PAUL SCHERRER INSTITUT

Marianne Liebi– Material Science at Large Scale Facilities

Small-angle scattering (SAXS/SANS)

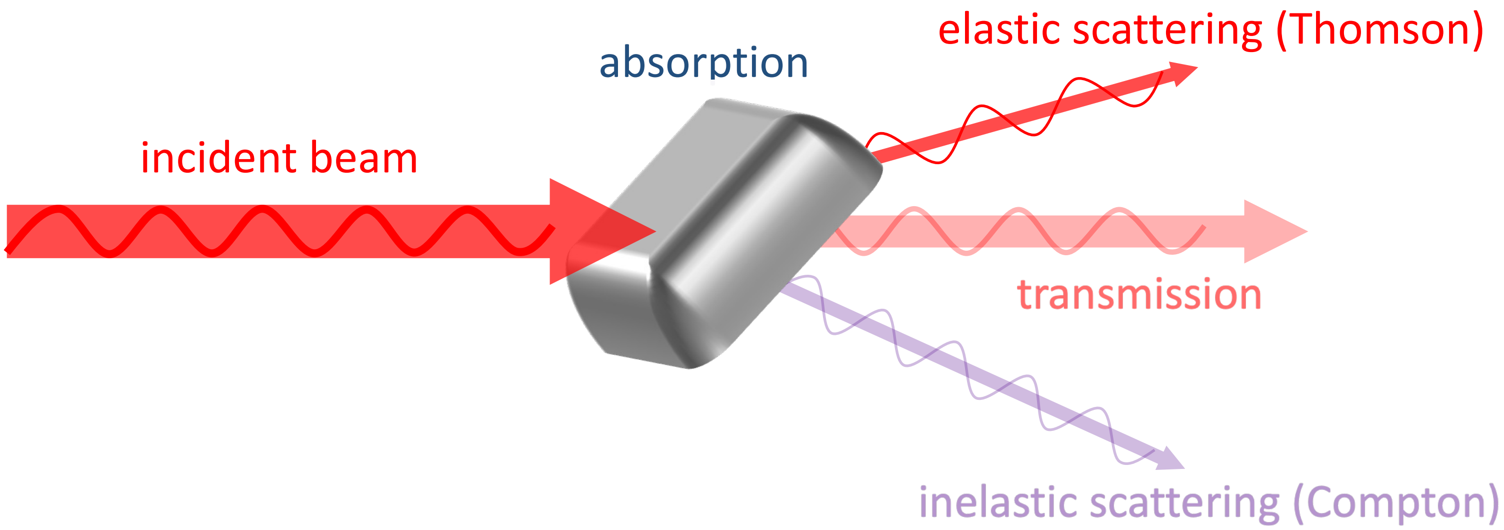
EPFL Master Course 2024 MSE435

Course program

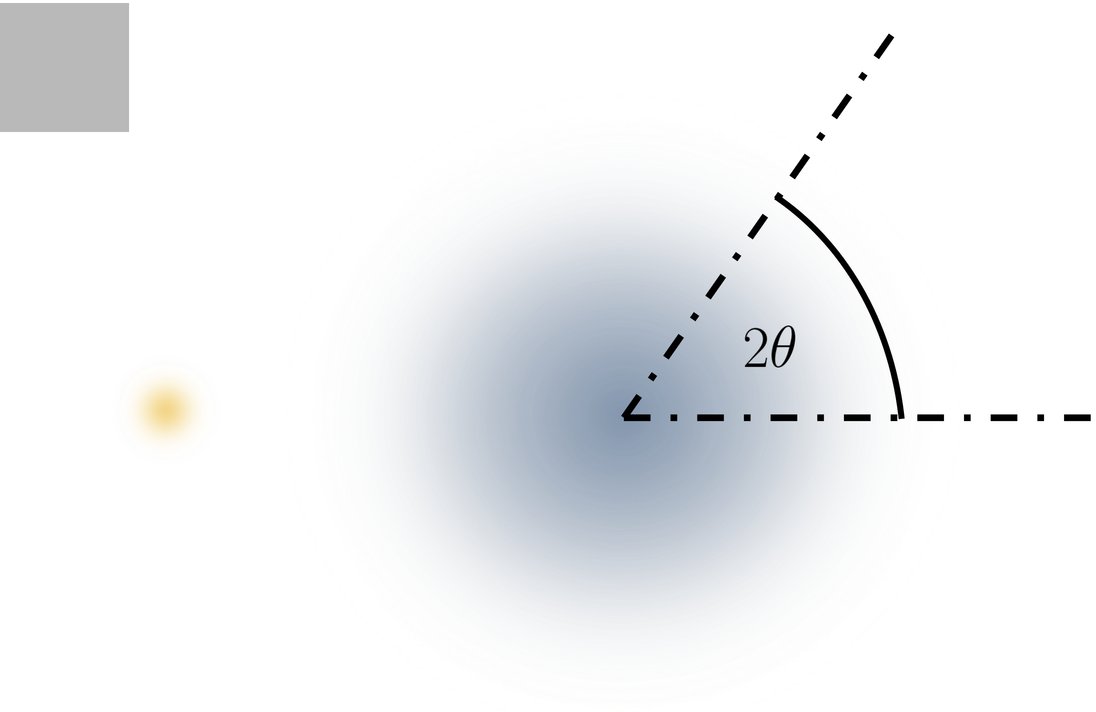
09.09.24	Introduction, sources, beamlines, detectors	Steven Van Petegem
16.09.24	Holiday	
23.09.24	Excursion to PSI	Steven Van Petegem / Marianne Liebi
30.09.24	Interaction with matter	Steven Van Petegem
07.10.24	Fluorescence	Marianne Liebi
14.10.24	Diffraction I	Steven Van Petegem
21.10.24	Break	
28.10.24	Small angle x-ray scattering	Marianne Liebi
04.11.24	Diffraction II / Magnetic scattering	Steven Van Petegem
11.11.24	XANES/EXAFS	Marianne Liebi
18.11.24	Phase contrast / Tomography	Steven Van Petegem
25.11.24	Coherent imaging	Marianne Liebi
02.12.24	Neutron imaging	Steven Van Petegem
09.12.24	PEEM/Muon	Steven Van Petegem
16.12.24	Case study presentations	Steven Van Petegem / Marianne Liebi

Interaction of X-rays with matter

interaction with electrons



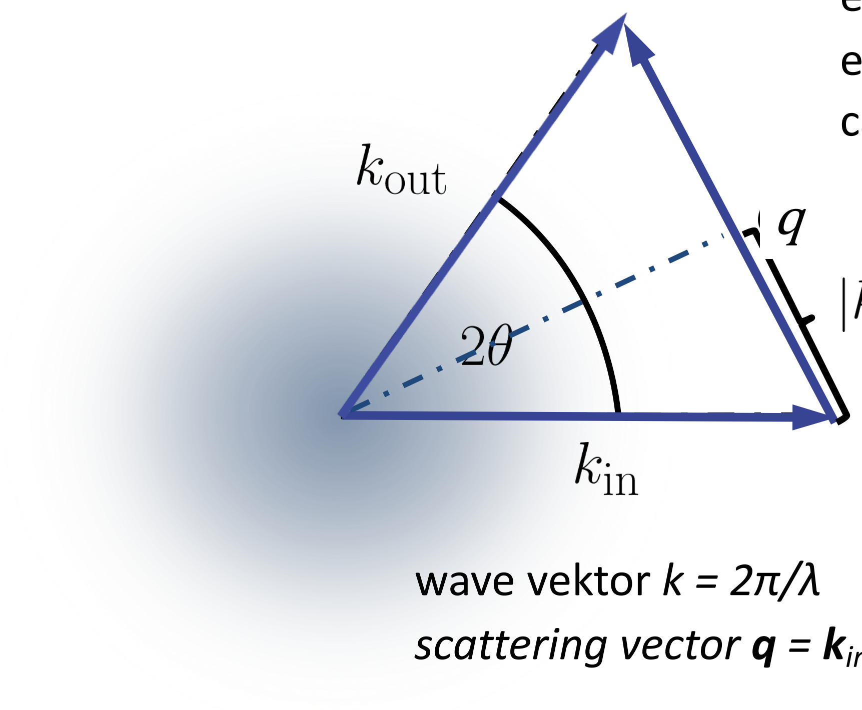
Elastic scattering of photons



elastic scattering: no loss in photon energy but direction or of the photon can change: scattering angle 2θ

Philip Willmott: Synchrotron and X-ray Free Electron Laser

Elastic scattering of photons



elastic scattering: no loss in photon energy but direction or of the photon can change: scattering angle 2θ

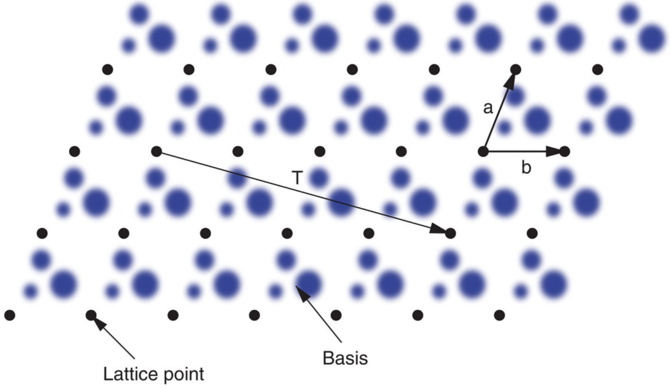
$$\boldsymbol{q} = 2|k|\sin\theta = (4\pi/\lambda)\sin\theta$$

wave vektor *k = 2π/λ*

scattering vector $\boldsymbol{q} = \boldsymbol{k}_{in} - \boldsymbol{k}_{out}$

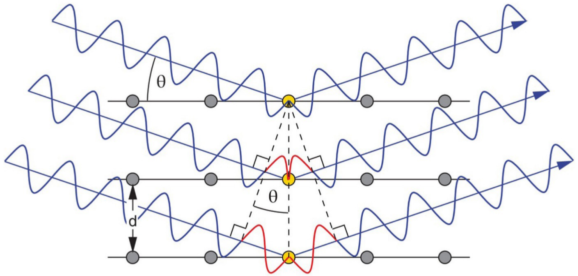
Philip Willmott: Synchrotron and X-ray Free Electron Laser

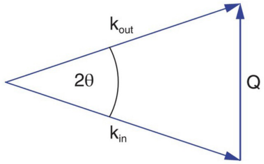
Diffraction on crystals and Bragg's law



If one derives it from an analogy with the slits, the distance between the atoms is the grating distance and the size of the atoms is the width of the slit.

Bragg's law

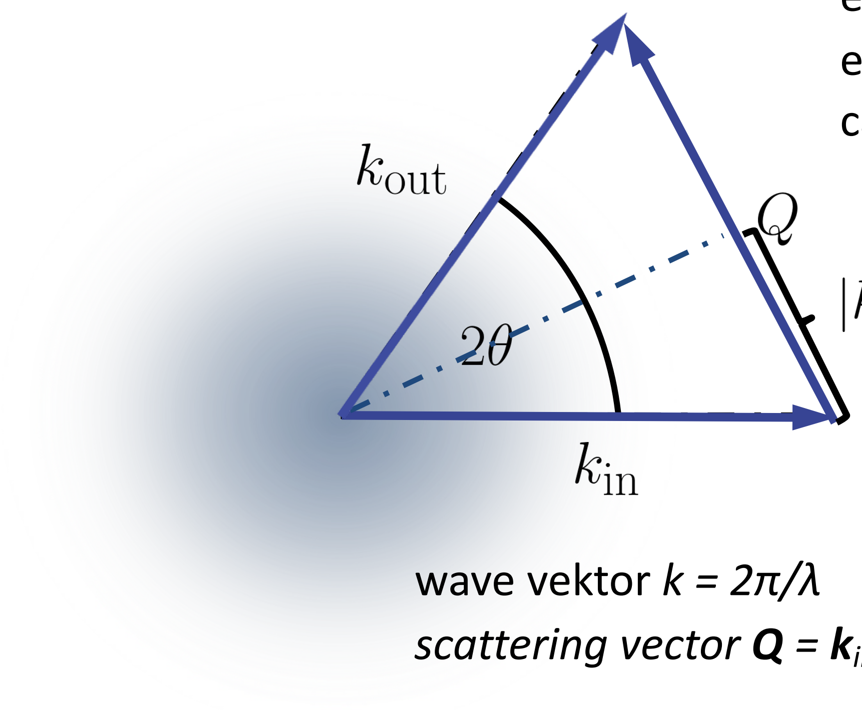




Willmott, P., John Wiley & Sons, Ltd: 2019 (2nd Edition).

$$m\lambda = 2d\sin\theta.$$

Elastic scattering of photons



elastic scattering: no loss in photon energy but direction or of the photon can change: scattering angle 2θ

$$Q = 2|k|\sin\theta = (4\pi/\lambda)\sin\theta$$

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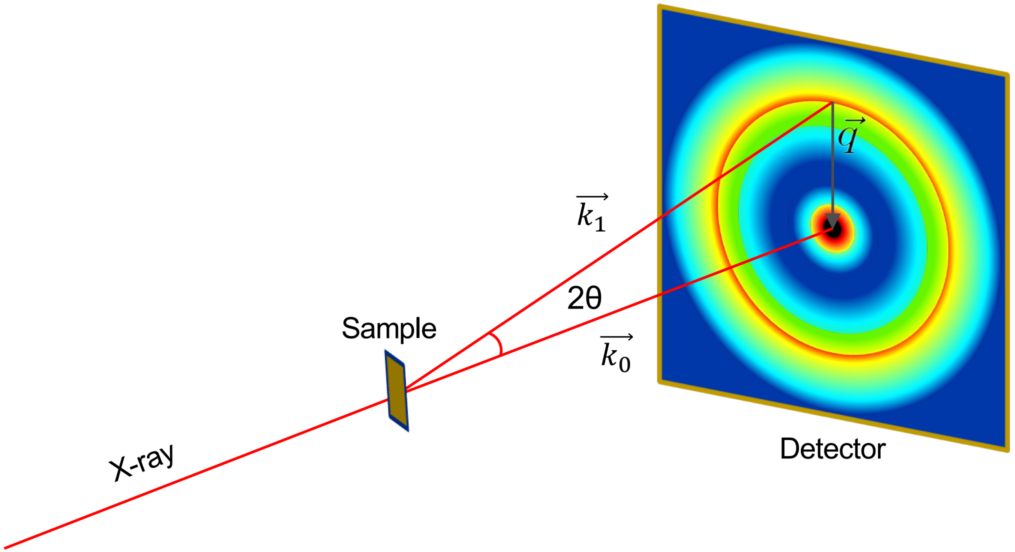
Philip Willmott: Synchrotron and X-ray Free Electron Laser

Scattering/Diffraction



$$\vec{q} = \vec{k_0} - \vec{k_1}$$

$$|\vec{q}| = q = \frac{4\pi \sin(\theta)}{\lambda}$$

Bragg's law

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

light λ = 400 to 600 nm

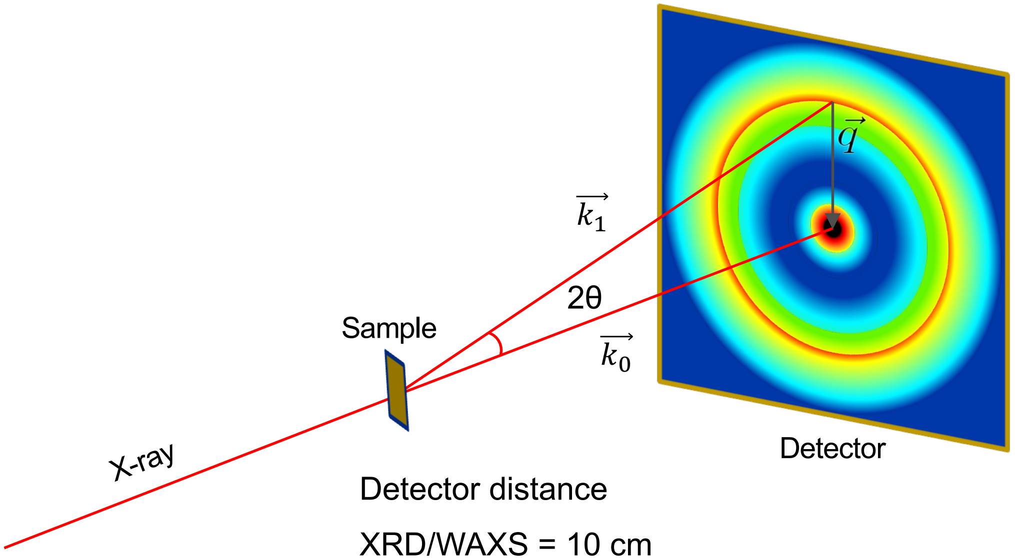
X-ray tube λ = 1 to 2 Å

synchrotron λ = 0.5 to 5 Å

thermal neutrons λ = 1 to 10 Å

Small-angle scattering

SAXS: scattering from variation in electron density distribution, NOT from single atoms as in XRD

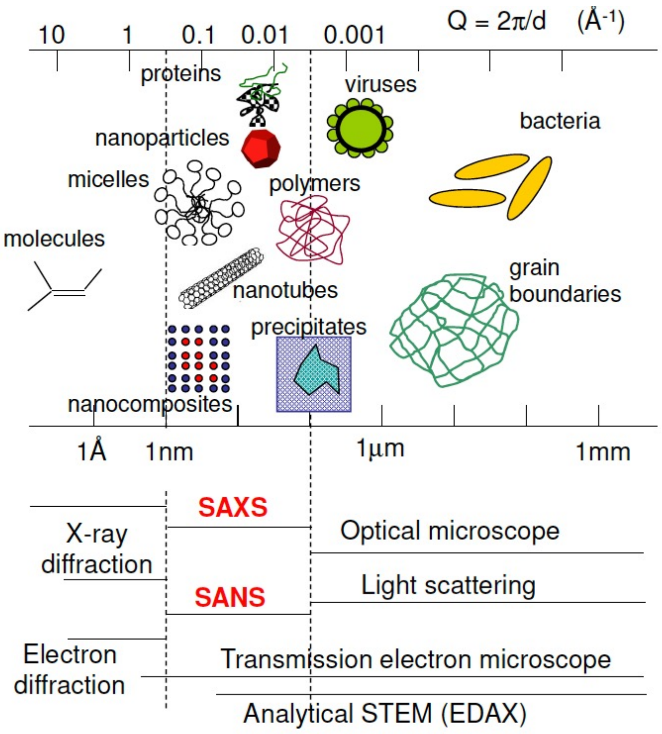


Detector distance

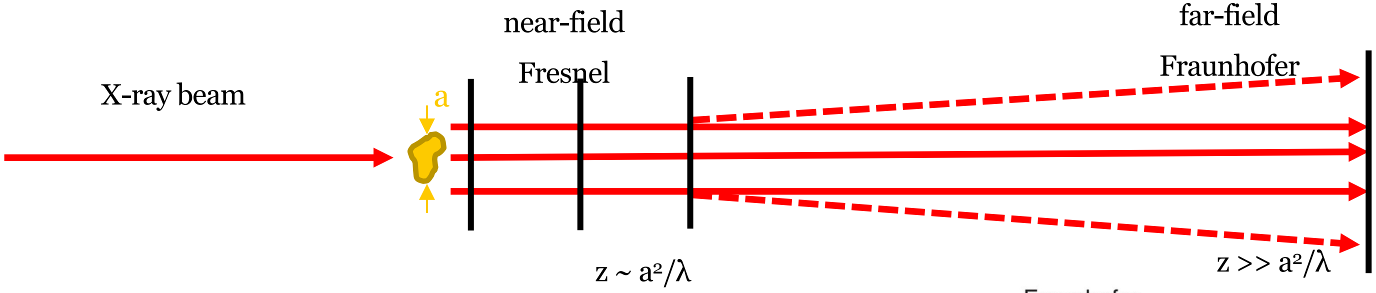
XRD/WAXS = 10 cm

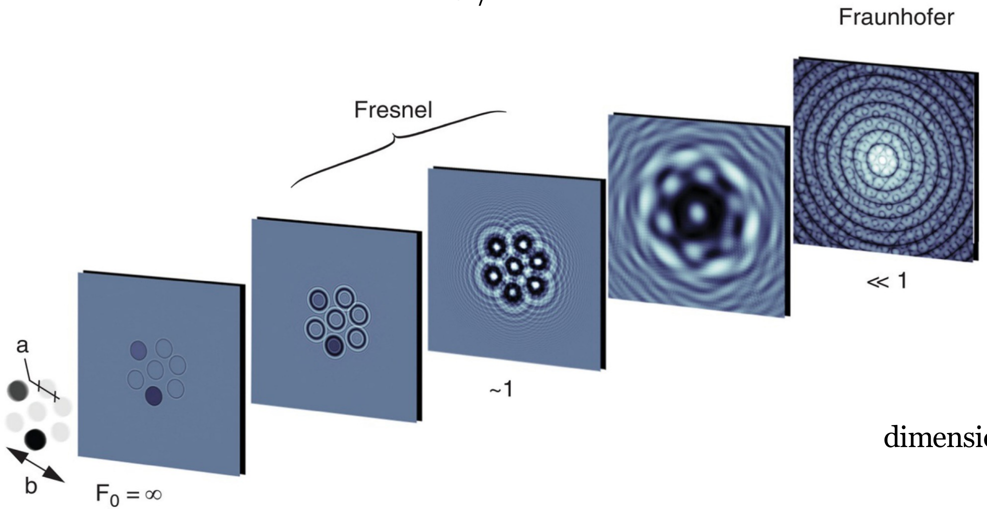
SAXS = several m

Size range comparison



Far-field Fraunhofer Regim





dimensionless Fresnel number $F_o = a^2/z\lambda$

Willmott, P., John Wiley & Sons, Ltd: 2019 (2nd Edition).

Demonstration: Fourier-Transform

Initial Python coding and refactoring:

Brian R. Pauw

http://www.lookingatnothing.com

With input from:

Samuel Tardif

Windows compatibility resolution:

David Mannicke

Chris Garvey

Windows compiled version:

Joachim Kohlbrecher

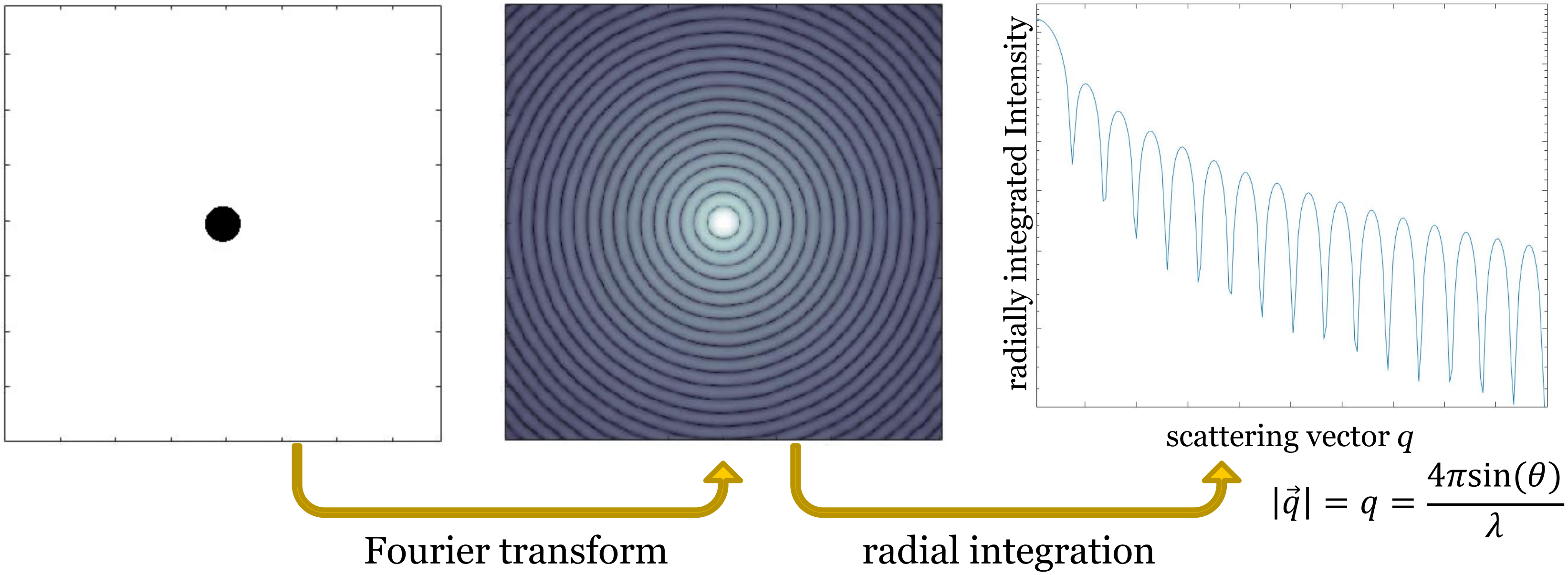
Sample images:

Joachim Kohlbrecher

simulation

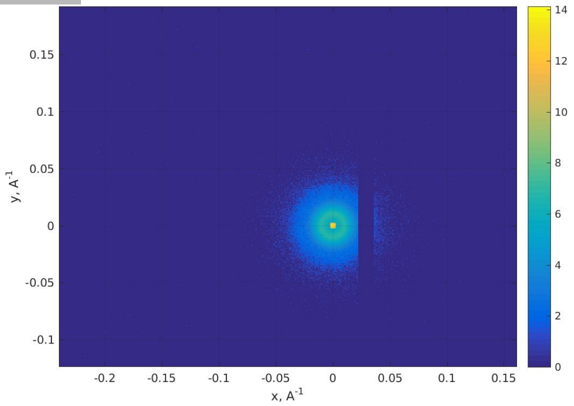
https://phet.colorado.edu/sims/html/wave-interference/latest/wave-interference_en.html

small-angle scattering



$$|\vec{q}| = q = \frac{4\pi\sin(\theta)}{\lambda}$$

small-angle scattering: first analysis step



raw data: 2D scattering pattern

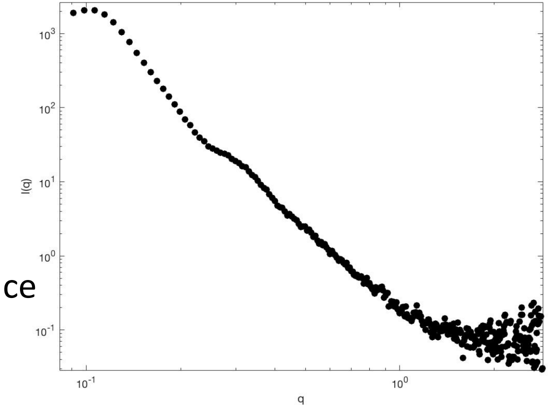
(example measured on a Labsource)

beam center

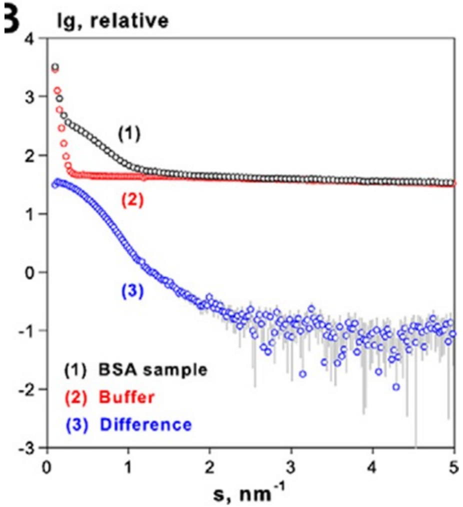
detector distance

wavelength λ

mask



average scattering profile I(q)

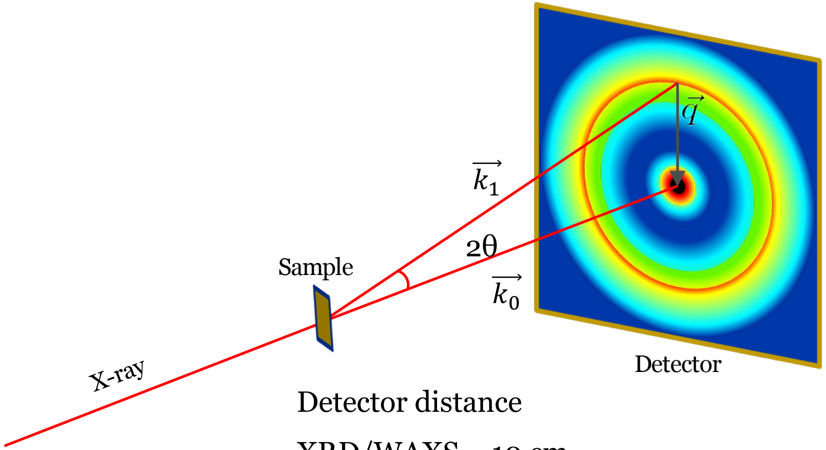


background substraction

particles in solution: measure only solvent

solid sample on support: measure only support material

SAXS/WAXS at a labsource



scattering vector q

$$\boldsymbol{q} = \boldsymbol{k}_0 - \boldsymbol{k}$$

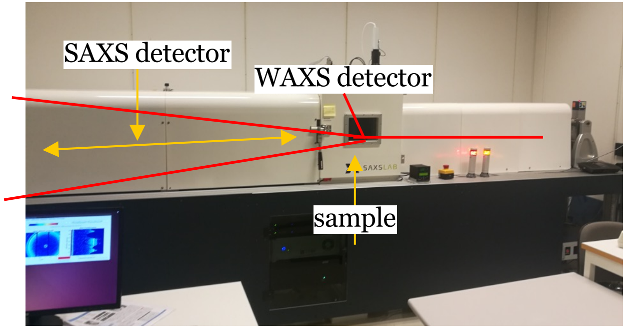
$$|\vec{q}| = q = \frac{4\pi \sin(\theta)}{\lambda}$$

Detector distance

XRD/WAXS = 10 cm

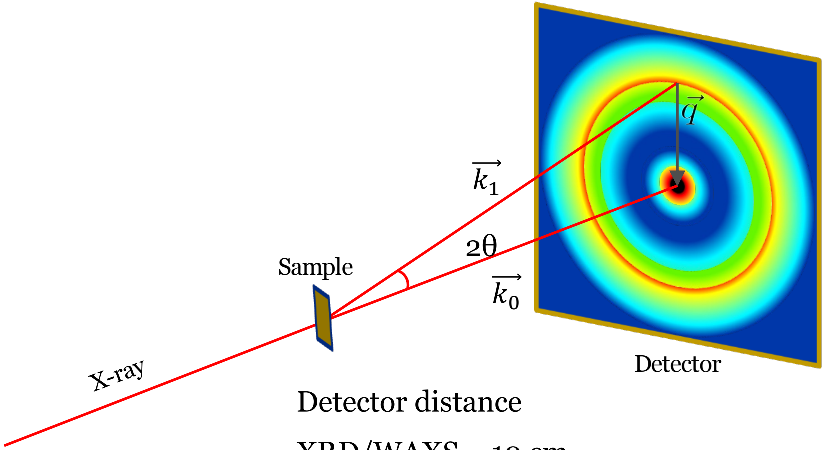
SAXS = several m

SAXSLAB instrument at CMAL, Chalmers



→ new Labsource SAXS available at EPFL!

SAXS/WAXS
at a synchrotron beamline



Detector distance

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$$\vec{q} = \vec{k_0} - \vec{k_1}$$

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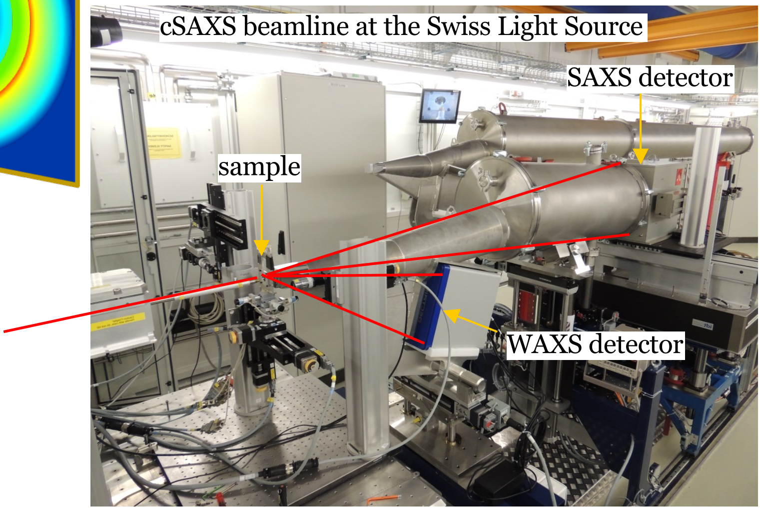
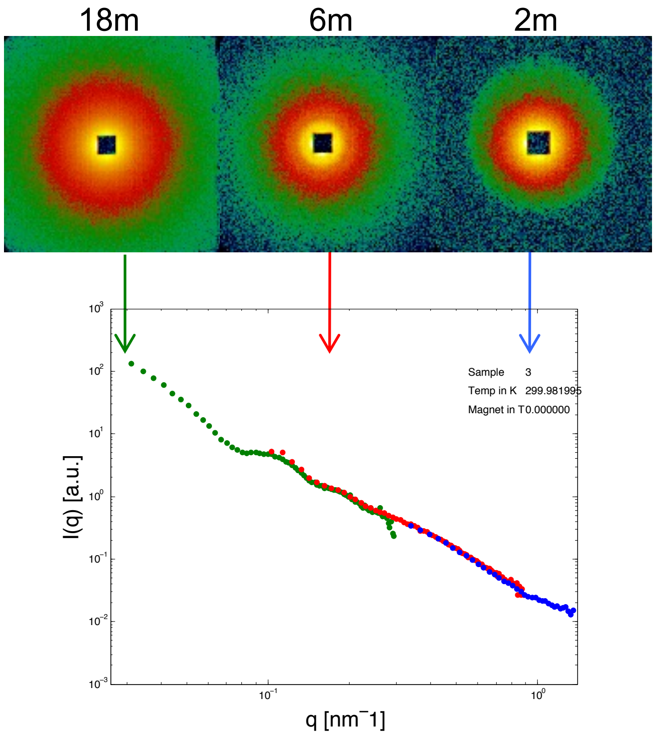


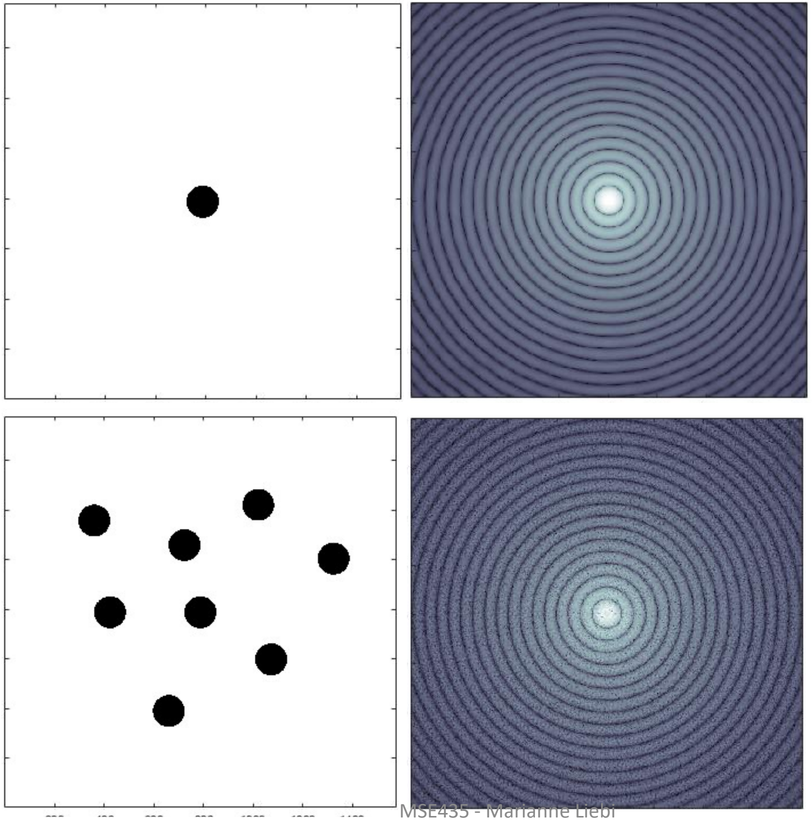
SANS: radial integration



vesicles July 2010

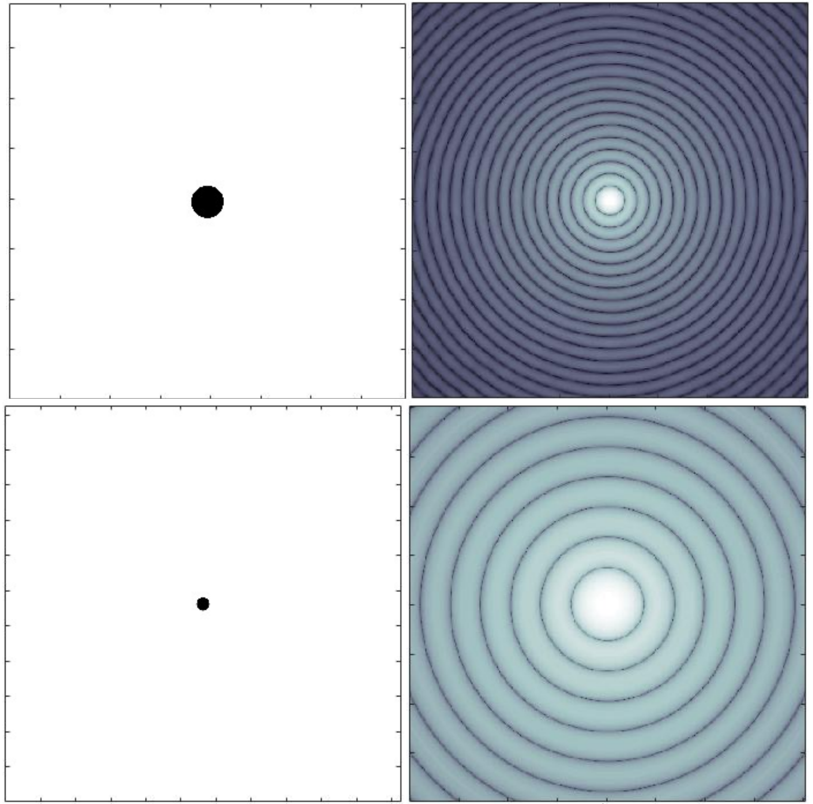
SANS instruments at SINQ

small-angle X-ray scattering



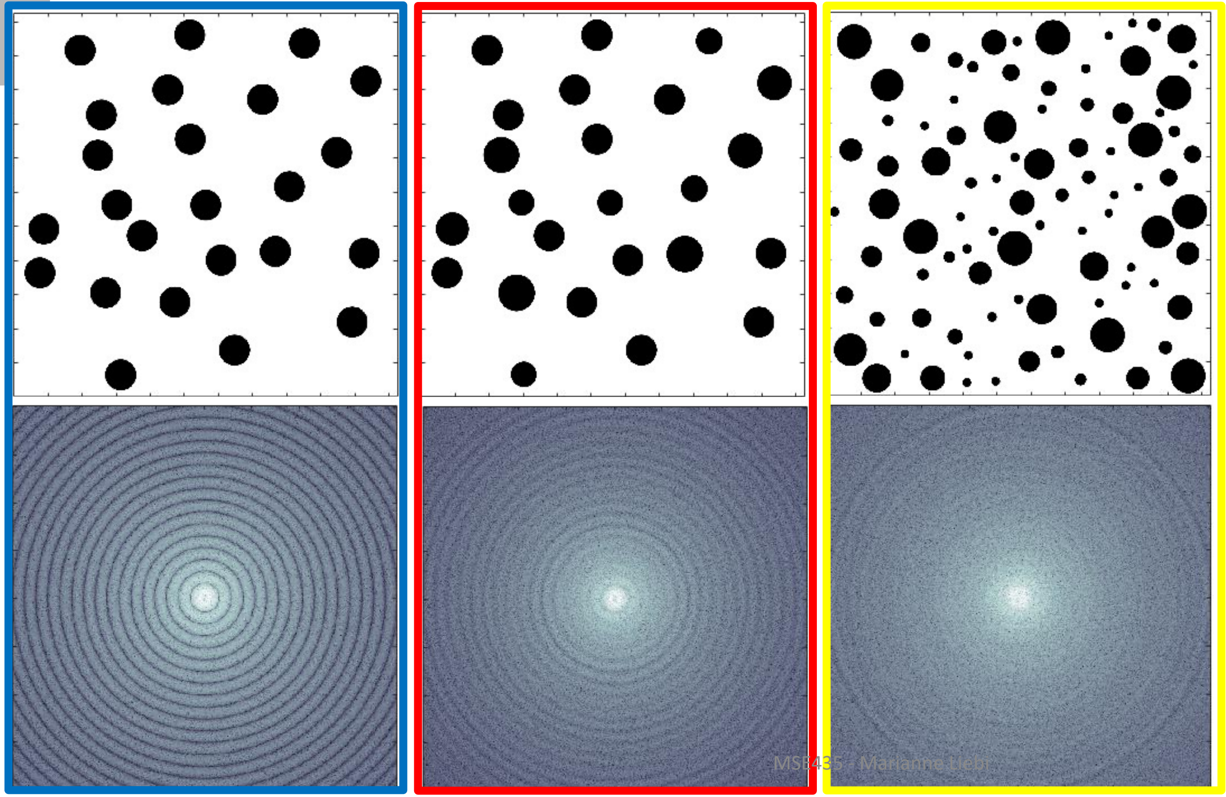
scattering pattern shows
average over particle ensemble

small-angle X-ray scattering size

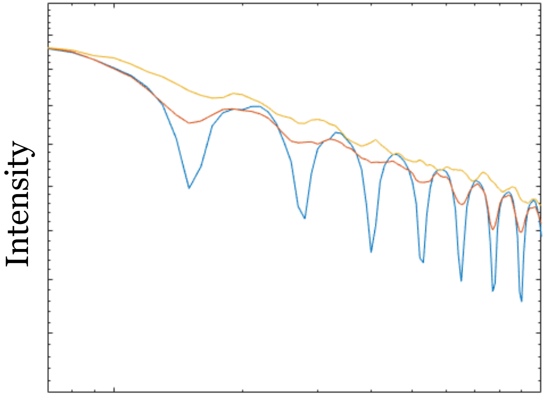


smaller structures scatter at larger angles

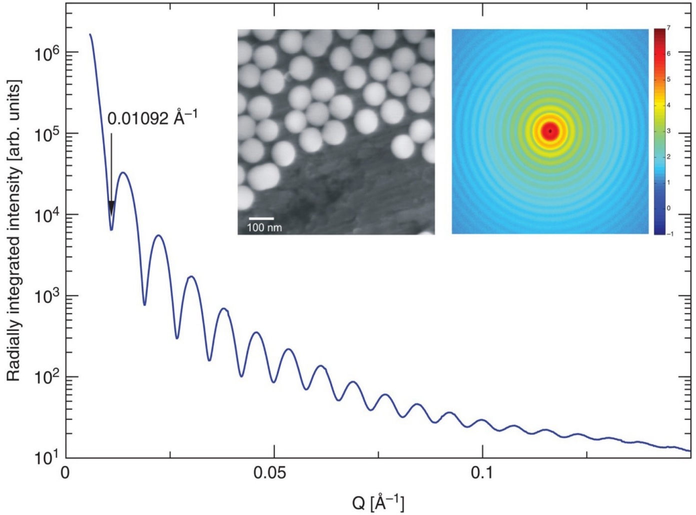
small-angle X-ray scattering polydispersity



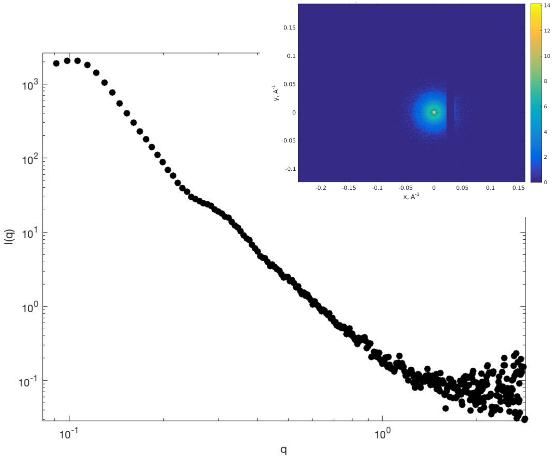
effect of polydispersity



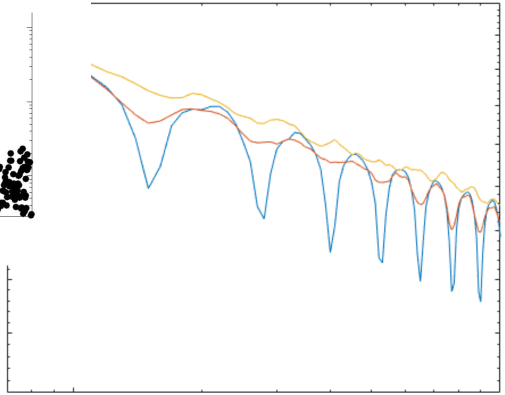
small-angle X-ray scattering polydispersity



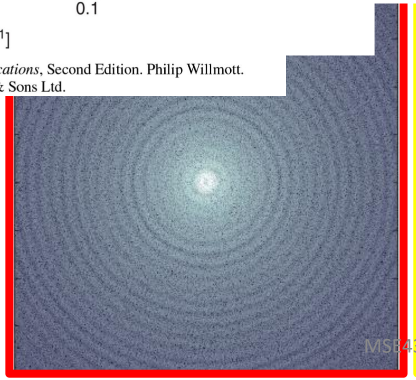
An *Introduction to Synchrotron Radiation: Techniques and Applications*, Second Edition. Philip Willmott.

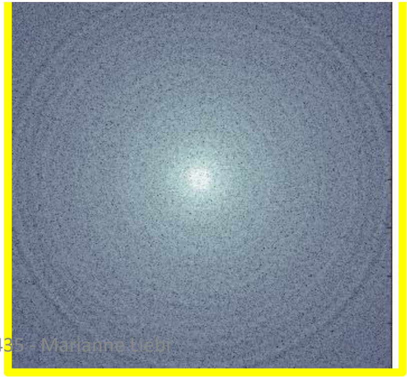


polydispersity

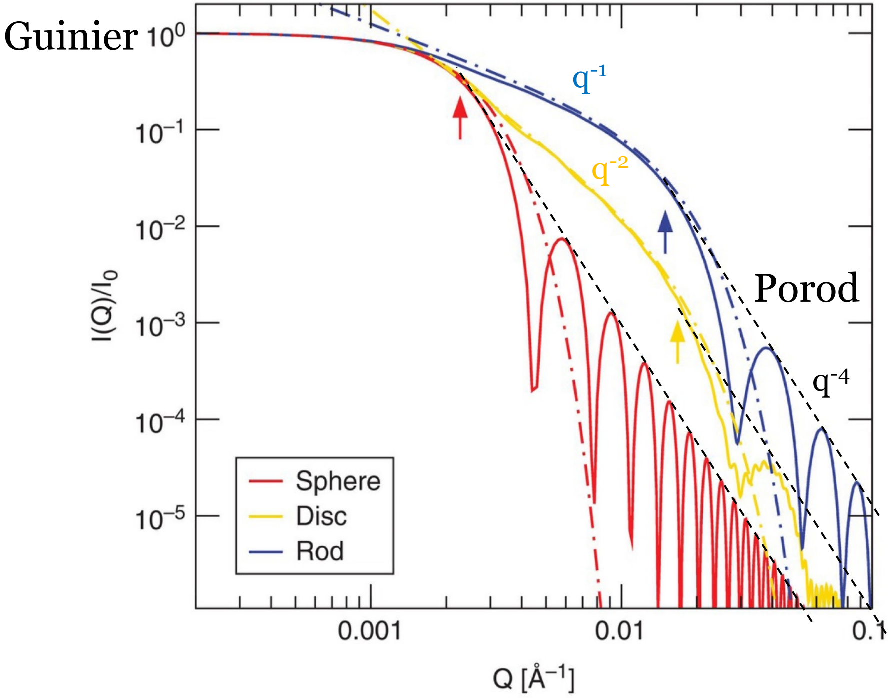


scattering vector q





small-angle X-ray scattering
size & shape



sphere, disc and rod with the same characteristic length (radius of gyration) → same scattering at low q (Guinier regime)

intermediate region depends on fractal dimension

q^{-1}: rod

q^{-2}: disk

at high q: Porod regime q^{-4}

An Introduction to Synchrotron Radiation: Techniques and Applications, Second Edition. Philip Willmott.

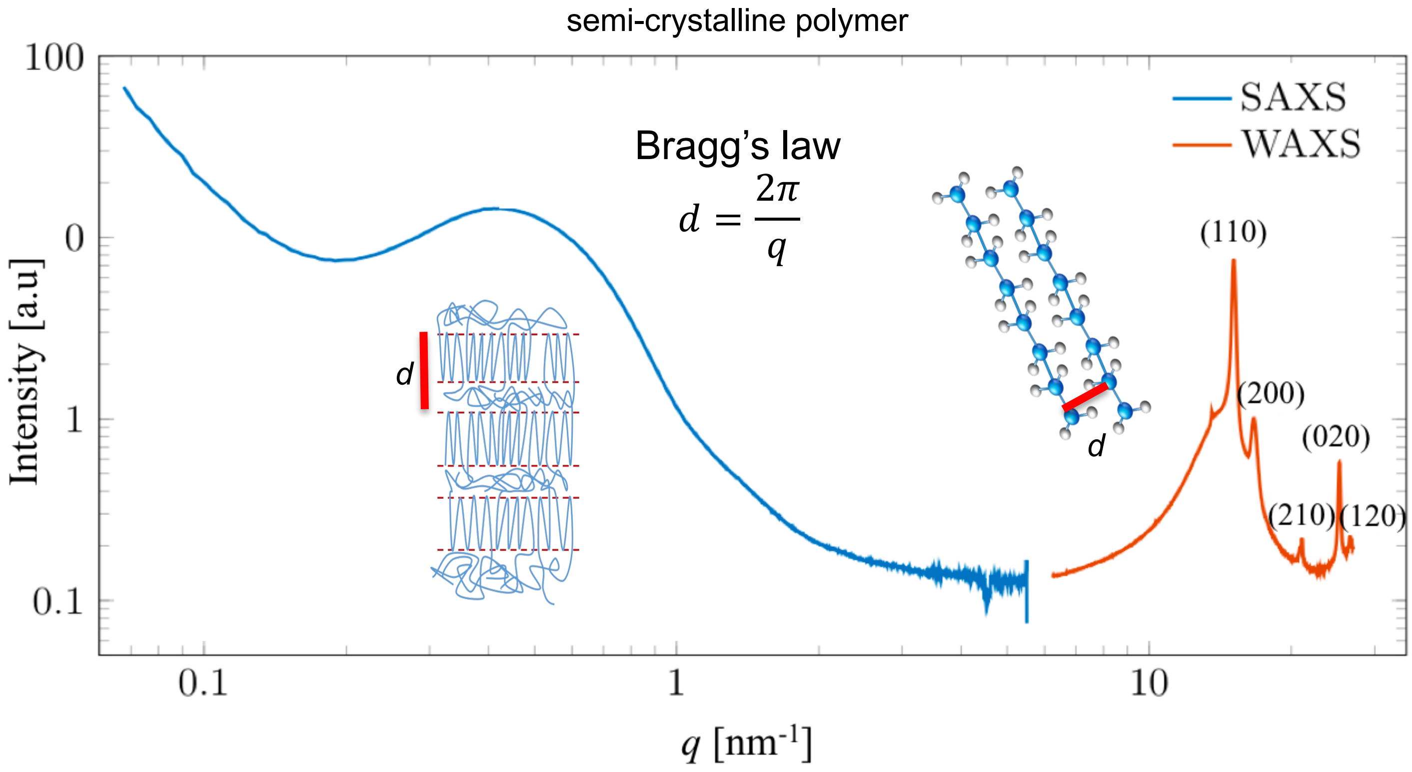
Small-angle scattering

- Fraunhofer approx. Fourier theorem:

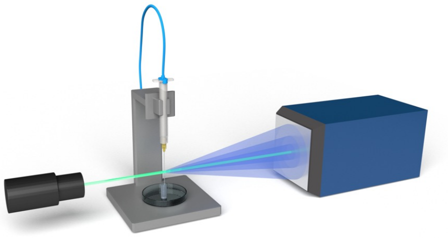
the field distribution at a distant detector is the Fourier transform of the electric field distribution in the exit plane of a sample
BUT we don't measure field but the intensity, which is the squared field: complex quantity: complex part (the phase) get lost → **the phase problem**

→we cannot directly calculate back the particles shape and size, different approaches to retrieve information from the scattering pattern
  - **model independent**
  - mathematically model the SAXS curve
  - pair distance distribution function (PDDF)
  - iterative phase retrival

Small-angle scattering: any peaks?

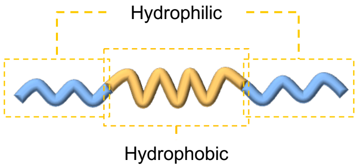


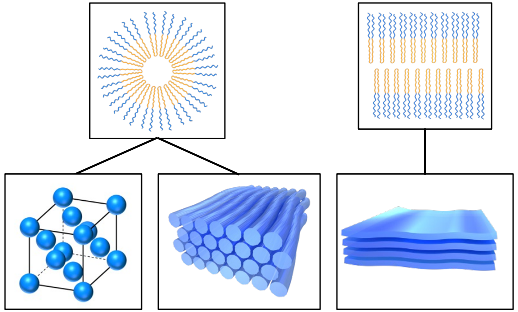
Small-angle scattering: any peaks?

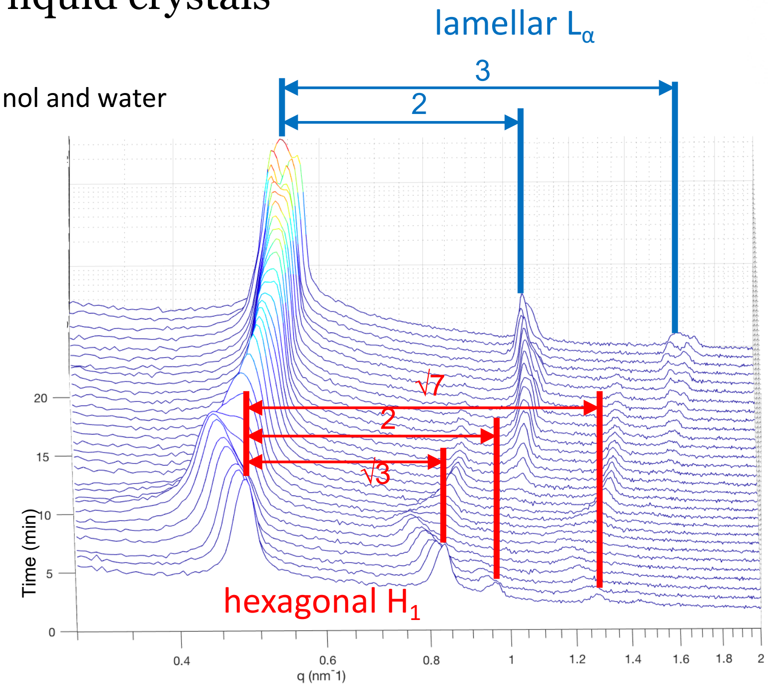


3D printing of lyotropic liquid crystals

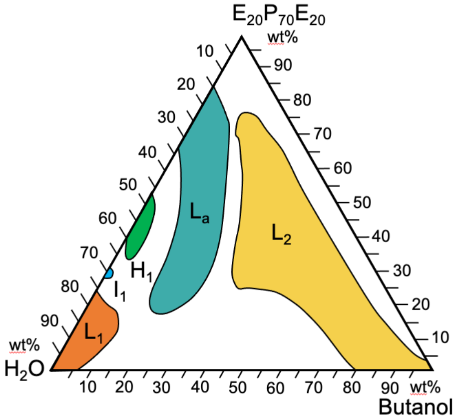
Pluronic F-127 ($EO_{100}PO_{70}EO_{100}$), 1-butanol and water







time-resolved measurements of phase changes after 3D printing



Rodriguez-Palomo A., Lutz-Bueno, V., Guizar Sicairos, M. , Kádár, R., Andersson, M., Liebi M. *Additive Manufacturing* **2021**, 47, 102289.

Small-angle scattering

low q: information about interaction s between the particles and particle size, no information about shape of particle
intermediate q: in the order of the particle size, particle shape
high q: Porod's region contrast at the interface between the particle and their surrounding, measure of surface area

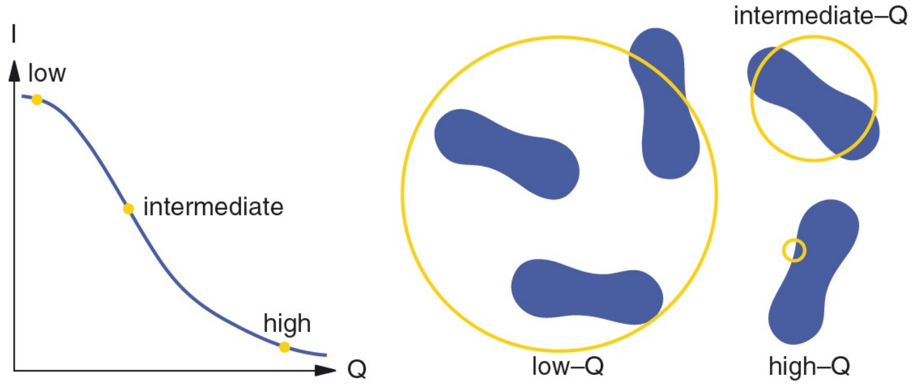
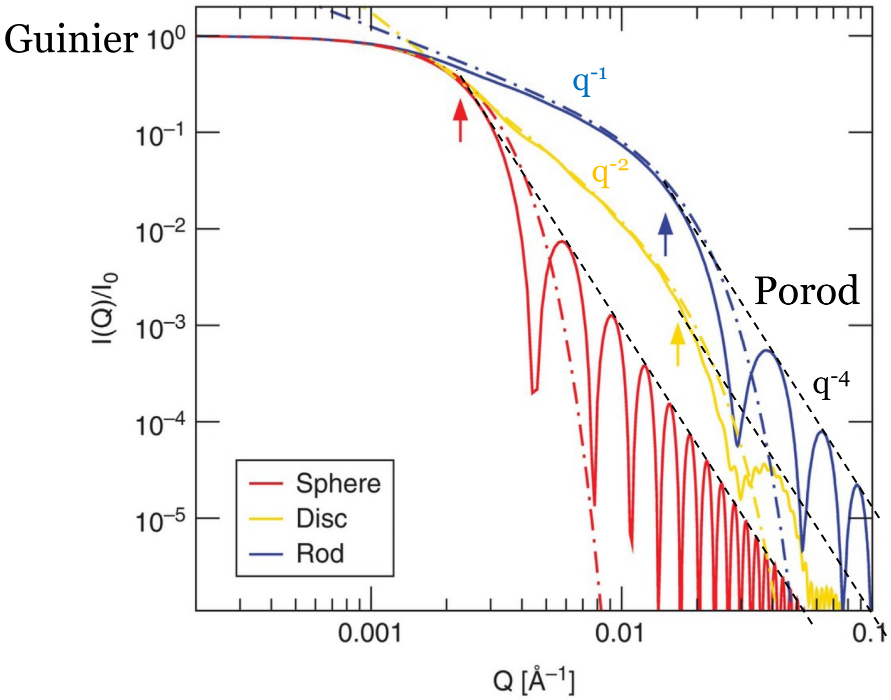


Figure 5.67 *The three Q-domains of SAXS.*

Willmott, P. (2011). Scattering Techniques. An Introduction to Synchrotron Radiation, John Wiley & Sons, Ltd: 133-221.

small-angle X-ray scattering
size & shape



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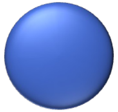
intermediate region depends on fractal dimension
q^{-1}: rod

q^{-2}: disk

at high q: Porod regime q^{-4}

Guinier approximation

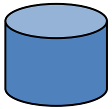
- Radius of gyration R_G: “weight average” of all radii present in the sample in analogy to mechanics



solid sphere radius *R*: $$R_G^2 = \frac{3}{5} R^2$$

thin rod length *L:* $$R_G^2 = \frac{1}{12} L^2$$

thin disc radius *R*: $$R_G^2 = \frac{1}{2} R^2$$

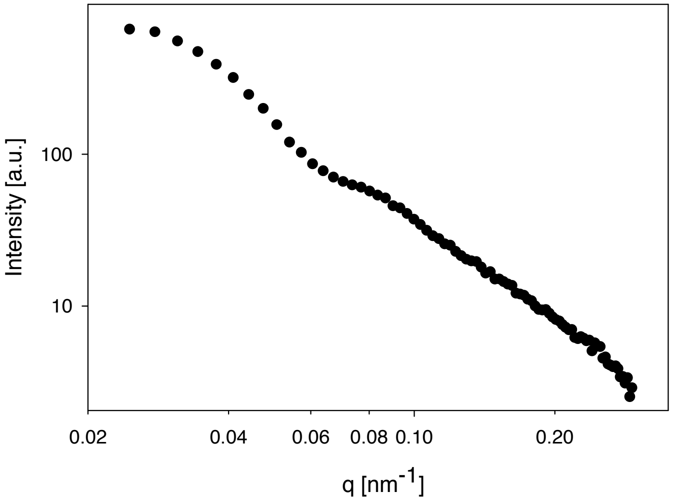


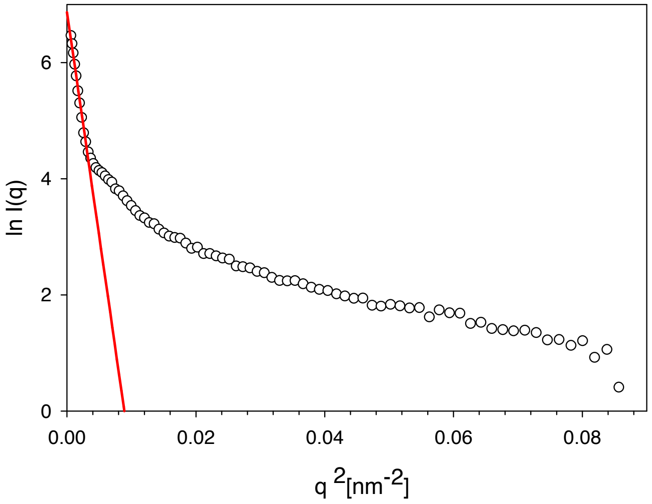
cylinder of height *h* and radius *R*: $$R_G^2 = \frac{R^2}{2} + \frac{h^2}{12}$$

Guinier approximation

Guinier approximation valid only in the region of small q values, R_G can be derived

$$I(q) \approx I(0)e^{-(1/3)q^2 R_G^2}$$

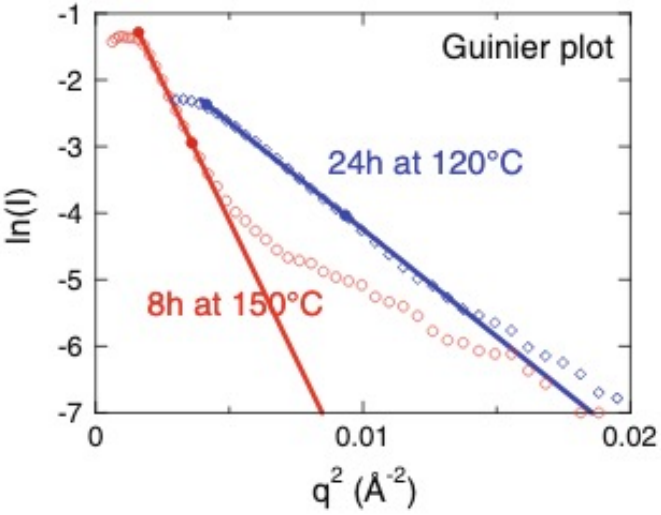




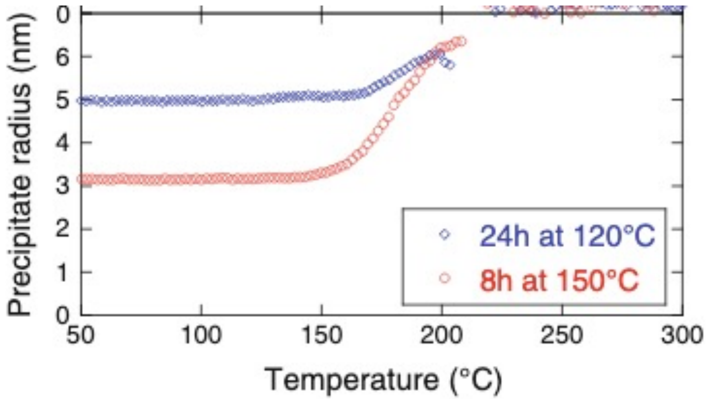
A not existing linear range indicates the presence of very large structures which scatter at low *q*, perhaps outside the accessible *q* range → change detector distance, change λ, check with SLS

SAXS on metal alloys

SAXS measurements on Al-Mg-Li alloy for two aging conditions



Evolution of precipitate radius during ramp heating experiments on these two initial aging conditions



Deschamps A. and De Geuser F. Metallurgical and Materials Transactions A, 44, 2013, 77-86

Small-angle scattering: Power law

Slope of the scattering curve: power law behavior

q^{-D} with D the **fractal dimension**

How does the mass changes as a function of the size

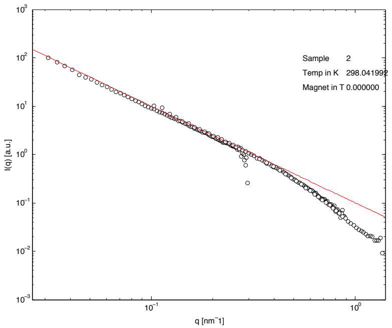
rod-like D=1

disk-like D=2

in general: the higher D, the more compact is the structure

D=4 Porod scattering

→ sharp interphase of two phases, information about surface area



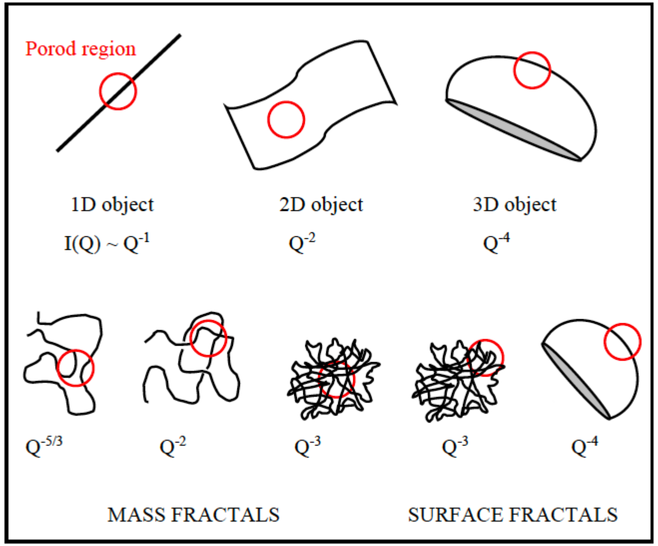
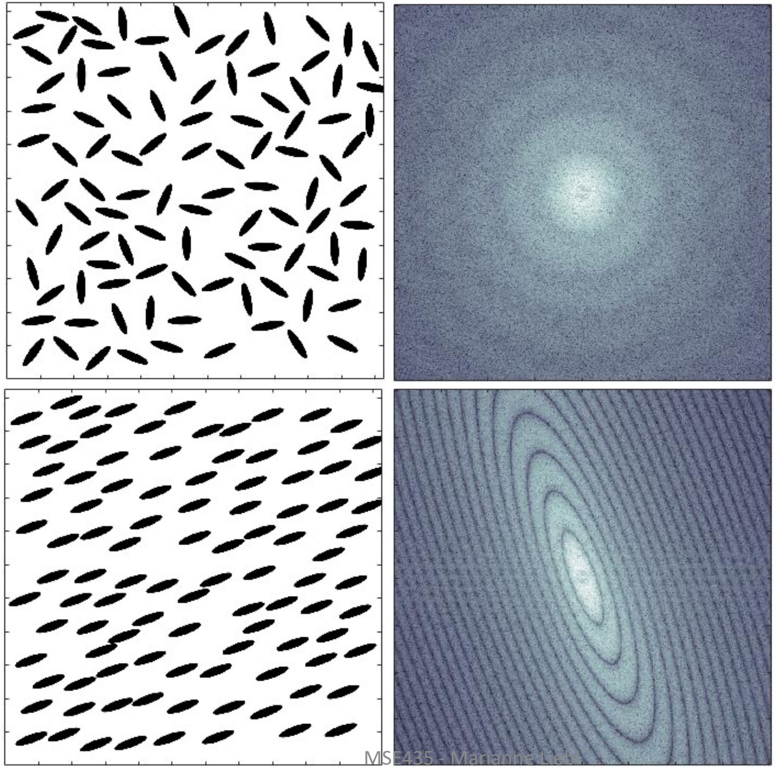


Figure 7: Assortment of Porod law behaviors for different shape objects.

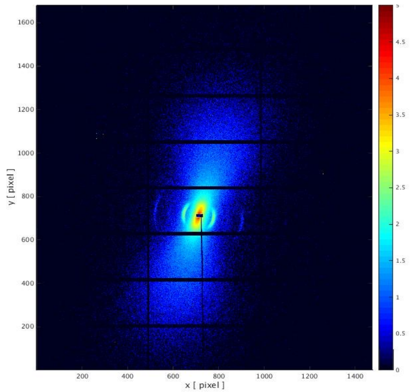
small-angle X-ray scattering: anisotropic particles



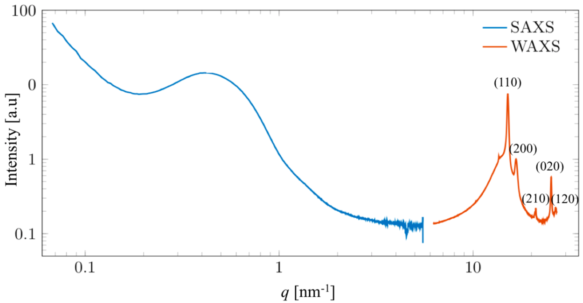
anisotropic and aligned particles produce anisotropic scattering

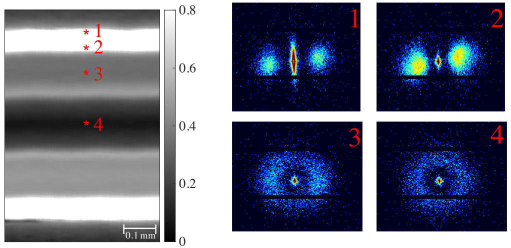
→ direct determination of orientation of nanoparticles!

SAXS of anisotropic materials

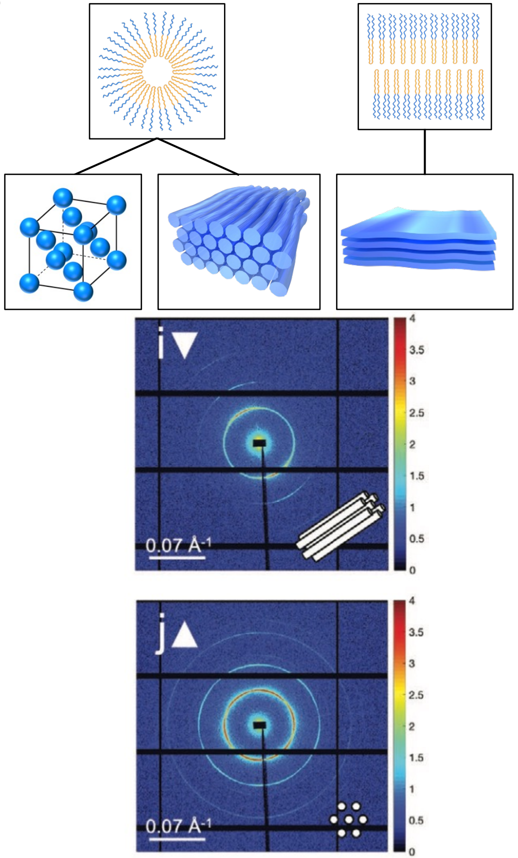


SAXS signal from mineralized collagen in human bone



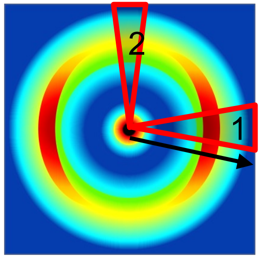


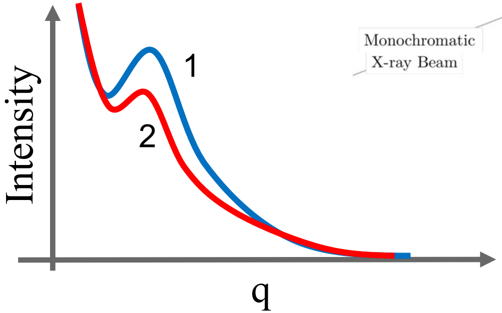
SAXS signal from different layers in injection-molded polymers

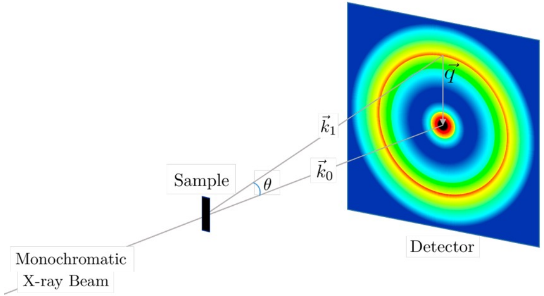


SAXS signal from liquid crystals oriented in flow

SAXS of anisotropic materials

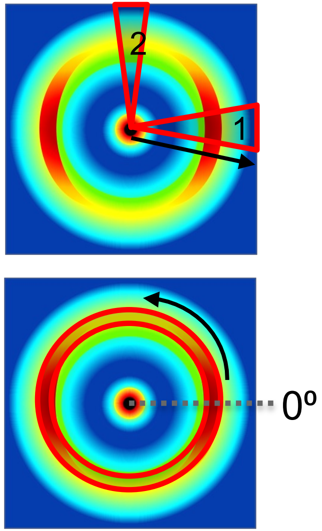


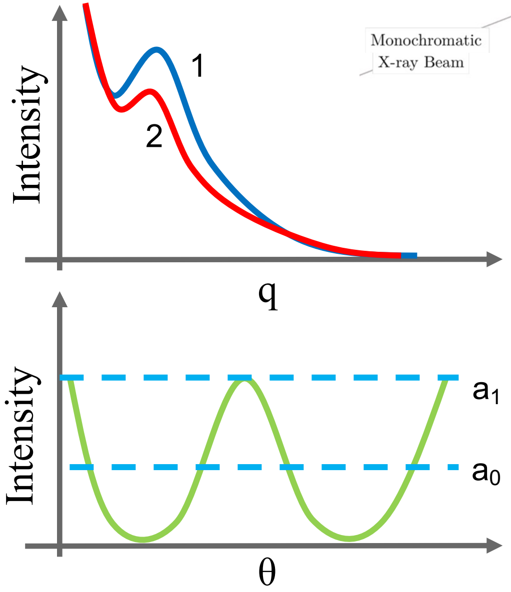


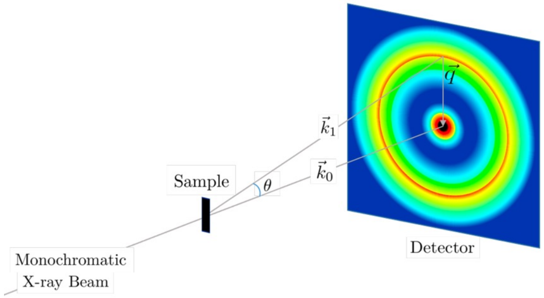


$$|\vec{q}| = q = \frac{4\pi}{\lambda} sin\frac{\theta}{2}$$

SAXS of anisotropic materials







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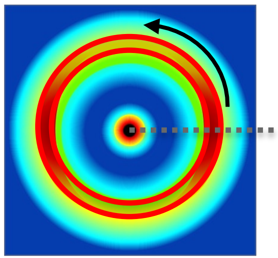

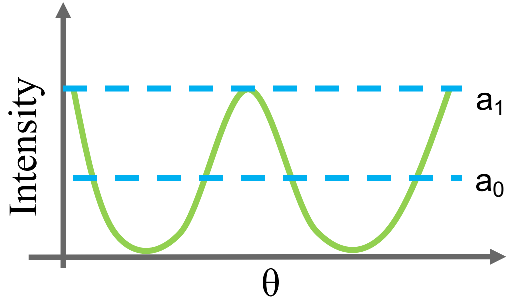

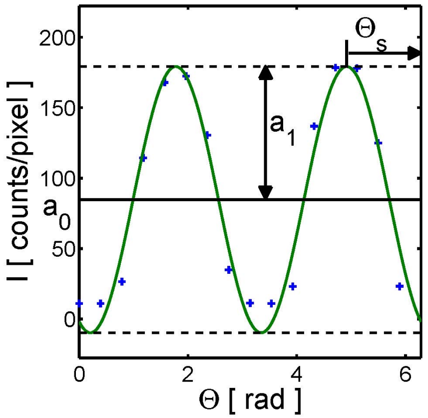

$$I\left(n_\Theta\right) \approx a_0 + a_1 \cos(2\pi n_\Theta / N_\Theta - \Theta_s)$$

$\frac{a_0}{a_1}$ degree of orientation

Bunk, O. *et al.* Multimodal x-ray scatter imaging. *New Journal of Physics* **11**, (2009).

Small-angle scattering

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BUT we don't measure field but the intensity, which is the squared field: complex quantity: complex part (the phase) get lost → **the phase problem**

→ we cannot directly calculate back the particles shape and size, different approaches to retrieve information from the scattering pattern
  - model independent
  - **mathematically model the SAXS curve**
  - pair distance distribution function (PDDF)
  - iterative phase retrival

Mathematical modelling of Small-angle scattering

$$I(q) = (\rho_{\mathrm{P}} - \rho_M)^2 N_P V_P^2 P(q) S(q)$$

$\rho_{\mathrm{P}} - \rho_M$: contrast in scattering length density between particle and matrix

N_{P}: number of particles

V_{P}: volume of particles

Formfactor P(q)

Intra-particle interference

shape, size

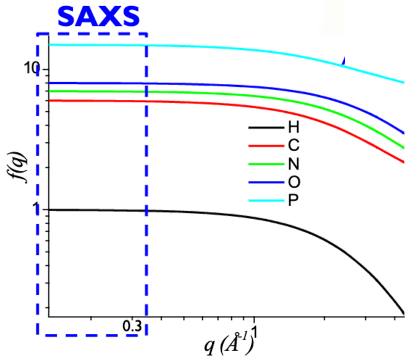
Structure factor S(q)

Inter-particle interference

spacing, interactions

for X-rays: electron density difference

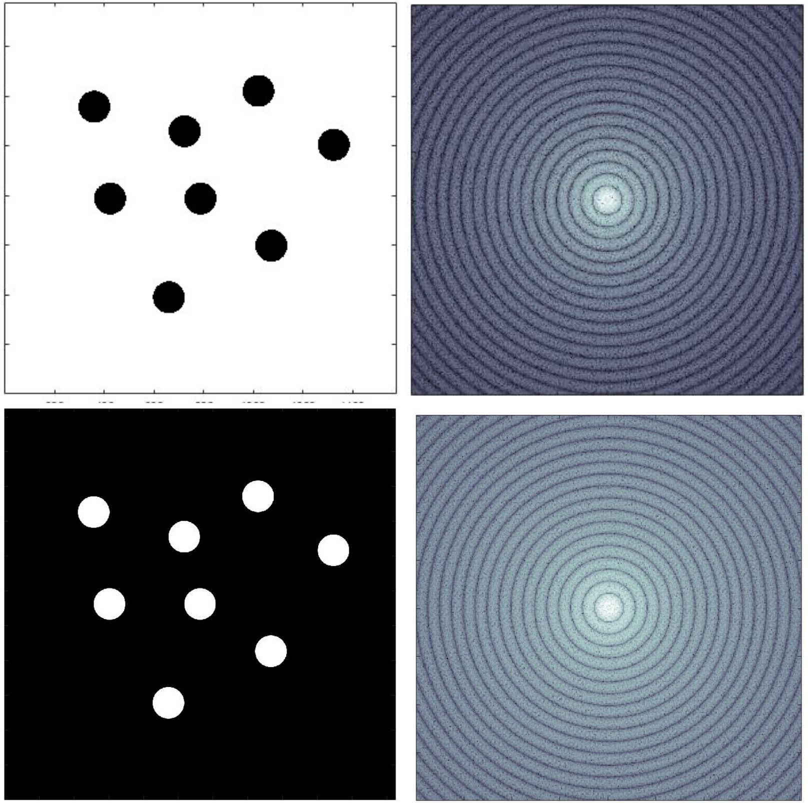
for neutrons: neutron scattering length density difference



Data taken from International Tables for Crystallography, Vol. C, Table 6.1.1.1

note that the atomic form factor in the SAXS regime is a constant

small-angle X-ray scattering



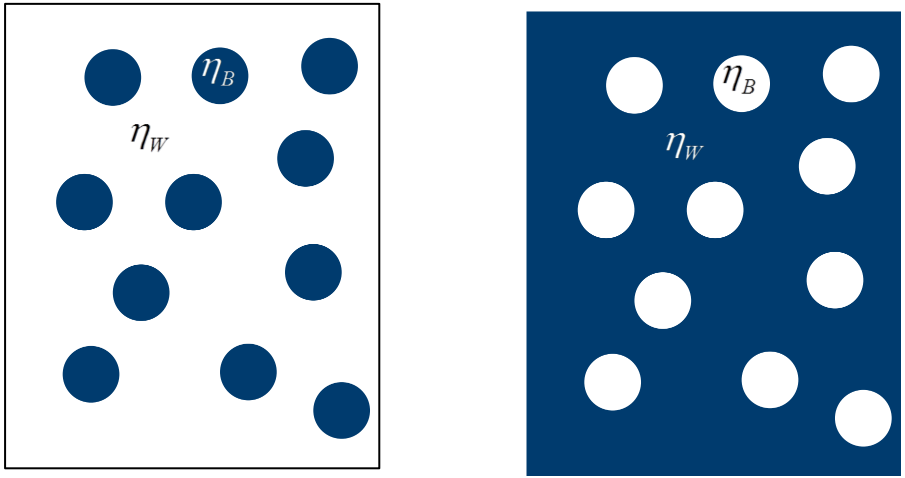
Babinet's principle:

particle vs. pores

same diffraction pattern apart from overall intensity

Babinet's principle: particles or pores?

two structures where only the scattering length densities are exchanged give the same scattering (incoherent scattering may be different)



$$I(\mathbf{q}) \propto (\eta_B - \eta_W)^2$$

- contrast is relative
- loss of phase information (is $\eta_B > \eta_W$?)

Model dependent fitting: Formfactor

$$I(q) = (\rho_P - \rho_M)^2 N_P V_P^2 P(q) S(q)$$

3.1. Spheres & Shells

3.1.1. Sphere.

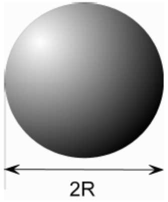


FIGURE 3.1. Sphere with diameter $2R$

$$I_{\text{Sphere}}(Q,R) = K^2(Q,R,\Delta\eta) \tag{3.1a}$$

with

$$K(Q,R,\Delta\eta) = \frac{4}{3}\pi R^3 \Delta\eta\, 3\frac{\sin QR - QR\cos QR}{(QR)^3} \tag{3.1b}$$

The forward scattering for $Q = 0$ is given by

$$\lim_{Q=0} I_{\text{Sphere}}(Q,R) = \left(\frac{4}{3}\pi R^3 \Delta\eta\right)^2$$

Input Parameters for model Sphere:

R: radius of sphere R
- - -: not used
- - -: not used
eta: scattering length density difference between particle and matrix $\Delta\eta$

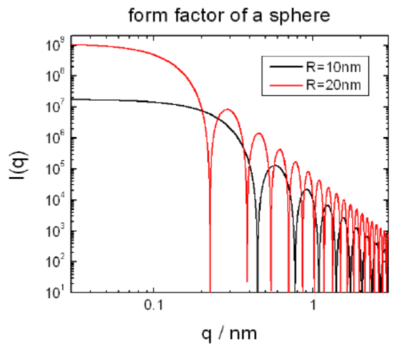


FIGURE 3.2. Scattering intensity of spheres with radii R = 10nm and R = 20nm. The scattering length density contrast is set to 1.

sasfit manual: https://kur.web.psi.ch/sans1/SANSSoft/sasfit.pdf

Model dependent fitting: Structure factor

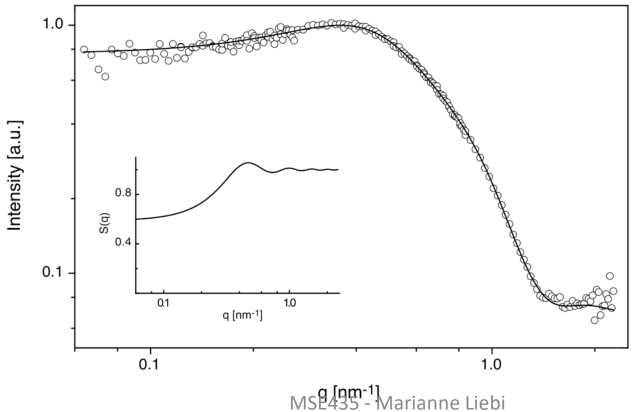
$$I(q) = (\rho_P - \rho_M)^2 N_P V_P^2 P(q) S(q)$$

Formfactor P(q)

Structure factor S(q)

Interacting particles

→Measure different concentrations



example: Phospholipid micelle

ellipsoidal form factor

hard sphere structure factor (hard sphere radius larger than radius of micelles)

→ self-assembly & surfactants

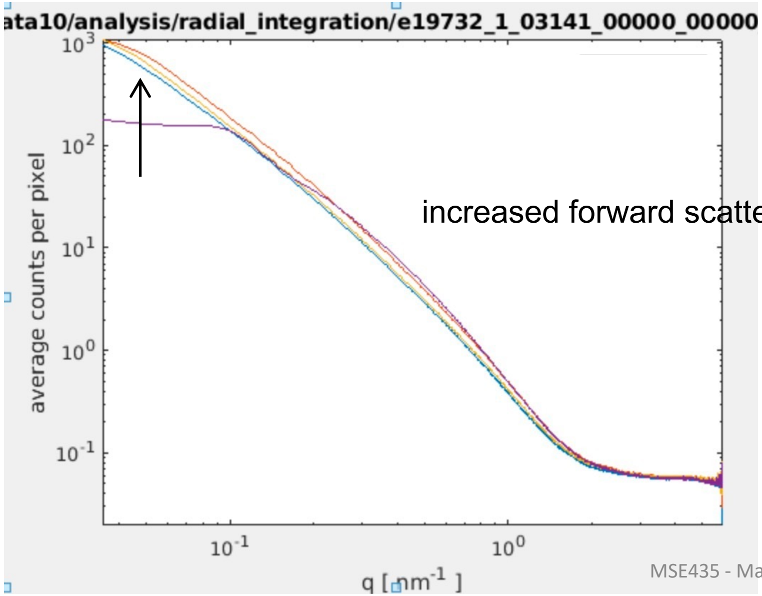
Beck, P., et al. (2010). Langmuir **26**(8): 5382-5387.

Model dependent fitting: Structure factor

$$I(q) = (\rho_P - \rho_M)^2 N_P V_P^2 P(q) S(q)$$

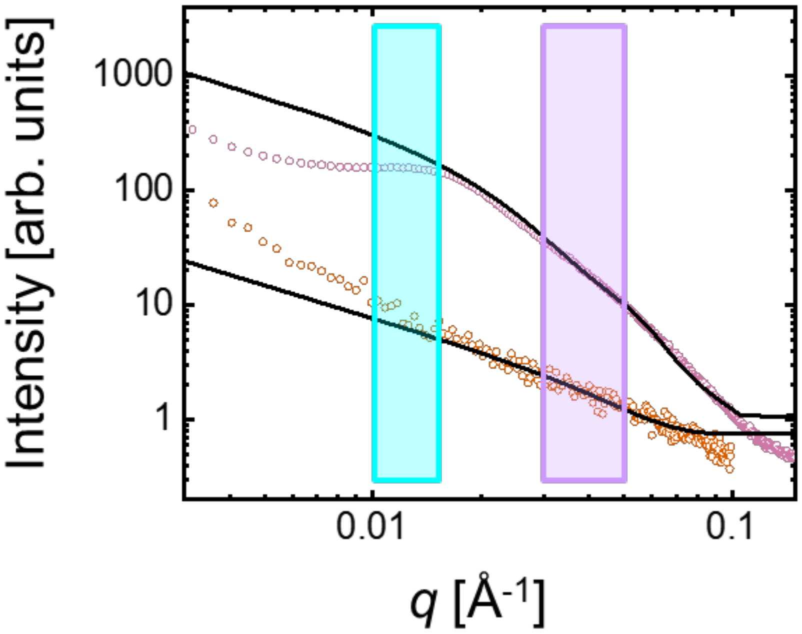
Structure factor S(q)

Interacting particles



increased forward scattering: typical sign of aggregation

Example: cellulose nano crystals (CNC) and cellulose nano fibrils (CNF)



4 wt% CNC dispersion (pink)

what does the slope say on the shape?

0.25 wt% CNF dispersion (orange)

Corona, P. T., Berke, B., Guizar-Sicairos, M., Leal, L. G., Liebi, M., & Helgeson, M. E. (2022). Fingerprinting soft material nanostructure response to complex flow histories. *Physical Review Materials*, *6*(4), 1–14. https://doi.org/10.1103/PhysRevMaterials.6.045603

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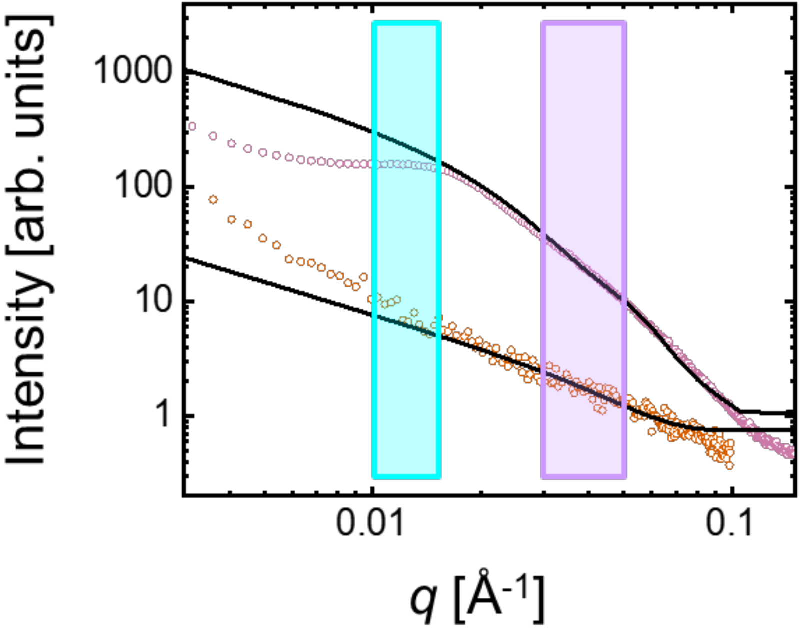
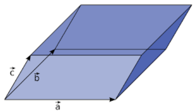
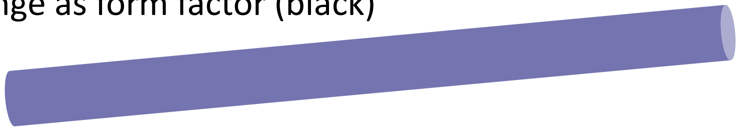


4 wt% CNC dispersion (pink): parallelepiped shape with cross section dimensions of 6 nm and 18 nm as form factor (black)



0.25 wt% CNF dispersion (orange): cylindrical shape with particle radius of 6 nm, length longer than the measured q-range as form factor (black)



what indicates the deviation from fit with a structure factor at low q?

Corona, P. T., Berke, B., Guizar-Sicairos, M., Leal, L. G., Liebi, M., & Helgeson, M. E. (2022). Fingerprinting soft material nanostructure response to complex flow histories. *Physical Review Materials*, *6*(4), 1–14. https://doi.org/10.1103/PhysRevMaterials.6.045603

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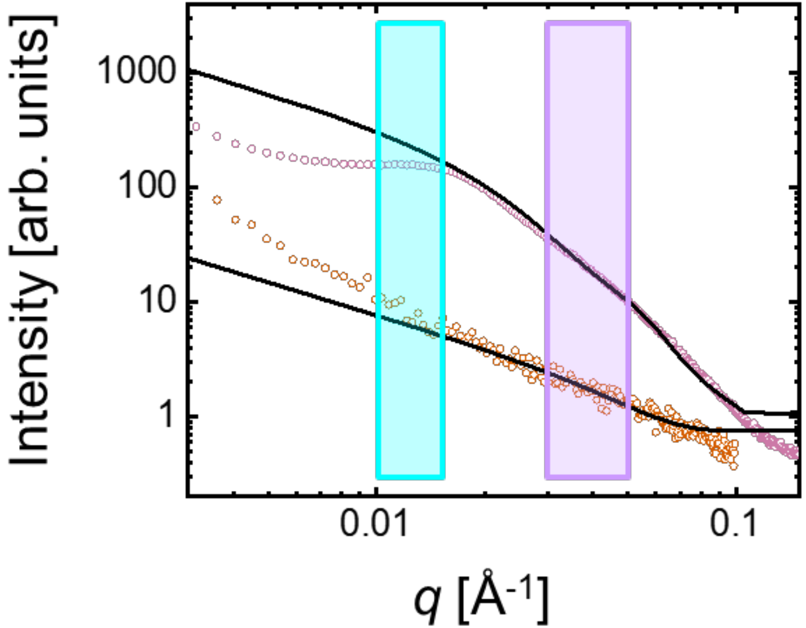
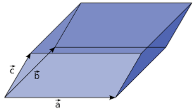


4 wt% CNC dispersion (pink): parallelepiped shape with cross section dimensions of 6 nm and 18 nm as form factor (black) at low q (blue box) deviation due to a **structure factor contribution for repulsive interaction**



0.25 wt% CNF dispersion (orange): cylindrical shape with particle radius of 6 nm, length longer than the measured q-range as form factor (black) at low q (starting from blue box) deviaiton due to a **structure factor contribution for attractive interaction**

Corona, P. T., Berke, B., Guizar-Sicairos, M., Leal, L. G., Liebi, M., & Helgeson, M. E. (2022). Fingerprinting soft material nanostructure response to complex flow histories. *Physical Review Materials*, *6*(4), 1–14. https://doi.org/10.1103/PhysRevMaterials.6.045603

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  - model independent
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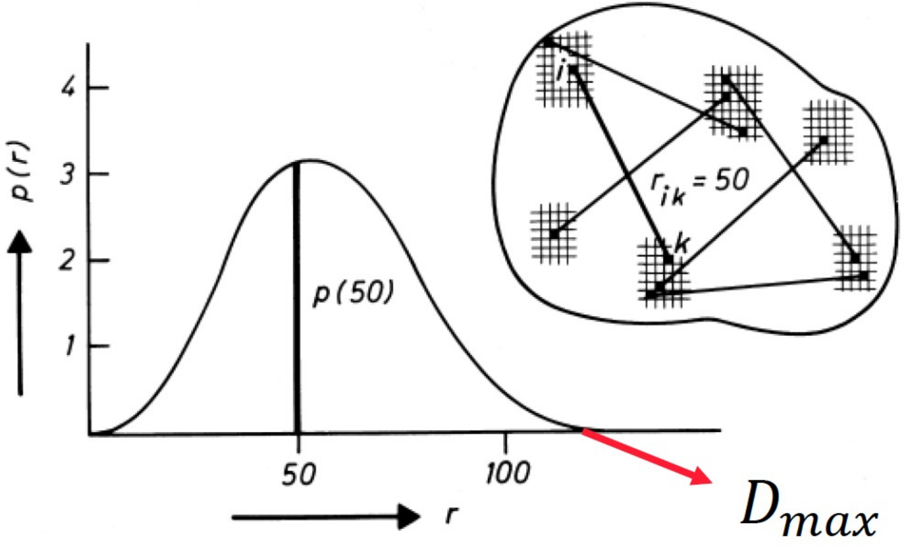
  - **pair distance distribution function (PDDF)**
  - iterative phase retrival

Pair distance distribution function

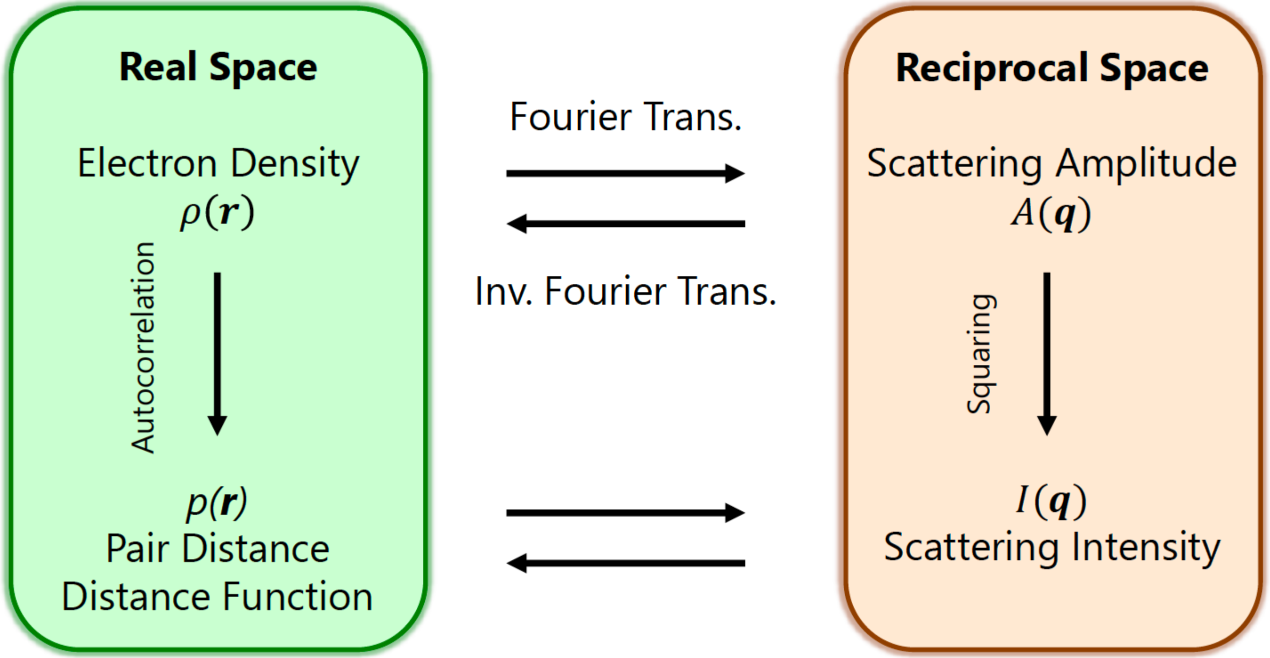
p(r) is the histogram of distances between all pairs of points inside the particle weighted by the respective electronic densities

$$p(\boldsymbol{r}) = r^2\gamma(\boldsymbol{r})$$



p(r) is the probability that two randomly chosen points in a particle are distance *r* apart.

Pair distance distribution function



Pair distance distribution function

The intensity function is linked to the pair distance distribution funcion p(r) by a Fourier transform.

$$I(q) = 4\pi \int_0^\infty p(r) \frac{\sin(qr)}{qr} dr$$

Then:

$$p(r) = \frac{r^2}{2\pi^2} \int_0^\infty q^2 I(q) \frac{\sin(qr)}{qr} dq$$

Problem: We **need** → I(q) from q=0 to ∞

We **have** → I(q) from q_{min} to q_{max}

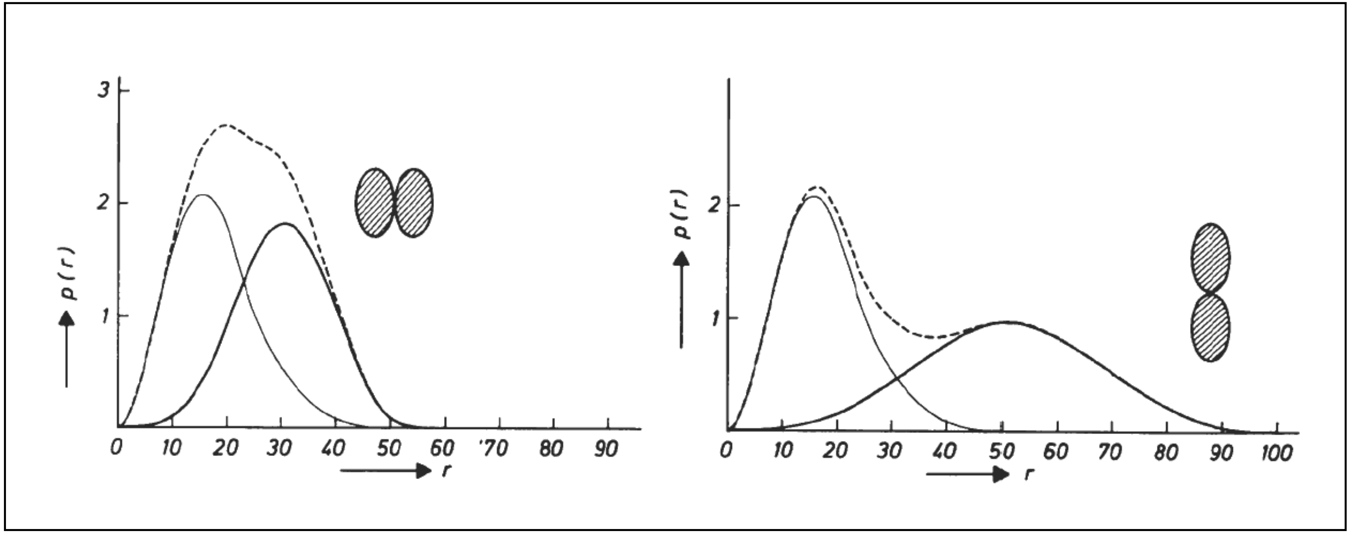
Pair distribution function (PDF)

pair distribution function:

$$p(r) = 4\pi r^2 \gamma_0(r)\, V$$

- the maximum size should be included (Guinier regim reached)
- Often used in analysis of proteins in solution can be calculated with:
  - http://www.bayesapp.org/ by Steen Hansen
  - Sasview http://www.sasview.org/
  - Gnom http://www.embl-hamburg.de/biosaxs/gnom.html
  - GIFT (generalized indirect fourier transform) by Otto Glatter, commercial

Pair distribution function (PDF)



$p(r)$ from dimer models built from prolate ellipsoids. Monomers (full line), dimers (broken line), and difference between dimers and monomers (thick full line). O. Glatter, J. Appl. Cryst. (1979). 12, 166-175

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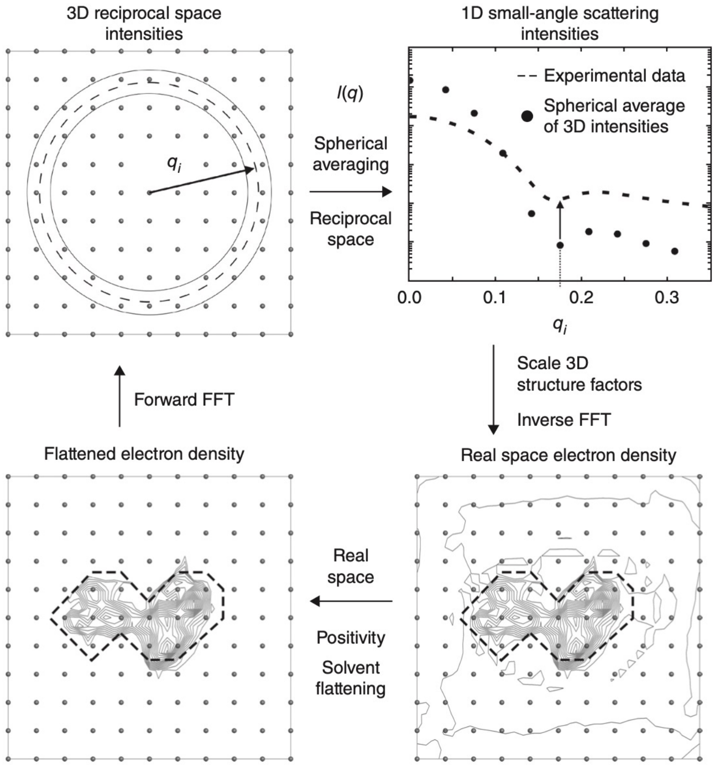
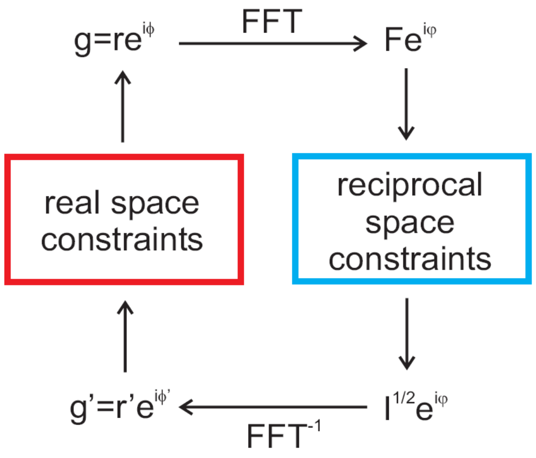
SAXS analysis: iterative approach



Grant, T. D., *Nature Methods* **2018,** *15*, 191.



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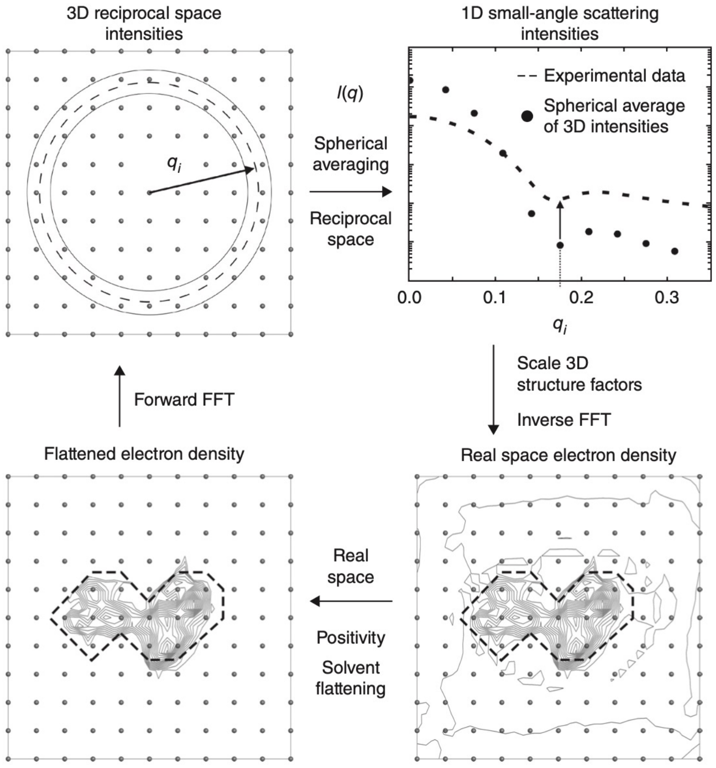

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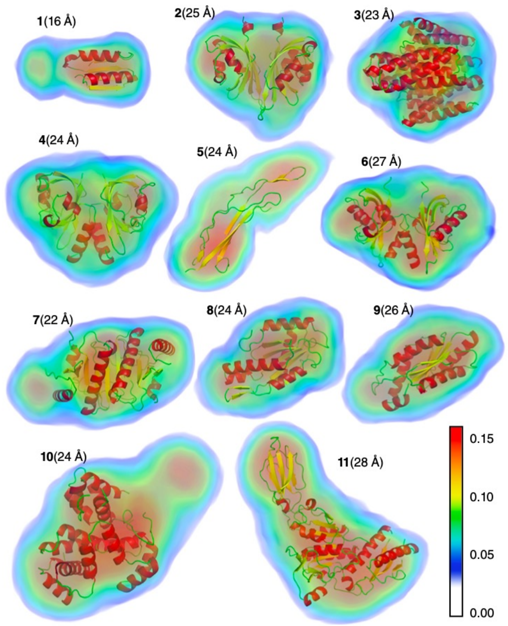
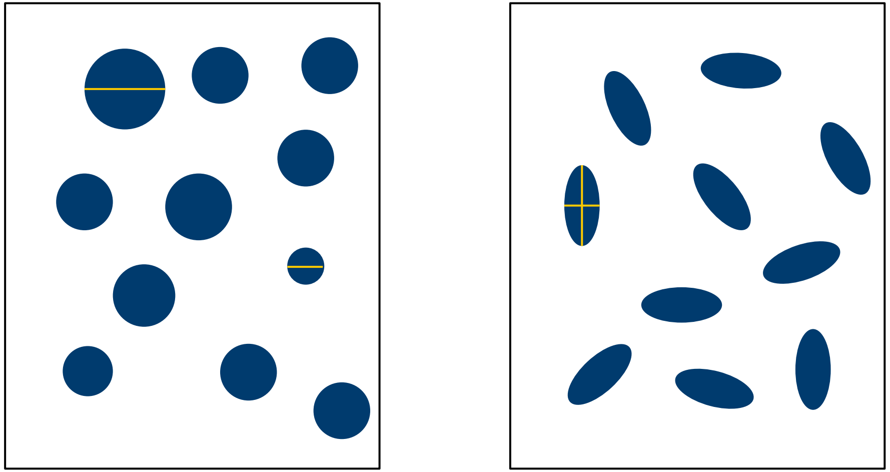


Figure 2 | Electron density reconstructions from experimental solution scattering data for samples 1–11 (**Supplementary Table 1**). Electron densities are shown as volumes colored according to density (color bar indicates electron density values in $e^-/Å^3$). X-ray crystal structures (for PDB IDs, see **Supplementary Table 1**) are shown in cartoon format. Estimated resolutions of the solution scattering reconstructions are shown next to sample ID (see Online Methods).

Polydispersity is the devil…

Small-angle scattering is a statistical method of all length scales in a sample

particle polydispersity or particle shape?



X-rays vs. neutrons

•Wavelengths in the order of atomic distances

•Penetrate into matter from µm to many cm deep

- scattered by nucleus of atoms
- scattering contrast depends on mass number A, is isotope-specific

$$n_{neutrons} = \sqrt{\frac{E_{kin} - \overline{V}}{E_{kin}}} \cong 1 - \frac{\overline{b} n_a}{2\pi} \lambda^2$$

→ contrast matching!

- Interact with magnetic moment in shell of atom

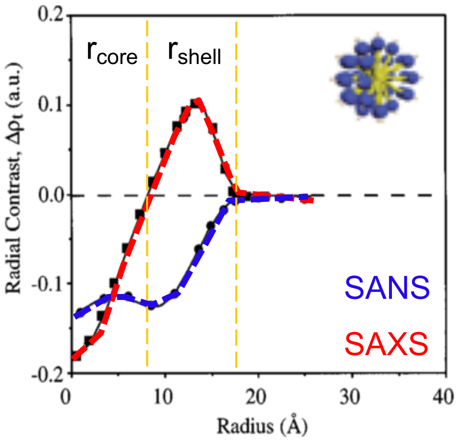
  →magnetic structures and magnetism

- scattered by electronic shell of atoms
- Scattering contrast proportional to order number (number of electrons)

$$n_{x-ray} = 1 - \frac{\overline{Z} r_e n_a}{2\pi} \lambda^2$$

- Larger flux possible→ faster, lower concentrations, smaller beam

SAXS vs. SANS as complementary contrast



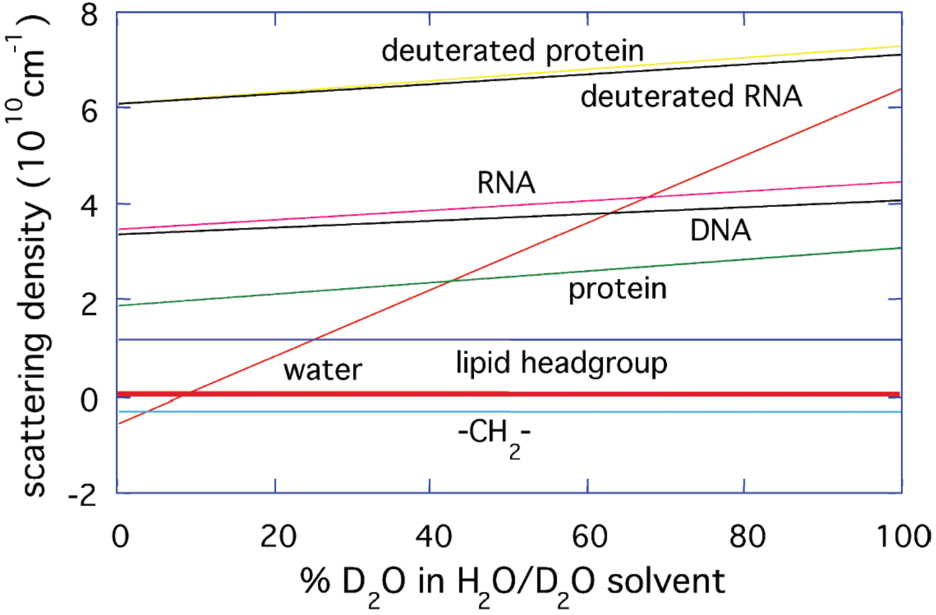
SANS contrast is mainly between the full micelle and the solvent

→ overall size of micelles

SAXS headgroups have a higher contrast then lipid tails

→ internal structures

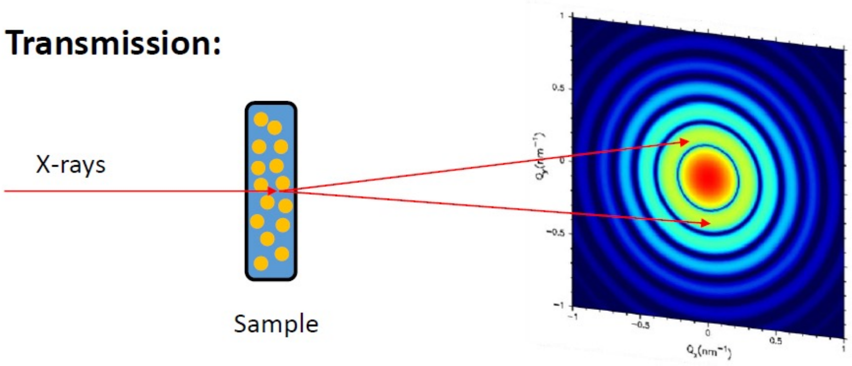
Contrast matching in SANS



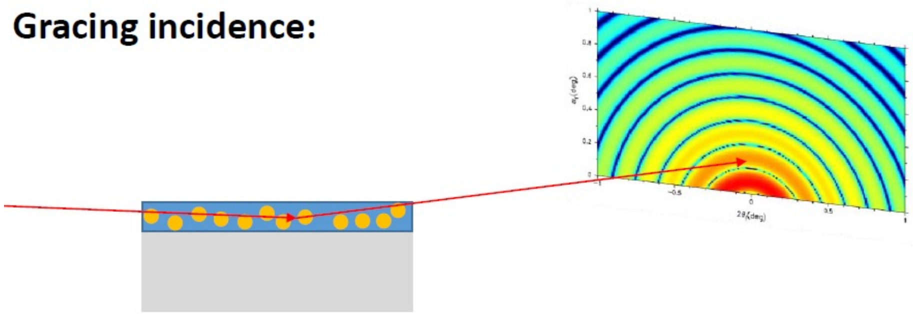
Scattering length density different for isotopes! Hydrogen and Deuterium!

SAXS at gracing incidence: GISAXS

Transmission:



Gracing incidence:



GISAXS

Extensive article on GISAXS including theoretical background, experimental consideration and application examples:

Renaud, G., Lazzari, R., & Leroy, F. (2009). Probing surface and interface morphology with Grazing Incidence Small Angle X-Ray Scattering. *Surface Science Reports*, *64*(8), 255–380. https://doi.org/10.1016/j.surfrep.2009.07.002

X-ray scattering at synchrotrons

High Brilliance allows for

Low divergence ⇒ high angular resolution scattering/diffraction patterns

Tight focus ⇒ small sample sizes e.g., protein crystals ~ 1 mm^3

Low emittance ⇒ large working distance between focussing optics and sample ⇒ bulky sample environments

High flux ⇒ rapid data acquisition, time-resolved studies down to ms regime or shorter

X-ray scattering at synchrotrons

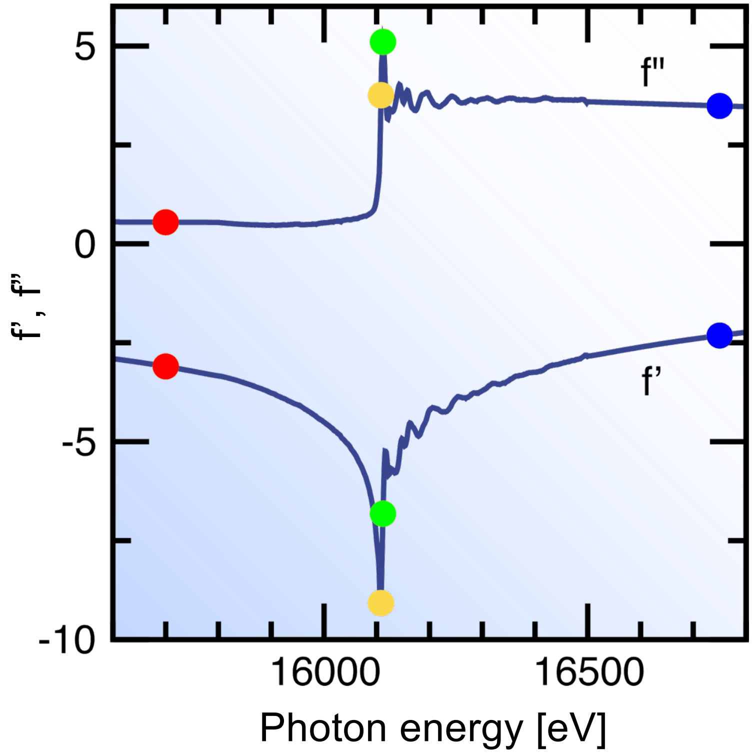
Acess to high photon energies:

Penetrate deep into samples, e.g., aeronautical components, large fossils, concrete, etc.

Tunability of energy:

Abrupt changes to atomic scattering amplitudes as one crosses an absorption edge

"Anomalous" signal

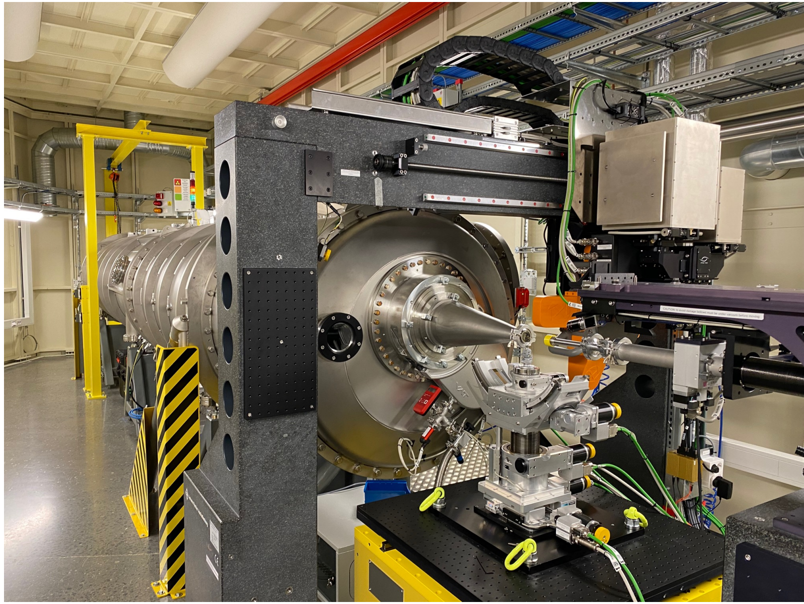


X-ray scattering at synchrotrons

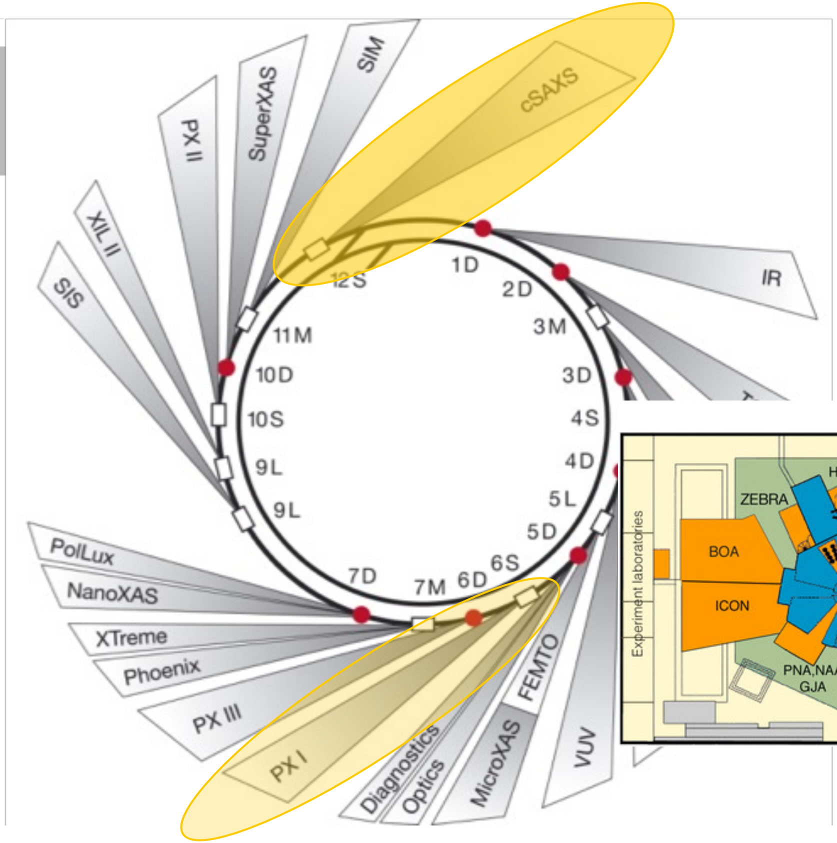
state-of the art detectors

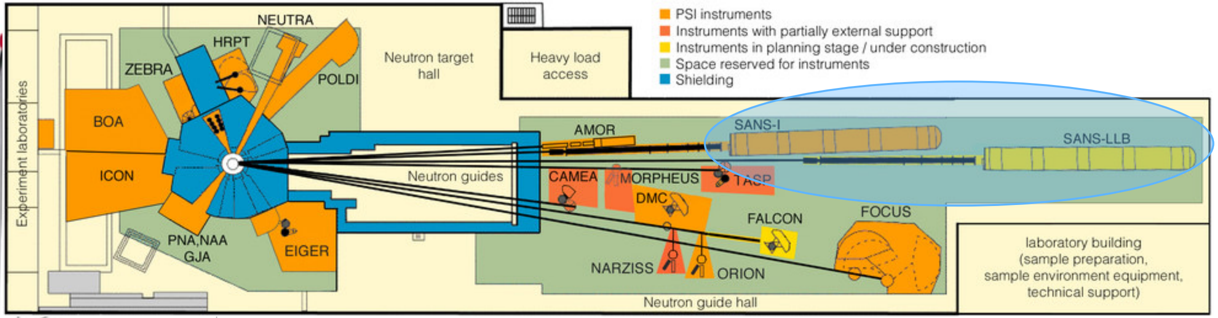
shared sample environemnts (e.g. Rheo-SAXS)

Large flight tubes and low emittance: Ultra small angle X-ray scattering



Small angle scattering at PSI: SAXS and SANS





Practical consideration for an experiment

X-ray vs. neutrons (vs. light)

what size range is of interest → q-range: detector distance and energy

beamsize: resolution vs. flux-density and beam damage

exposure time: signal to noise, detector speed

detector saturation

thickness of sample, for X-rays energy:

- number of scatterer proportional to intensity $I(q) = (\rho_P - \rho_M)^2 \boldsymbol{N_P} V_P^2 P(q) S(q)$
- but absorption (Lambert-Beer law): intensity decays exponentially with thickness $I = I_0\, e^{-N_i \sigma z}$
- maximum at the absorption length i.e. where transmission is 1/e, ~ 30%

Sample thickness and X-ray energy