EXPLORING SAXS AND USAXS TO MEASURE SEVERAL PROPERTIES OF SOFT MATTER USING SMALL AMOUNT OF SAMPLE

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WHAT IS SAXS

SMALL ANGLE X-RAY SCATTERING

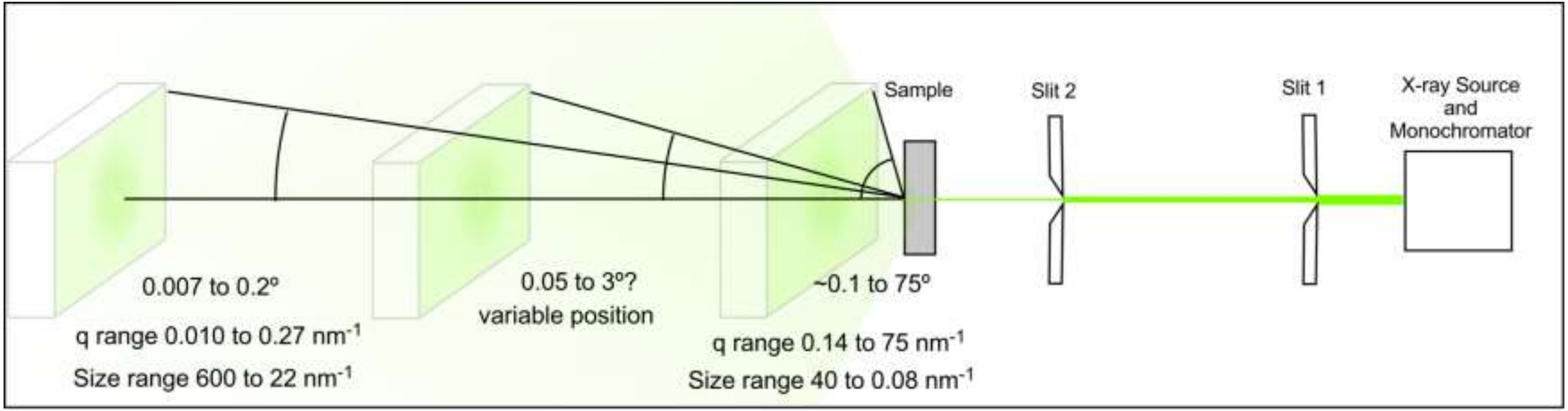
Measures intensity of scattered (X-ray) light versus and angle

Ensemble average technique (good statistics)

Small angle → Large structure (SAXS)
Large Angle → Small structure (WAXS)

SAXS SETUP

X-RAY – COLLIMATION – SAMPLE – DETECTOR (MOVEABLE)



Scattering vector $q = \frac{4\pi}{\lambda} \, sin(\Theta)$

$\lambda_{Cu} = 0.154$ nm

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

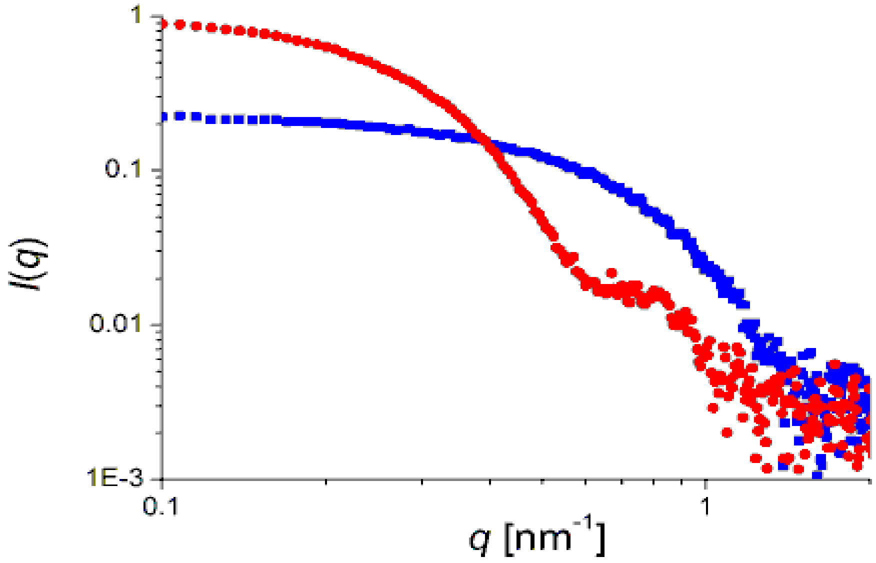
MEASUREMENT

DATA REDUCED TO 1D (FROM 2D SCATTERING)

- I(q) = Intensity of X-ray scattered
  as a function of q

- q = Scattering vector
- q = 4 π sin(θ) / λ

- θ = scattering angle
- λ = wavelength

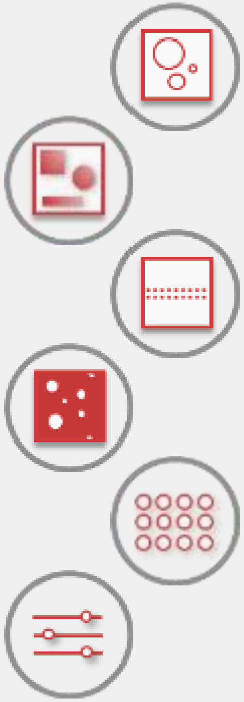


TYPICAL SAMPLES & RESULTS

- Nanoparticle dispersions
- Proteins in solution
- Surfactants, emulsions
- Liquid crystals
- Catalysts
- Mesoporous materials
- Polymers
- Composite materials
- Fibers
- Surfaces, thin films

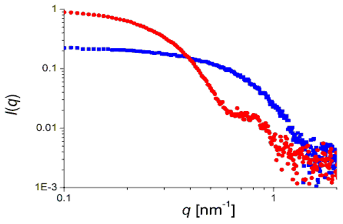
SAXS

- Size, size distribution
- Shape
- Internal structure
- Porosity, specific surface area
- Crystallinity
- Orientation

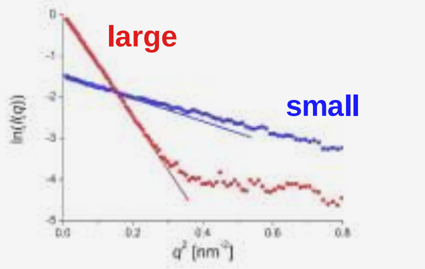


PRINCIPLE DATA EVALUATION ROUTES

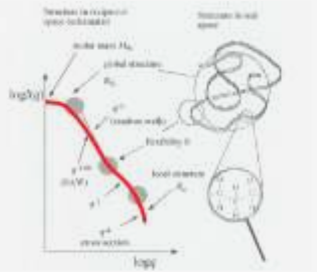
MEASUREMENT



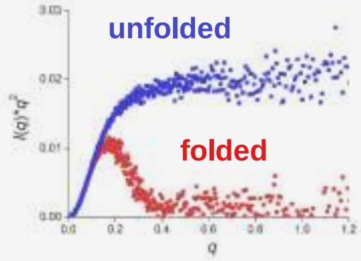
Guinier | Size estimate



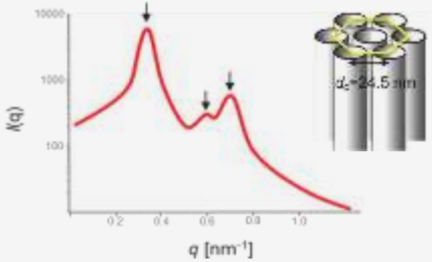
Slope analysis



Kratky plot | Folding state

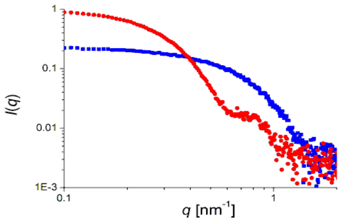


Peak analysis



PRINCIPLE DATA EVALUATION ROUTES

MEASUREMENT



Fourier transformation

- GIFT
- ATSAS

Monte Carlo approach

- McSAS

Model fitting

- SasView
- SASfit
- … many more

SAXS FOR SOFT MATTERS

APPLICATIONS TO FOLLOW:

- Surfactants
- Particle size
- Surface area of porous materials (BET like)
- Mesoporous materials
- Phase transitions
- Micrometric size measurements using USAXS

SURFACTANTS

- Example showing RheoSAXS of surfactants forming lamellar and onion-like mesophase

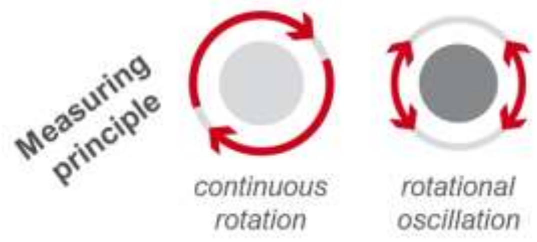
RHEOSAXS: RHEOLOGY WITH SCATTERING

MOTIVATION

- Determine rheological and structural properties of a material simultaneously

RheoSAXS measuring set-up

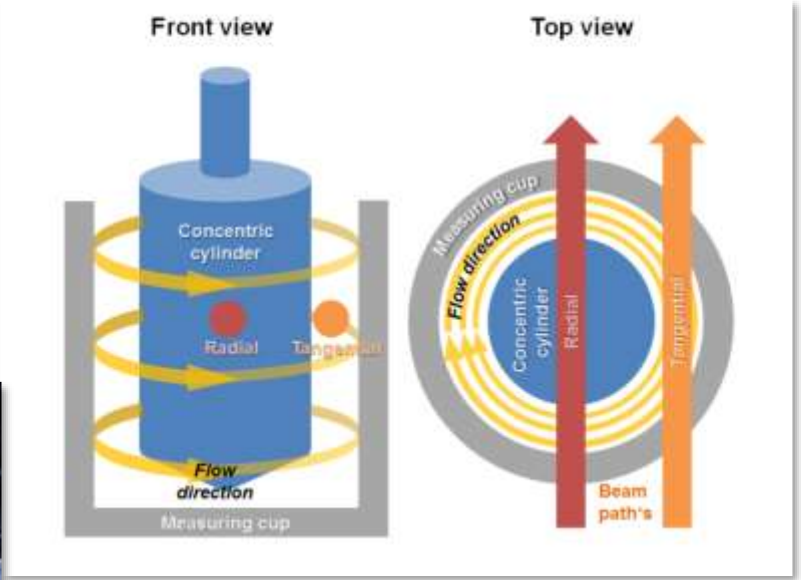
- DSR 502 measuring head with air bearing
- Temperature control: ambient to 200 °C
- Min. torque (rotation): 10 nNm



RHEOSAXS: RHEOLOGY WITH SCATTERING

EXPERIMENTAL SET-UP

- Offering two measurement geometries: **radial & tangential**
- The radial beam (R) probes perpendicular to the flow direction.
- The tangential beam (T) probes parallel to the flow direction

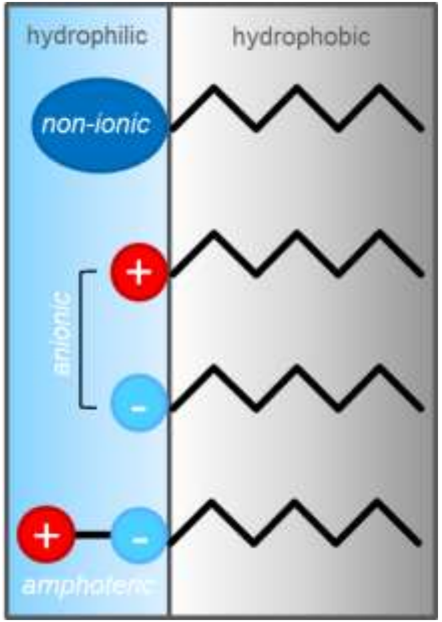


RHEOSAXS: RHEOLOGY WITH SCATTERING

NON-IONIC SURFACTANTS

- Used in a wide field of applications:
  - detergents
  - wetting agents
  - emulsifiers and solubilizers in cosmetics
  - personal and health care

- Compared to ionic surfactants, some non-ionic surfactants have superior properties like:
  - superior cleaning performance
  - enhanced solubility (especially in hard water)
  - better chemical stability



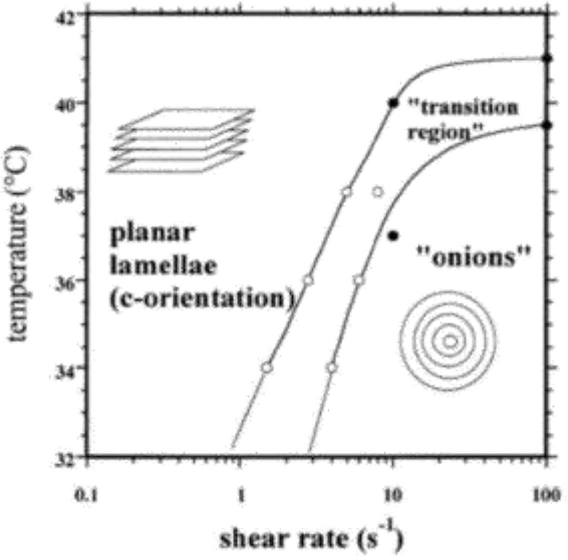
RHEOSAXS: RHEOLOGY WITH SCATTERING

SAMPLE INFO & EXPERIMENTAL SET-UP

- polyoxyethylene alkyl ether (C_mE_n)-water two-component system (40 % w/w)
- Formation of planar lamellae at no shear or low shear rates
- Onion-like structures can evolve at higher shear rates and in dependence of the temperature

Measurement set-up

- Axial mode
- $0.05\ nm^{-1} < q < 2.5\ nm^{-1}$
- T = 25, 30, 35 and 40 °C

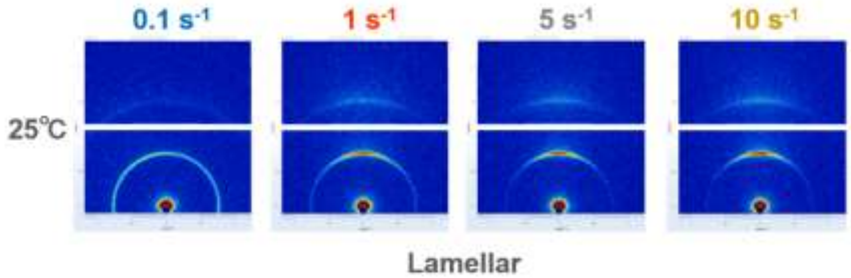


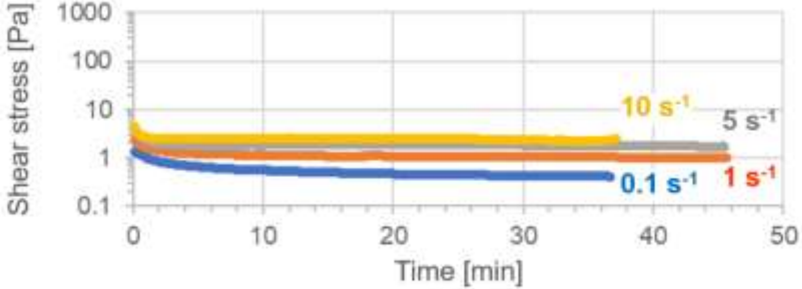
Oliviero C., et al., *Colloids Surf. A: Physicochem. Eng. Asp*. 228 (2003) 85)

RHEOSAXS: RHEOLOGY WITH SCATTERING

RESULTS AT 25 °C

- Characteristic scattering pattern of a lamellar structure is seen
- With increasing shear stress, the initially isotropic structure is oriented and leads to an anisotropic pattern
- Shear stress slightly decreases at the beginning and then settles to a constant value

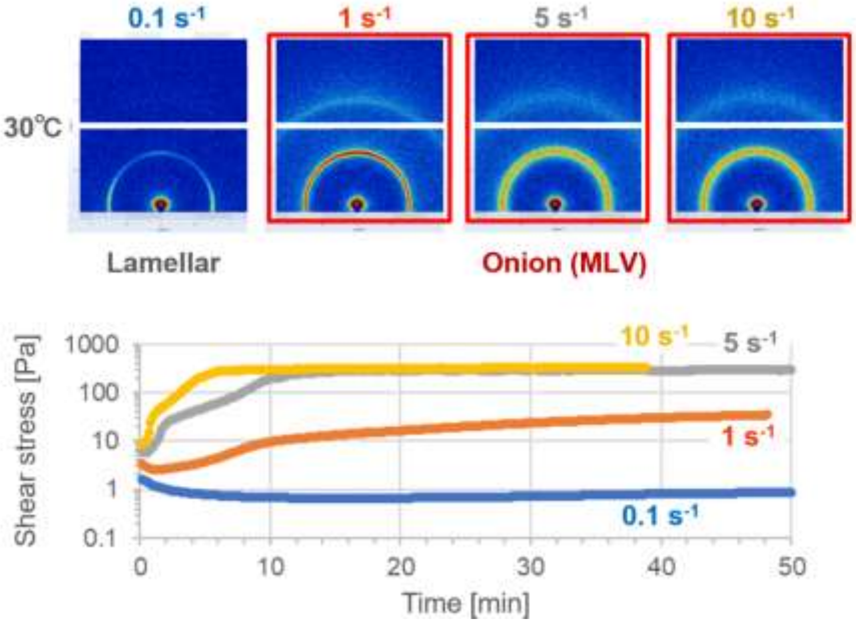




RHEOSAXS: RHEOLOGY WITH SCATTERING

RESULTS AT 30 °C

- Initial structure is still lamellar
- Already at a shear rate of 1 s^{-1} and higher, the shear stress increases significantly
- Lamellar peak in the scattering pattern changes to an (isotropic) ring
  ⇨ change to an onion-like multi-layer vesicle (MLV) structure



RHEOSAXS: RHEOLOGY WITH SCATTERING

LAMELLAR STRUCTURES AT 25 °C

- The scattering intensity *I(q)* is proportional to the product of the Form factor *P(q)* and the Structure factor *S(q)*
  - number of bilayers
  - the lamellar *d*-spacing
  - Caillé parameter (bilayer flexibility)

- Upon shear stress, the bilayers strongly arrange and the flexibility or rippling of the structure is suppressed

$$I(q) \propto P(q)\, S(q)$$

Shear rate in s^{-1}	Caillé parameter
0.1	0.257
1	0.203
5	0.198
10	0.194

RHEOSAXS: RHEOLOGY WITH SCATTERING

ONION STRUCTURE AT ≥ 30 °C

- Conclusions to be drawn:
  - the number of bilayers decreases with increasing shear rate
  - the *d*-spacing becomes narrower when changing from lamellar to onion
  - the Caillé parameter becomes smaller with increasing shear rate (rippling fluctuation of the bilayer is suppressed at higher shearing force)

Shear rate in s^{-1}	No. of bilayers	d-spacing in nm	Caillé parameter
0.1	18.6	8.43	0.271
1	19.4	8.34	0.230
5	7.75	8.12	0.231
10	7.76	8.07	0.246

  - Either number of bilayers from the outside of MLVs is decreasing or the stacked lamellar structure on the outside of MLVs is disturbed at high shear rates

PARTICLE SIZE

- Example showing High-resolution SAXS measurement of SiO_2 nanoparticles

PUSHING SAXS RESOLUTION

MOTIVATION

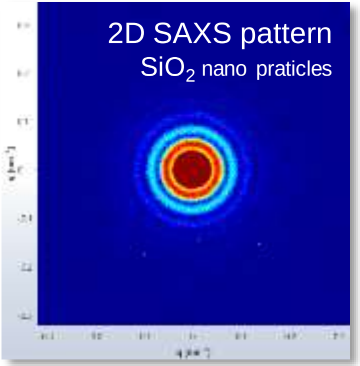
- Resolving very large nanostructures by SAXS (diameter ≤ 314 nm, d-spacing ≤ 628 nm) requires scattering data at very low angles

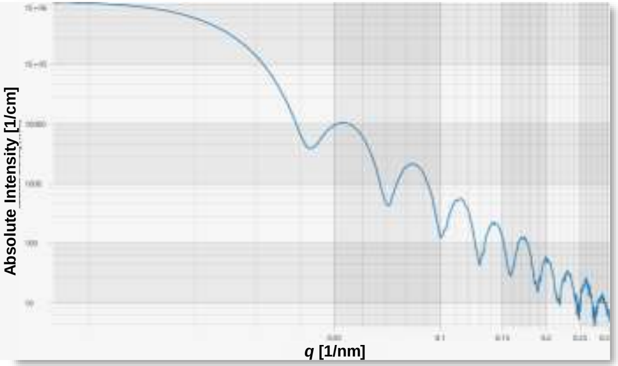
CHALLENGE

- Measuring high-resolution SAXS data in short time requires high quality and design of the used instrument and its beam-forming components: X-ray source, optics, collimation

Infos

Batch:	SiO_2-R-L4026-1
Mean Diameter [µm]:	0.213
Standard Deviation [µm]:	0.006
CV [%]:	2.9
Solids Content [wt.-%]:	5

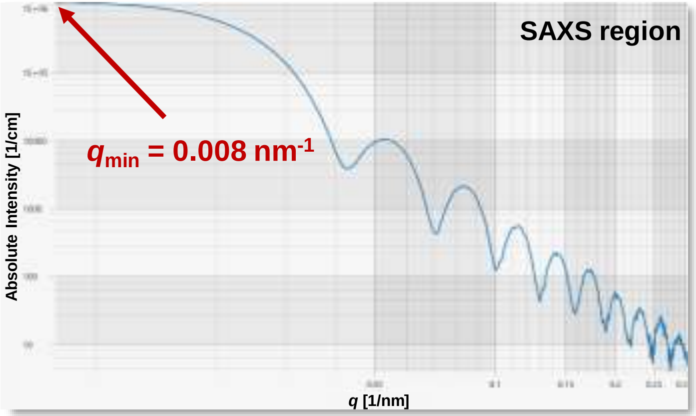


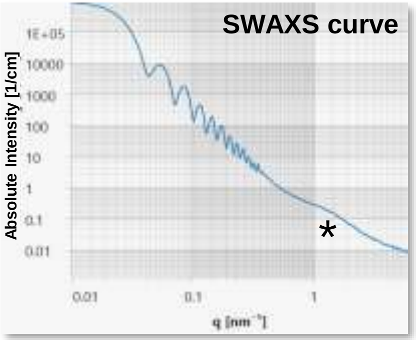


LARGE HOLLOW SiO_2 SPHERES

EXPERIMENTAL & RESULTS

- High-resolution SAXS measurement of SiO_2 nano-particle solution after background subtraction
  - ⇨ Exposure time: 1 hour
  - ⇨ High performance optic
  - ⇨ Beamstop-less
  - ⇨ 1st useable data point at 0.008 nm^{-1}
- The pronounced minima in the scattering curve relate to the form factor of the highly monodisperse particles. A second length scale (lower image *) corresponds to the shell thickness of the spheres.
- d_{max} = 211 nm (PCG, Glatter et al.)





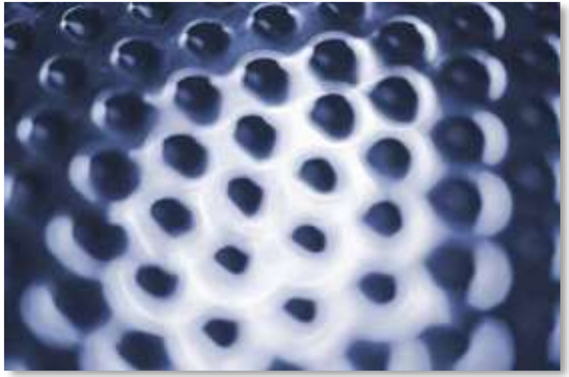
SURFACE AREA

- Example showing surface area measurement (BET like) of porous materials

SPECIFIC SURFACE AREA

MOTIVATION

- Porous materials can be found in a very wide range of applications.
- Knowing the **specific surface area** of energy storage materials, construction materials and catalysts is crucial
  - ⇨ Structural characterization of materials
  - ⇨ Development of new materials
  - ⇨ Product quality control



CHALLENGE

- Establishing SAXS as an alternative method to the well established gas adsorption (BET) technique

SPECIFIC SURFACE AREA

GAS ADSORPTION vs. SAXS

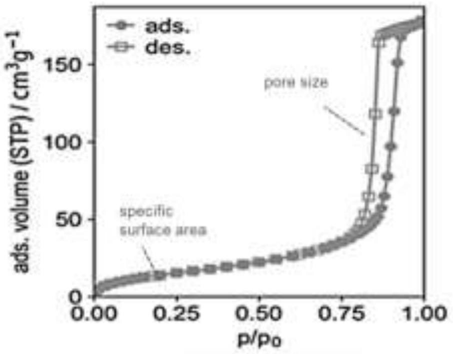
- Both methods probe the same length scale
  - ⇨ Structures from approx. 1 to 300 nm

SPECIFIC SURFACE AREA by SAXS

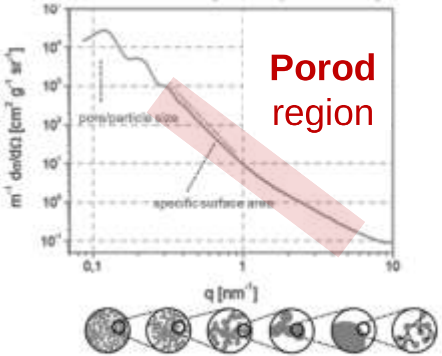
- Information on the specific surface area (SSA) is found at higher scattering angles: **Porod region**
- The basis for calculating the SSA is **Porod's law**

$$\lim_{q\to\infty} I(q) = A + K \cdot q^{-4}$$

Gas adsorption



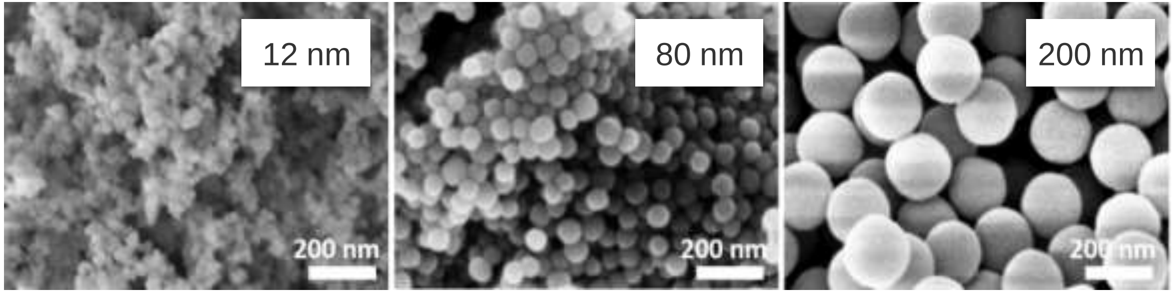
SAXS

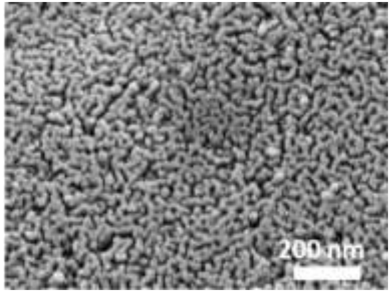


SPECIFIC SURFACE AREA

EXPERIMENTAL

- SAXS measurements were performed with the SAXSpoint system using the Heated Sampler
- The goal was to validate the SAXS method for determining the SSA of the non-microrporous reference materials





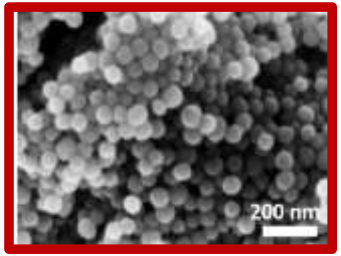
Silica particles with different diameter

Controlled pore glass (CPG) ERM-FD-121

Schlumberger et al., Microporous and Mesoporous Materials 329 (2022) 111554

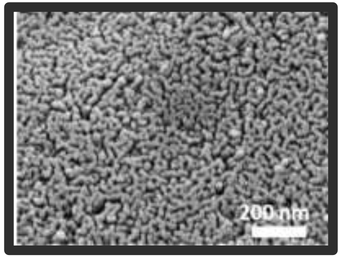
Anton Paar

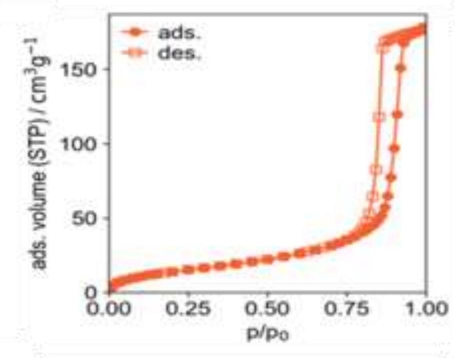
SPECIFIC SURFACE AREA

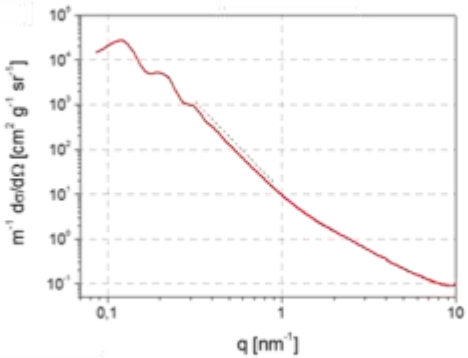


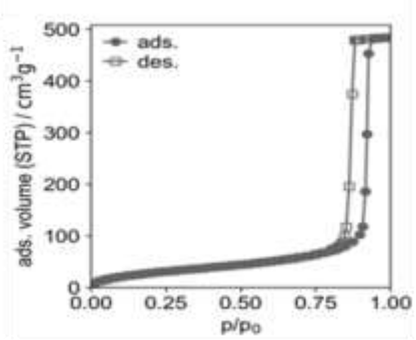
SiO_2 particles
***d* = 80 nm**
SSA = 47 m²/g

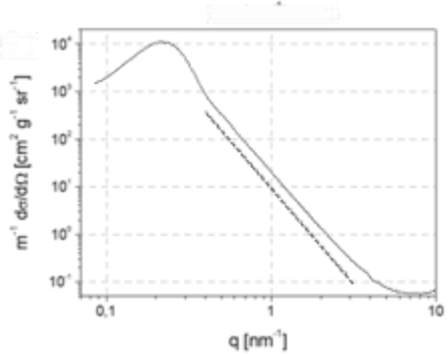
Controlled pore glass
SSA = 147 m²/g











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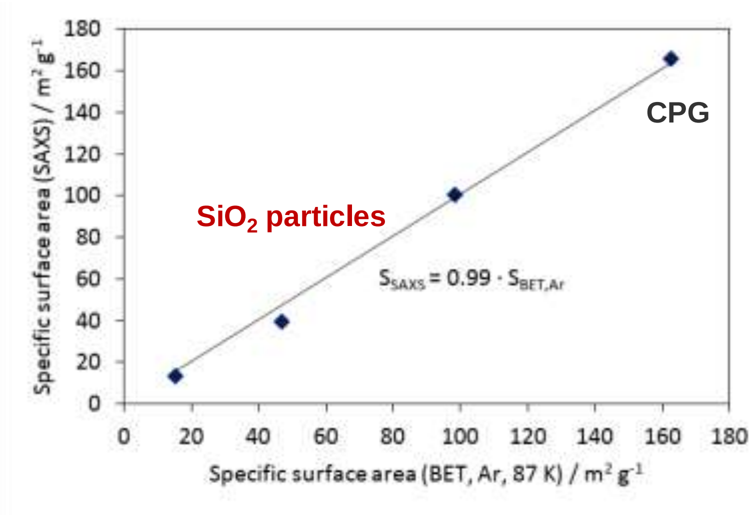
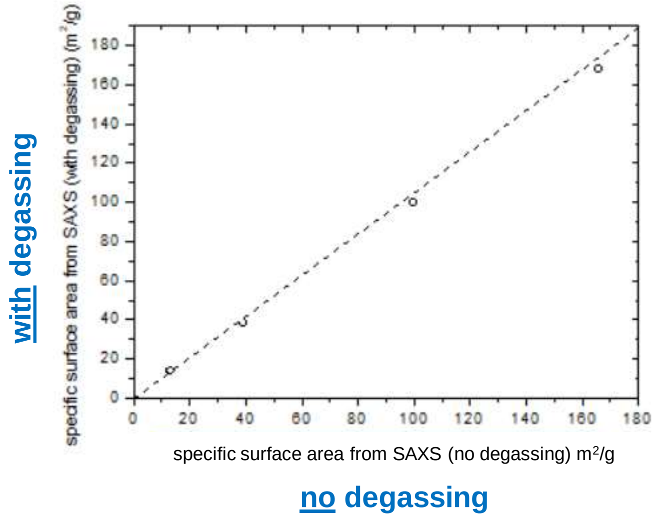
SPECIFIC SURFACE AREA

RESULTS

- Specific surface area obtained by SAXS and Ar BET match very well





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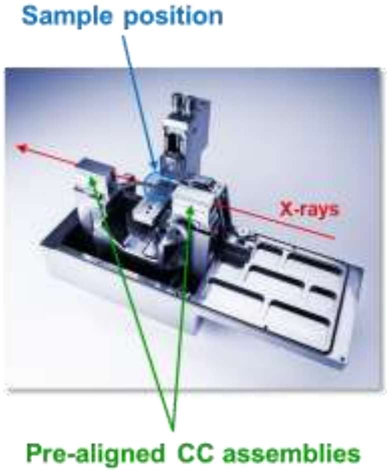
PARTICLE SIZE

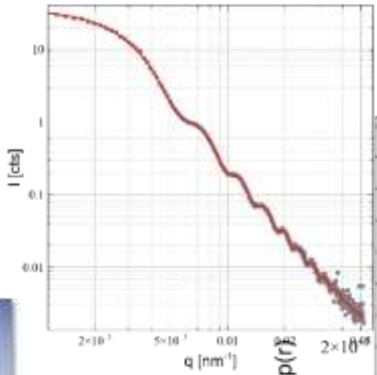
- Example showing USAXS (Ultra-Small Angle X-ray Scattering)

USAXS – ULTRA SMALL-ANGLE X-RAY SCATTERING

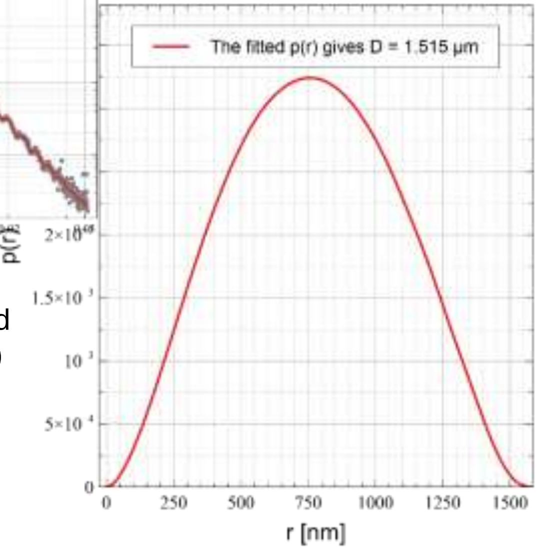
RESULTS

- SiO_2 particles with a verified diameter of 1.53 ± 0.02 µm
- Continuous flow stirring of the solution ➔ prevention of sedimentation
- IFT: PDDF with maximum dimension of 1.52 µm





1D *q*-plot (background subtracted)



Pair distance distribution function

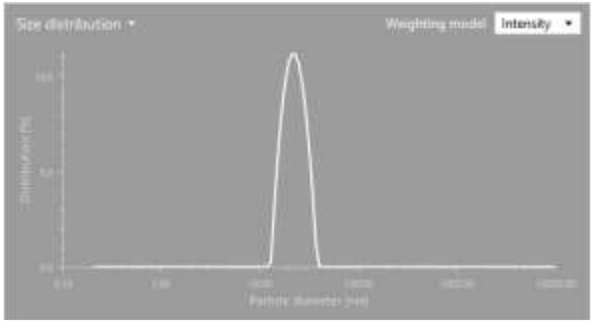
PARTICLE SHAPE

- Example showing shape of rod-like material

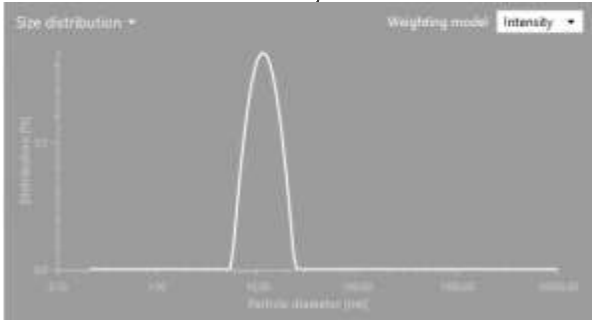
SAXS AND DLS

DLS & ELS RESULTS

- DLS determines the mean hydro-dynamic diameter (only size, no shape):
  - Ferric carboxymaltose: 24.4 nm
  - Iron sucrose: 11.9 nm
- Both samples show a narrow size distribution (polydispersity index < 20 %)
- ELS determines the zeta potential, i.e. the stability of the colloidal dispersion:
  - Ferric carboxymaltose: 6.8 mV
  - Iron sucrose: -29.5 mV



Size distribution of ferric carboxymaltose nanoparticles determined by DLS

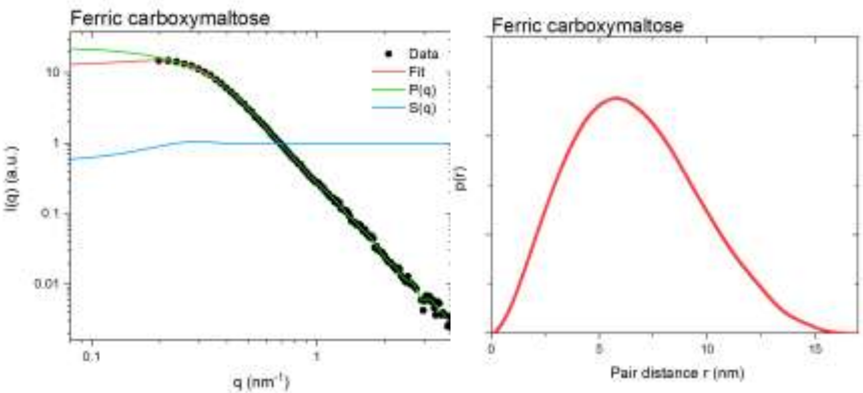


Size distribution of iron sucrose nanoparticles determined by DLS

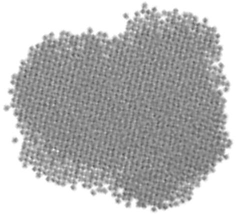
SAXS AND DLS

SAXS RESULTS

- SAXS determines the size and shape
- Ferric carboxymaltose
  - The calculated pair-distance distribution function (using program GIFT*) indicates a slightly elongated/prolate shape
    - Max. dimension: 17 nm
    - Averaged radius: ~ 6 nm
- A low-resolution 3D shape was calculated using the ATSAS** software



Scattering curves and pair-distance distribution function



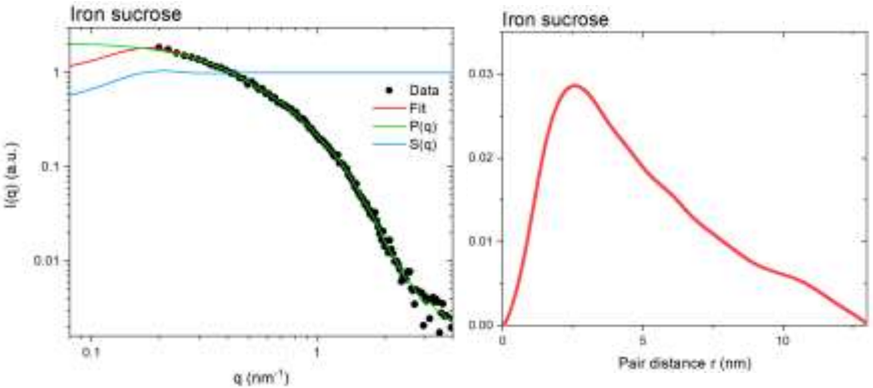
Averaged 3D shape (below) of ferric carboxymaltose

*O. Glatter, J. Phys.: Condens. Matter 18 (2006) 2403 **D. Franke, D.I. Svergun, J. Appl. Cryst. 42 3

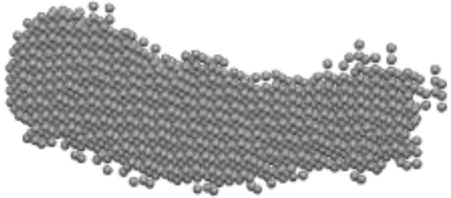
SAXS AND DLS

SAXS RESULTS

- Iron sucrose
  - The calculated pair-distance distribution function (using program GIFT) indicates a cylindrical shape
    - Averaged length: 13 nm
    - Averaged width: ~ 3 nm
- A low-resolution 3D shape was calculated using the ATSAS software



Scattering curves and pair-distance distribution function



Averaged 3D shape (below) of iron sucrose

O. Kratky and O. Glatter, Small-angle X-ray Scattering, Academic Press Inc. (1982)

SAXSpoint 5.0

APPLICATIONS

Thank you!

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