Small-angle X-ray scattering (SAXS) with synchrotron radiation

Martin Müller
Institut für Experimentelle und Angewandte Physik
der Christian-Albrechts-Universität zu Kiel

- Introduction to small-angle scattering
- Instrumentation
- Examples of research with SAXS

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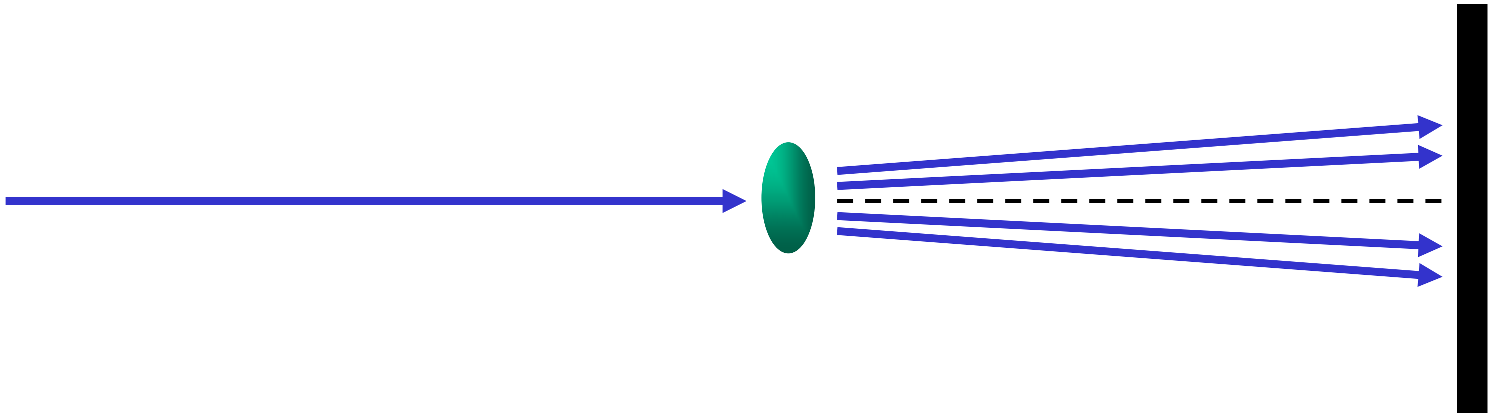
What is small-angle scattering?

elastic scattering in the vicinity
of the primary beam (angles $2\theta < 2°$)
at inhomogeneities (= density fluctuations)



typical dimensions in the sample:
0.5 nm (unit cell, X-ray diffraction)
to 1 µm (light scattering!)

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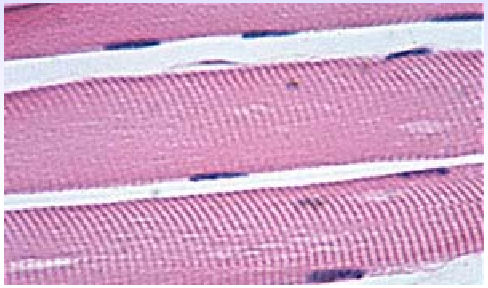
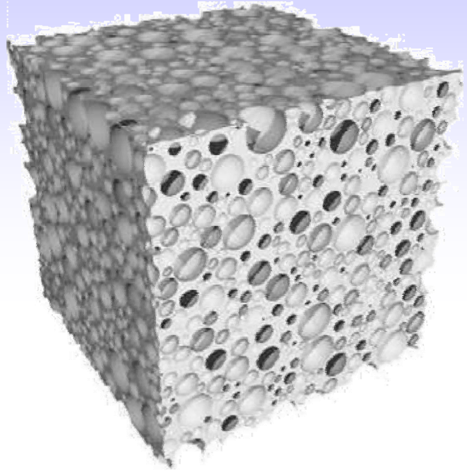
What is small-angle scattering?

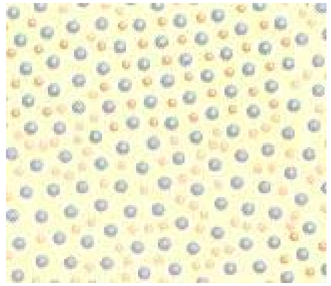
fibres

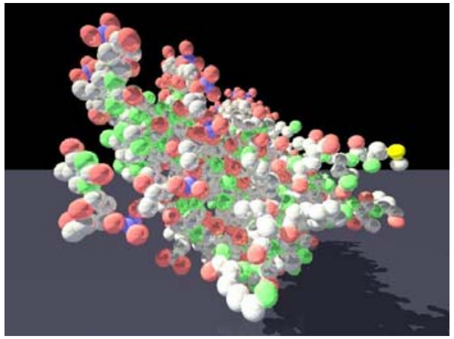




pores

colloids





proteins

polymer morphology

X-ray scattering (SAXS):
electron density

neutron scattering (SANS):
scattering length

} **contrast**

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On the importance of contrast …

When the monster came, Lola, like the peppered moth and the arctic hare, remained motionless and undetected. Harold, of course, was immediately devoured.

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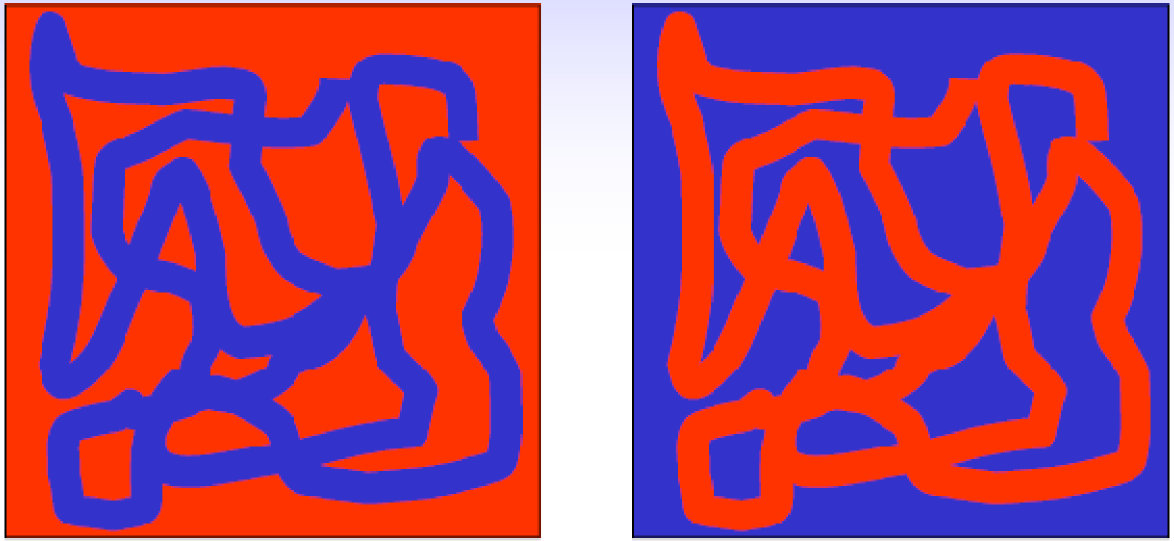
Scattering contrast is relative

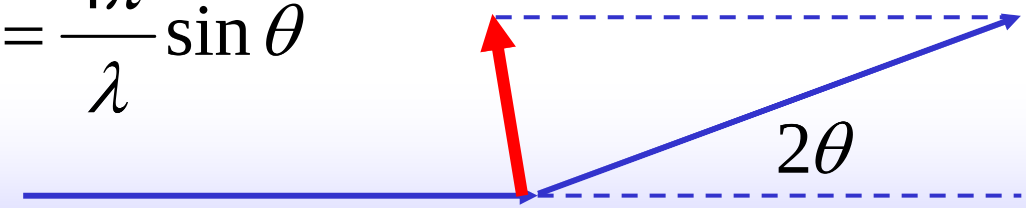
Babinet's principle



two different structures may give the same scattering:

$$I(Q) \propto (\rho_1 - \rho_2)^2$$

scattering vector $\left|\vec{Q}\right| = \dfrac{4\pi}{\lambda}\sin\theta$



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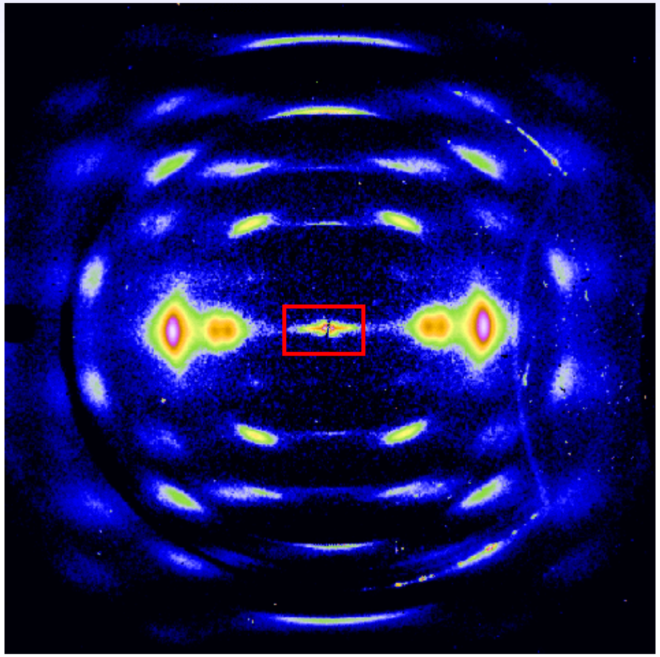
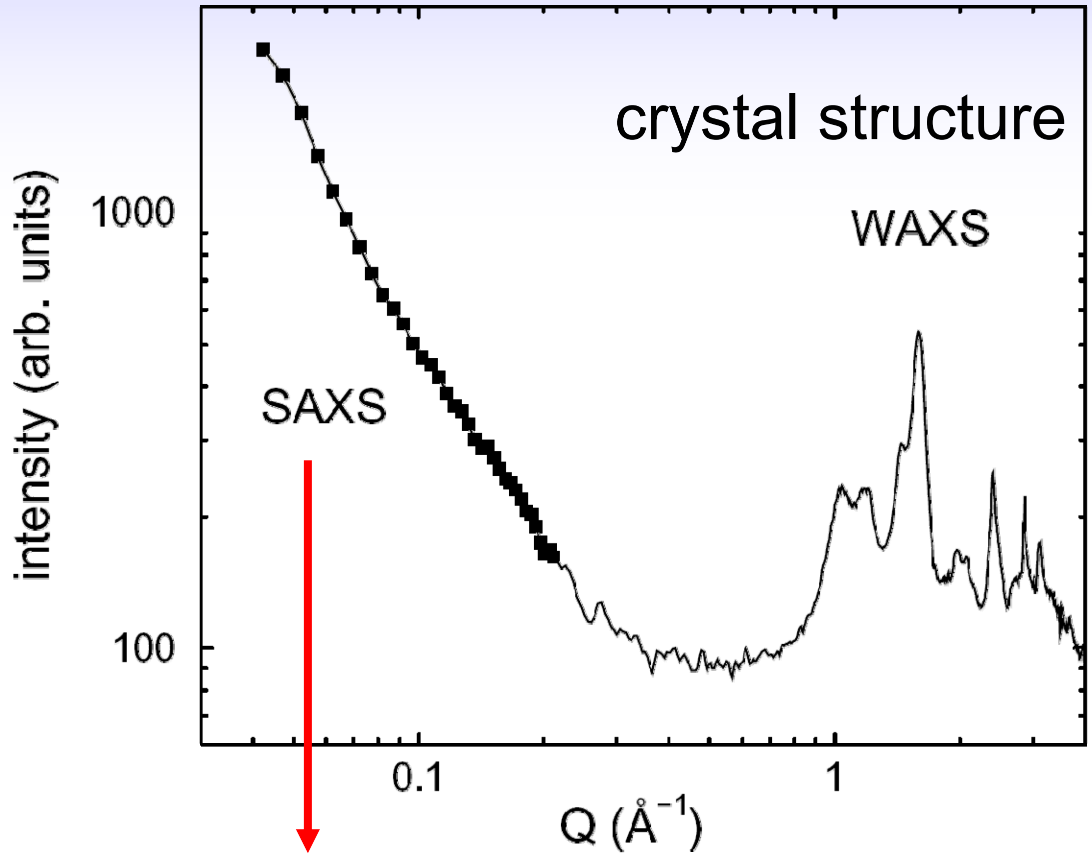
Diffraction and small-angle scattering

cellulose fibre





scattering contrast
crystals - matrix

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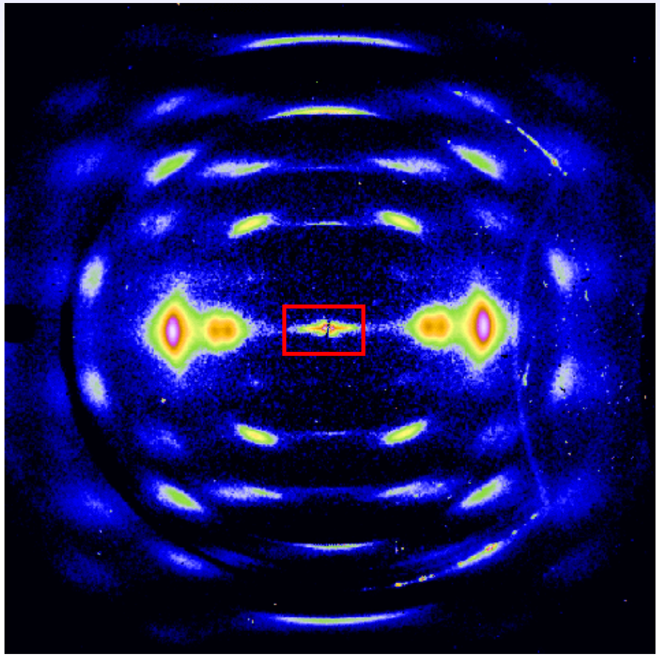
M. Müller, C. Czihak, M. Burghammer, C. Riekel.
J. Appl. Cryst. **33**, 817-819 (2000)

Diffraction and small-angle scattering



Diffraction:

$$I(Q) = \left| \sum_l f(Q)\, e^{i\vec{Q}\cdot\vec{R}_l} \right|^2$$

atomic form factor, electron distribution

lattice interference $\Rightarrow$ Bragg peaks

small-angle scattering:

- *form factor* = Fourier transform of particle shape
- *structure factor* = interparticle interference

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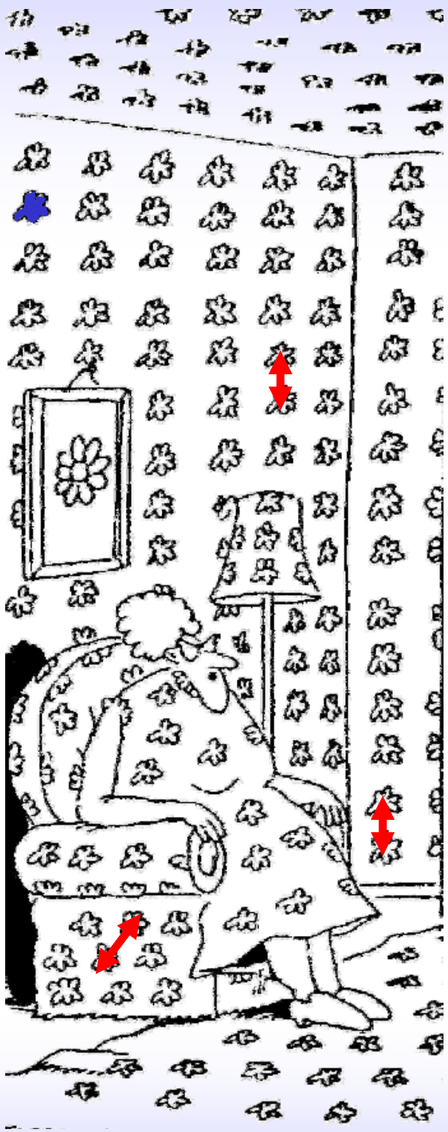
Form factor and structure factor

form factor:
particle shape

structure factor:
(mean) particle distance



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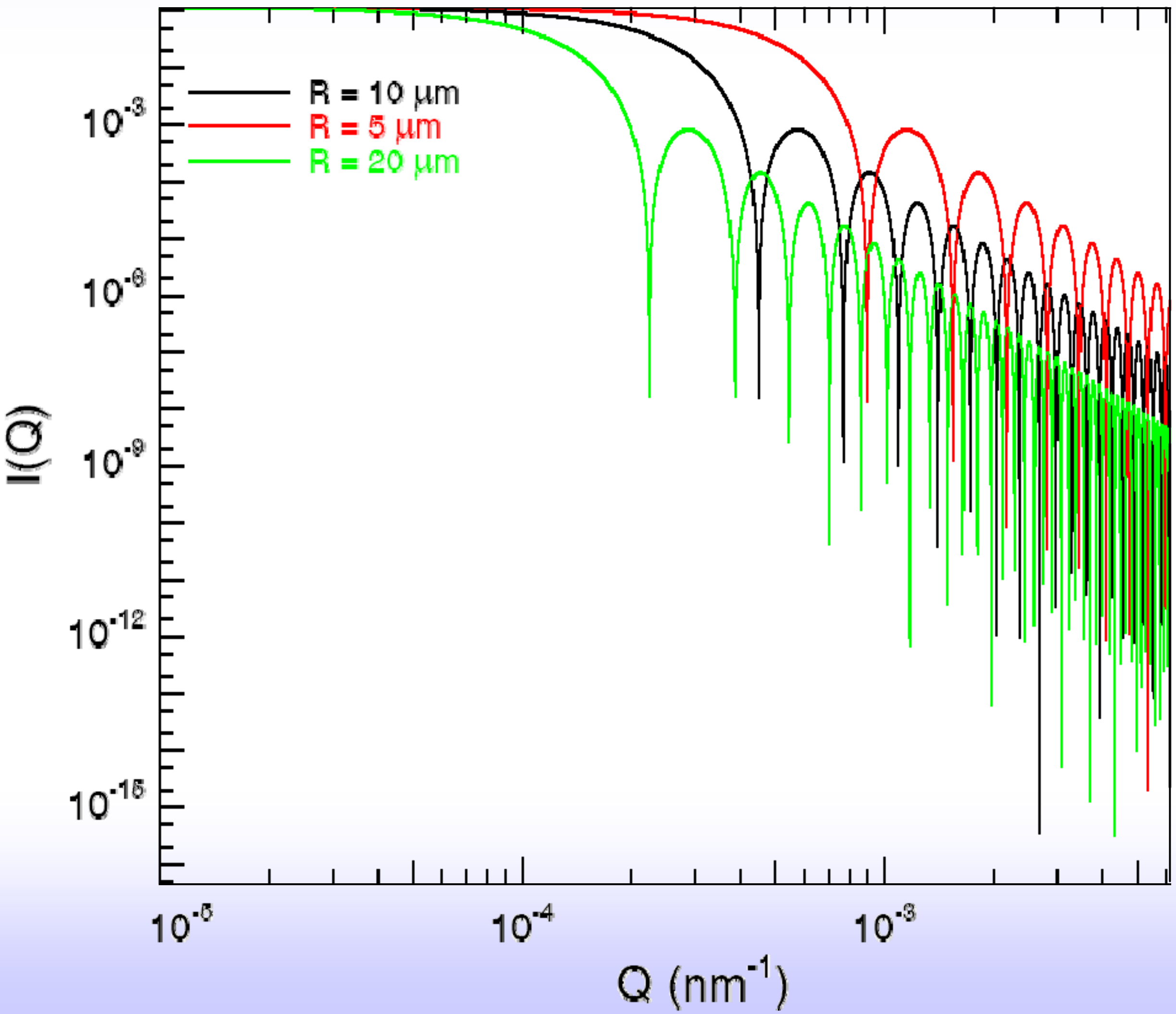
Form factor (dilute systems)

sphere: $$I(Q) \propto \left| \frac{3(\sin QR - QR\cos QR)}{Q^3R^3} \right|^2$$



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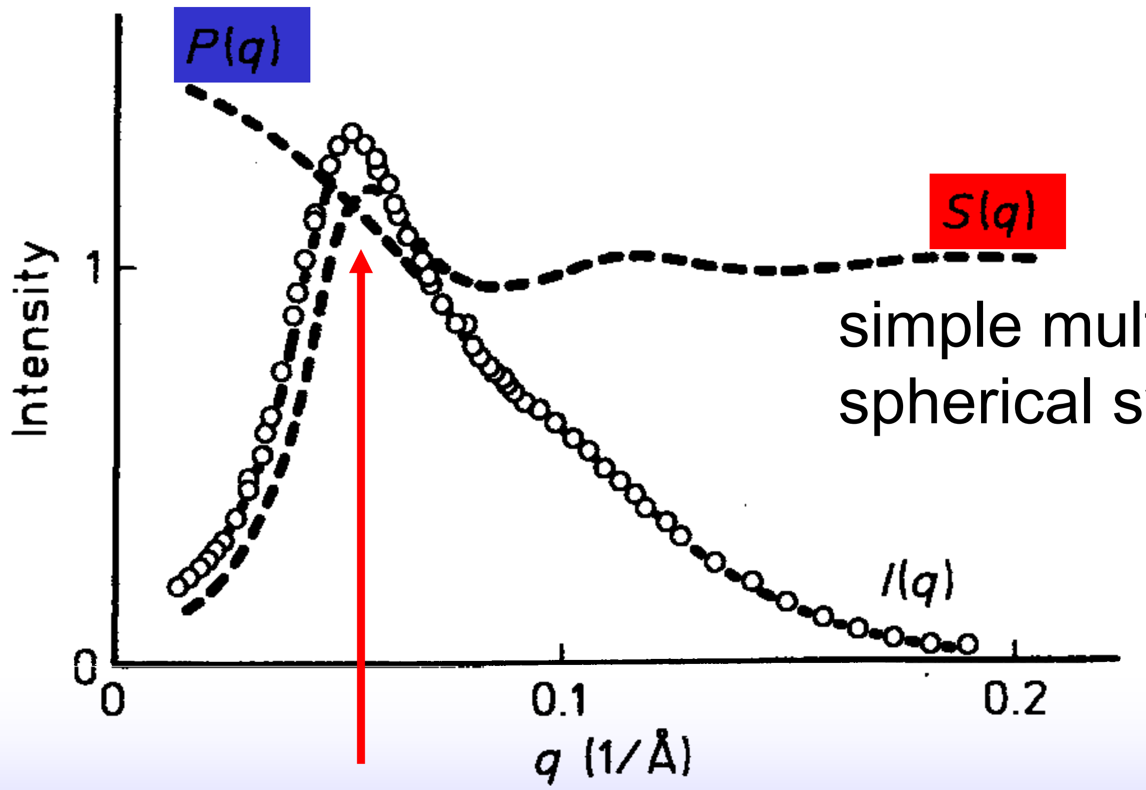
Form factor and structure factor (non-dilute)

basic principle as in diffraction:

- form factor (as before): single particles, **dilute** systems
- structure factor: interparticle distances of the order of particle size ⇒ **interference**



simple multiplication only for spherical symmetry!

„long-range **Bragg** peak“ ($d = 2\pi/q \approx 120$ Å)

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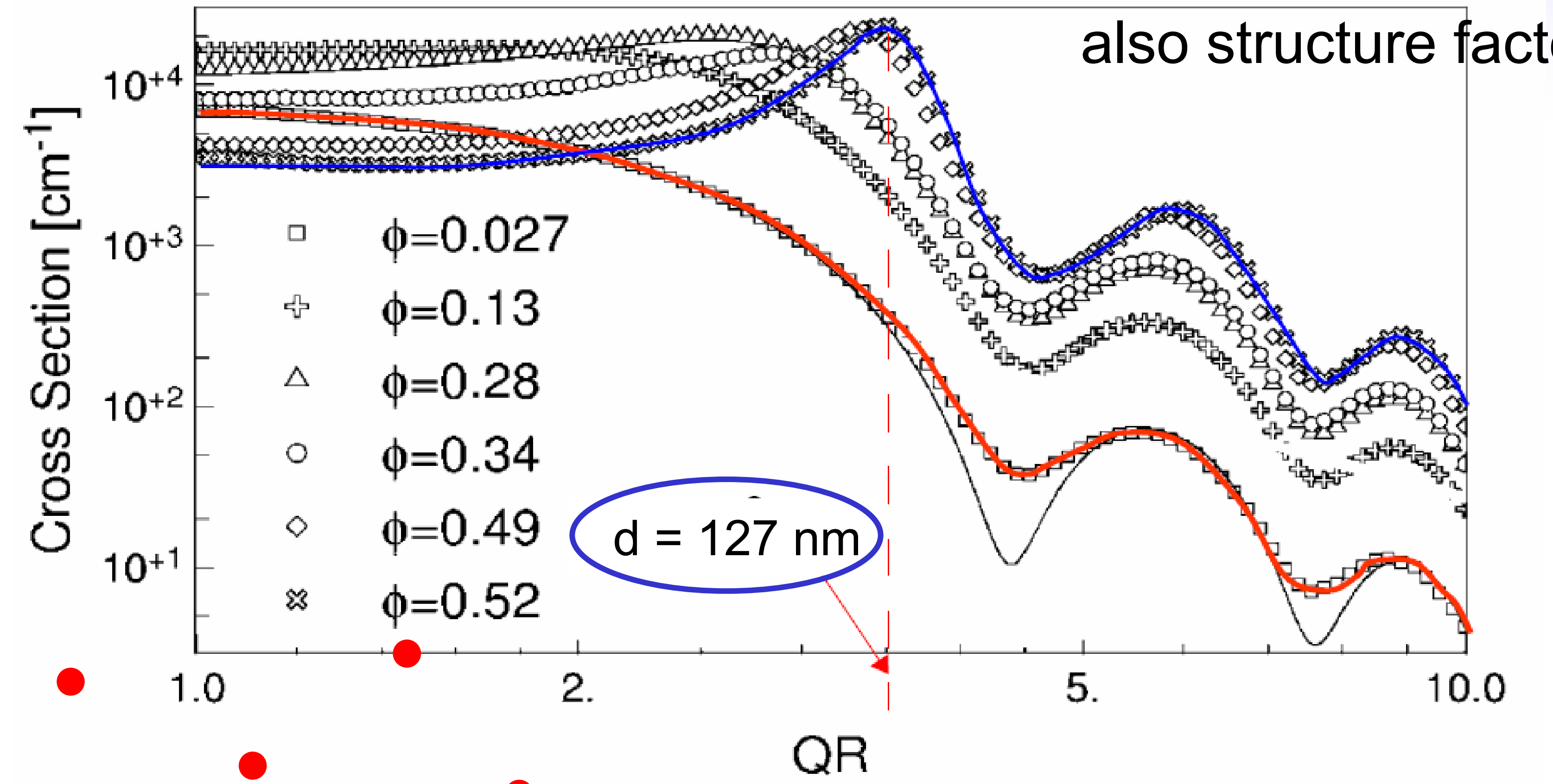
Polystyrene spheres (71 nm radius) in glycerol

concentrated: also structure factor

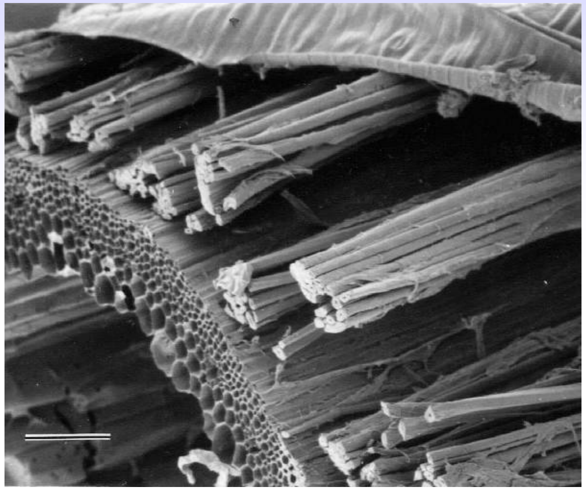


dilute: only form factor

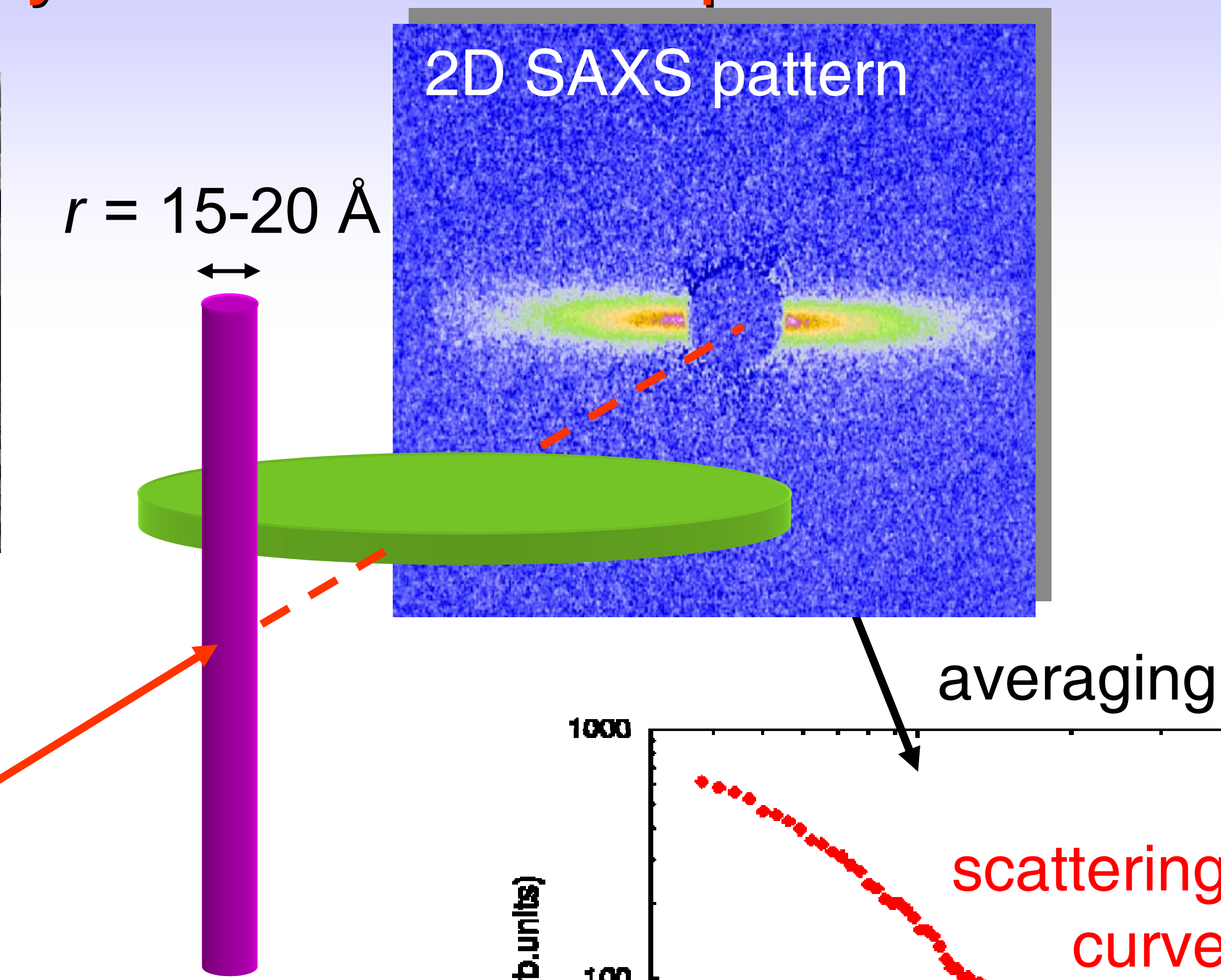
d: mean distance

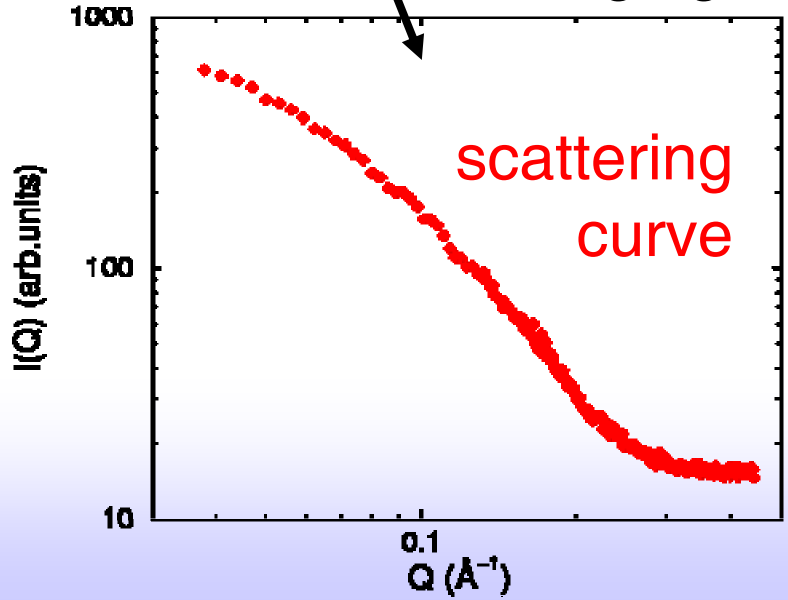
L. B. Lurio et al., *Phys. Rev. Lett.* **84**, 785 (2000)

Data analysis of a SAXS experiment



flax fibres



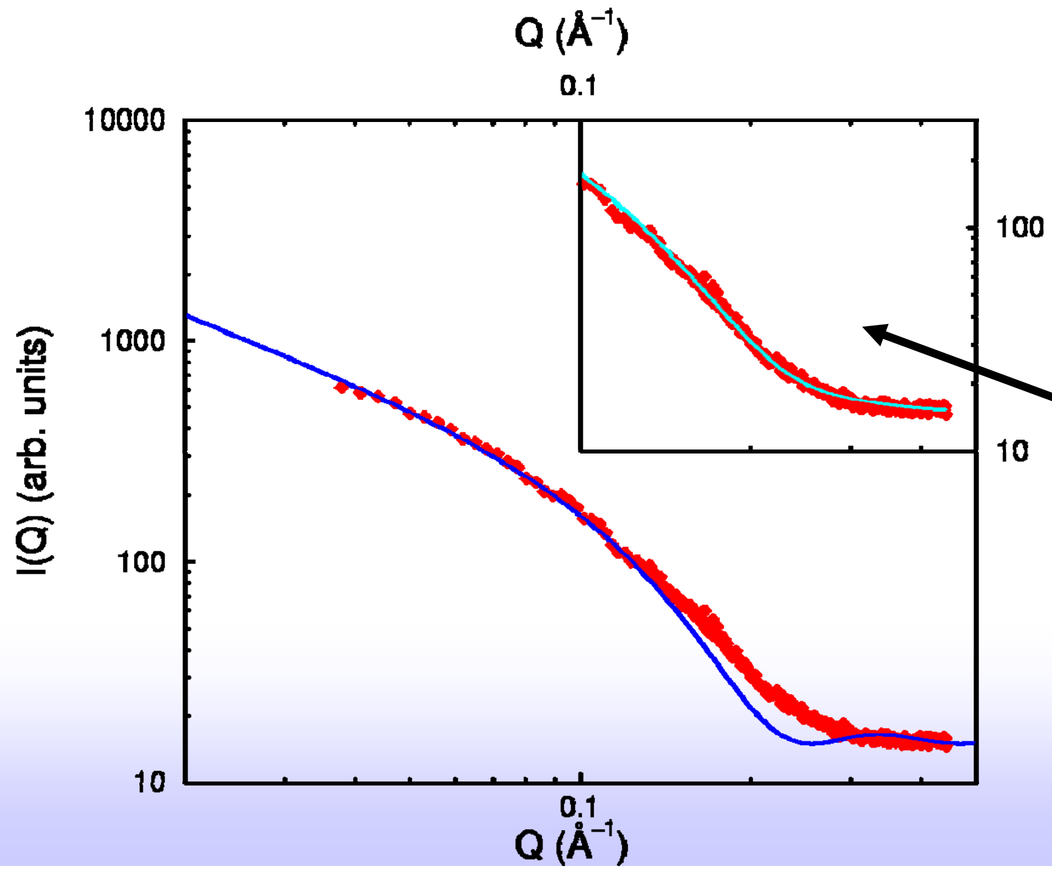


cellulose crystallites
(= microfibrils)
in amorphous matrix
(density contrast)

Form factor: fit with model function

cellulose microfibrils in flax fibres,
long cylinder with radius *r* (= 15 Å) yields:

$$I(Q) = b + c \cdot \frac{r^4}{Q} \left(\frac{2 J_1(Qr)}{Qr} \right)^2$$



better fit with
assumption of
size distribution
(± 4 Å)
= **polydispersity**

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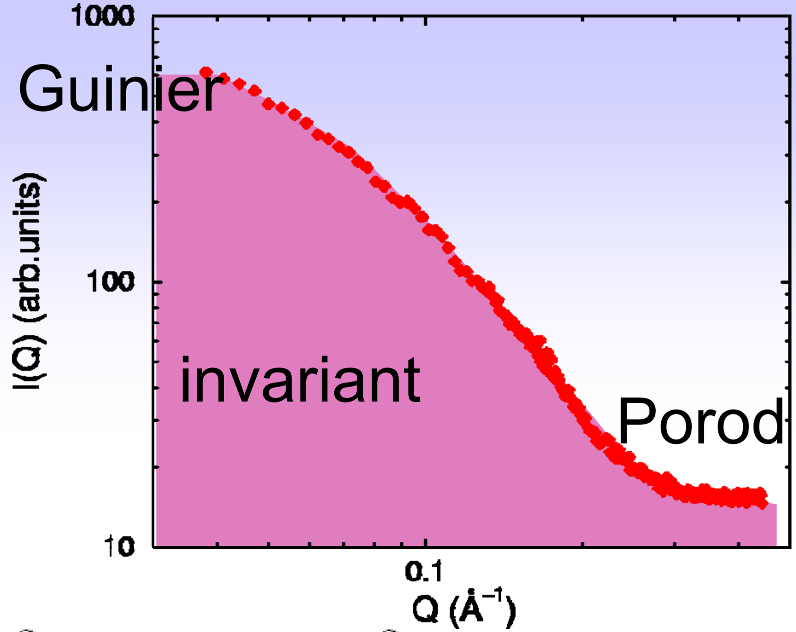
Model-free parameter determination



single particle scattering, 2 phases; independent of topology and geometry

- **invariant**

$$I = \frac{1}{V}\int_0^\infty Q^2 I(Q)\,\mathrm{d}Q = 2\pi^2\,\phi_1\phi_2\,(\Delta\rho)^2$$

volume fractions — scattering contrast

- **Porod limit**

for distances larger than typical distances in the sample and sharp interfaces:

$$\lim_{Q\to\infty} Q^4 I(Q) = 2\pi(\Delta\rho)^2 V\cdot\mathcal{A}$$

specific (inner) surface

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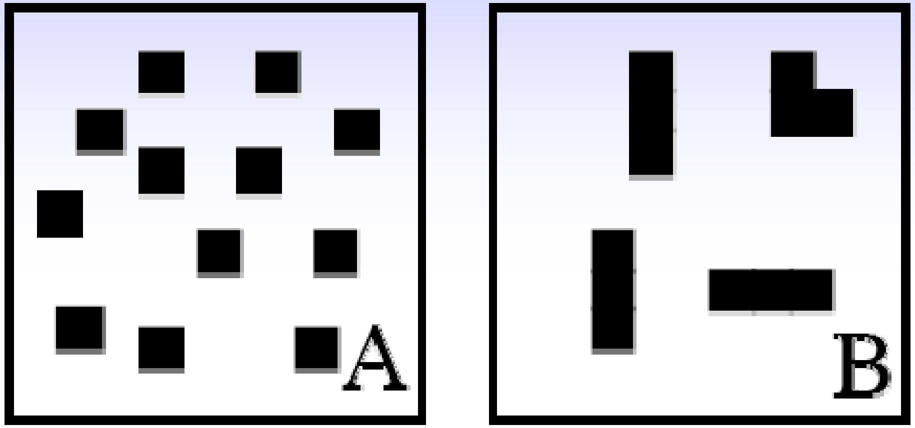
Invariant and Porod scattering

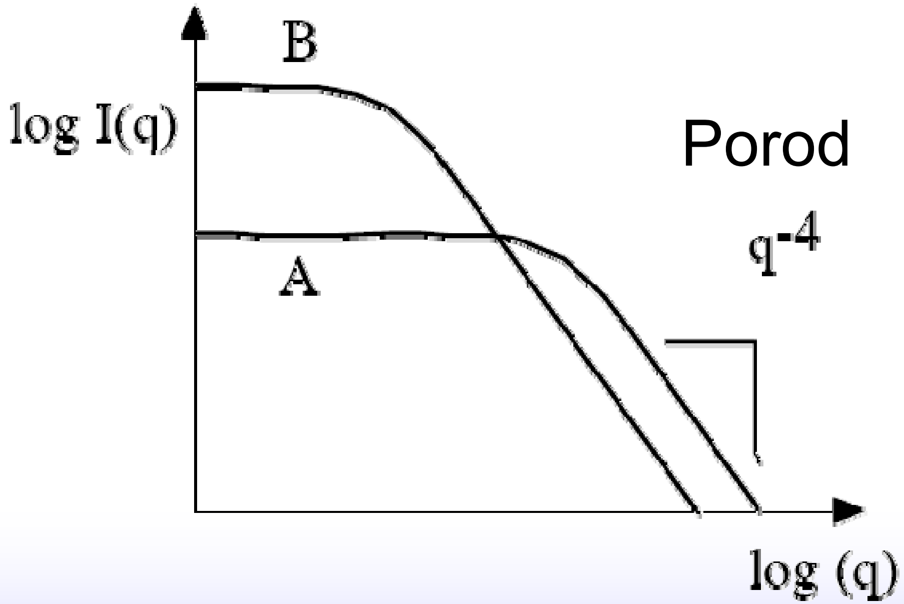
- 90 % white
- 10 % black

different scattered intensity, but **same invariant**



specific (inner) surface:

larger for **A**



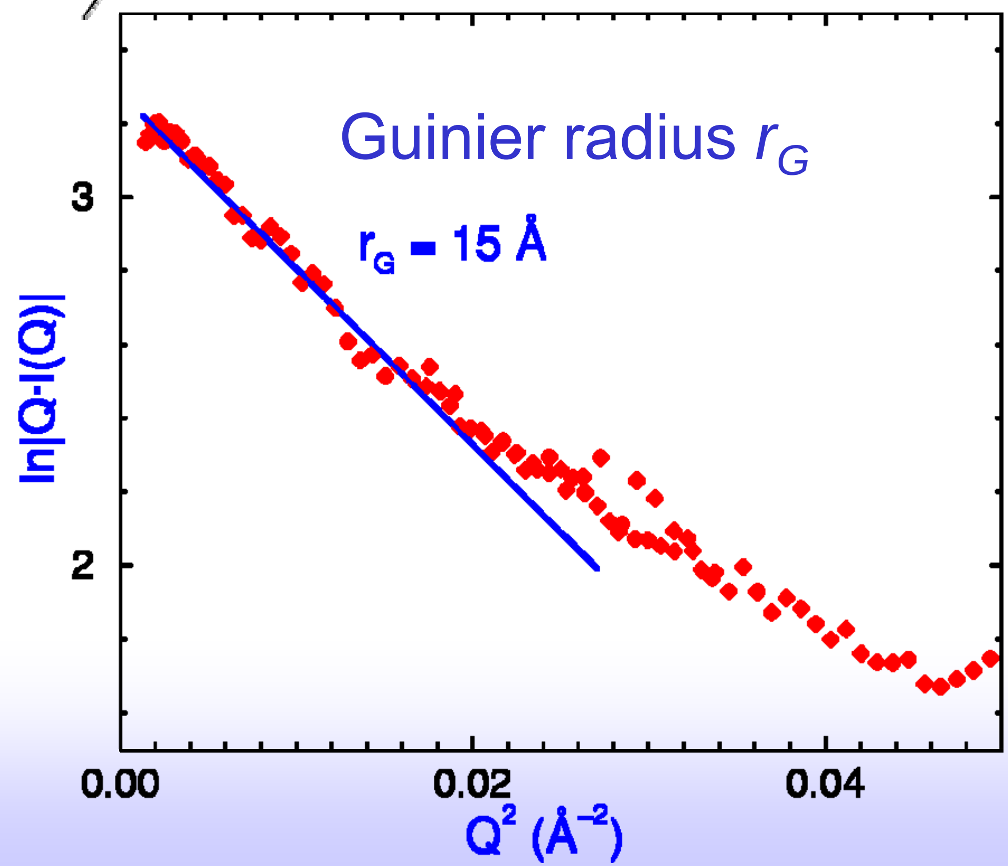
Guinier analysis

Guinier (1938): For very small angles scattering function independent of particle shape, only dependent on size:

$$I(Q) = I_0 \exp\left(-\frac{Q^2 r_G^2}{3}\right)$$

for $Q r_G \ll 1$

(details „not seen“ at low angles)



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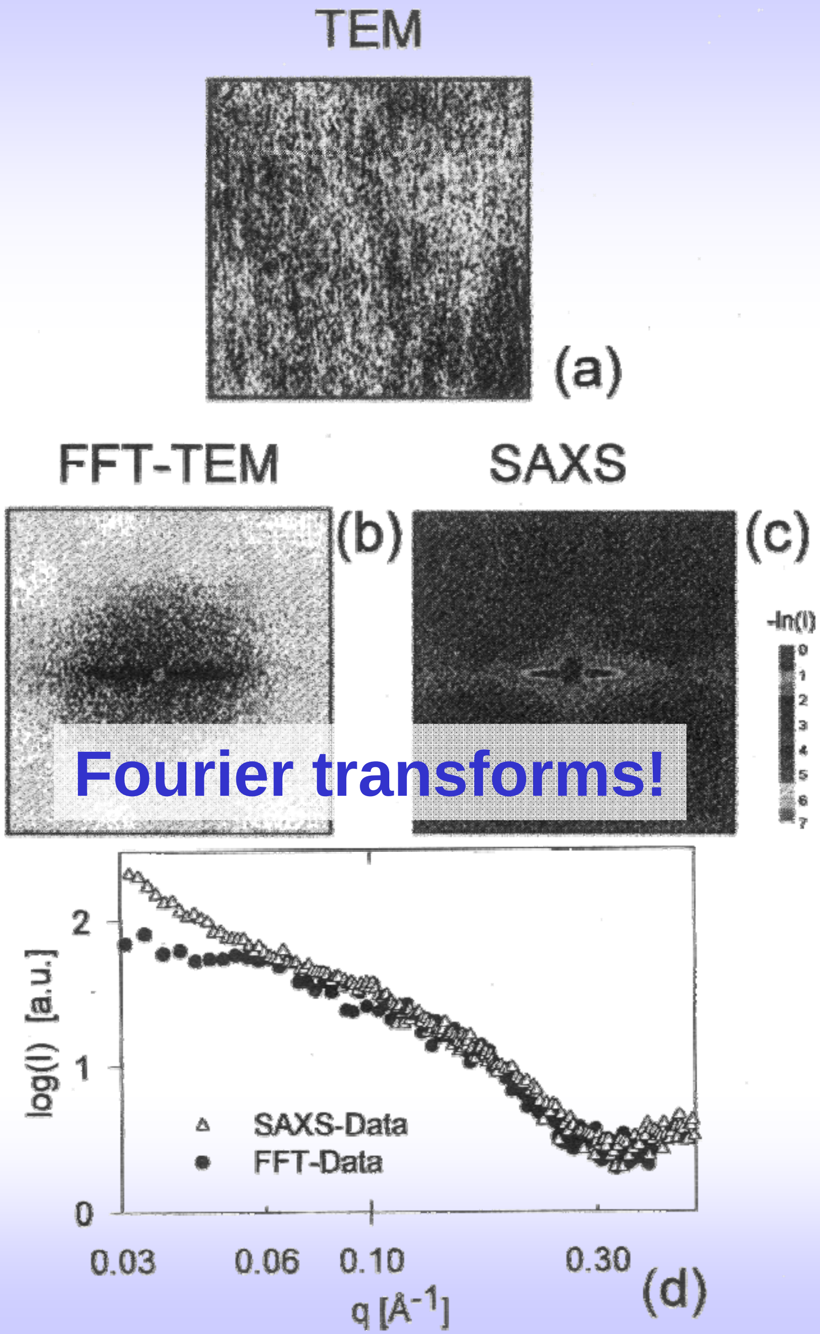
Why an indirect method?

- non-destructive, no tedious sample preparation (sectioning, staining…)
- averaging of larger areas
- simultaneous information on several length scales in combination with e. g. diffraction
- soft matter: liquids, solutions, emulsions, biological samples…



H. F. Jakob et al., *Macromolecules* **28**, 8782 (1995)

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Small-angle X-ray scattering (SAXS) with synchrotron radiation

- Introduction to small-angle scattering
- Instrumentation
- Examples of research with SAXS

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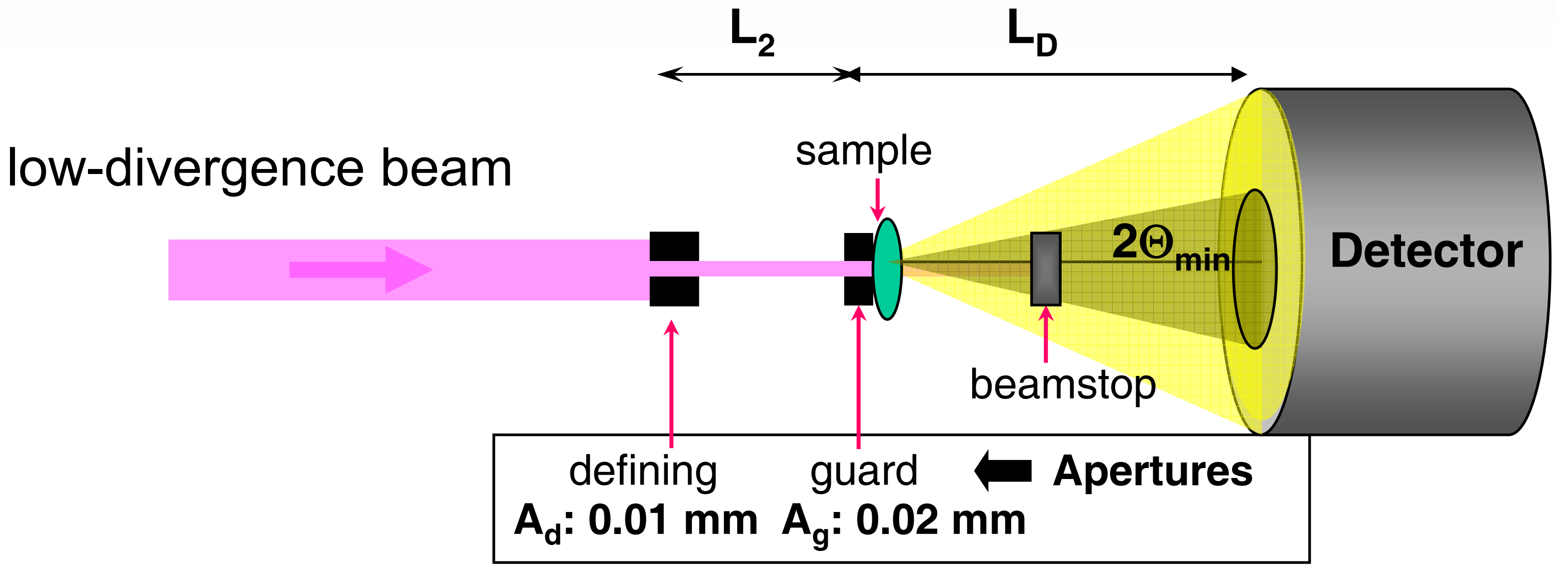
Pinhole SAS camera

long distance
for high resolution



beam shaping

detector protection
without cutting SAXS signal

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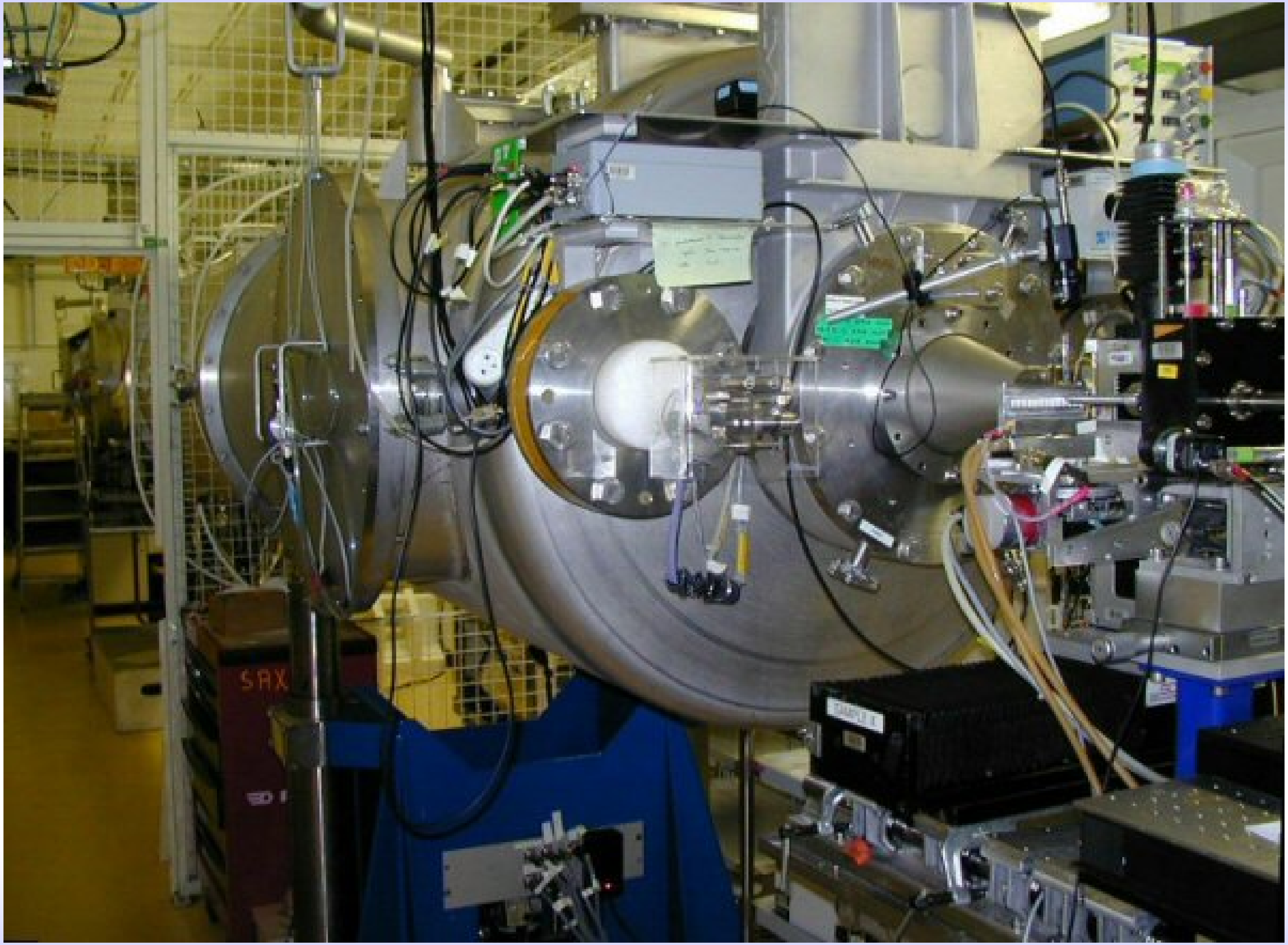
Pinhole camera ID02 at ESRF



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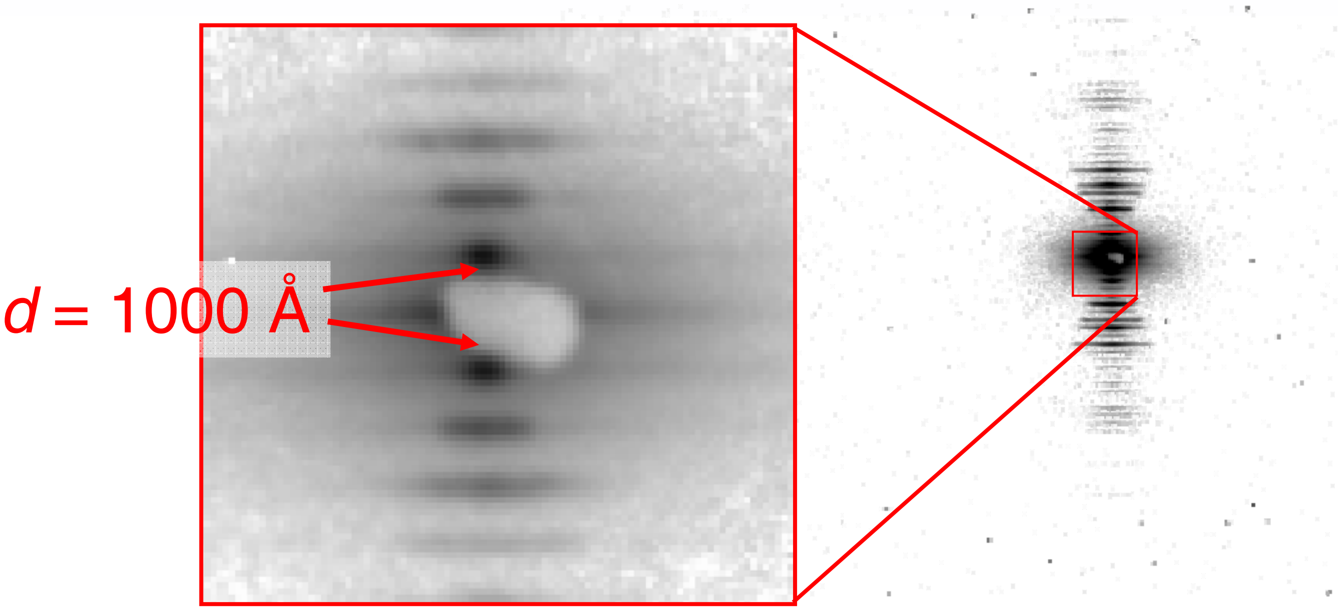
"Resolution" in small-angle scattering

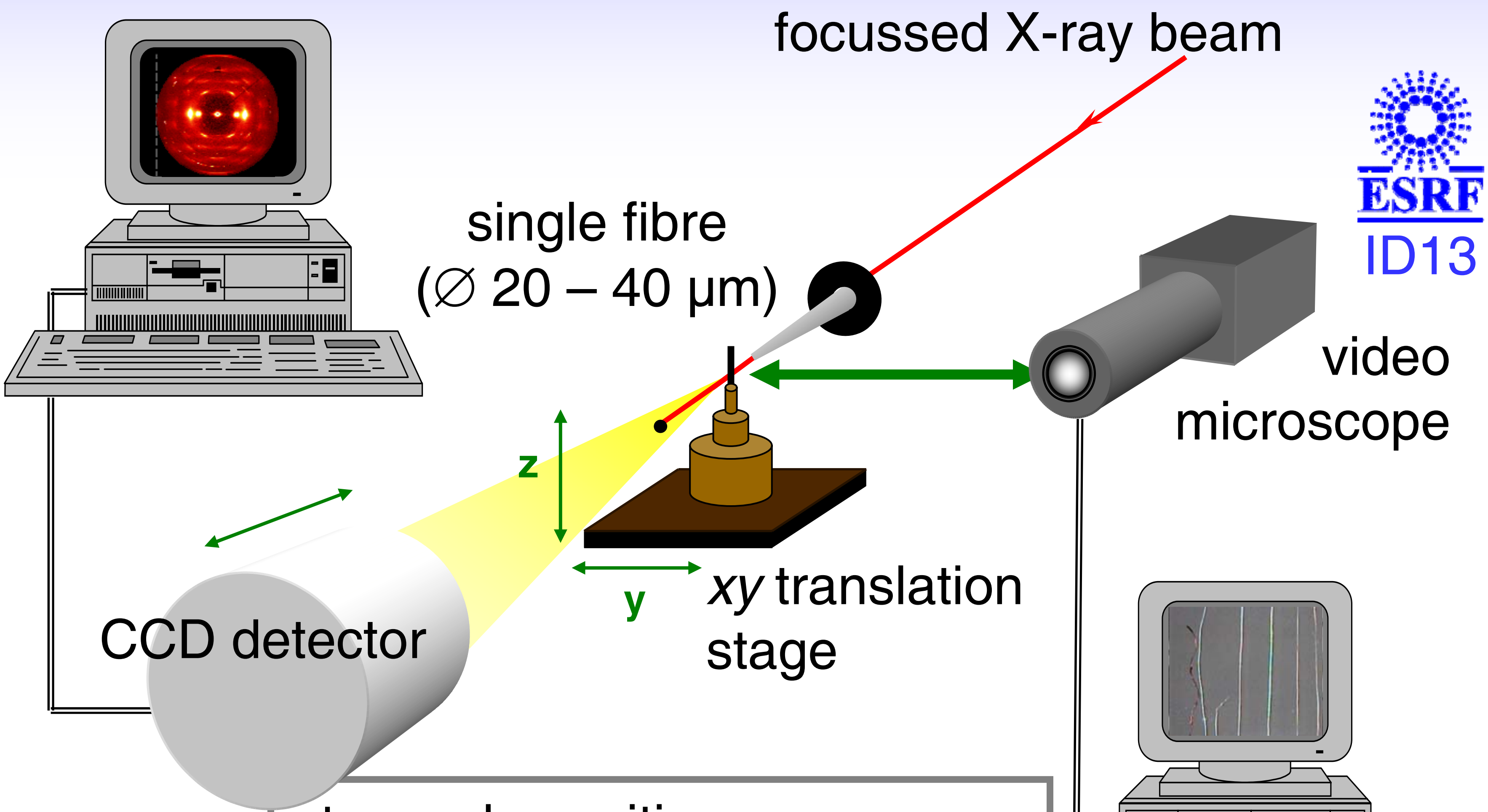
SAXS resolution: $2\theta_{min} \rightarrow d_{max}$



standard calibration material: rat tail collagen
(periodic structure: 67 nm)

M. Müller, M. Burghammer, C. Riekel
Nucl. Instrum. Meth. A **467-468**, 958-961 (2001)

Microdiffraction and µSAXS at the ESRF Microfocus Beamline



at sample position:

- beam size ∅ 0.5 - 2 µm
- flux 10^{10} - 10^{11} ph/s @ 13 keV

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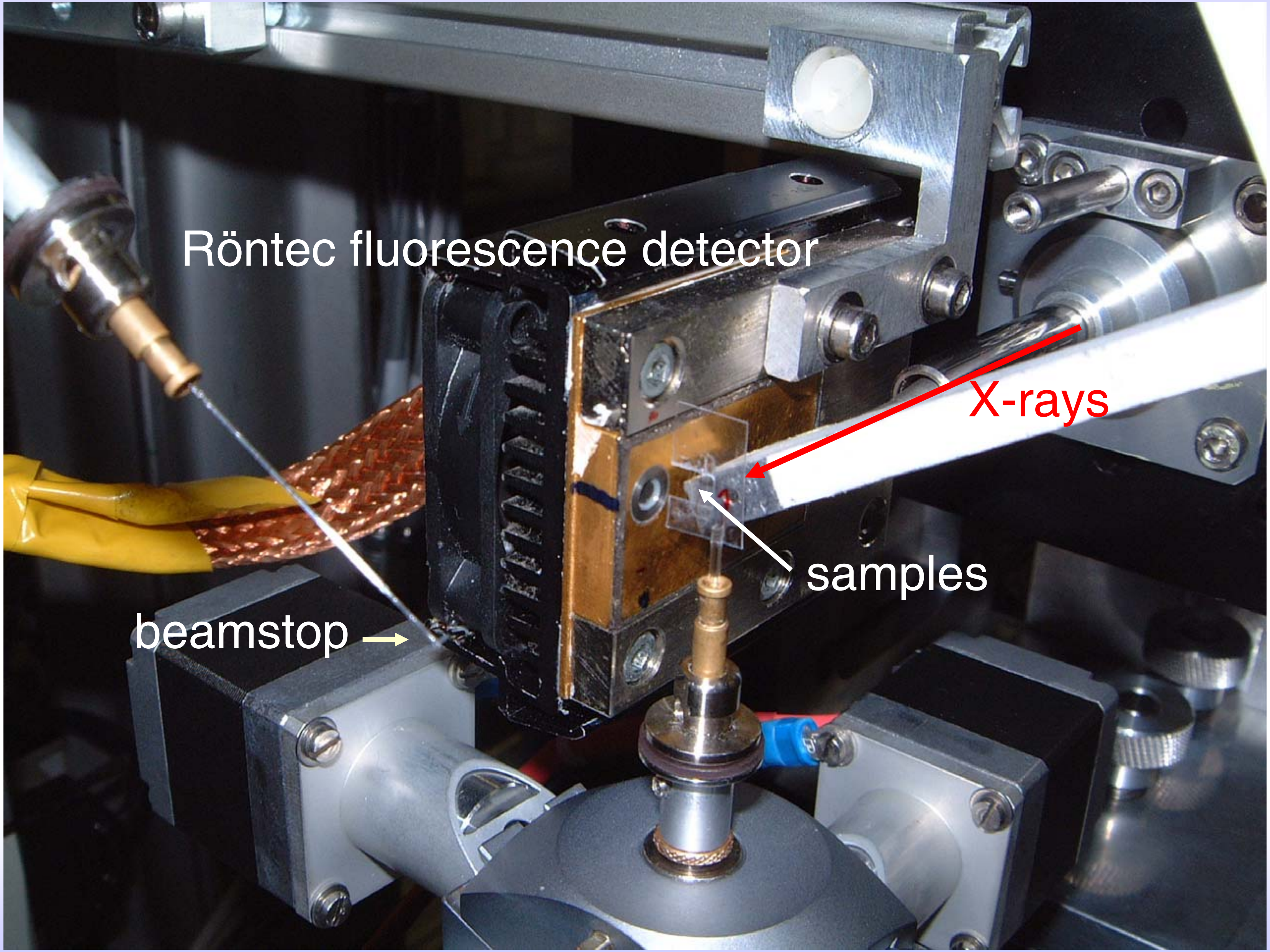
Combination with microfluorescence

ESRF
ID13



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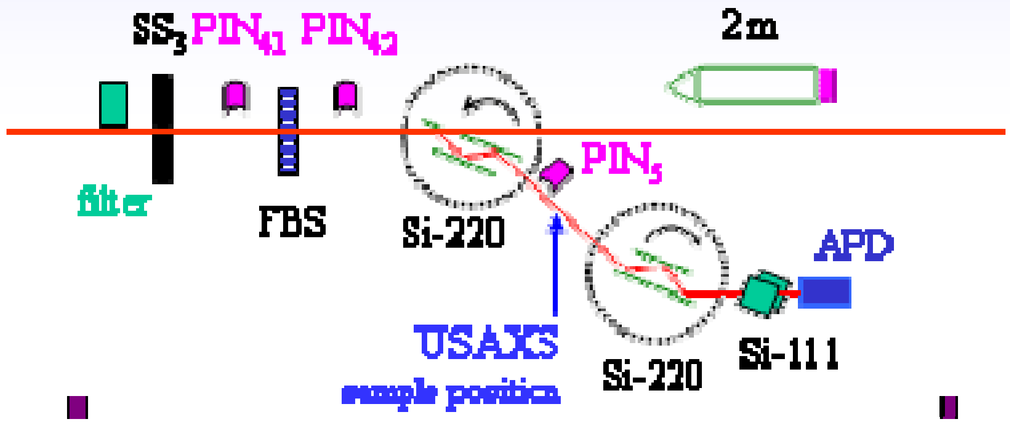
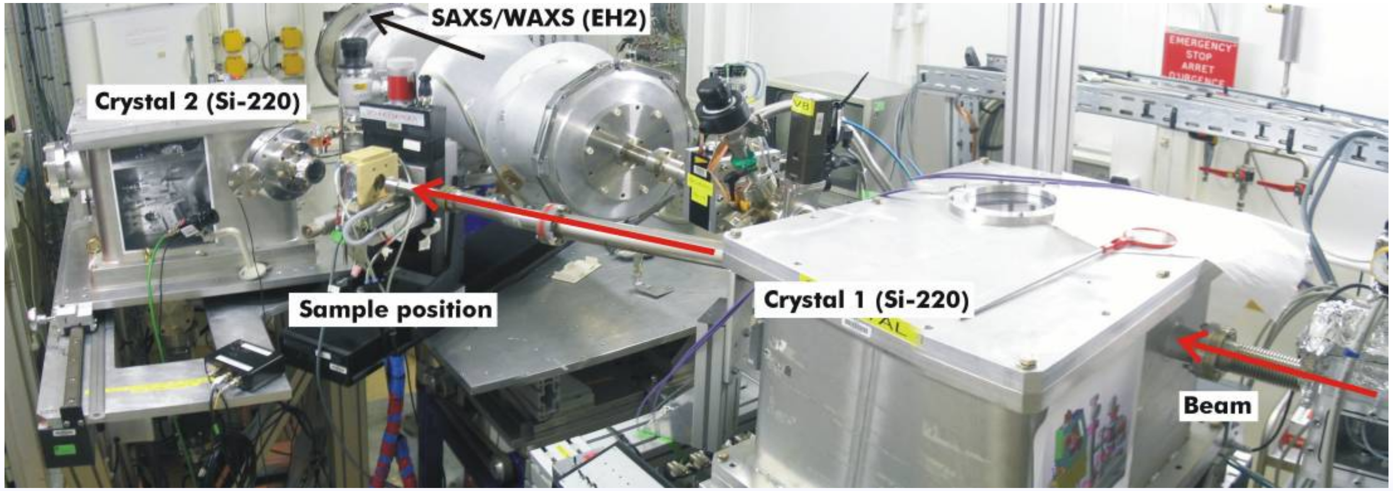
Bonse-Hart camera

apertures / slits replaced by **Si single crystals** (very low angular aceptance):

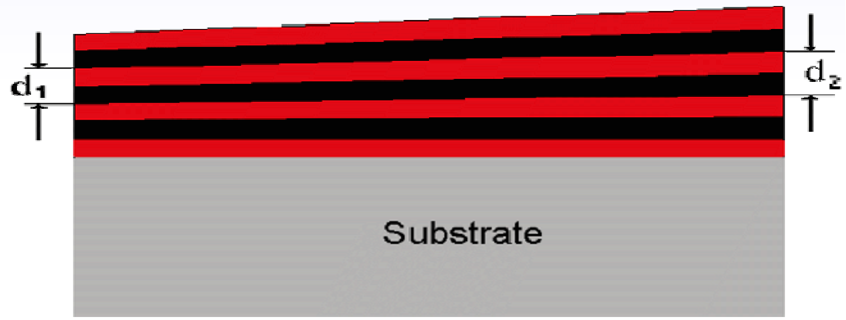




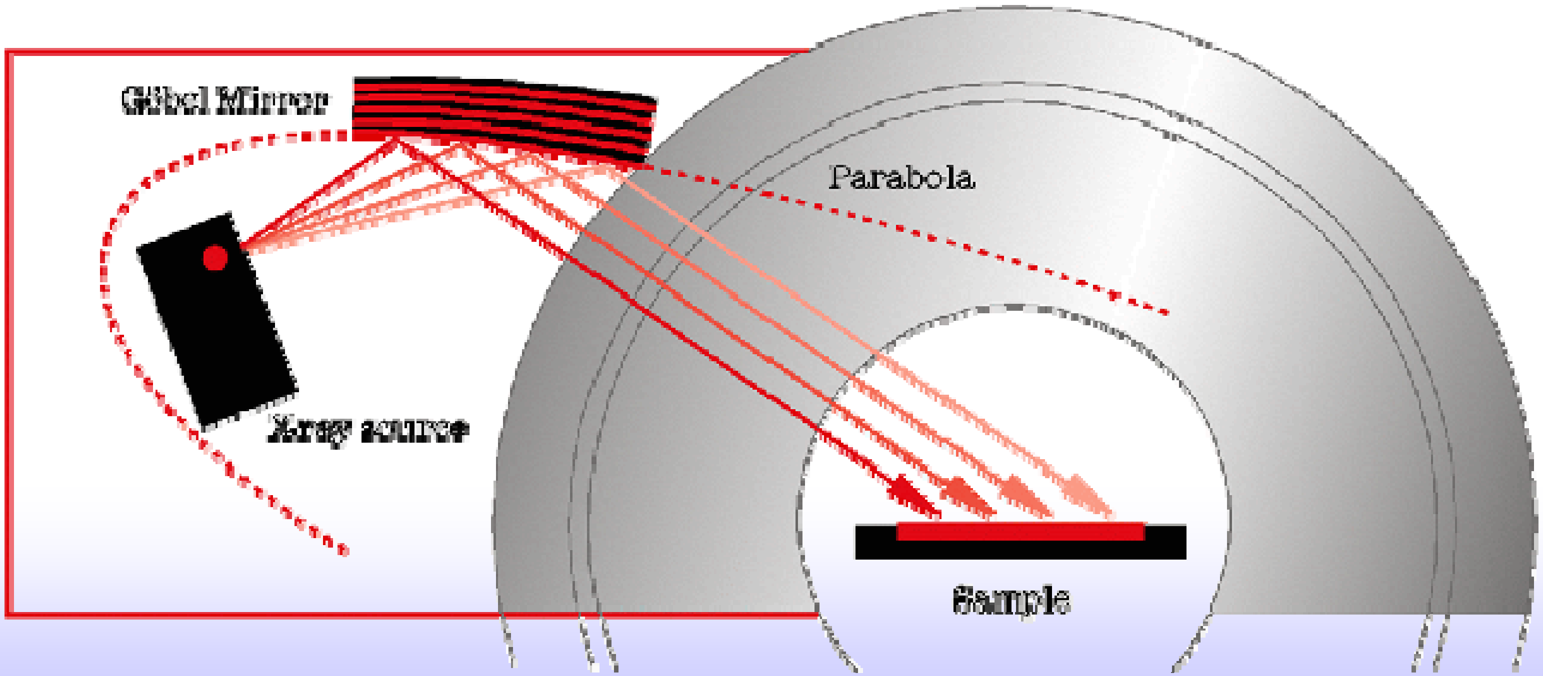
+ extremely high resolution (d_{max} = 7 µm)
- low flexibility in flux and resolution

SAXS in the laboratory

very parallel radiation (low divergence)
with **Göbel mirrors** (graded multilayers)



but: lower flux, fixed energy



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Small-angle X-ray scattering (SAXS) with synchrotron radiation

- Introduction to small-angle scattering
- Instrumentation
- Examples of research with SAXS
    - SAXS with a microbeam: cellulose
    - porosity development in carbon fibres

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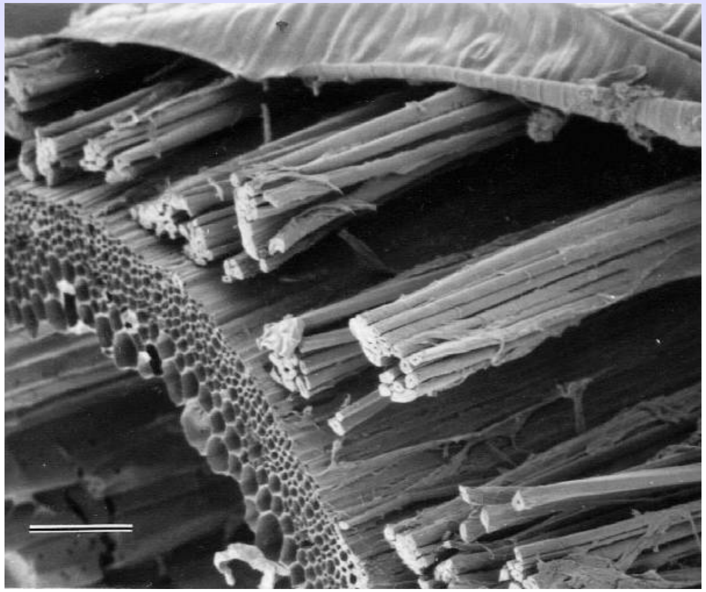
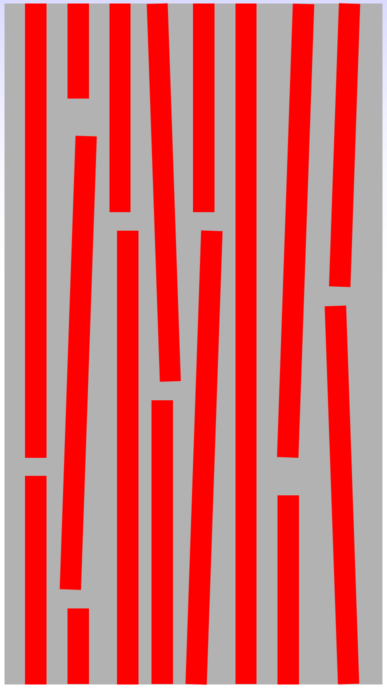
Microfibril orientation in cellulose fibres



flax fibres



orientation of crystalline microfibrils responsible for mechanical strength and stiffness

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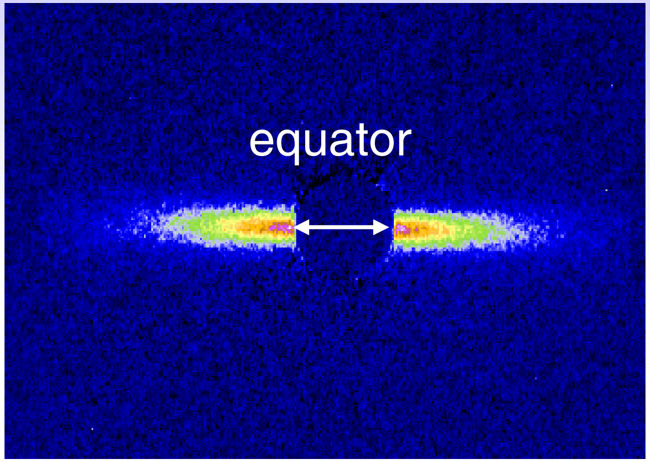
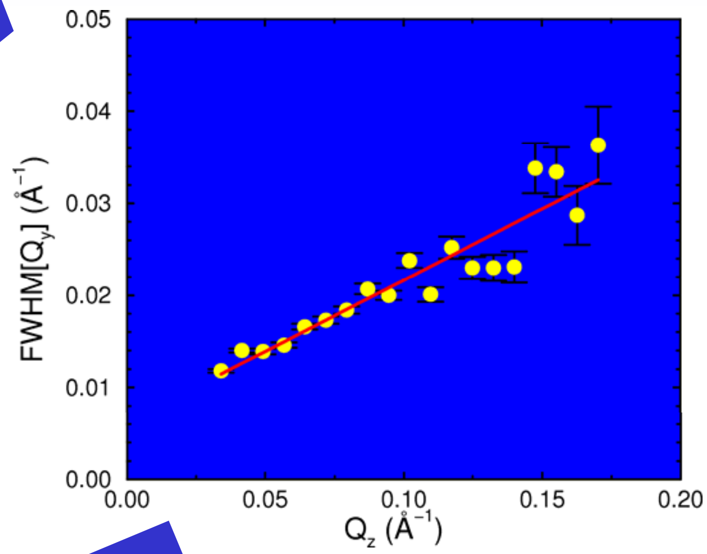
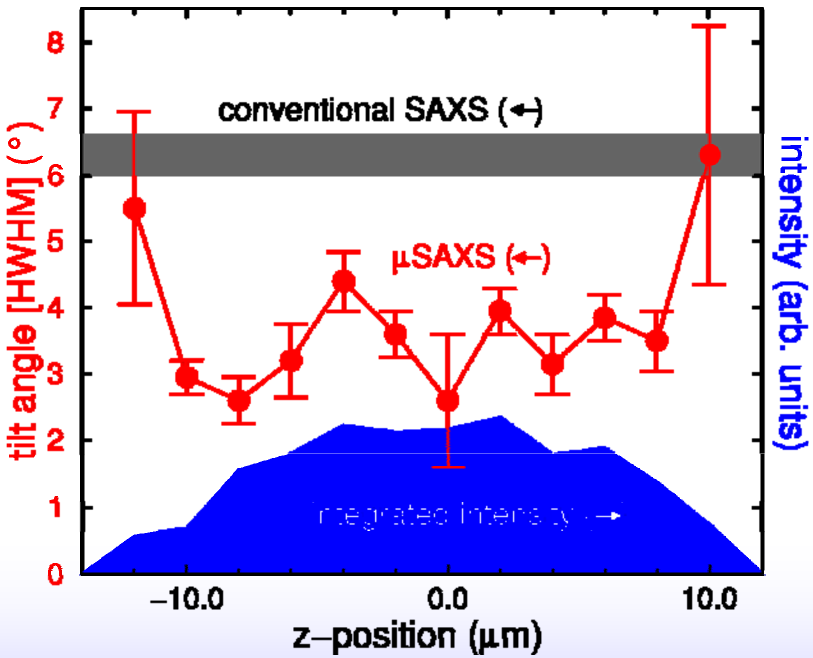
measurement with µSAXS (2 µm beam size) on **single** fibres

Micro-SAXS on flax cellulose fibres



increasing width
of streak with Q





position dependence of
microfibril alignment

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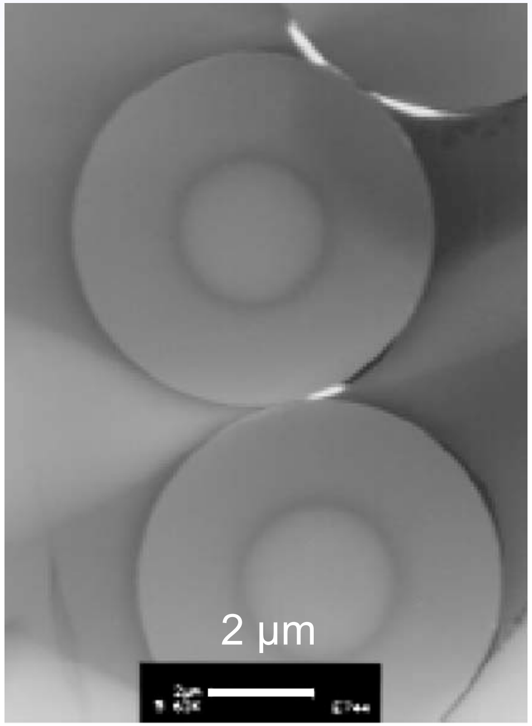
M. Müller, C. Czihak, G. Vogl, P. Fratzl, H. Schober, C. Riekel
Macromolecules **31**, 3953-3957 (1998)

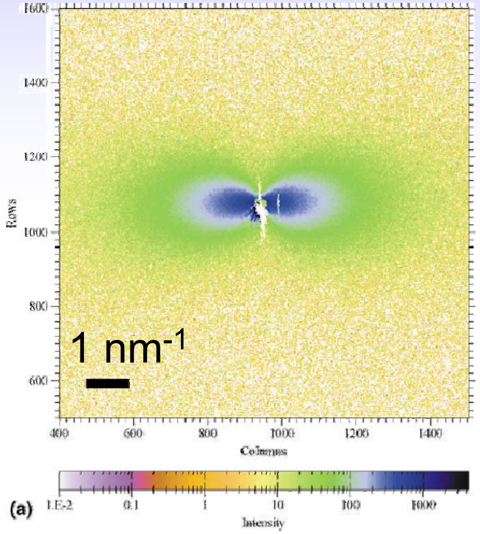
Porosity development in carbon fibres

PAN-based carbon fibre
with skin-core structure

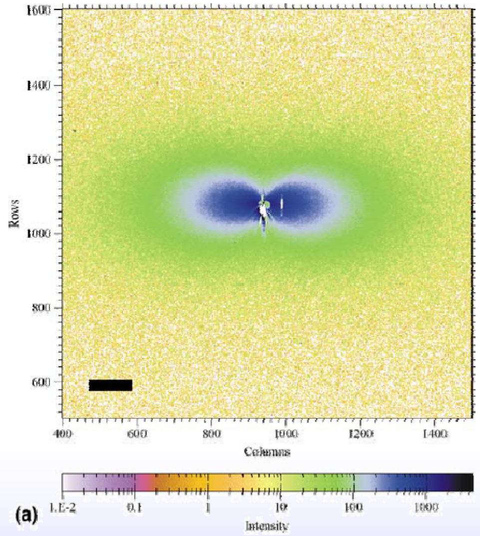


2D µSAXS patterns:

untreated



after activation
with **NaOH**
(2 h at 750 °C)



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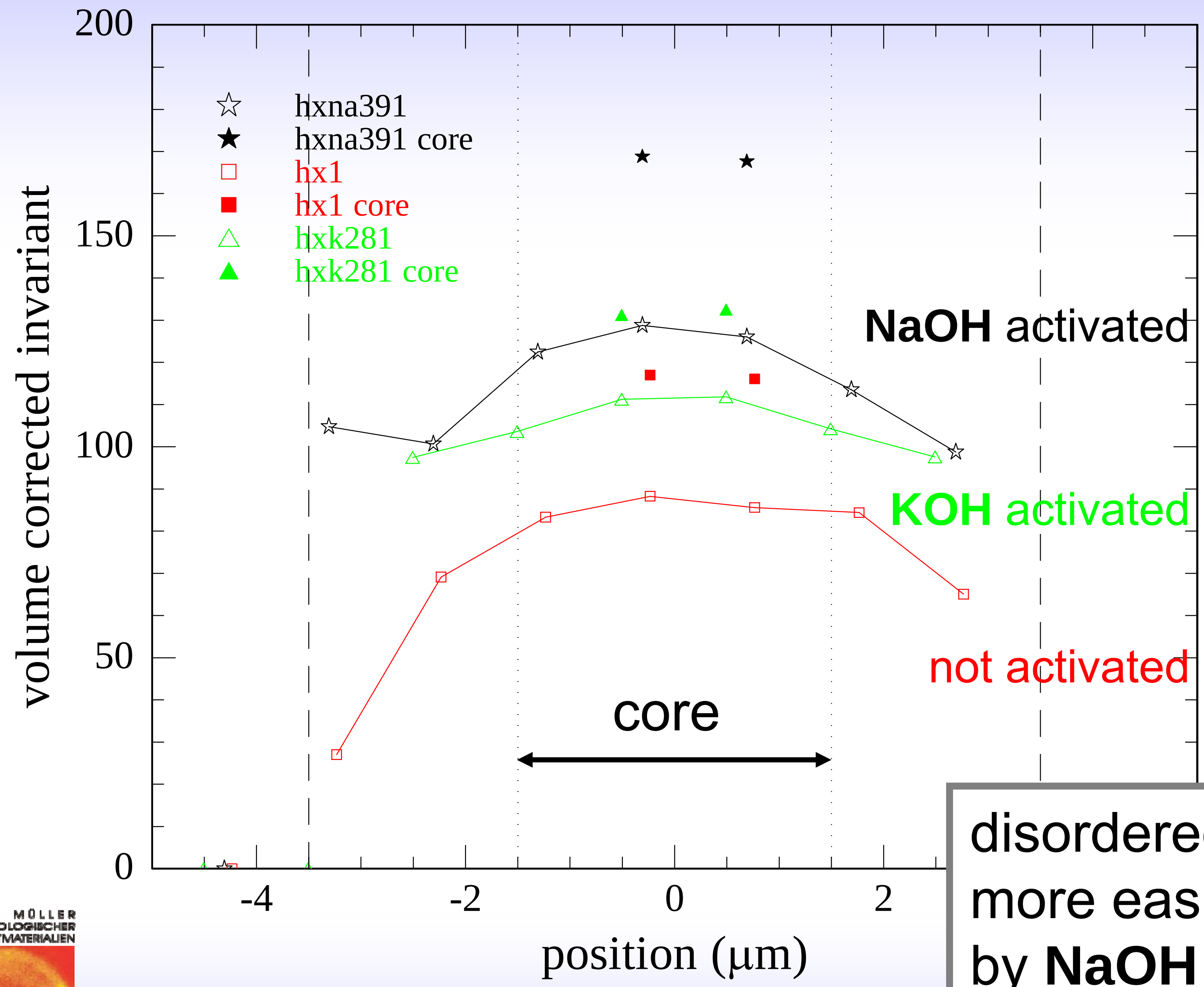
D. Lozano Castelló, J. A. Maciá Agulló, D. Cazorla Amorós, A. Linares Solano, M. Müller, M. Burghammer, C. Riekel. *Carbon* **44**, 1121–1129 (2006)

Porosity development in carbon fibres



(beam size 0.5 µm)

disordered core region more easily activated by **NaOH** than by **KOH**

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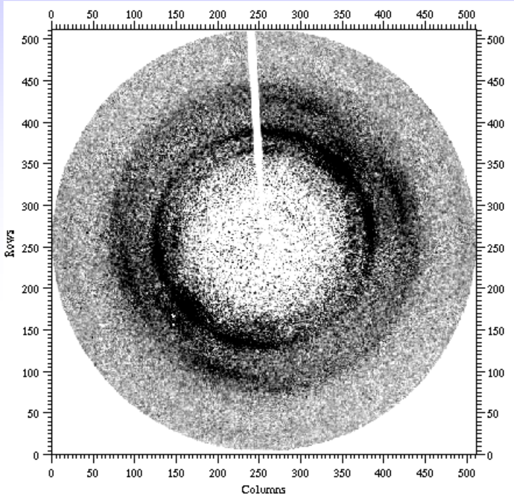
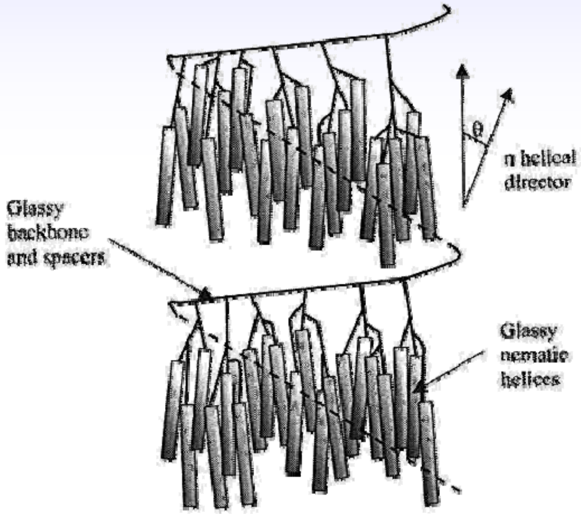
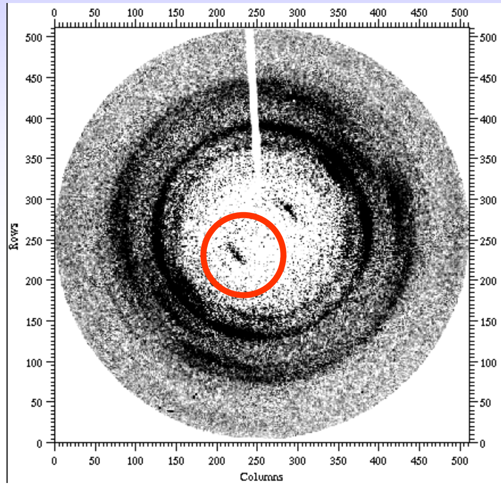
Micro-SAXS on single starch granules

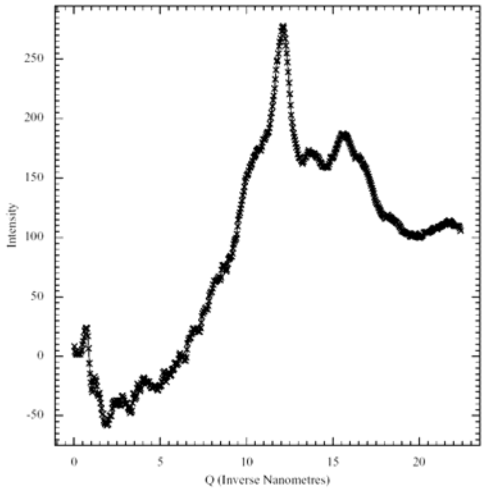
dry

wet

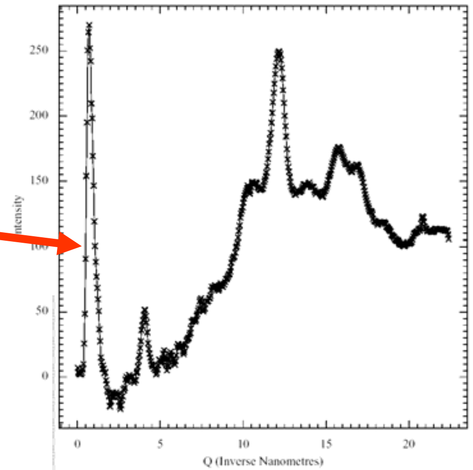


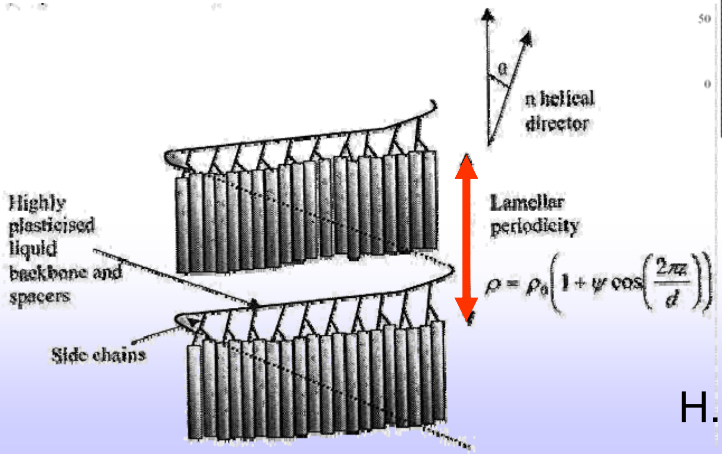






appearance of new reflections at 1.6 nm





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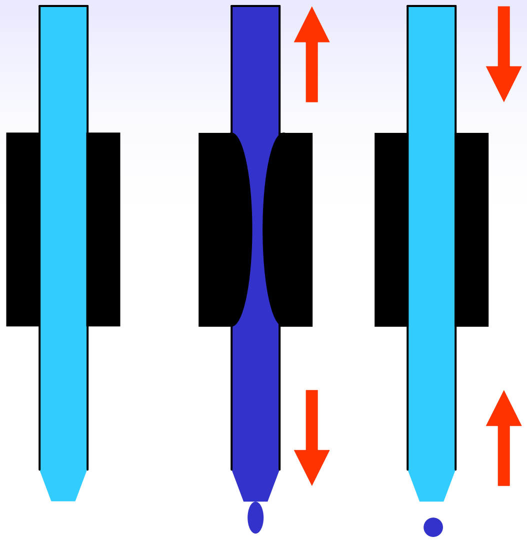
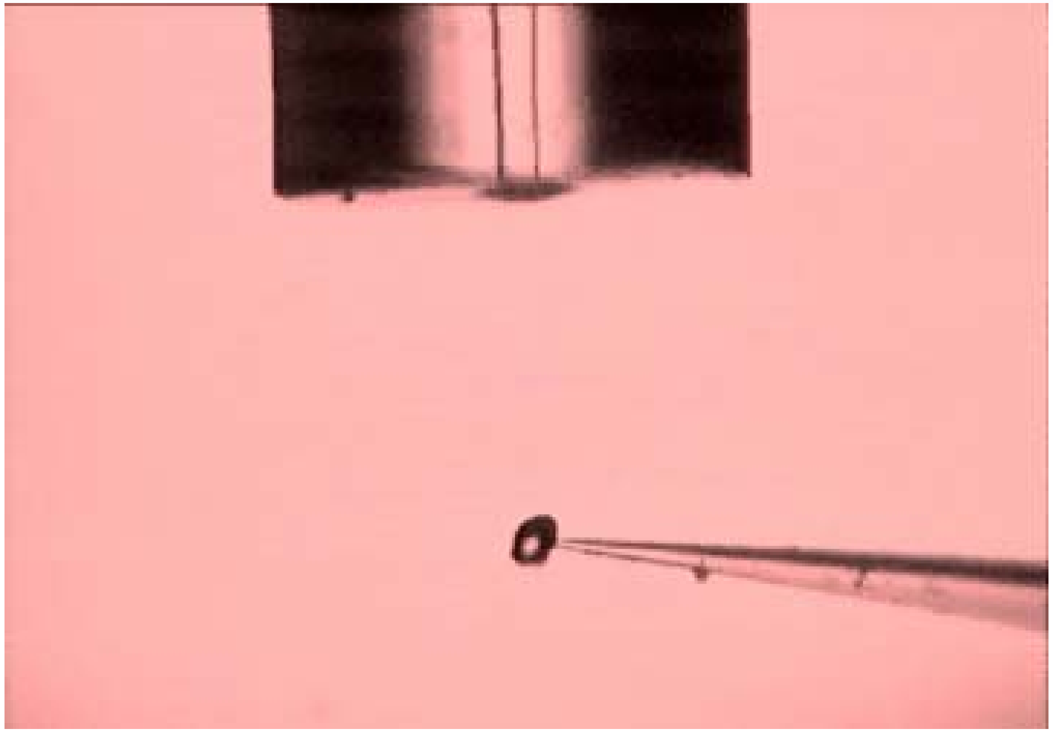
DER CAU ZU KIEL

H. Lemke, C. Riekel (2003)

Microdroplet generator





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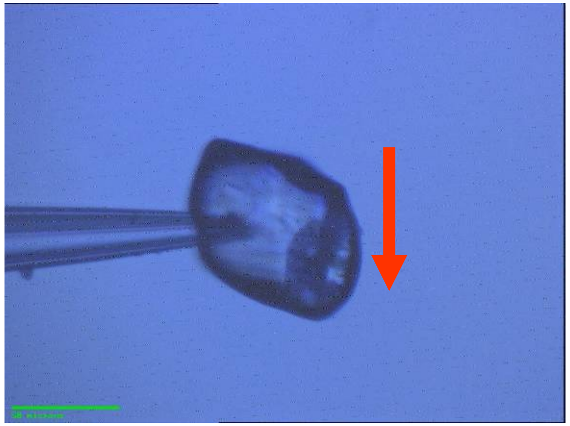
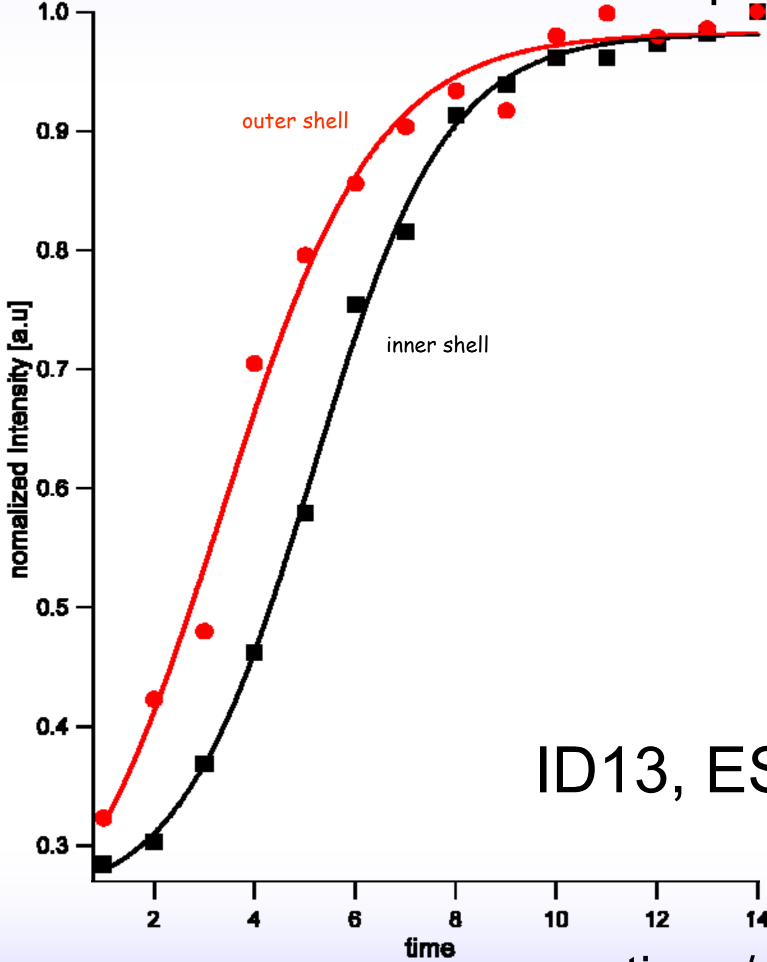
Time-resolved kinetics (seconds): Hydratisation of starch granules



scanning of a single starch grain during the hydratisation reaction

droplet frequency 1 s^{-1}

intensities of the 1.6nm peak



ID13, ESRF

time / 4 s

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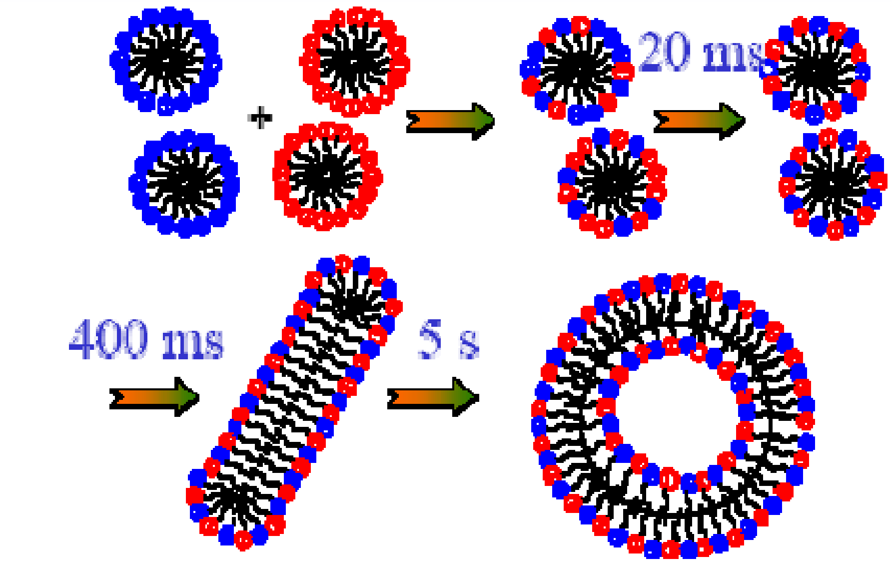
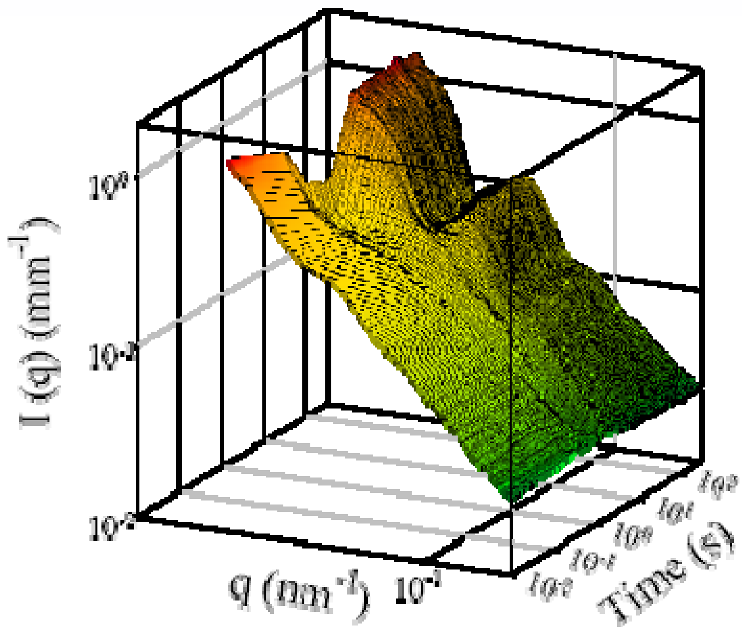
Time-resolved kinetics (milliseconds): Self-assembly of ionic surfactants





Schmoelzer *et al.* *Phys.Rev.Lett.* **88**, 258301, (2002)

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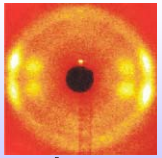

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ID02, ESRF; **20 ms** exposure!

Anomalous X-ray scattering

energy-dependent atomic scattering factors (up to 20 % variation) close to X-ray absorption edge:

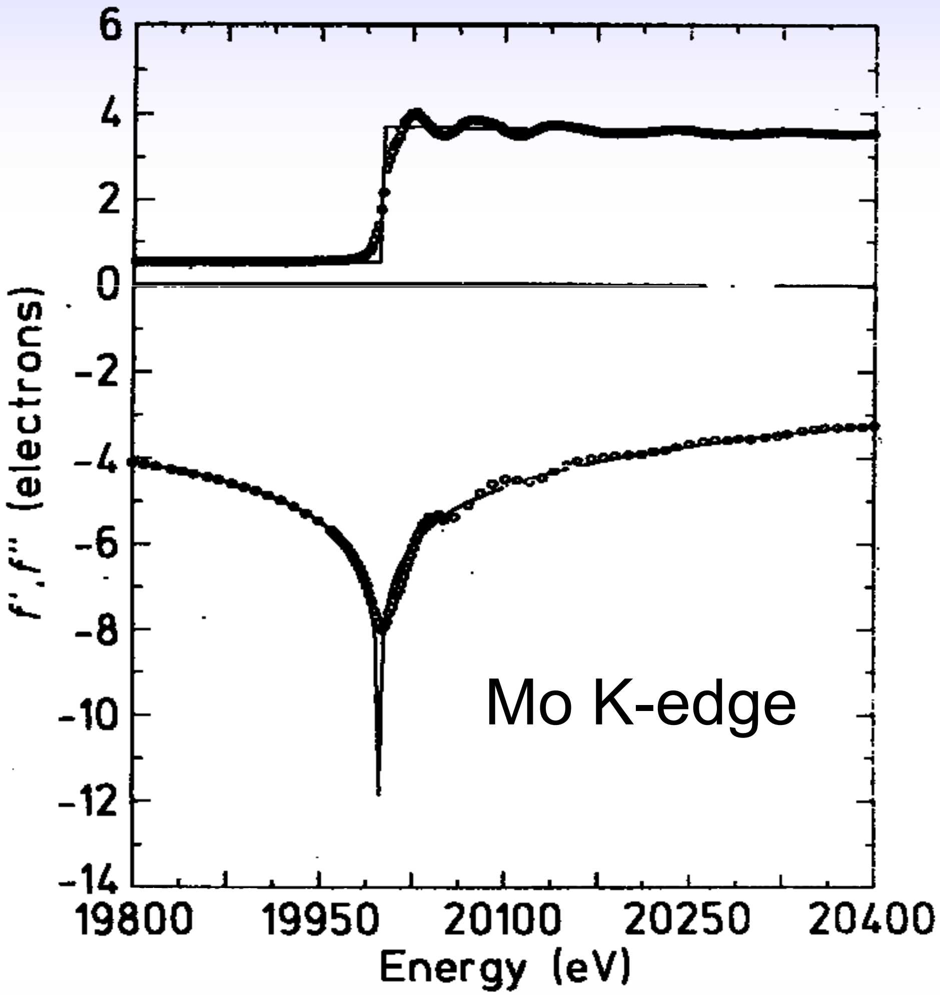
$$f(E) = Z + f'(E) + if''(E)$$

atomic number

anomalous scattering factor

absorption

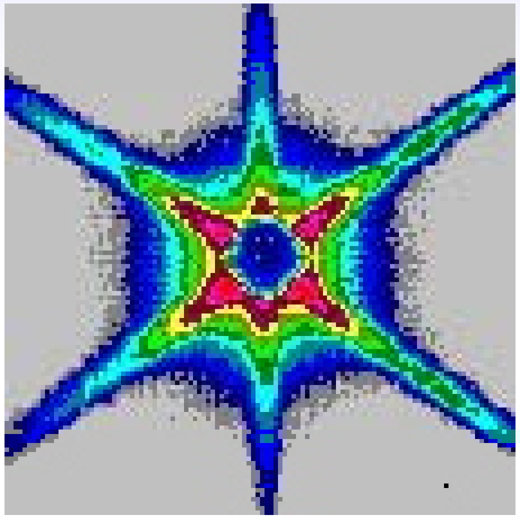
⇒ contrast variation



Iron oxide precipitates in copper single crystal containing 1 at% Fe

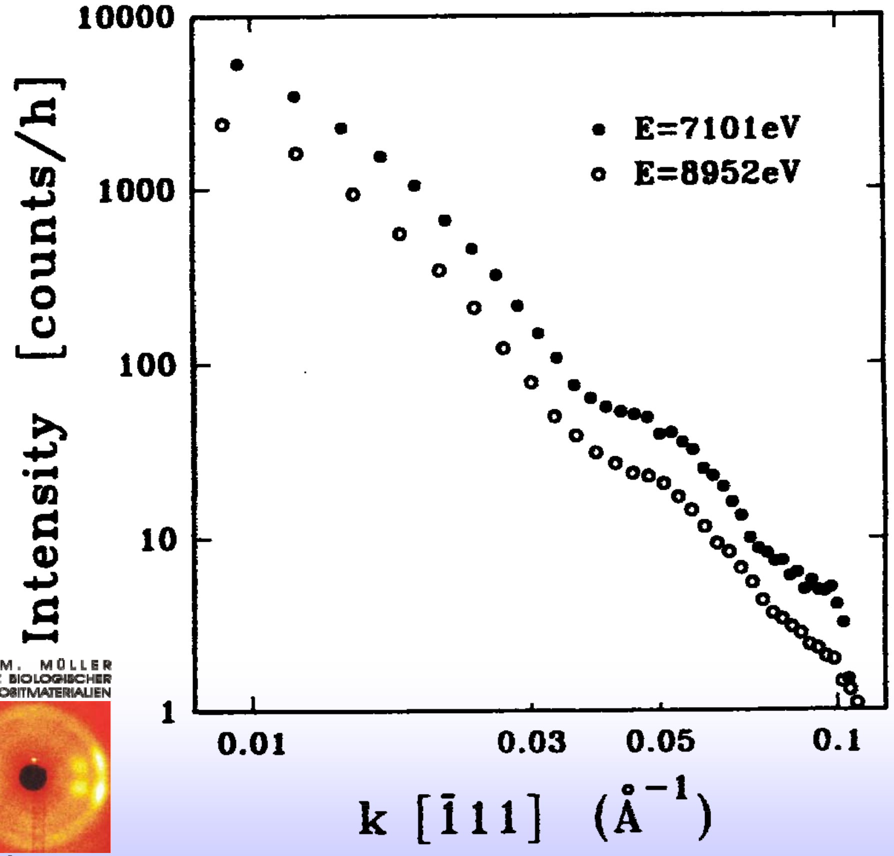
2 species of iron oxide precipitates:
(1) platelets with 200 Å ∅ on {111}
(2) platelets with 330 Å ∅ on {100}

(2)



(1)

(1)



contrast variation by measuring at Cu and Fe edges:
(1) Fe_3O_4
(2) γ-Fe_2O_3

O. Paris et al., Acta metall. Mater. **42**, 2019 (1994)

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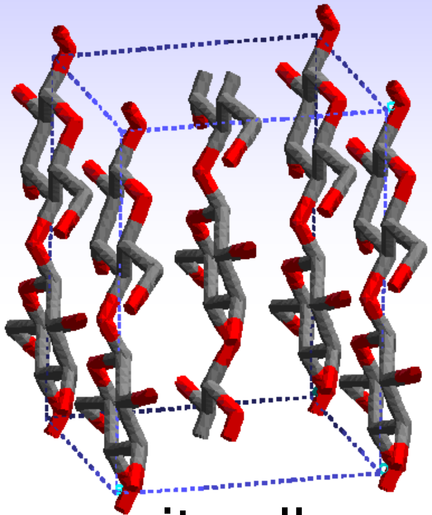
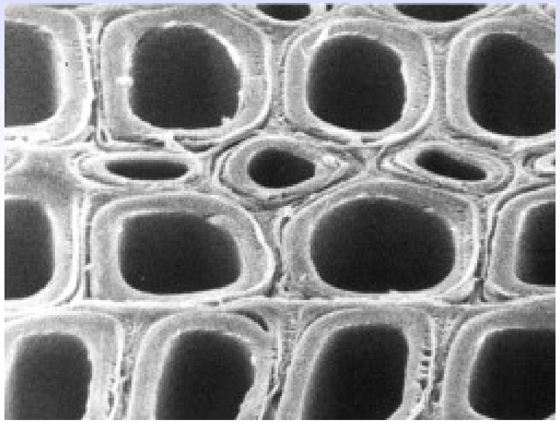
Hierarchical cellulose structure

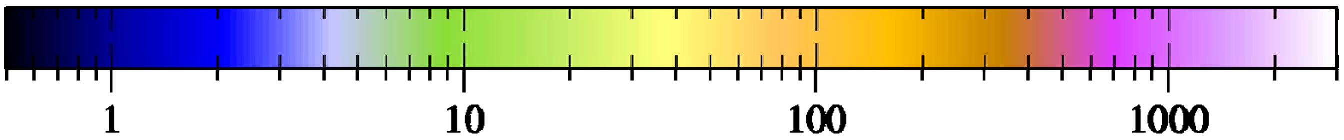


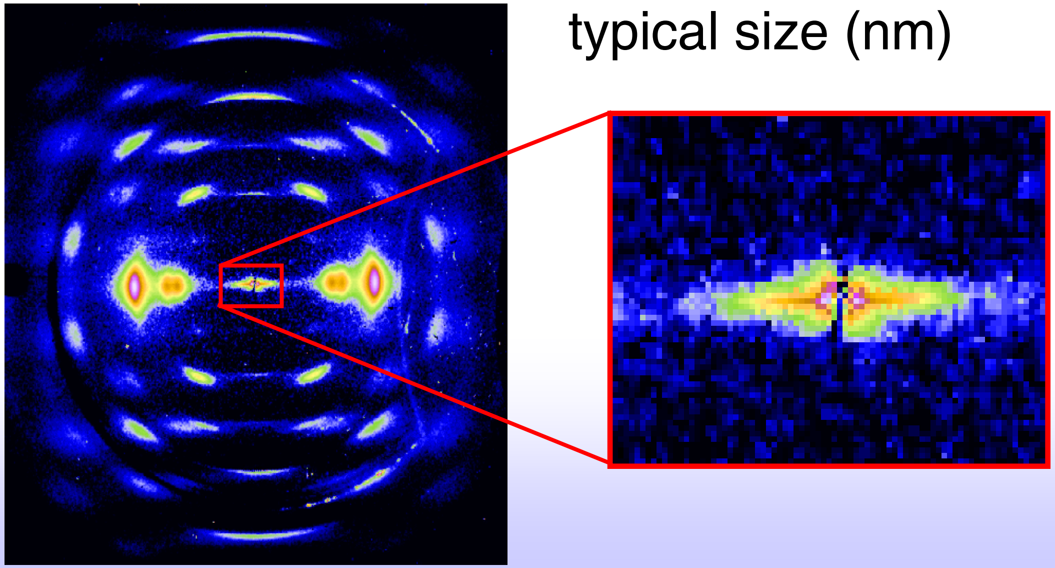
unit cell

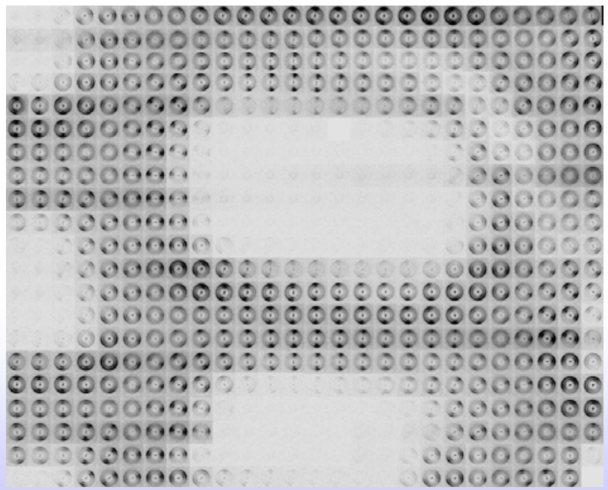
microfibrils



plant cell walls







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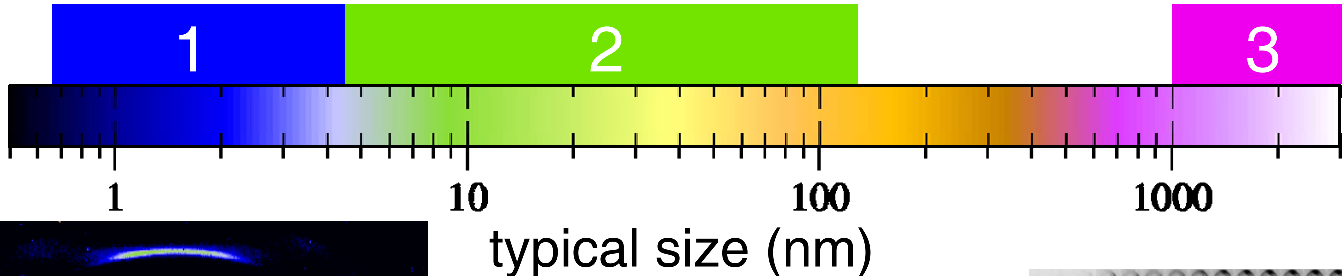
Position-resolved X-ray diffraction and small-angle scattering with a microbeam

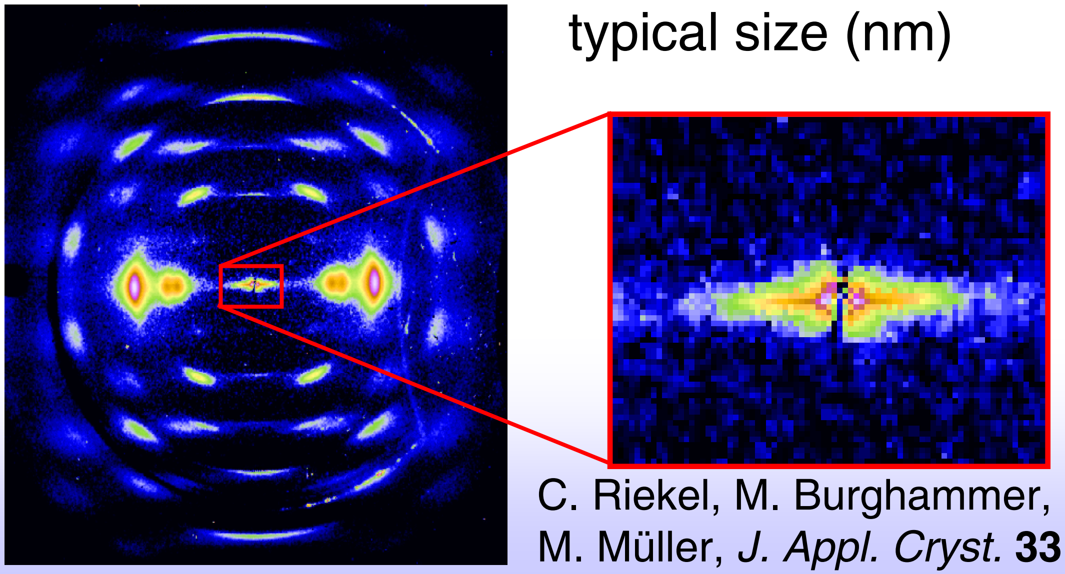
Simultaneous information on three length scales:

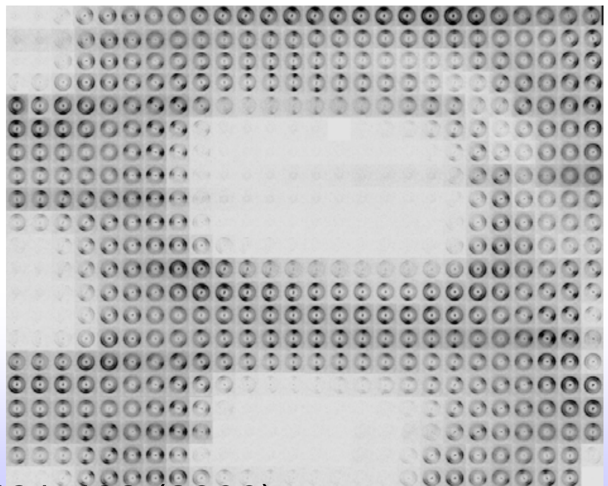
diffraction (WAXS): unit cell

SAXS: pores, particles

position resolution: optical microscopy







C. Riekel, M. Burghammer, M. Müller, *J. Appl. Cryst.* **33**, 421-423 (2000)

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