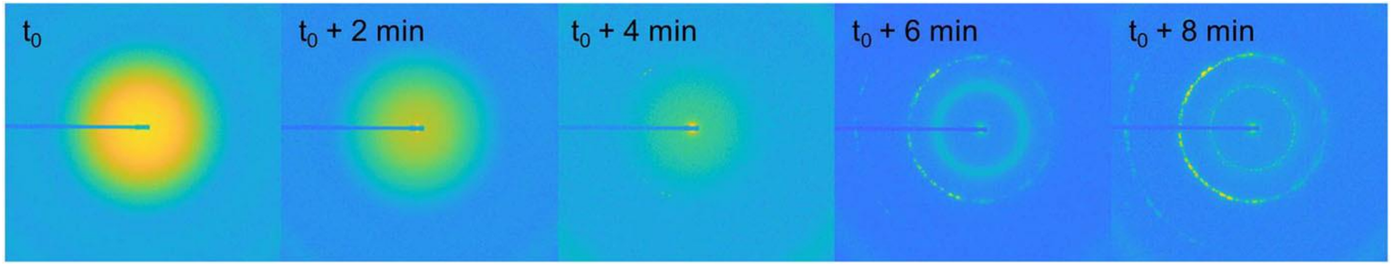


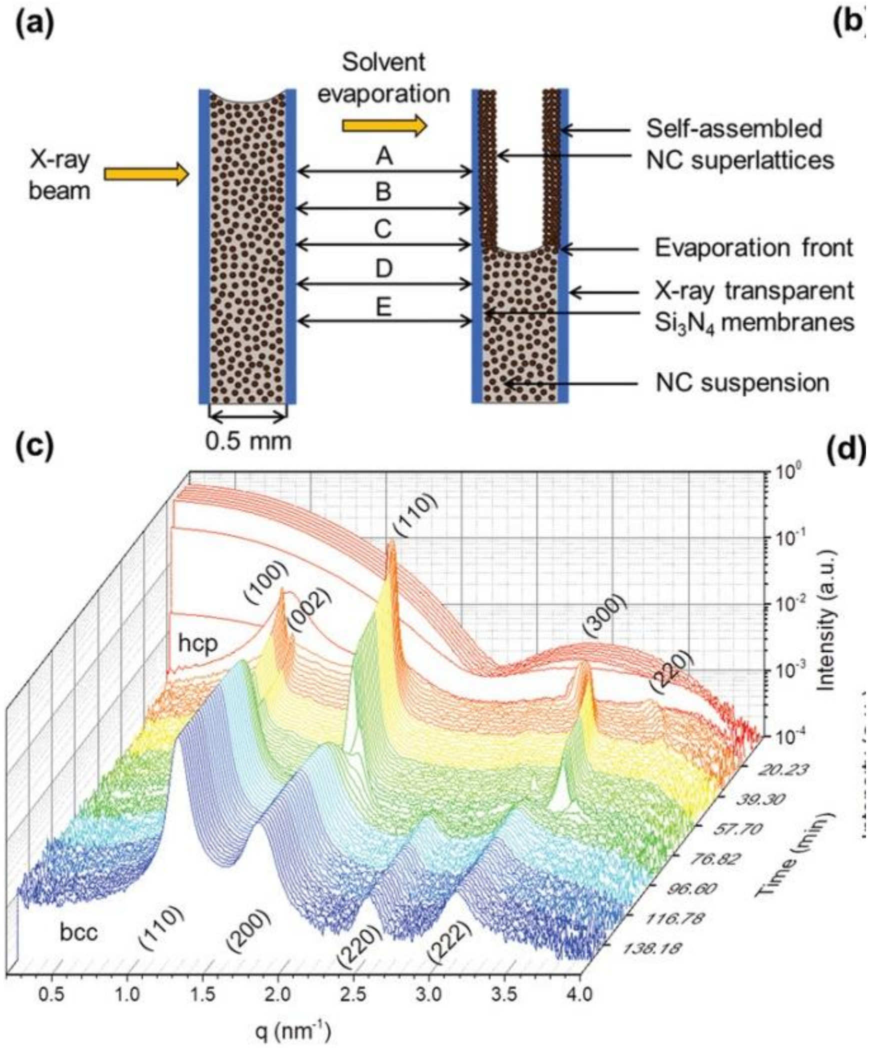


B. Abecassis et al. Nano Lett. 15, 2620 (2015)

Example 4: Self assembly of quantum dots / nanoparticles

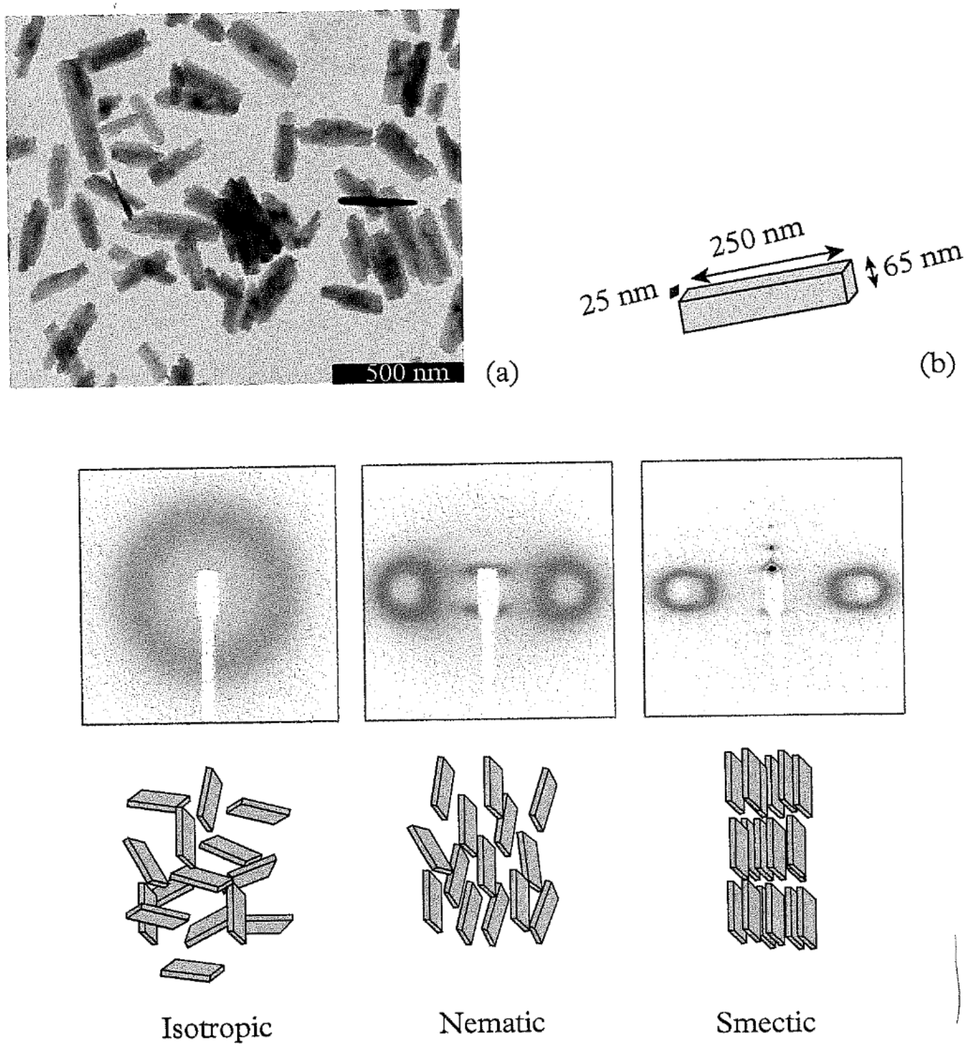
- Lead sulfate particles (3.9 nm diameter) in heptane / toluene / hexane …
- Self-assembly to ordered structures upon solvent evaporation → standard route to obtain functional materials made from such nanocrystals
- Track assembly over time: complex phase behaviour





I. Lokteva et al. RSI 90, 036103 (2019) & small 15, 1900438 (2019)

Example 5: Phase transitions in liquid crystals



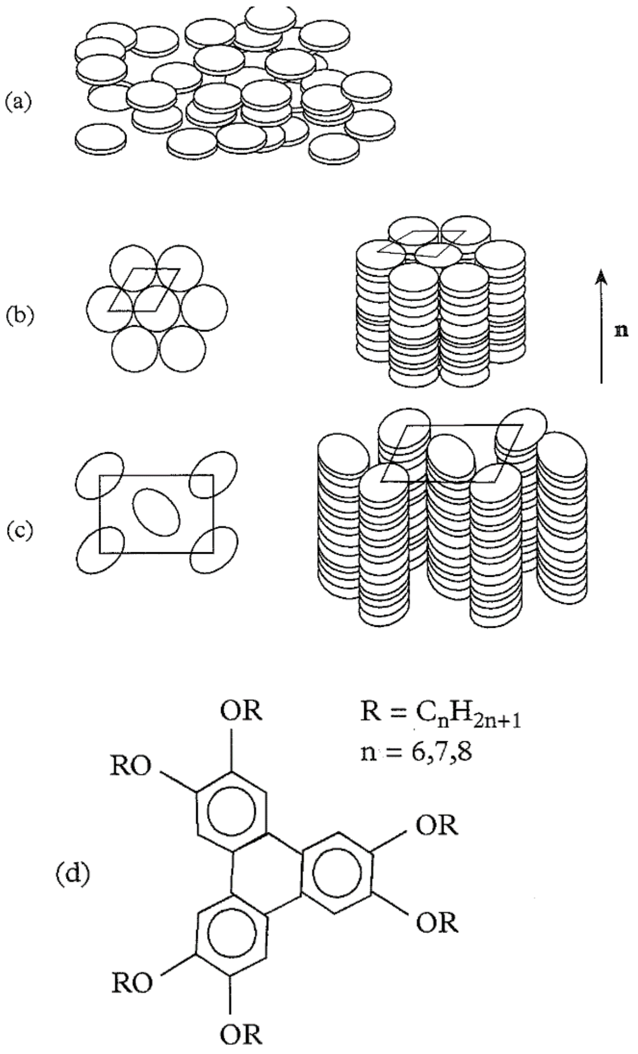
Goethite [α-FeO(OH)] particles in water may form

- Isotropic
- Nematic
- Smectic

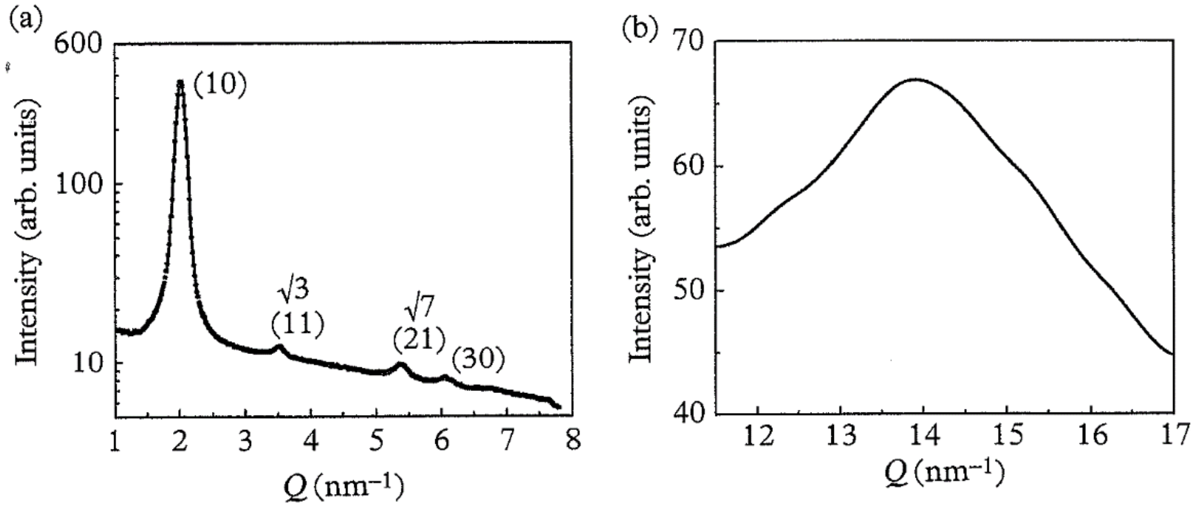
Phases → SAXS

de Jeu: "Basic X-ray scattering for Soft Matter", 2016

Example 5: Phase transitions in liquid crystals



Disc-systems
(a) Discotic nematic phase
(b) Hexagonal columnar phase
(c) Rectangular columnar phase



Combined SAXS/WAXS from columnar phase
- SAXS: hexagonal intercolumnar order
- WAXS: disorder inside column

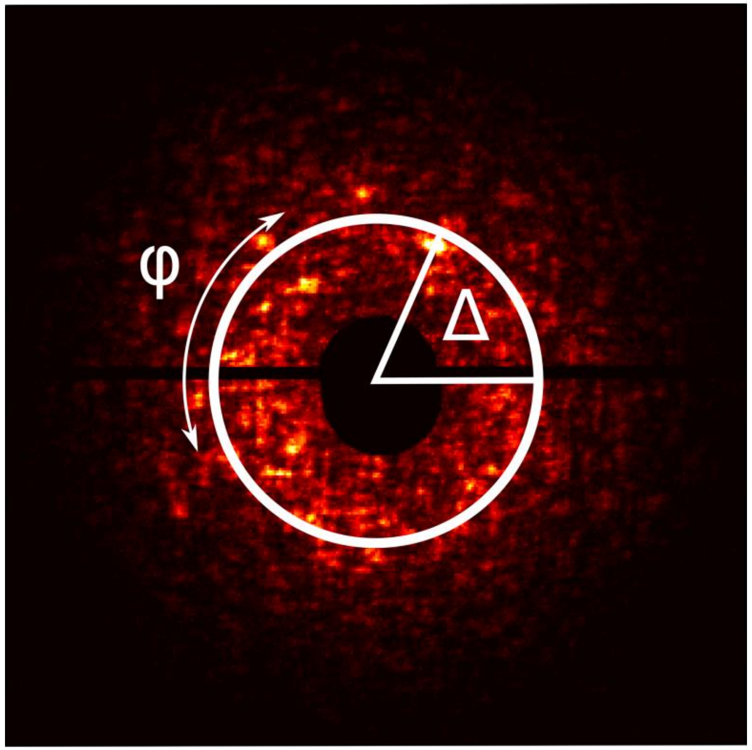
de Jeu: "Basic X-ray scattering for Soft Matter", 2016

Further methods and applications

- Anomalous SAXS → ASAXS
- Scanning SAXS
- Phase transitions and self-assembly
- Time resolved techniques
- SAXS tomography
- BioSAXS
- Grazing-incidence SAXS (GISAXS)
- …

X-ray cross correlation analysis

SAXS: 1D information (typically)
→ How to make use of the 2D information obtained from a 2D scattering pattern?
→ Angular correlations



1D information (standard SAXS)

- $I(\mathbf{q}) = \langle I(q,\varphi)\rangle_\varphi = I(q)$

2D information: Angular correlations

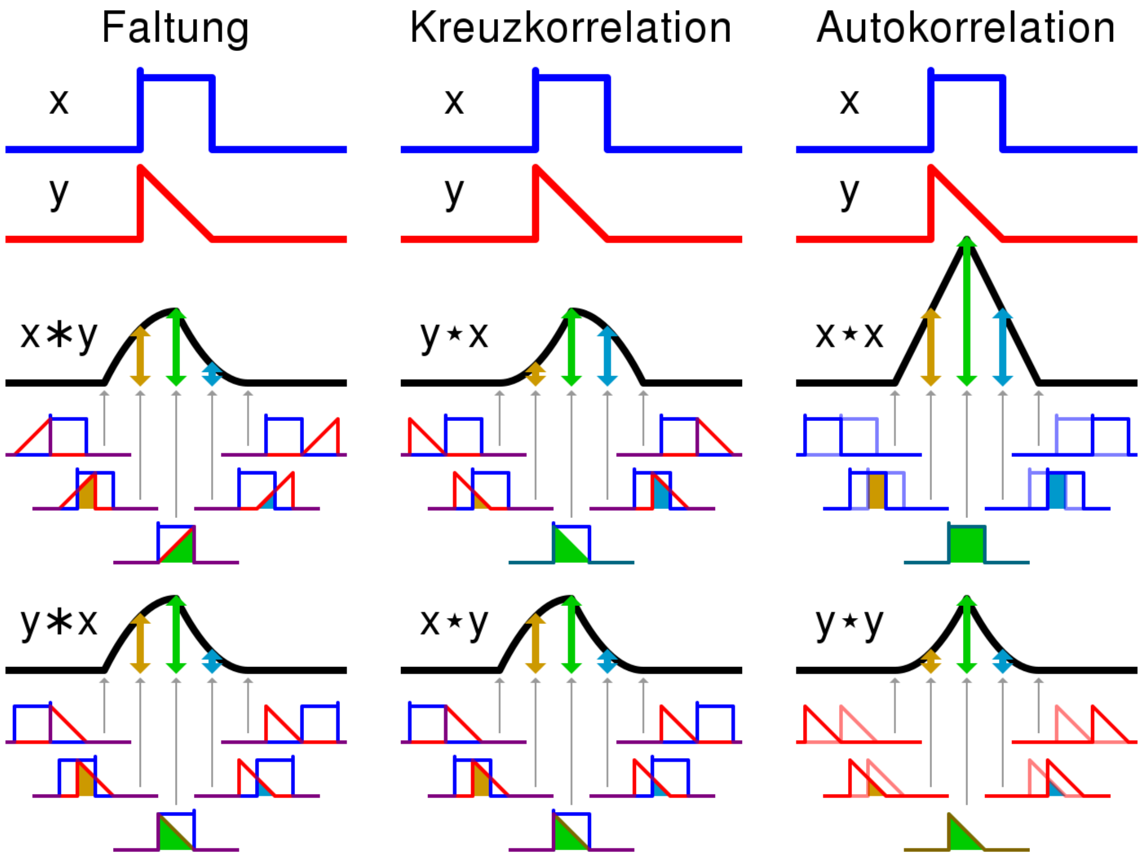
- $C(q,\Delta) = \frac{\langle I(q,\phi)I(q,\phi+\Delta)\rangle_\phi - \langle I(q,\phi)\rangle_\phi^2}{\langle I(q,\phi)\rangle_\phi^2}$, i.e. correlations of fluctuations

- Coherent X-rays

- Two possibilities:
  - Solve structures in solution
  - Hidden symmetries

Correlation functions

- Quantify correlation (similarity) between two (or more) entities
- Example from signal processing: convolution, cross correlation, autocorrelation



Common correlation function

- $C(r) = \langle I(r_1)I(r_1 + r)\rangle_{r_1}$

→ compares a signal (intensity) between two points as a function between their (spatial, temporal, …) difference r

- **XCCA**: angular correlations $C(\Delta) = \langle I(\varphi)I(\varphi + \Delta)\rangle_{\varphi}$
- **XPCS**: temporal correlations $C(\tau) = \langle I(t)I(t + \tau)\rangle_t$

X-ray cross correlation analysis

Consider coherent X-ray scattering experiment in transmission geometry (e.g. SAXS) with 2D detector on disordered sample of N identical particles

$$A_j(\mathbf{q}) = \int \rho_j(\mathbf{r}) e^{i\mathbf{q}\mathbf{r}} \mathrm{d}\mathbf{r} \;\rightarrow \mathrm{I}(\mathbf{q}) = \sum_{j_1,j_2=1}^{N} e^{i\mathbf{q}\mathbf{R}(j_1,j_2)} A_{j_1}^*(\mathbf{q}) A_{j_2}(\mathbf{q})$$

$$= \sum_{j_1,j_2=1}^{N} \int\int \rho_{j_1}^*(\mathbf{r_1}) \rho_{j_2}(\mathbf{r_2}) e^{i\mathbf{q}(\mathbf{R}(j_1,j_2)+\mathbf{r}_{21})} d\mathbf{r_1} d\mathbf{r_2}$$

Partially coherent illumination and dilute system (particles distance > coherence length) → interparticle correlations can be neglected:

$$I(\mathbf{q}) = \sum_{j=1}^{N} I_j(\mathbf{q}) = \sum_{j=1}^{N} \left|A_j(\mathbf{q})\right|^2$$

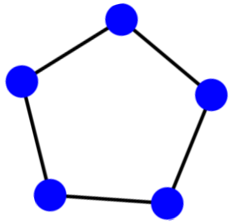
Angular information: Fourier decomposition

$$I(\mathbf{q}) = I(q,\phi) = \sum_{l=-\infty}^{\infty} \hat{\mathrm{I}}_\ell(q) e^{il\phi}\,; \qquad \hat{\mathrm{I}}_\ell(q) = \frac{1}{2\pi} \int_0^{2\pi} I(q,\phi) e^{-i\ell\phi}\, \mathrm{d}\phi$$

X-ray cross correlation analysis

Now consider 2D disordered system in the dilute limit, e.g. pentagonal arrangement of particles (polar coordinates, R_0 radius of pentagon, $\theta_j = \frac{2\pi j}{5}$)

$$\rho(r,\theta) = \frac{\delta(r - R_0)}{R_0} \sum_{j=1}^{5} \delta(\theta - \theta_j)$$



Expansion of scattering amplitude in Fourier series yields

$$A(q,\phi) = \sum_{\ell=-\infty}^{\infty} \hat{a}_\ell(q) e^{il\phi} \qquad (1)$$

with Fourier coefficients

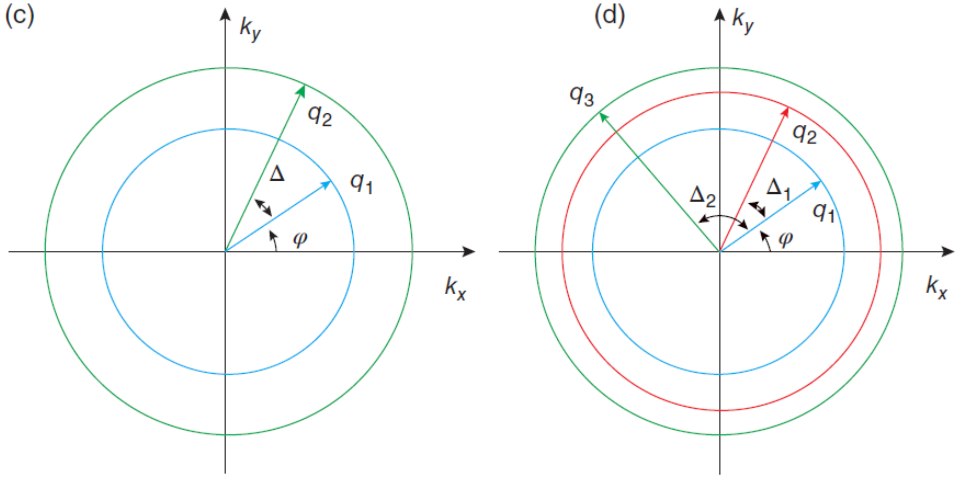
$$\hat{a}_\ell(q) = i^{-\ell} J_\ell(qR_0) \textstyle\sum_{j=1}^{5} e_j^{il\theta_j} \qquad (2)$$

- Pentagonal symmetry: only contribution if $\ell = 0 \bmod 5$ in (2).
- Odd terms cancel out pairwise (e.g. $\ell = 5$ and $\ell = -5$) in (1) → Friedel's law!
- Only contributions with $\ell = 0 \bmod 10$
- $F_l(q) \propto J_\ell(qR_0)$ → higher-order terms at large q

X-ray cross correlation analysis

- Corresponding correlation function $C(q,\Delta) = \frac{\langle I(q,\phi)I(q,\phi+\Delta)\rangle_\phi - \langle I(q,\phi)\rangle_\phi^2}{\langle I(q,\phi)\rangle_\phi^2}$ with Fourier coefficients $\hat{c}_\ell(q) = \left|\hat{I}_\ell(q)\right|^2$ (Wiener–Khinchin theorem)

- Correlations between different q possible

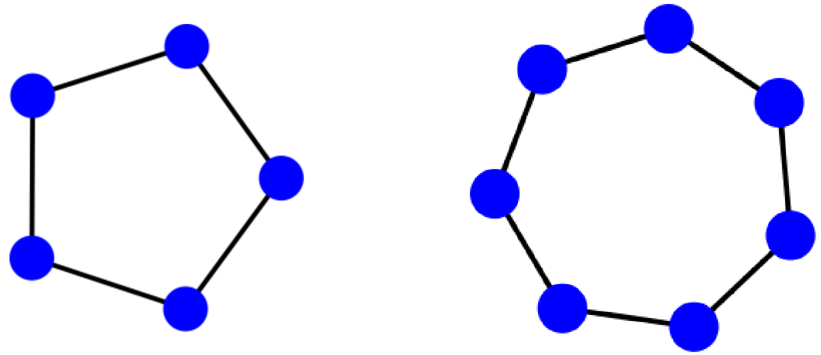


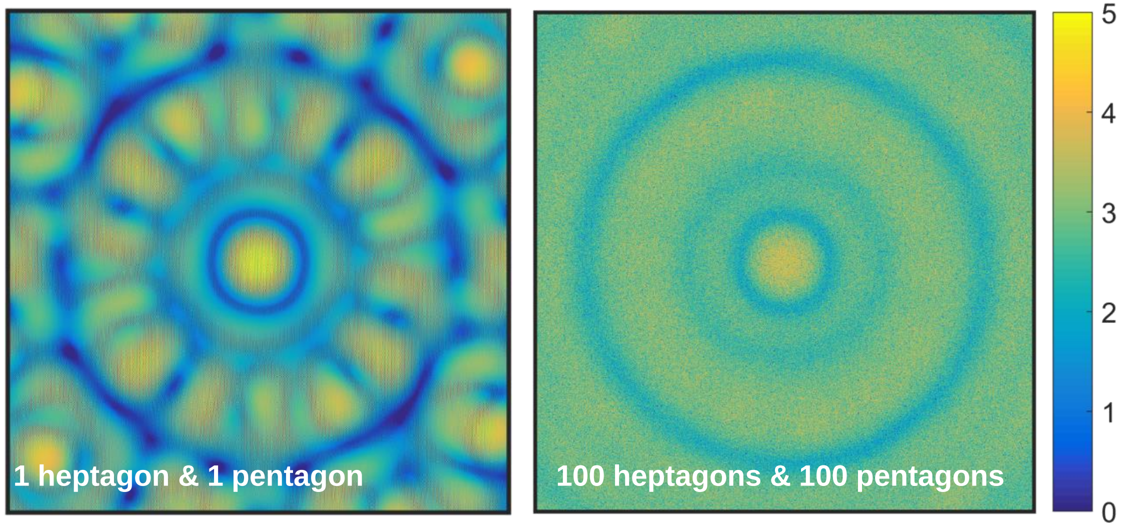
Adv. Chem. Phys. 161, 1 (2016)

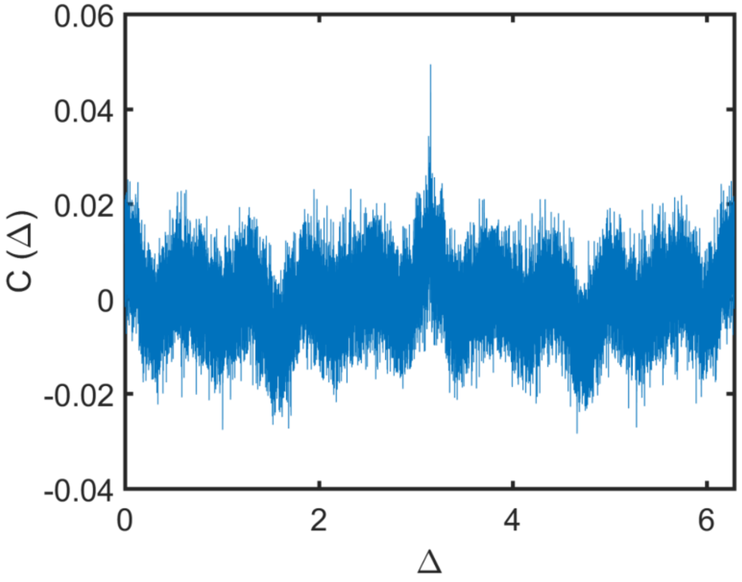
- 3D systems: curvature of Ewald sphere → odd symmetries

X-ray cross correlation analysis

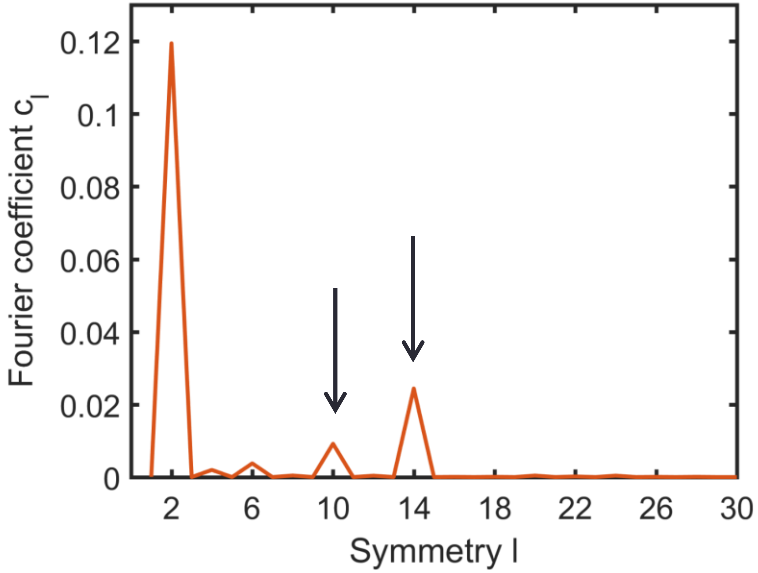
2D model system: Heptagons and Pentagons



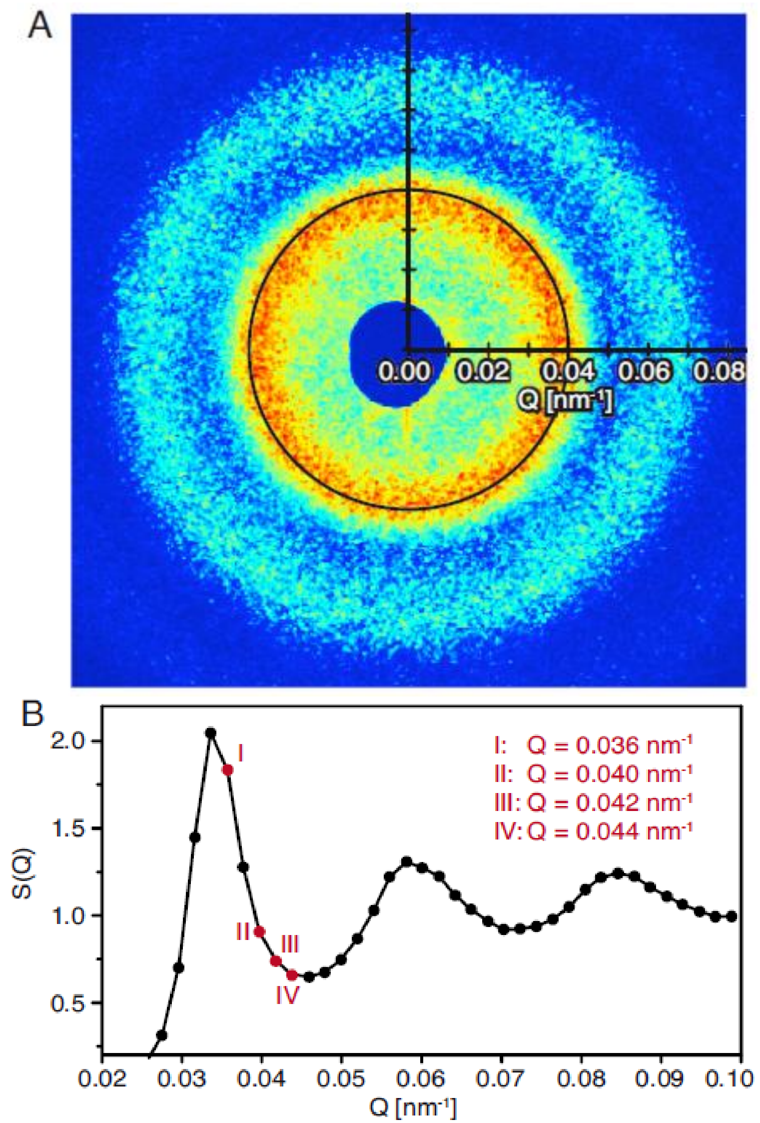


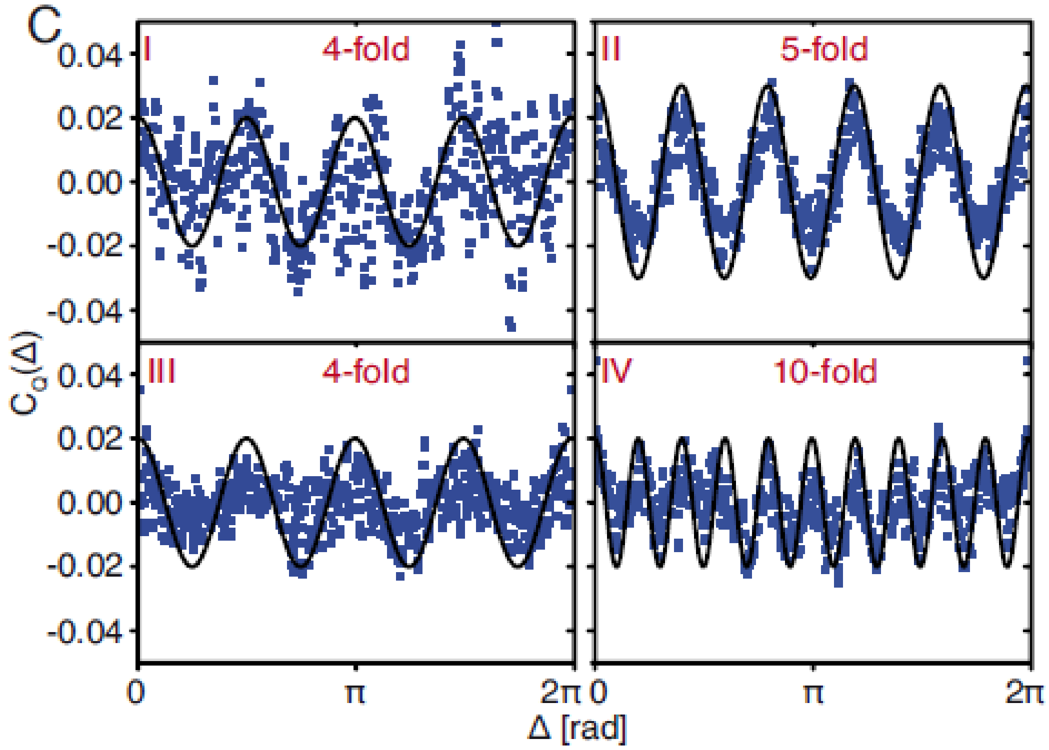


Averaged over 10 patterns



XCCA example 1: Hard-sphere glass

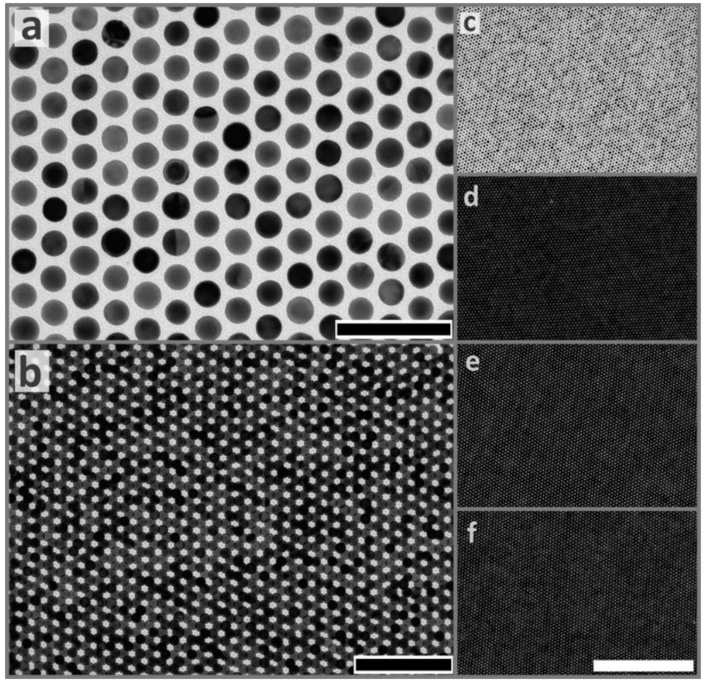


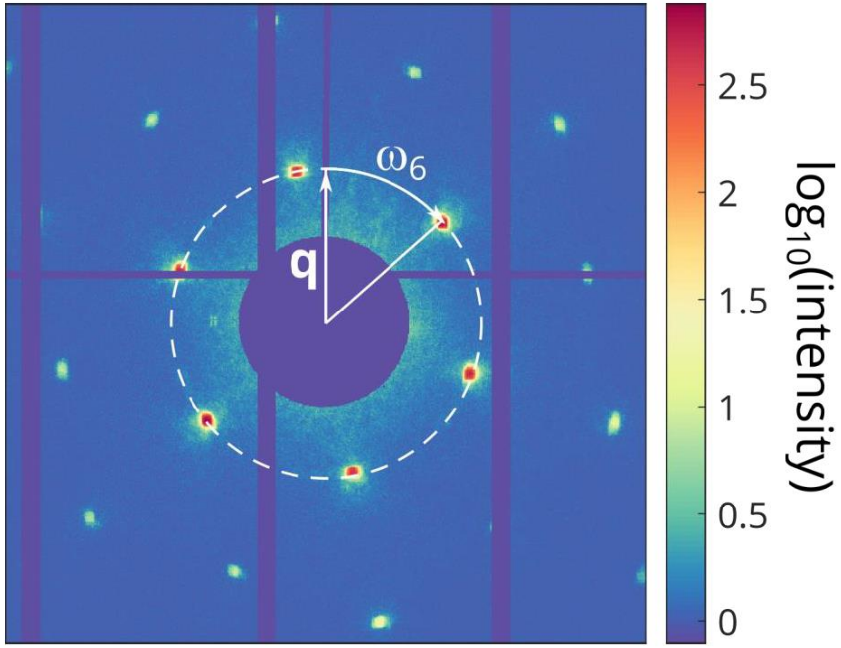


→ Hidden symmetries
→ Structural information beyond SAXS

PNAS 109, 11511 (2009)

XCCA example 2: Self-assembled nanoparticle films





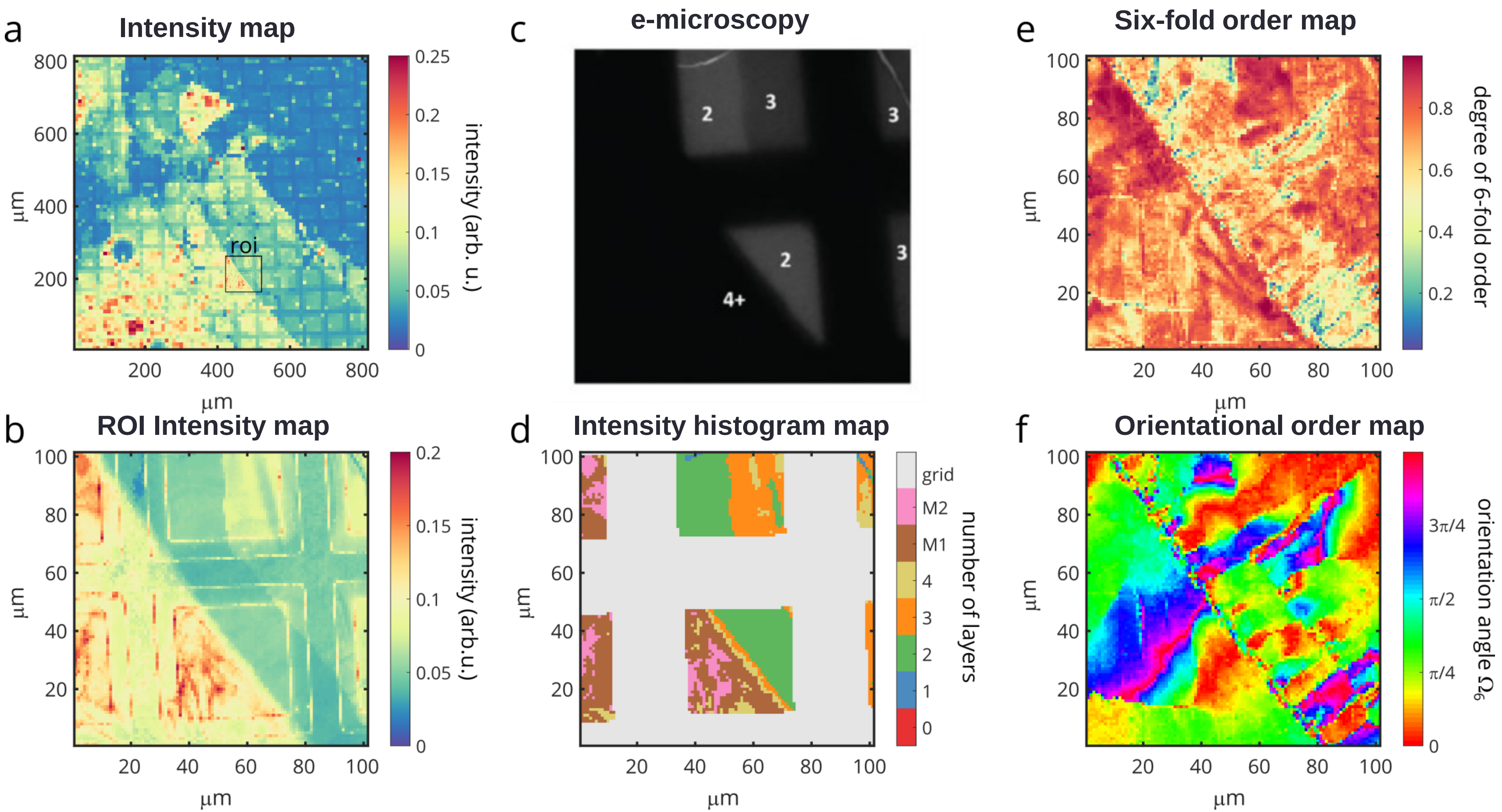
Films of assembled gold particles (12 nm radius): special plasmonic and optical properties

From mono- to multilayers

Diffraction pattern: 2D hexagonal lattice

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

XCCA example 2: Self-assembled nanoparticle films



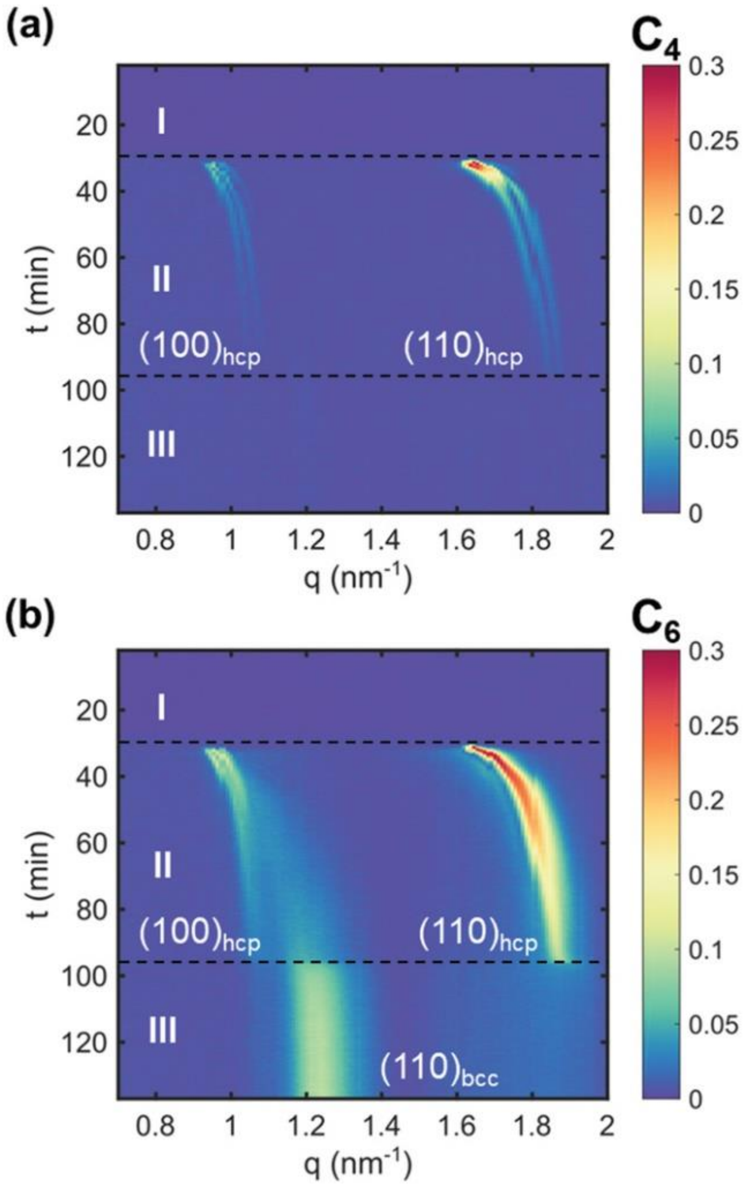
Adv. Mater. Interf. 7, 2000919 (2020)

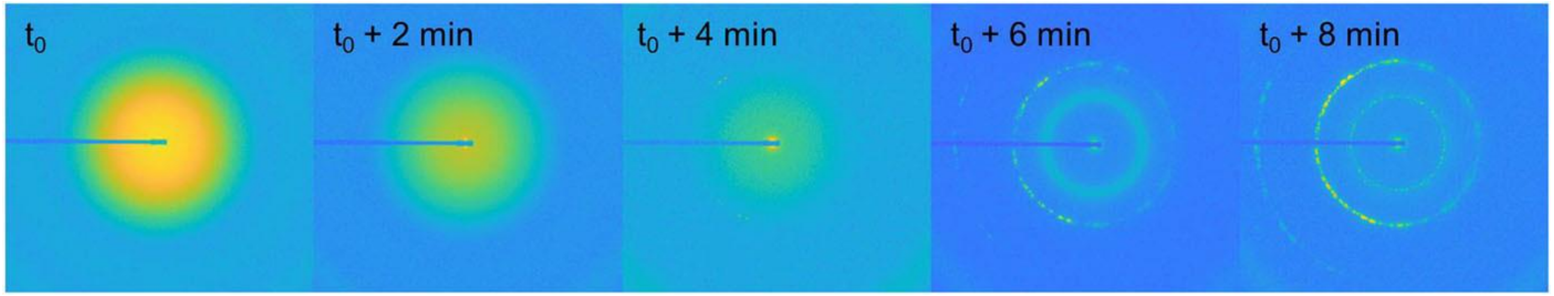
XCCA example 2: Self-assembled nanoparticle films

- The fourth and the sixth Fourier coefficients of the cross-correlation function from Bragg reflections during in-situ self-assembly

- Support SAXS data
  - (I) colloidal suspension
  - (II) swollen hcp superlattice
  - (III) dried bcc superlattice

- Coexisting bcc phase in II





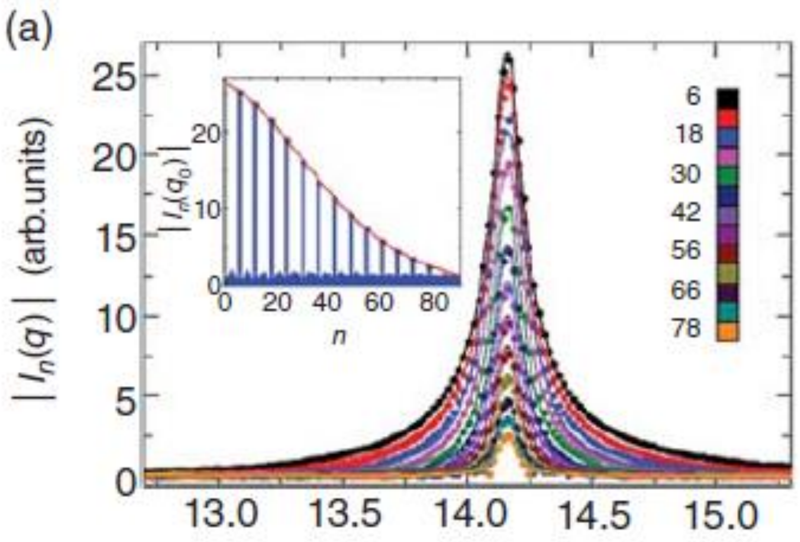
I. Lokteva et al. RSI 90, 036103 (2019) & small 15, 1900438 (2019)

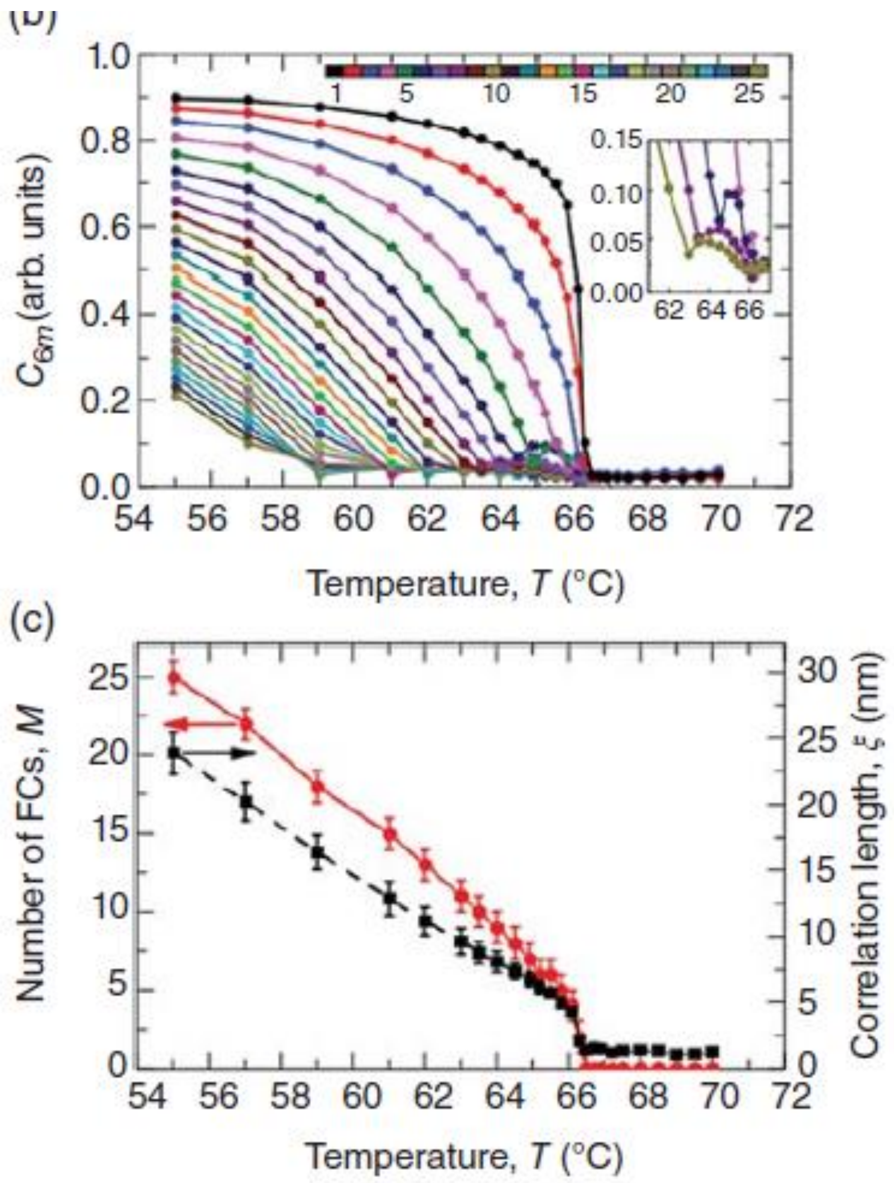
XCCA example 3: Liquid crystals

High number of symmetries → strongly developed hexatic order

Measure of correlation length

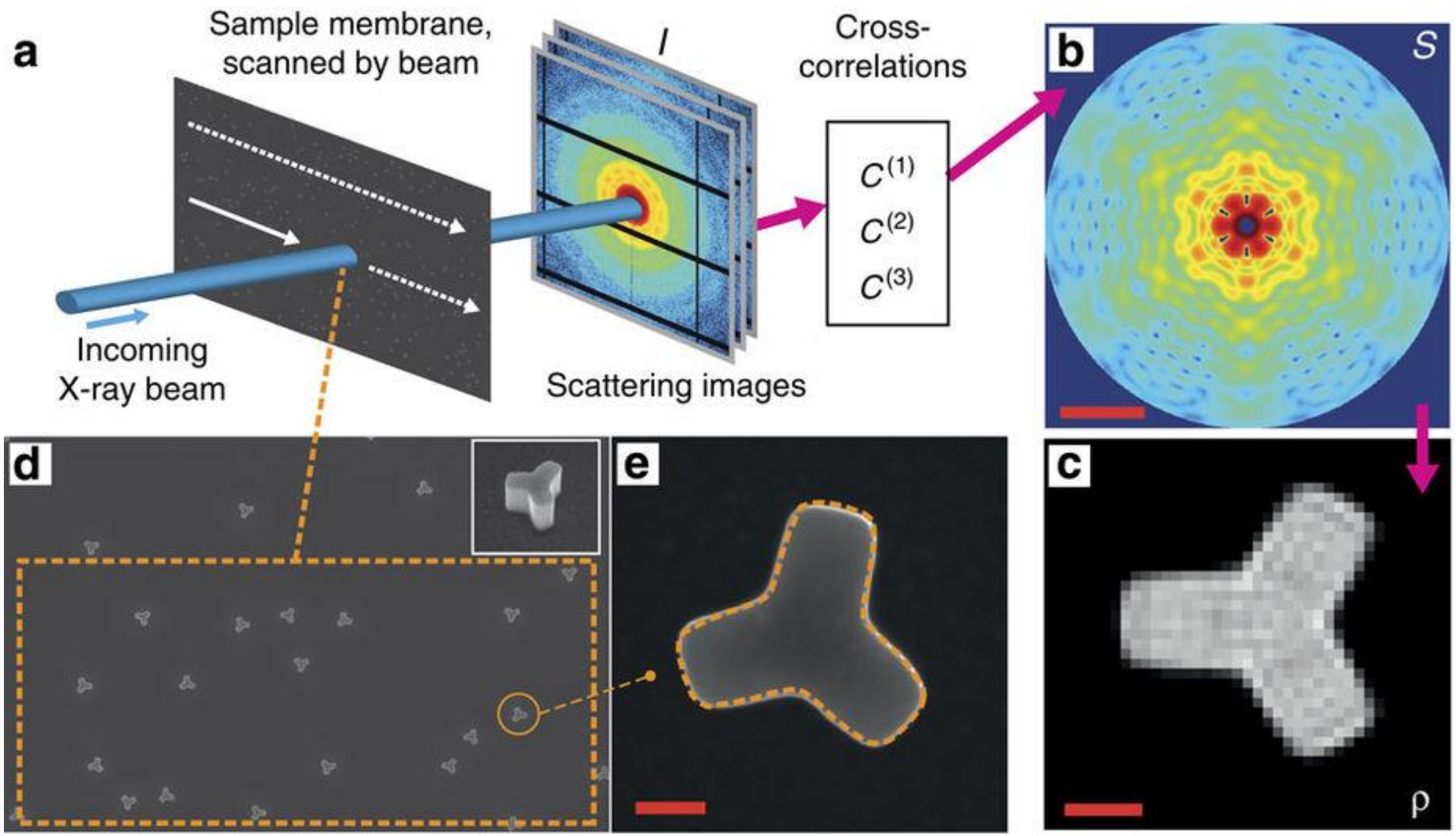
XCCA to provide measure of degree of order and as order parameter for phase transitions





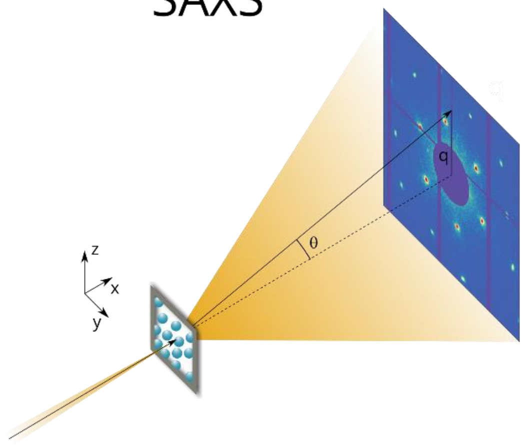
Adv. Chem. Phys. 161, 1 (2016)

XCCA example 4: Sample reconstruction

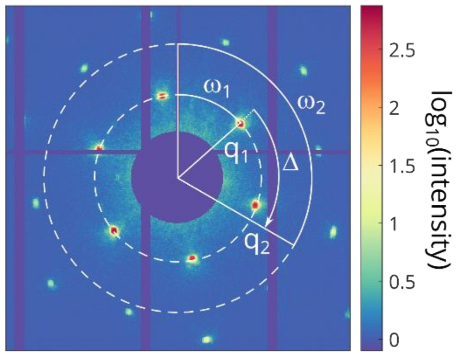


Nat. Comm. 4, 1647 (2013)

SAXS



XCCA



GISAXS