Introduction to Small-Angle Scattering

SAXS & ASAXS

HZB Helmholtz Zentrum Berlin

Dr. Armin Hoell

Lecture series: Modern Methods in heterogeneous catalysis research: FHI, WS 2014-2015

Helmholtz Zentrum Berlin für Materialien und Energie

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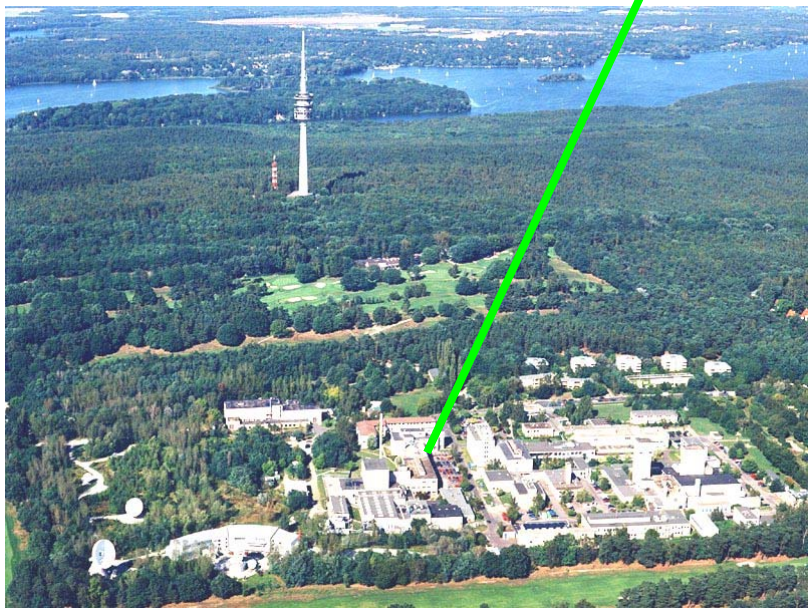
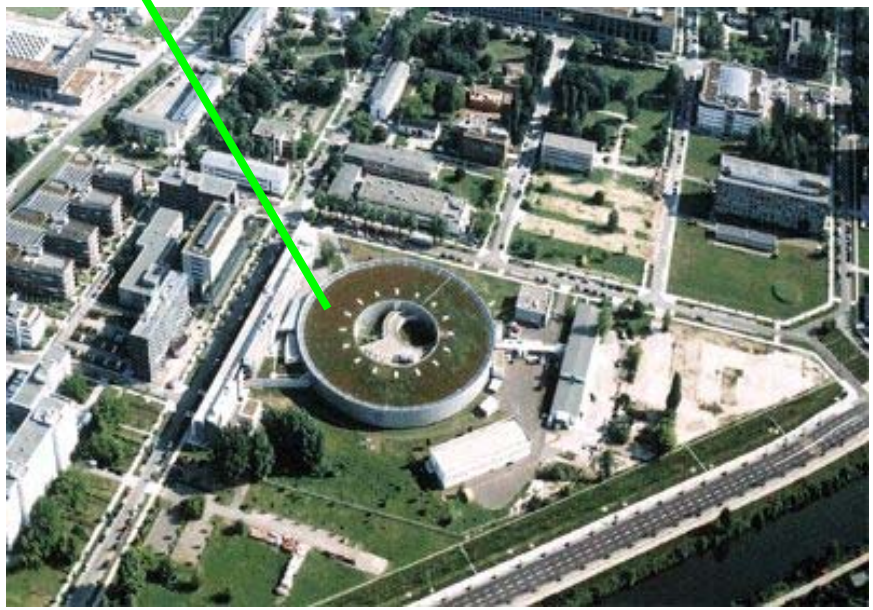
Liese-Meitner-Campus Wannsee
-Neutron reaktor as neutron source:
BER II
-solarenergie research

Wilhelm-Conrad-Roentgen Campus Adlershof
-Synchrotron source: BESSY II
-solarenergie research





Outline

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Introduction SAS: -some historical remarks

-when can small-angle scattering be used

-kind of samples

Small-Angle Scattering:

-scattering vector, size range to be investigated

-theoretical remarks

-structural parameters, the scattering contrast

-Which are possible structural results of SAS

Model scattering curves:

Example of instrumentation: -ASAXS instrument at BESSY II

Contrast variation: -ASAXS; resonant Small-Angle X-ray Scattering

Examples: -RuSe – catalyst for fuel cells

-degradation of $PtNi_3$ catalysts studied by ASAXS

References: Small-Angle Scattering (SAS)

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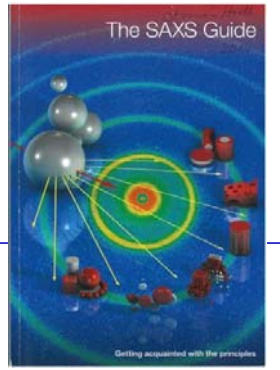

Heimo Schnablegger: „**The SAXS Guide**“ Firma Anton Paar, Austria
online available from institute ILL / Grenoble in France

Guinier (1956/1994) “X-ray diffraction. In crystals, imperfect crystals, and amorphous bodies”, Chapter 10 Small-angle x-ray scattering.

Glatter & Kratky (ed.) (1982) “Small Angle X-ray Scattering”. (http://physchem.kfunigraz.ac.at/sm/Software.htm)

Feigin & Svergun (1987) “Structure analysis by small-angle X-ray and neutron scattering”, (http://www.embl-hamburg.de/ExternalInfo/Research/Sax/reprints/feigin_svergun_1987.pdf)

Guinier & Fournet, (1955), “Small-angle scattering of X-rays”, New York

Otto Kratky (1983) “Die Welt der vernachlässigten Dimensionen und die Kleinwinkelstreuung der Röntgen-Strahlen und Neutronen an biologischen Makromolekülen”, Nova Acta Leopoldina, Halle.

27. IFF-Ferienkurs (1996) “Streumethoden zur Untersuchung kondensierter Materie”, Jülich. ISBN 3-89336-180-4

Software to analyse the Small-Angle Scattering curves. **SASFIT** / Joachim Kohlbrecher: PSI
https://kur.web.psi.ch/sans1/SANSSoft/sasfit.html

Structural determination of different materials

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Direct methods

Indirect methods

Electron microscopy

Atomic force microscopy

Optical microscopy

Electron diffraction

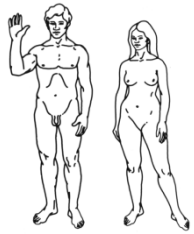
Static and dynamic light scattering

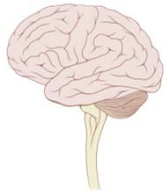
USAXS SAXS

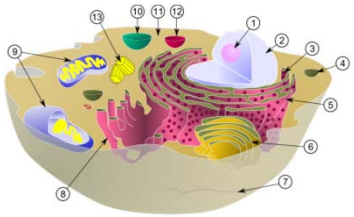
WAXS XRD

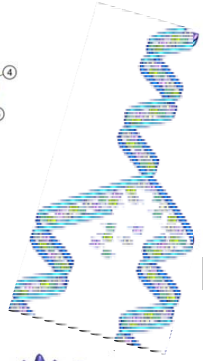
Biggest advantage of X-ray scattering:
-In situ measurements
-Statistical average

1 m **1 mm** **1 μm** **1 nm** **1 pm**

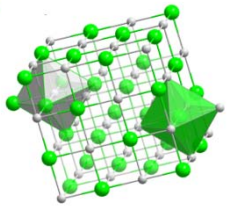


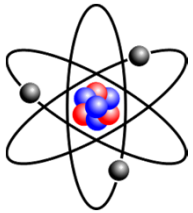




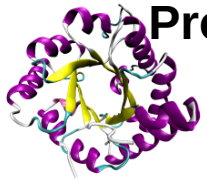


DNA





Liquid crystals



Proteins

History: SAXS and Anomalous SAXS

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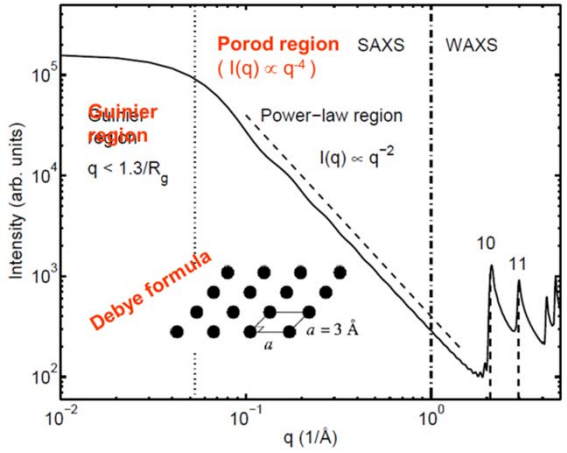
1930 Krishnamurti, P. A
Indian J. Phys., *5*, 473–500 (1930). "Studies in X-Ray Diffraction. Part I: The Structure of Amorphous Scattering. Part II: Colloidal Solutions and Liquid Mixtures." Particle size and molecular weights related to extent of small-angle scattering.

1940 – 1960 Guinier, Debye, Luzatti, Porod and others develop interpretation for the basic features in SAXS patterns



1980 Stuhrmann (EMBL Hamburg; instrument X15) **first ASAXS** on Ferritin and Hemoglobin

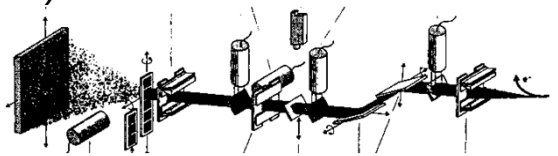
J.P. Simon; O. Lyon; France
ASAXS on alloys and theory

A. Bienenstock; Stanford, USA

HASYLAB JUSIFA instrument at B1 (Haubold; FZ Juelich)

1991 ASAXS at A1 (lower energy range, organic materials) Stuhrmann

No real dedicated ASAXS instruments furthermore:
ID01 & BM02 @ ESRF; 12ID at APS

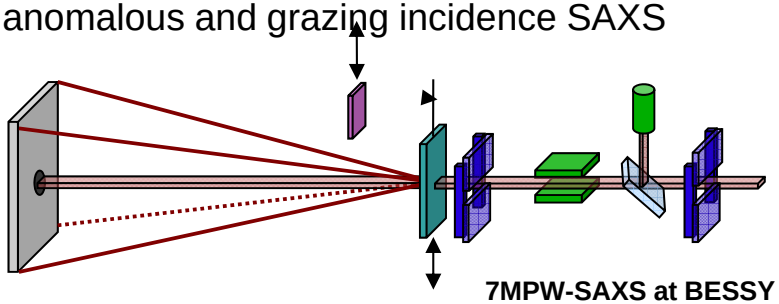


HMI - SAXS instrument at BESSY: dedicated to anomalous and grazing incidence SAXS

3/2006

Our goals:

- Application of ASAXS in the material science field and materials for renewable energy sources
- Increase the sensitivity and accuracy of ASAXS
- Further development of ASAXS theory



7MPW-SAXS at BESSY

What can be characterized by Small Angle Scattering?

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-in general all nanostructures containing materials

(in state of solid plates, powders, or liquids)

Examples:

-immiscibility regions and beginning crystallization in e.g. glasses

-precipitations in alloys

-concentrations fluctuations at phase boundaries (e.g. hydrogen storage)

-grain boundaries in polycrystalline materials

-pore structures in aero gels, porous glasses …

-morphology of biological cells, DNS, bones, woods

-polymers

-colloidal liquids: protein structures, magnetic fluids

-catalysts; especially nonoparticles on different supports

Some Examples

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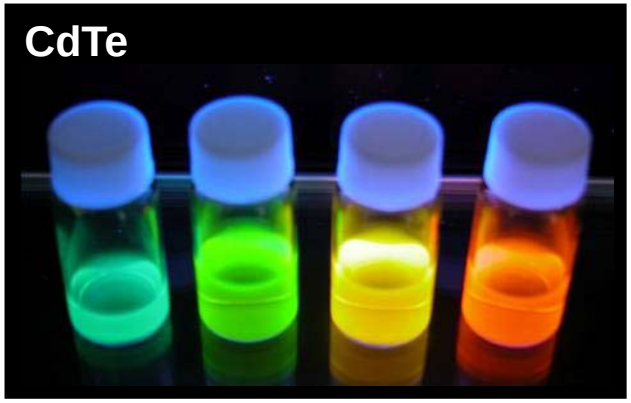
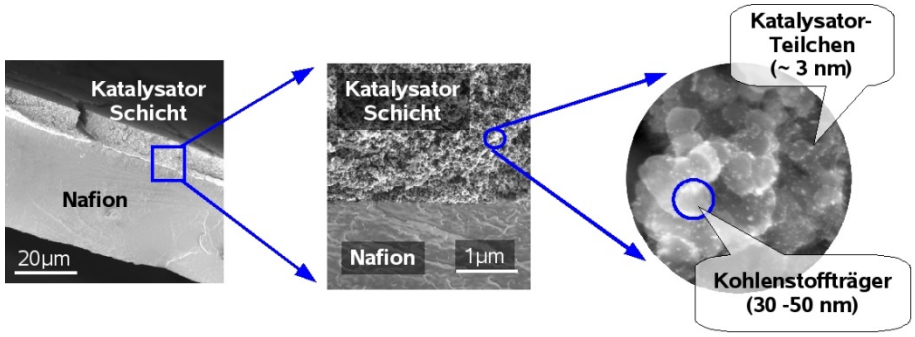
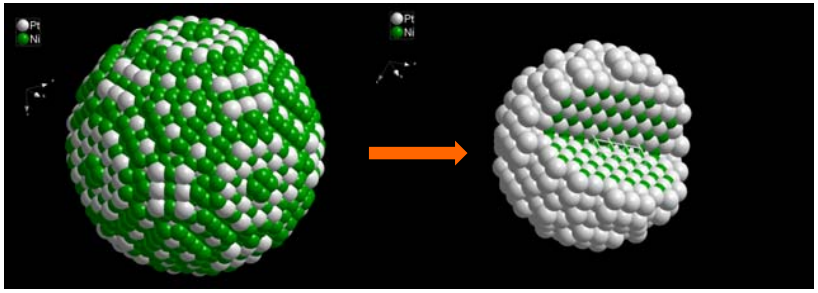
Luminescent Nano- crystals:



Different catalysts:



$PtNi_3$



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Historical Gold-Ruby Glass: old roman

Lycurgus cup

nature photonics | VOL 1 | APRIL 2007 | www.nature.com/naturephotonics

OPTICAL METAMATERIALS

Invisibility cup

Ulf Leonhardt

Cloaking devices for visible light come a step closer to reality by combining the modern form of a Roman technology with ideas from ancient Greece.

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e-mail: ulf@st-and.ac.uk

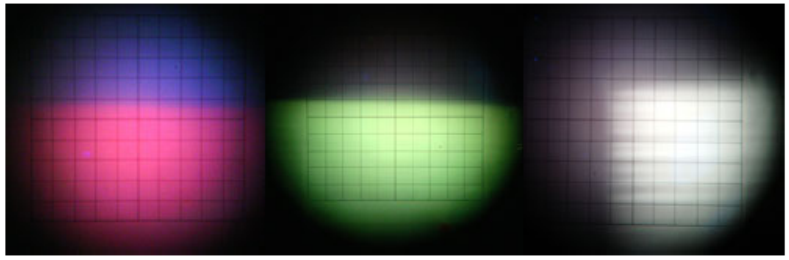
One of the things the Romans did for us was the invention of the first optical metamaterial — ruby glass. They probably did not know it, but their recipe for ruby glass contained one crucial ingredient[1]: tiny gold droplets, typically 5–60 nm in size. These gold particles colour the glass in an extraordinary way, as demonstrated by the exquisite Lycurgus Cup (Fig. 1). In daylight the cup appears a greenish colour, but illuminate it from the inside and it glows ruby. On page 224 of this issue, Cai *et al.*[2] present theoretical simulations that show that a modified Roman cup based on modern nanofabrication technology will act as an invisibility device, albeit for one polarization and one specific colour of light. Any object you put inside will

Lumineszierende Gläser

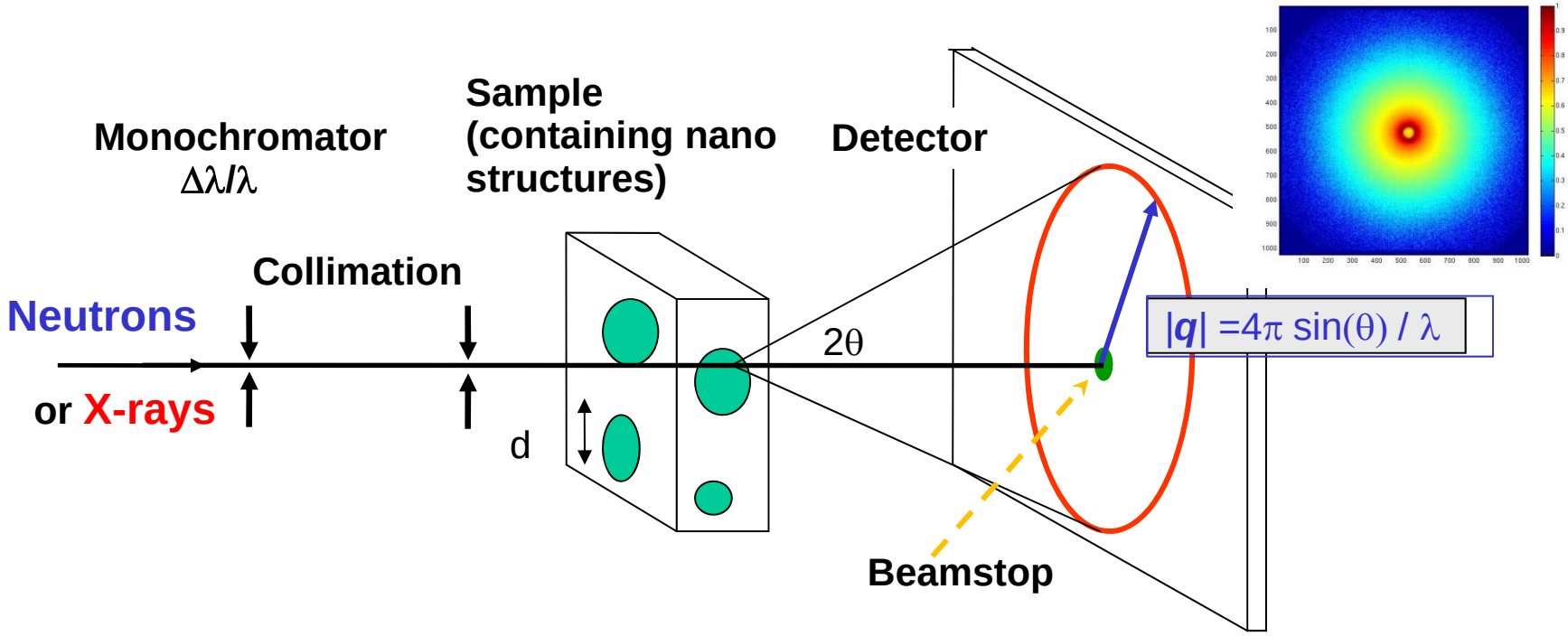
DOI: 10.1002/anie.200123456

Intensive rote, grüne und weiße Lumineszenz in photoaktivierten gold- und silberhaltigen Silicatgläsern**

Maik Eichelbaum, Klaus Rademann, Wilfried Weigel, Armin Hoell, Dragomir M. Tatchev*



Principle of Small-Angle Scattering (SAS)



Inhomogeneity of densities, composition fluctuations and magnetisation in size ranges of d: ~ 0.5 – 100 nm

One can get: Size distributions, distances, compositions, volume fractions

Intensity I(q) **q = 2π/d**

Scattering angle 2θ: 0.1 – 6°

important: sample properties

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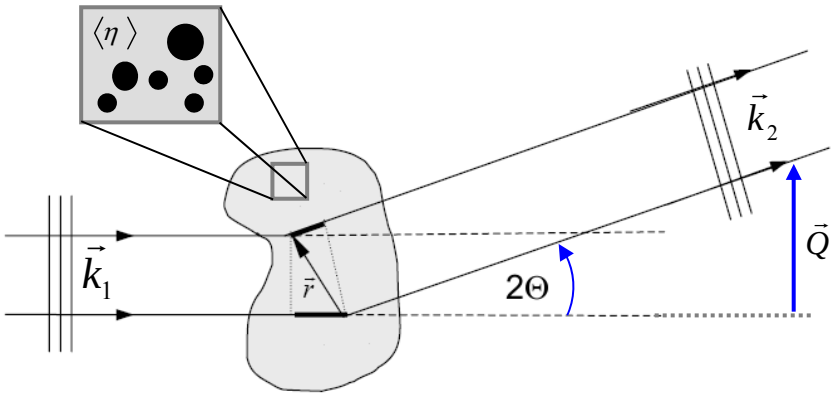
Scattering cross-section



Material:
that contains
nanostructures

Scattering vector: $\vec{Q} = \vec{k}_2 - \vec{k}_1$

$$\left|\vec{Q}\right| = Q = \frac{4\pi}{\lambda}\sin(\theta)$$

Resolution limit: $r_{\min} = \frac{\pi}{Q_{\max}}$

SAS range: $0 \le Q \le \frac{\pi}{d_A}$

$\Rightarrow$ Colloidal dimensions: ~ 1 – 100 nm

How can colloidal structures be investigated?

Magnitude of the scattering vector

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

Bragg-equation

$$2d \sin(\theta) = \lambda$$

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

Threshold value: $|\vec{q}| \rightarrow 0 \qquad d \rightarrow \infty$

Scattering also allows to investigate structures in the nm- and µm- range.

→ Small-Angle Scattering (SAXS, SANS, USAXS, USANS) ←

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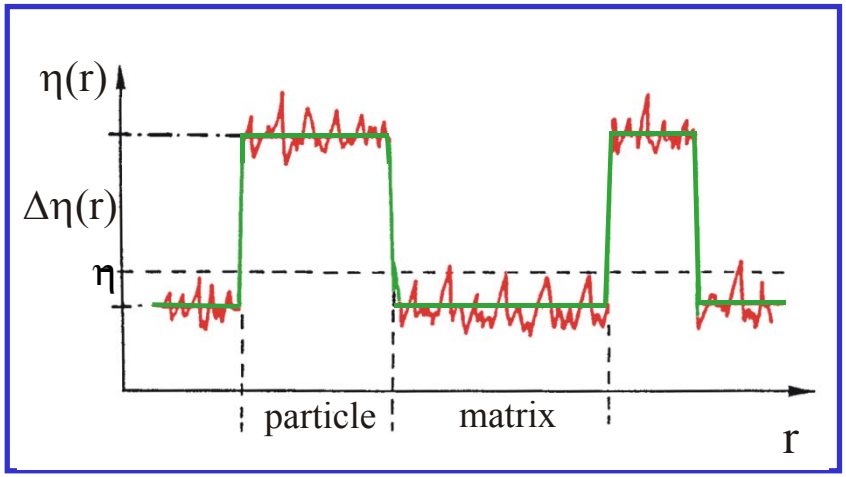
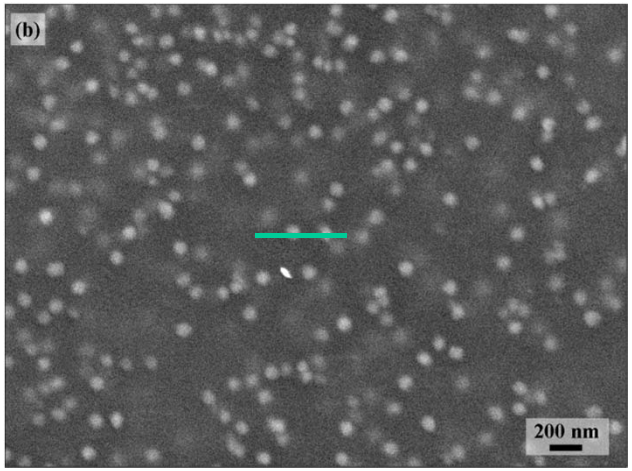
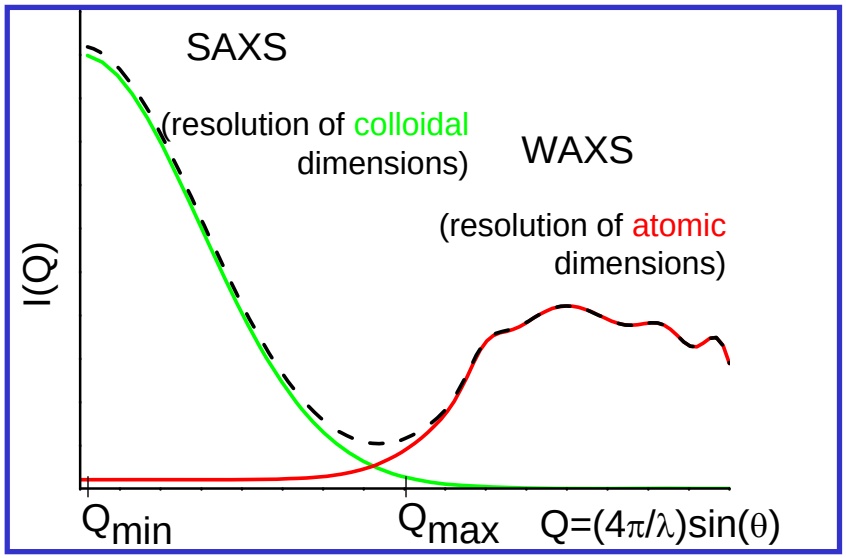
Inhomogenities of scattering lenghtdensity, η, in a size range of: ~ 0.5 - 200 nm [introduction scattering length density later]







Resolution limit: $r_{min} = \frac{\pi}{Q_{max}}$

View field limit: $r_{max} = \frac{\pi}{Q_{min}}$

SAS does not have resolution for interatomic distances.

Therefore, SAS alone can not distinguish whether a nanostructure is crystalline or amorphous.

Small- and Wide-Angle X-ray Scattering (SAXS & WAXS)

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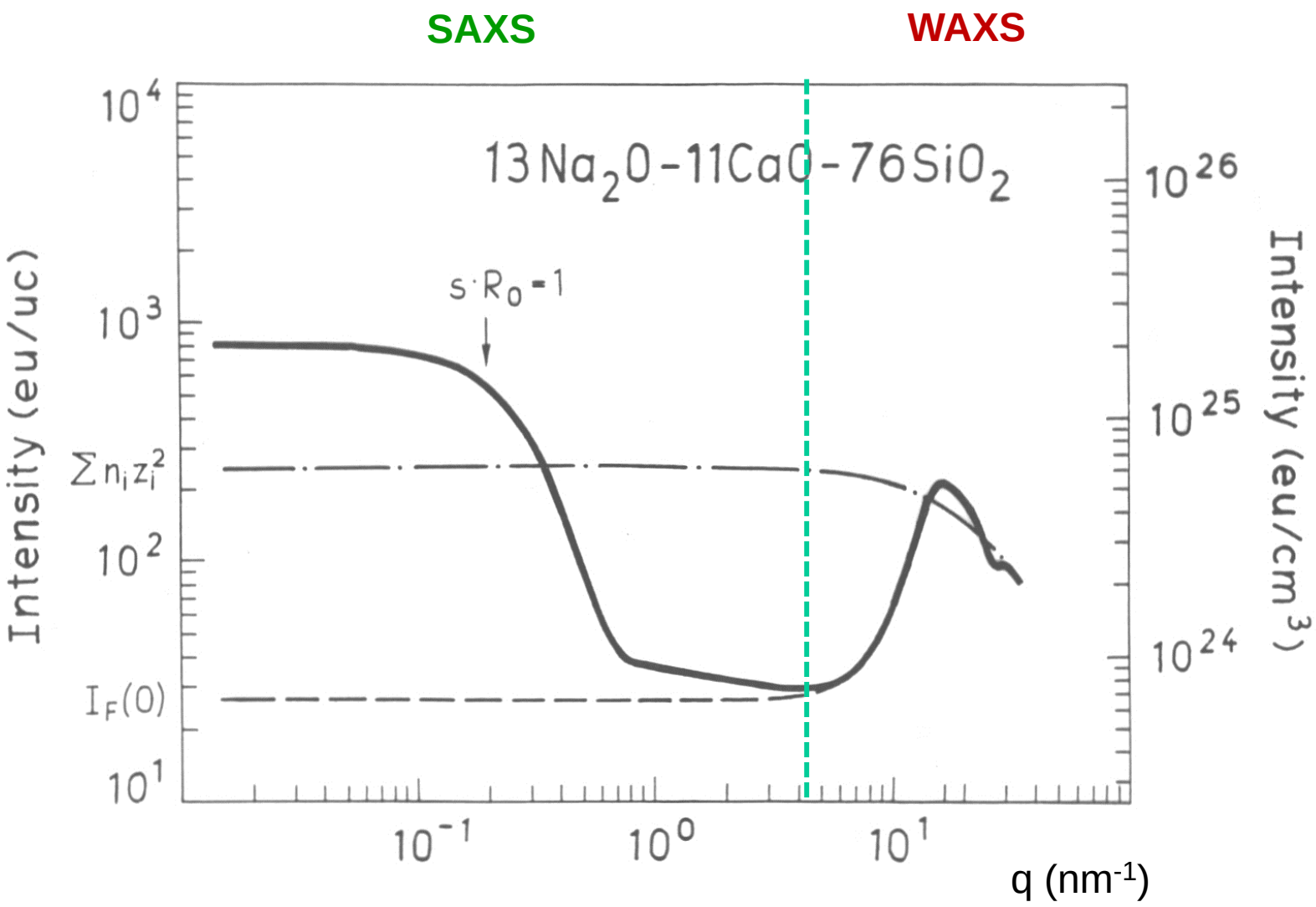

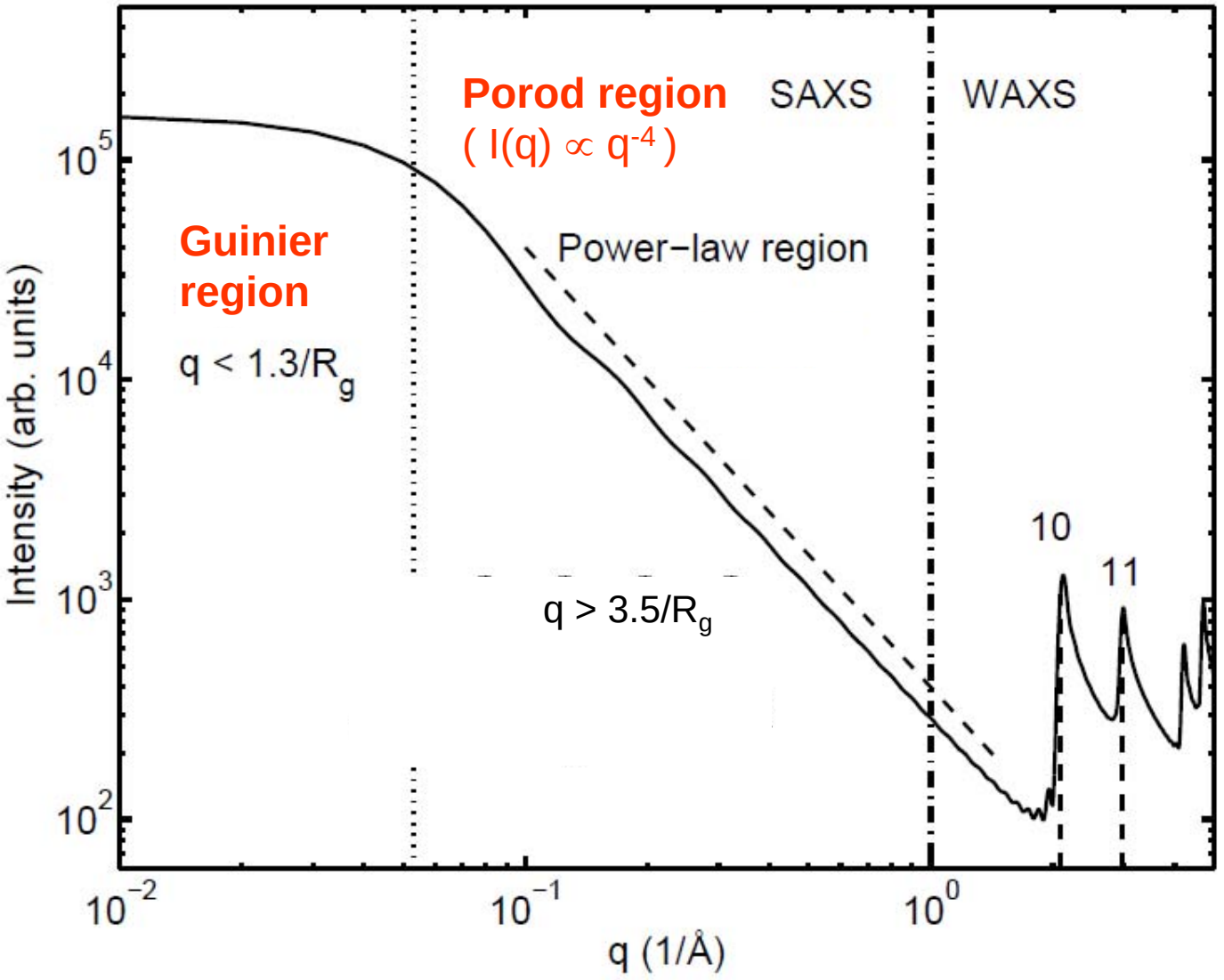
Porod region
(I(q) ∝ q-4)
SAXS
WAXS
Guinier region
q < 1.3/Rg
Power−law region
q > 3.5/Rg
10
11
Intensity (arb. units)
10^5
10^4
10^3
10^2
10^−2
10^−1
10^0
q (1/Å)

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Scattering Intensity:

$$I(Q) = N_V (\Delta\rho)^2 V^2 F(Q,R)^2$$

Fluctuations of electron density:

$$\Delta\rho(r) = \rho(r) - \overline{\rho}$$

Scattering Amplitude of a sphere of radius *R*:

$$F(Q,R) = 3\frac{\sin(QR) - QR\cos(QR)}{(QR)^3}$$

A

Guinier region: for Q ⇒ 0

$$I(Q) = I(0)\exp(-R_0^2 Q^2 / 3)$$

$$R_0^2 = -3\lim_{Q\to 0}\left[\frac{d\ln(I(Q))}{d(Q^2)}\right]$$

R_0: radius of gyration

B

Porod region: for large Q

$$I(Q) \approx K_1 / Q^4$$

$$K_1 = \lim_{Q\to\infty}\left[Q^4 I(Q)\right] = 2\pi(\Delta\rho)^2 S_V$$

S_V: interphase surface area

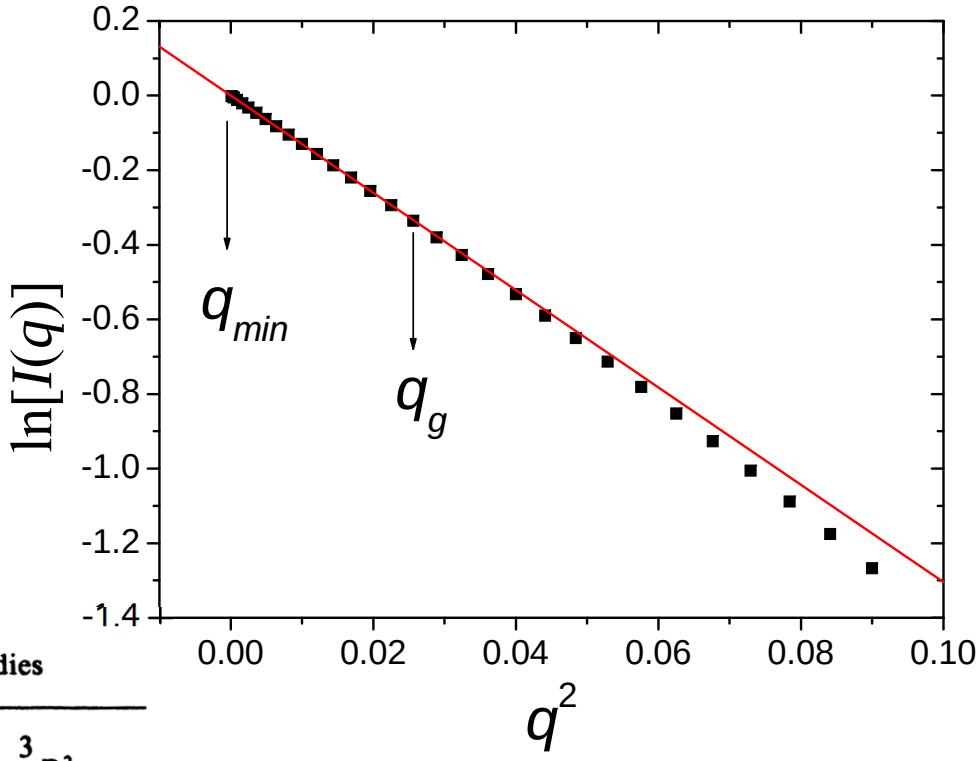
Guinier approximation A

Approximation at small q

$$q \to 0; \quad R_g q_g < 1$$

$$I(q) = I(0)\exp(-q^2 R_g^2/3)$$

$$R_g = \sqrt{\frac{\int_V \Delta\rho(\vec{r})\vec{r}d\vec{r}}{\int_V \Delta\rho(\vec{r})d\vec{r}}}$$



Guinier plot

$$\ln[I(q)] = \ln[I(0)] - (R_g^2/3)q^2$$

Table 3.1. Radii of Gyration of Some Homogeneous Bodies

Sphere of radius R	$R_g^2 = \frac{3}{5}R^2$
Spherical shell with radii $R_1 > R_2$	$R_g^2 = \frac{3}{5}\frac{R_1^5 - R_2^5}{R_1^3 - R_2^3}$
Ellipse with semiaxes a and b	$R_g^2 = \frac{a^2 + b^2}{4}$
Ellipsoid with semiaxes a, b, and c	$R_g^2 = \frac{a^2 + b^2 + c^2}{5}$

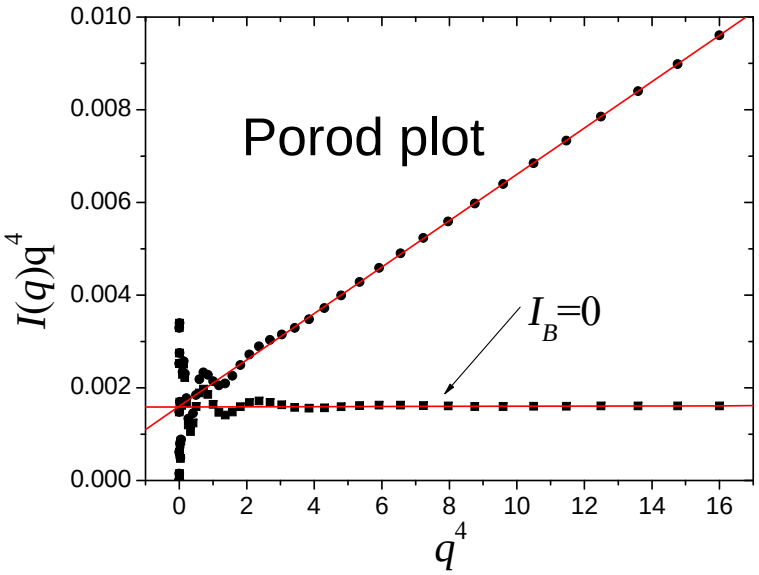
Porod approximation B

Approximation at large q $\quad q \to \infty$

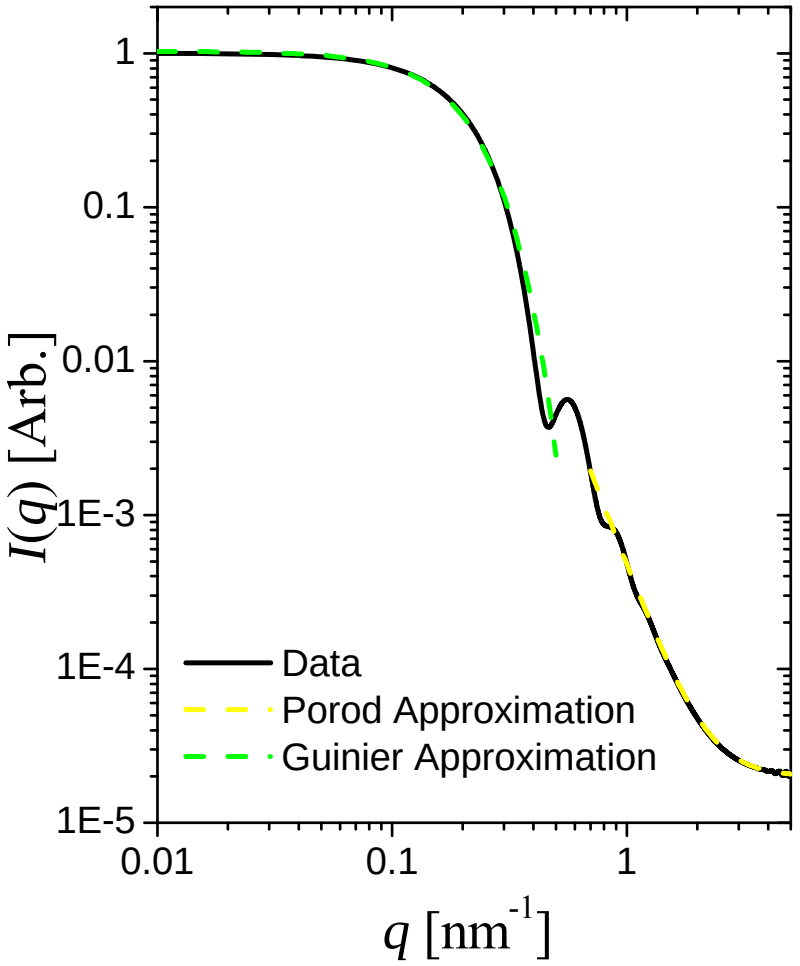
$$I(q) \approx K_P / q^4 \quad I(q) \approx \tilde{K}_P / q^3$$

$$I(q) \approx K_P / q^n + I_B$$

$$K_P = 2\pi(\Delta\rho)^2 S$$



$$I(q)q^n \approx K_P + I_B q^n$$



K_p – proportional to the interphase surface area

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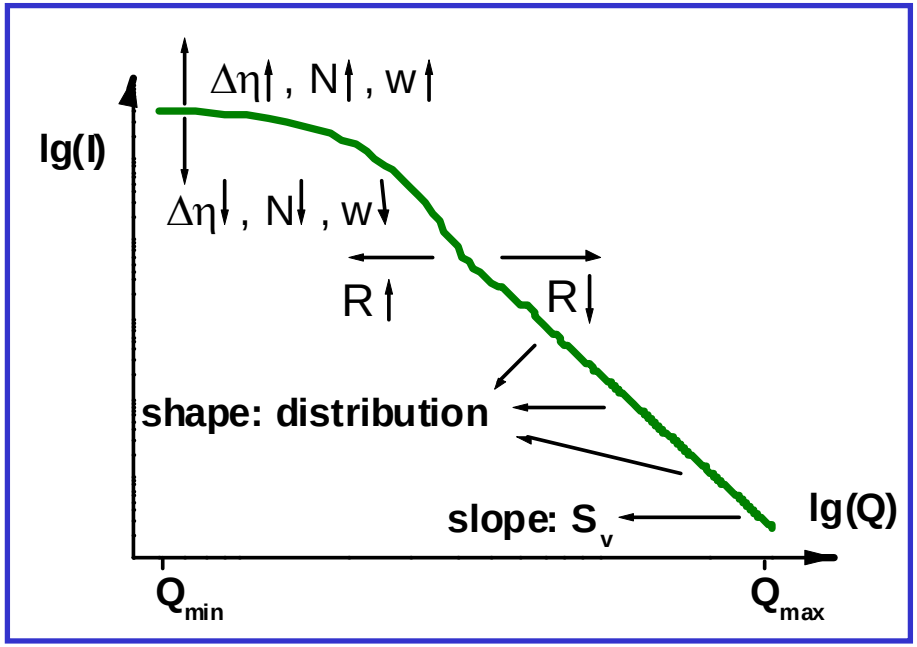
$$I(Q) = N_p \int \{\Delta\eta V_p(R)\, F(QR)\}^2\, S(QR_{hc})\, N(R)\, dR$$

Size distribution

Inter-particle interference

Particle shape factor

Contrast: $\Delta\eta = \eta_{particle} - \eta_{matrix}$



The scattering contrast: $(\Delta\rho)^2$

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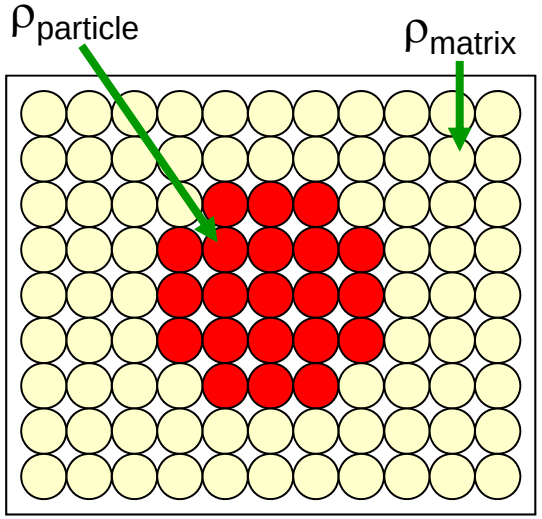
electron density:

$$\rho = \frac{N_A D \sum_i c_i z_i}{M_C}$$

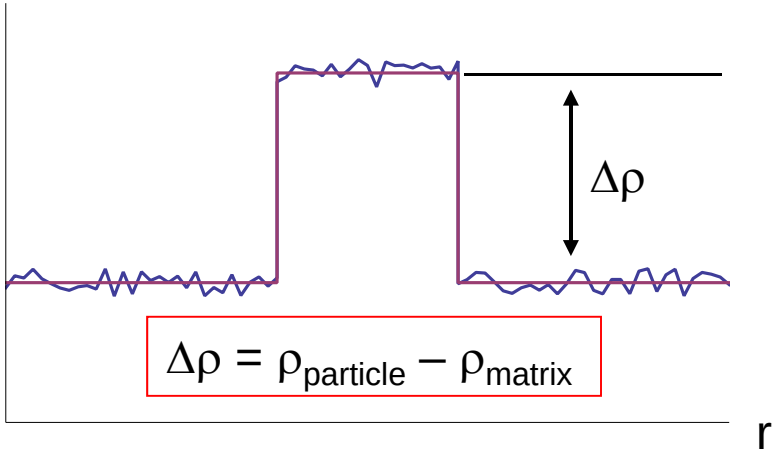
general:

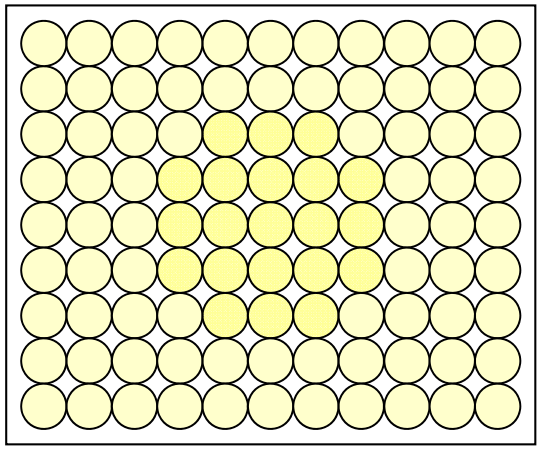
Scattering length density



Electron density: ρ(r)

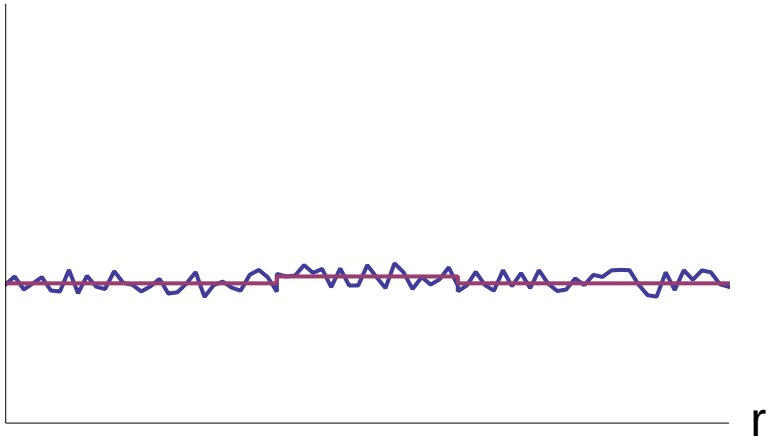
$(\Delta\rho)^2 > 0$



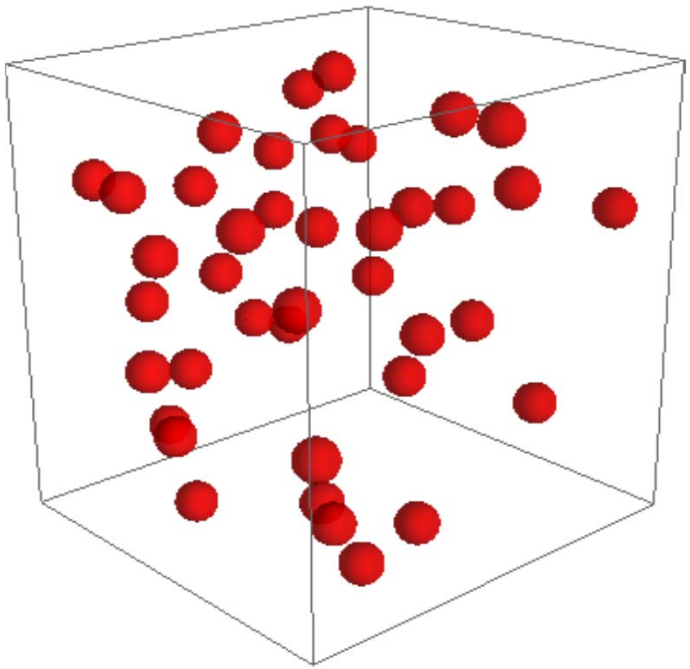


Electron density : ρ(r)

$(\Delta\rho)^2 \cong 0$



Case 1: Monodisperse spherical particles in a solution (matrix)



$$I(q) = N_P \times (\Delta\rho)^2 \times V_P{}^2(R) \times F^2(q,R)$$

Number of particles

Scattering contrast

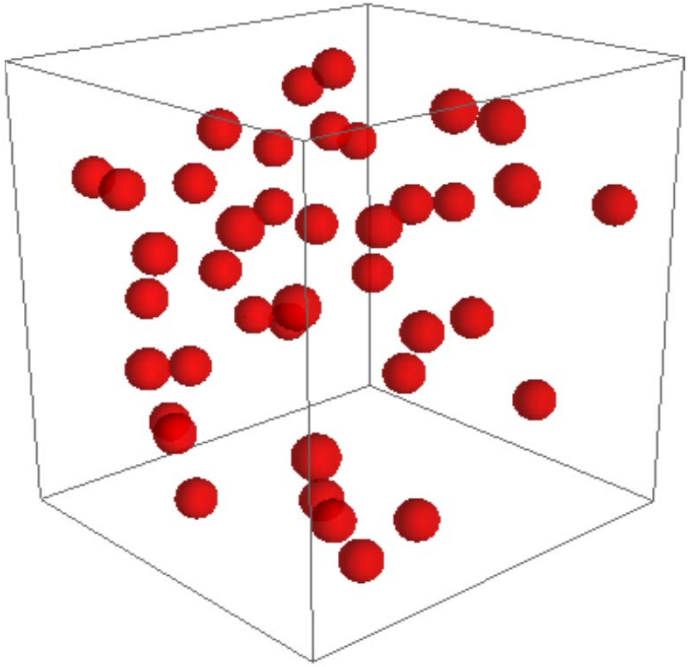
Particle volume

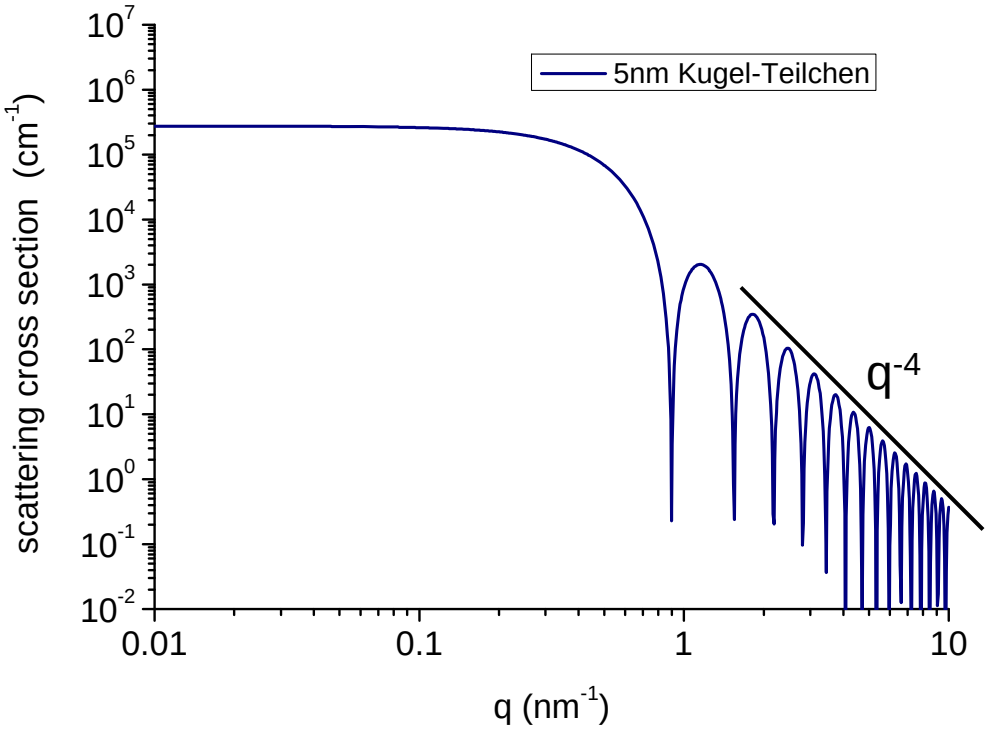
Formfactor

Scattering amplitude of a homogeneous sphere:

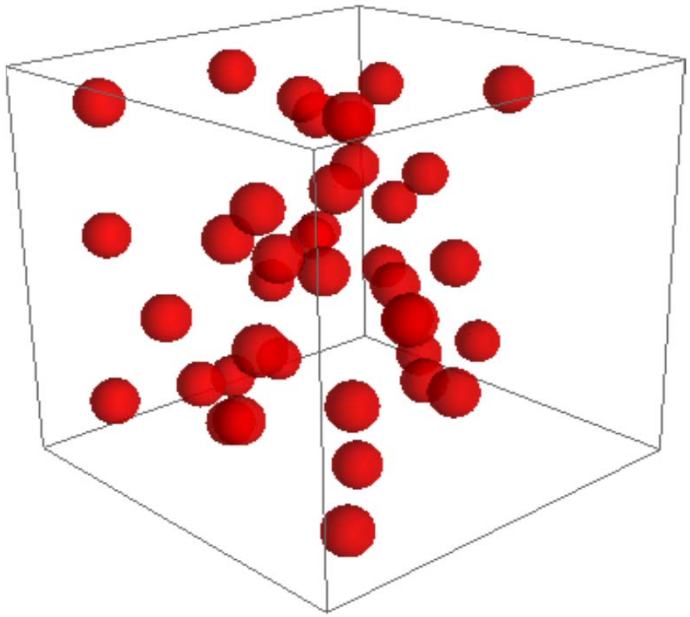
$$F(Q,R) = 3\frac{\sin(QR) - QR\cos(QR)}{(QR)^3}$$

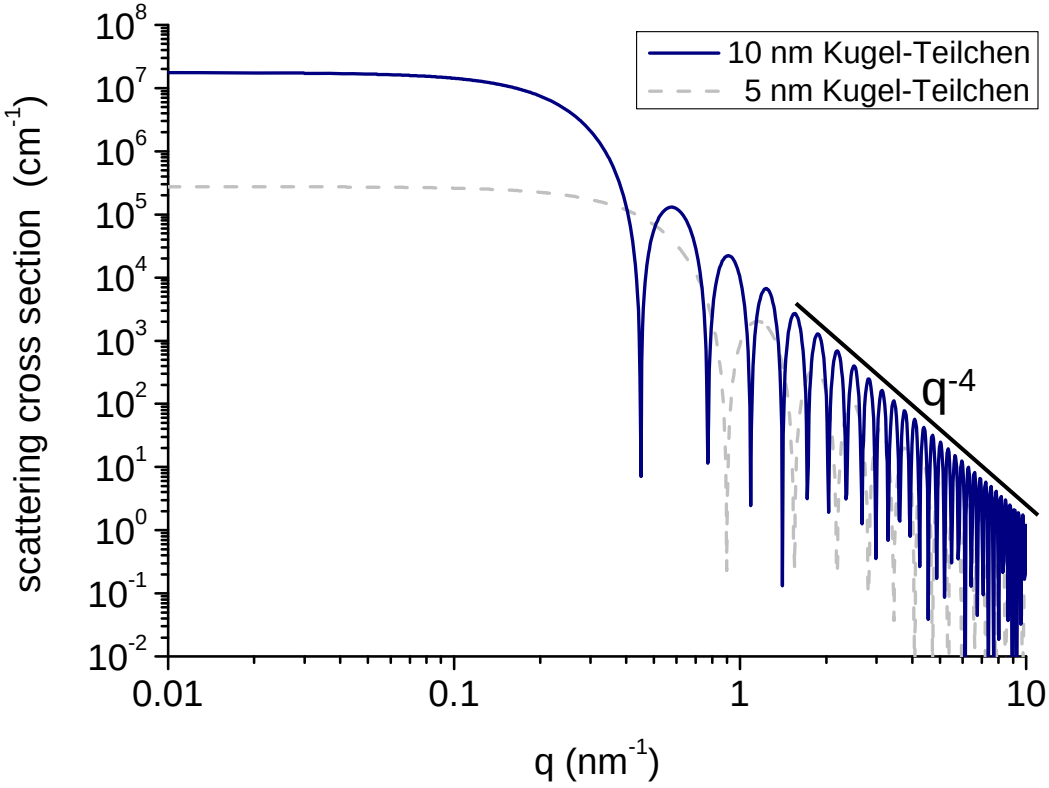
Case 1: Monodisperse spherical particles in a solution (matrix)





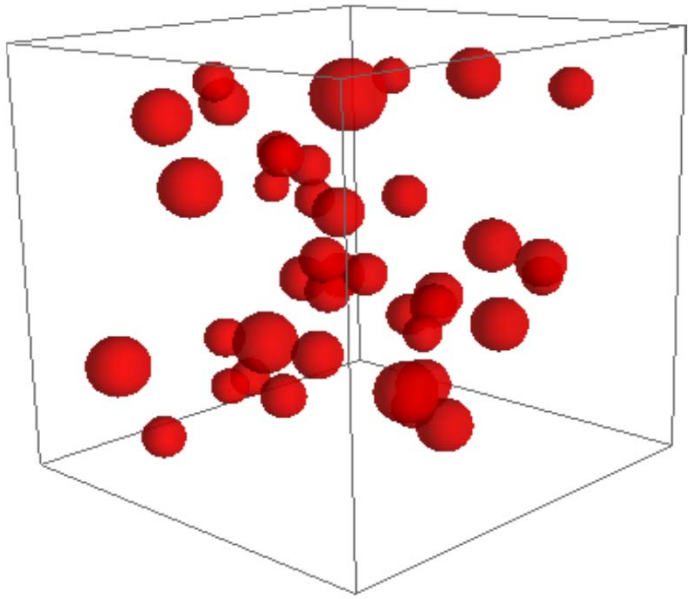
Case 1: Monodisperse spherical particles in a solution (matrix)





Case 2: Polydisperse spherical particles in a solution (matrix) (diluted system)

$$I(q) = N_P \times (\Delta\rho)^2 \times \int P(\tilde{R}) \times V_P{}^2(\tilde{R}) \times F^2(q, \tilde{R}) d\tilde{R}$$



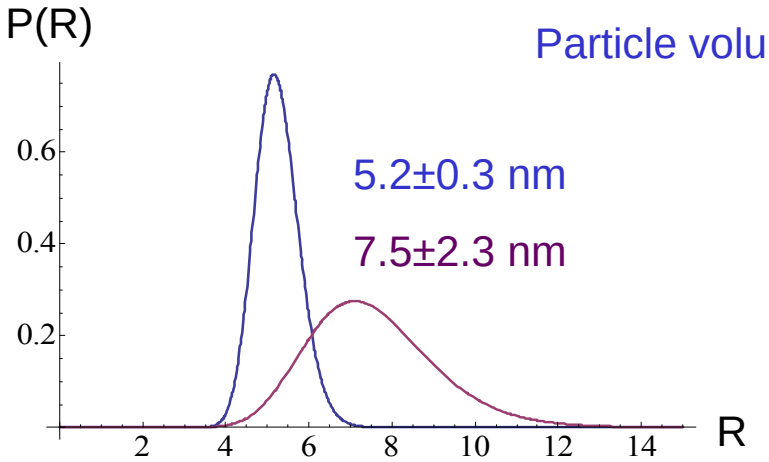
Particle number

Scattering contrast

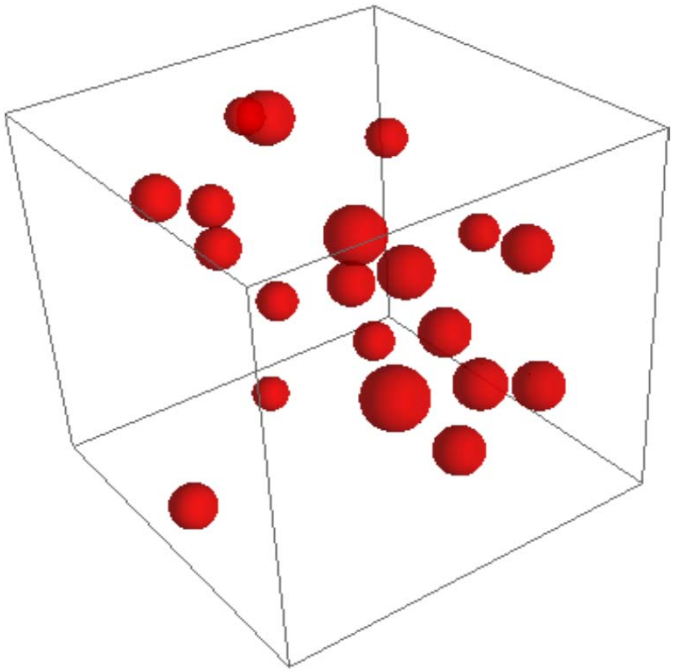
Size distribution

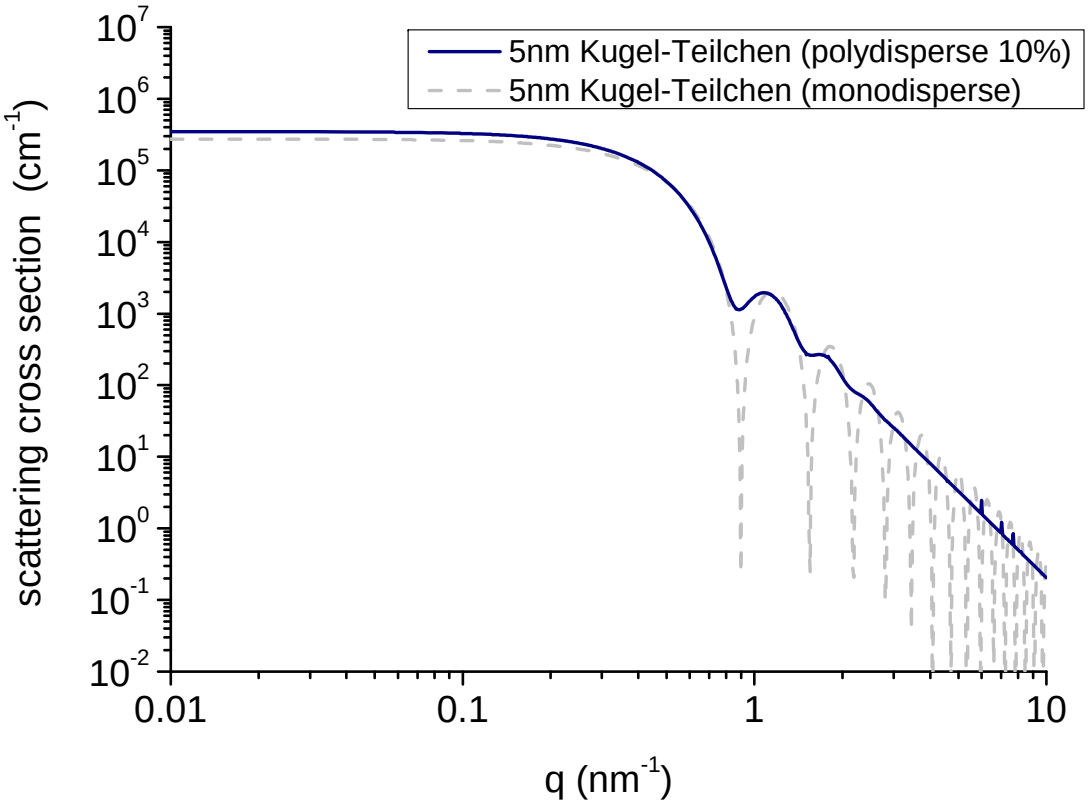
Particle volume

Formfactor

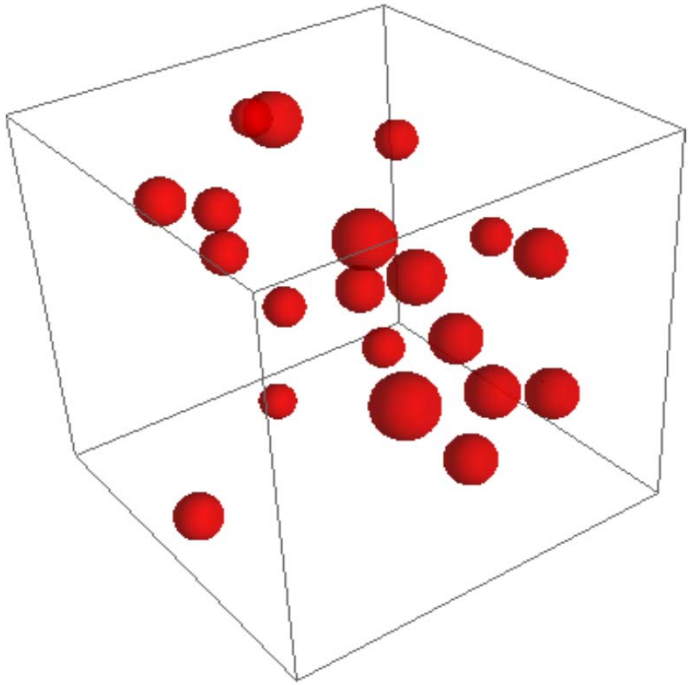


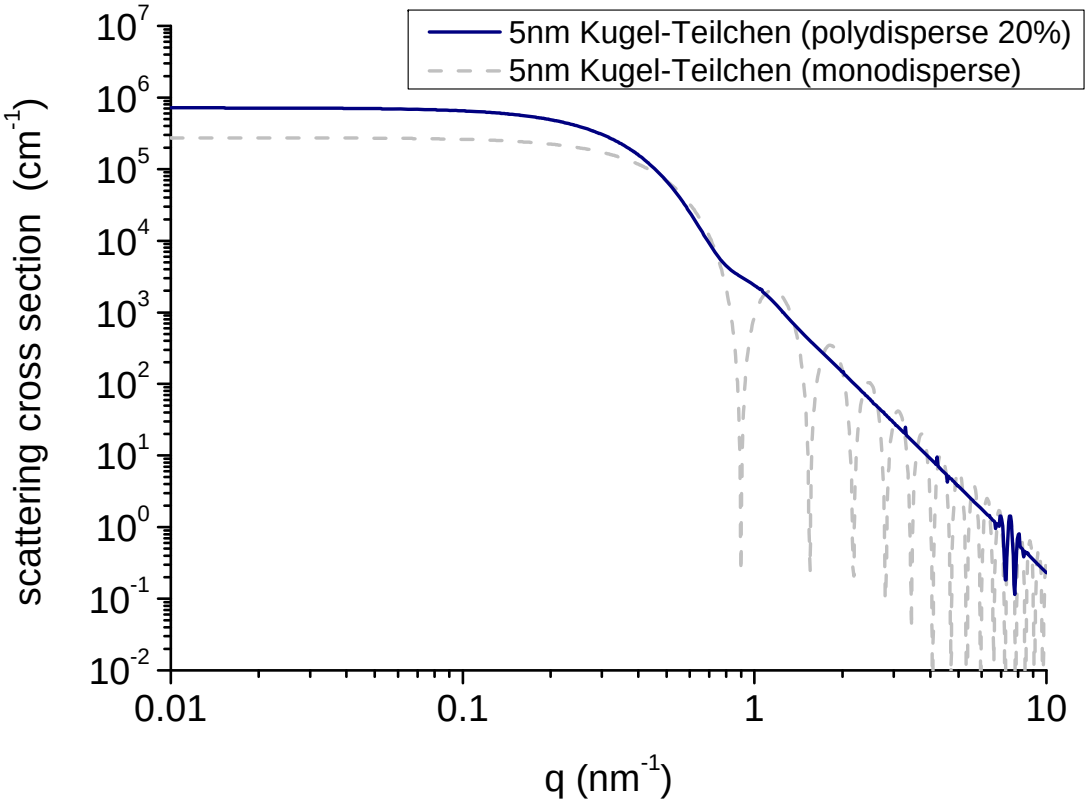
Case 2: Polydisperse spherical particles in a solution (matrix) (diluted system)



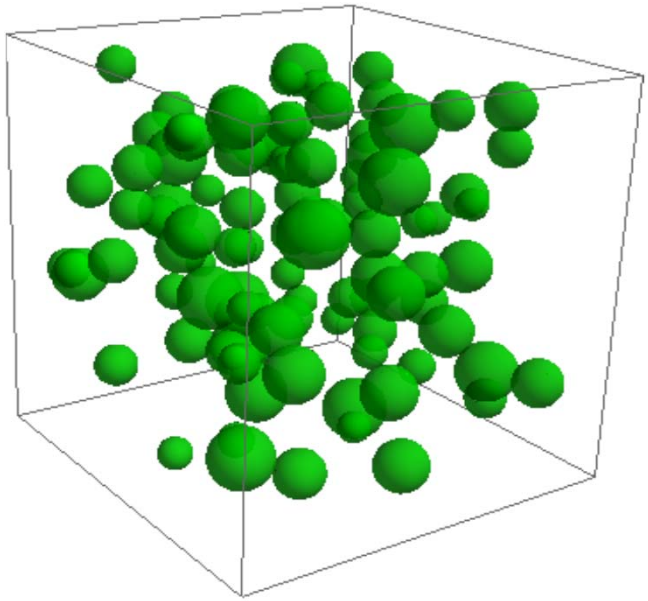


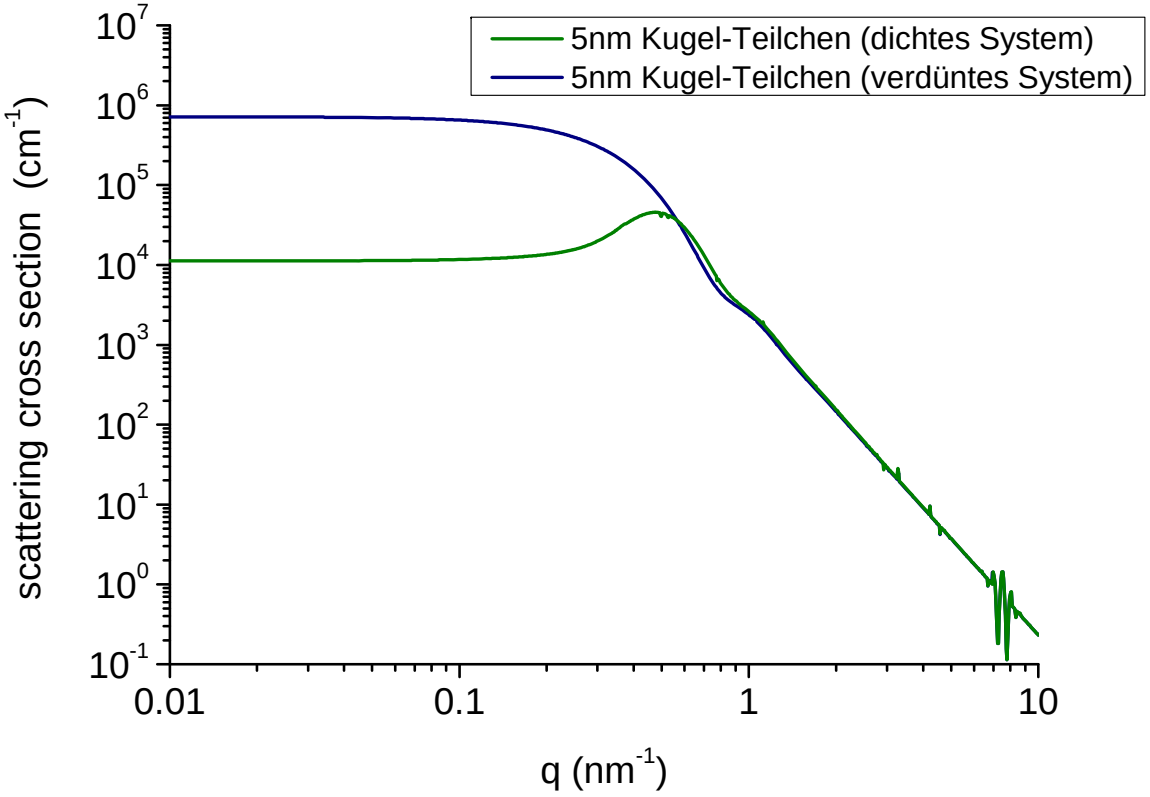
Case 2: Polydisperse spherical particles in a solution (matrix) (diluted system)





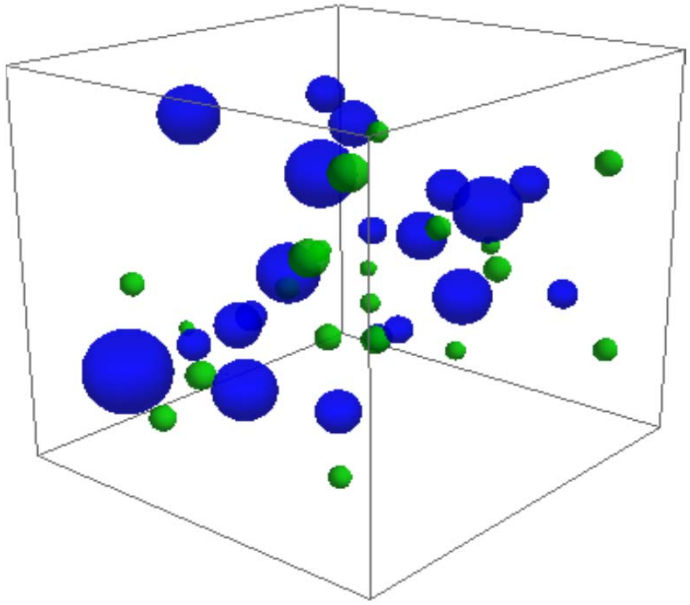
Case 3: Polydisperse spherical particles in a solution (matrix) (dense system)

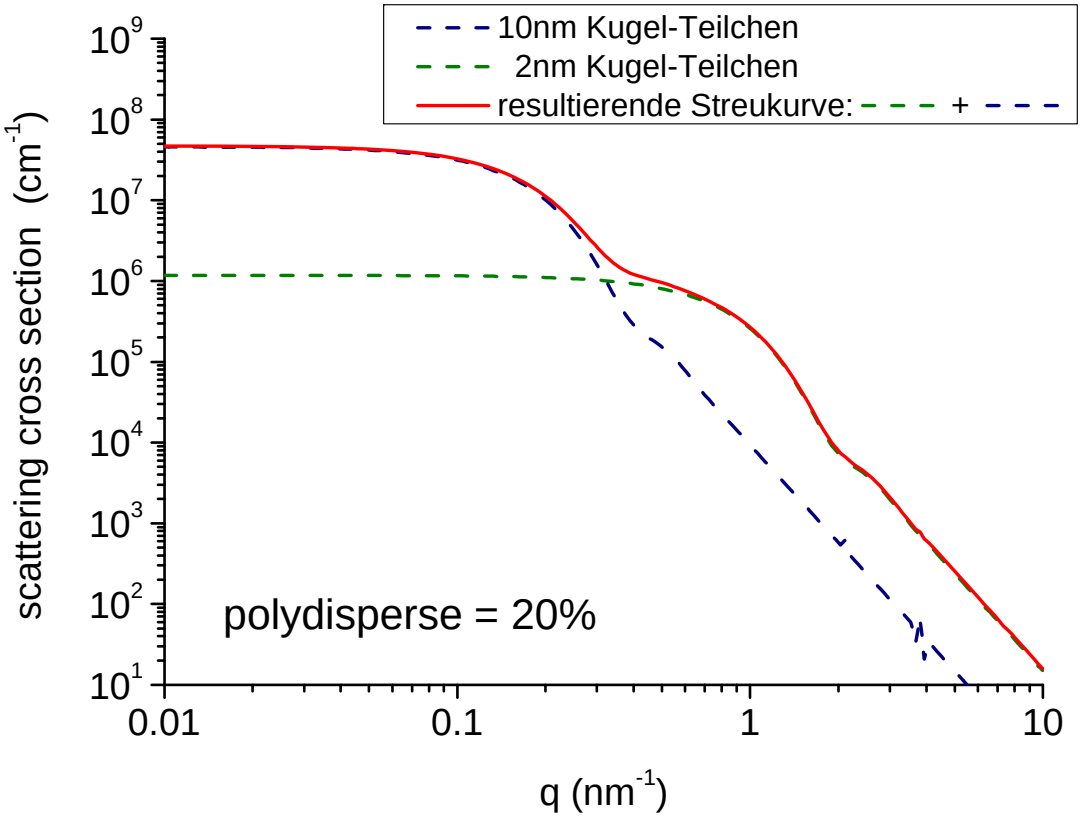




➢ Interferences between the scattering of single particles

Case 4: Sum of two sort of particles with different size distributions

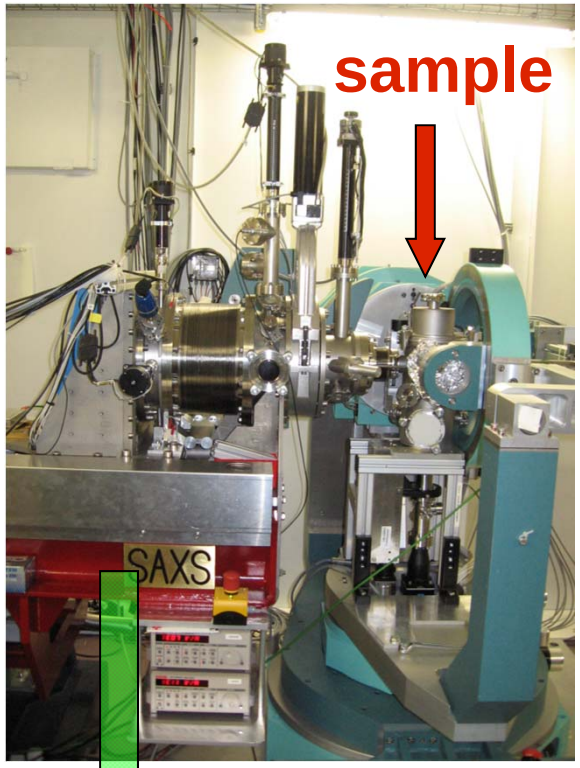


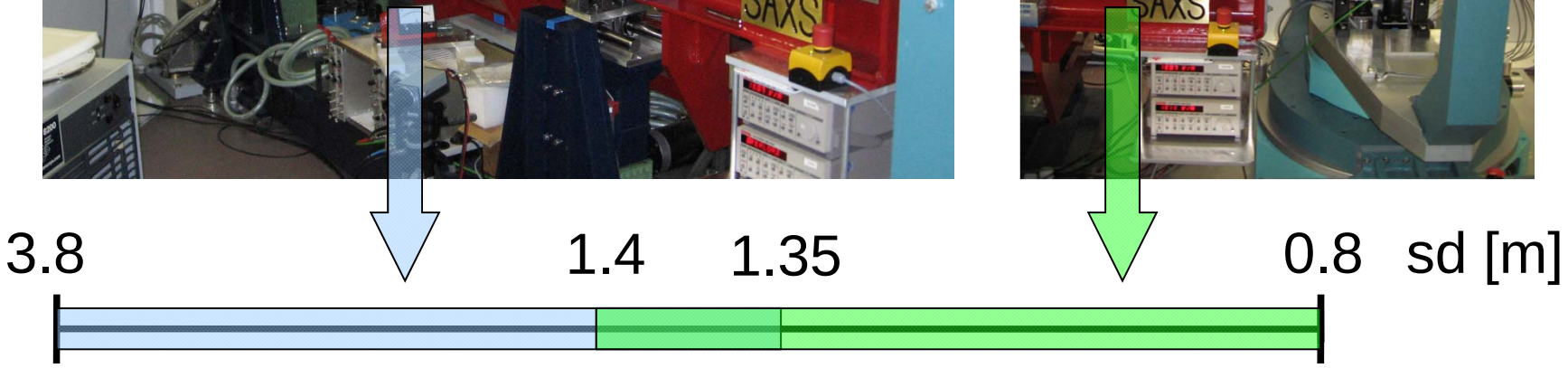


One example of small angle scattering instrumentation

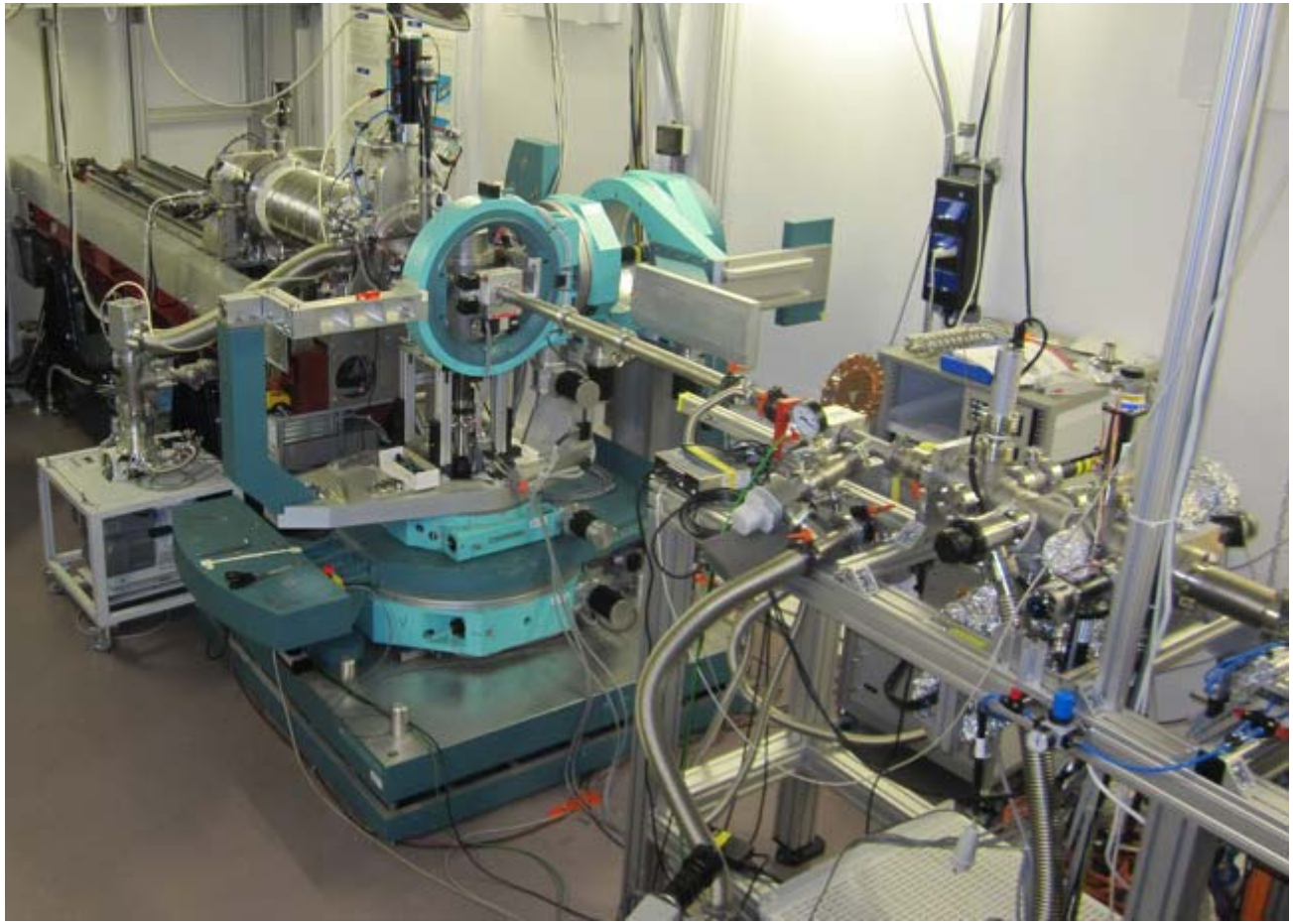
The ASAXS-Instrument at the Synchrotron BESSY II

HZB Helmholtz Zentrum Berlin





The ASAXS-Instrument from top



Some sample environments for SAXS

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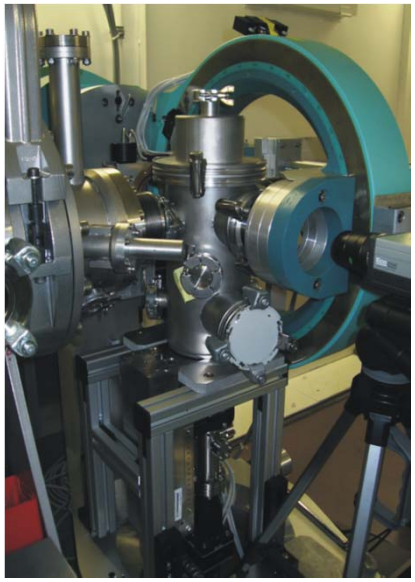
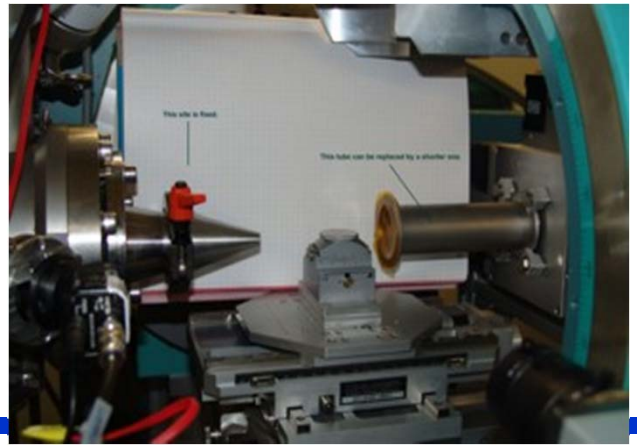
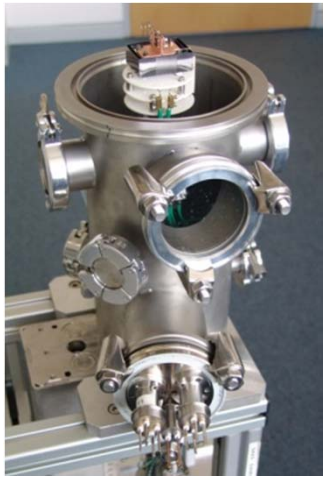
Sample chamber under vacuum

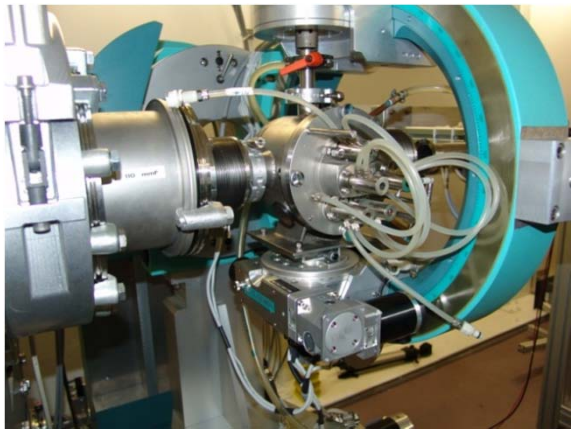


Sample changer on air

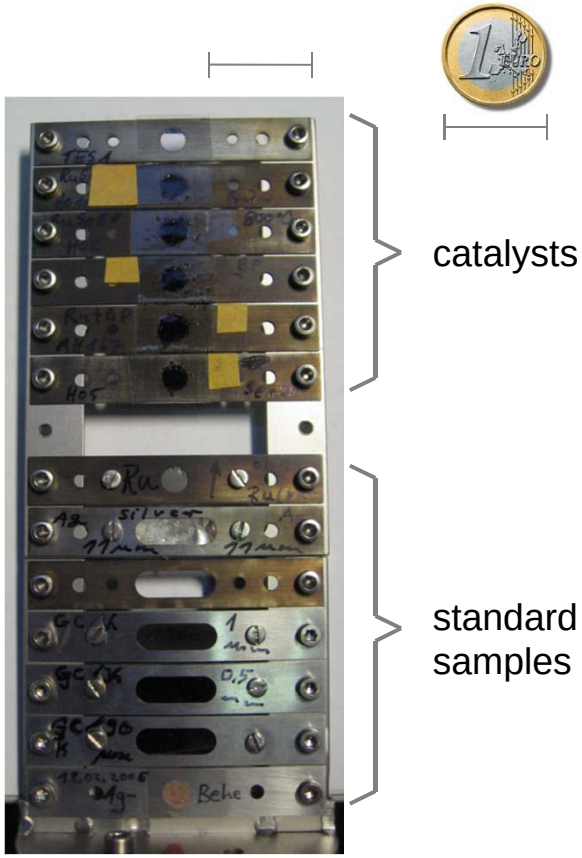


furnaces (293K – 1450K)





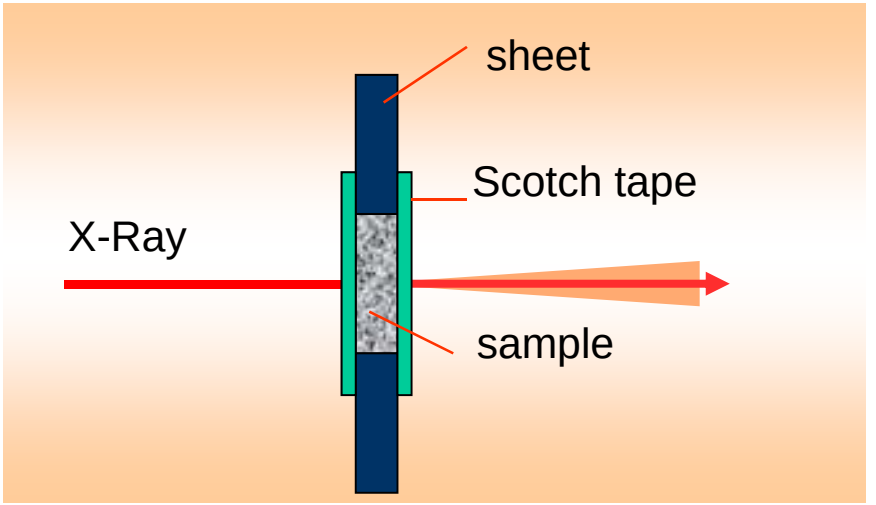
ASAXS-Instrument at BESSY II: collection of sample holders



optimal sample thickness:

$\tau = exp^{-\mu d}$ $\tau \sim 0.36$

Powder samples



Liquid samples

HZB Helmholtz Zentrum Berlin

Why: more complex systems, mixture of different phases

decide between different structural model solutions

How:

1. Combined use of X-ray and Neutron Small Angle Scattering

2. Isotope substitution in case of neutrons
   lack: set of different samples to be prepared

3. Magnetic contrast variation in case of neutrons (polarised N.)

4. Anomalous Small Angle Scattering (ASAXS)
   in case of X-rays

Scattering length densities, ρ: X-rays and Neutrons

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X-rays

$\rho \sum c_i z_i / M_i$

c_i: composition ρ: density

z_i: electron number

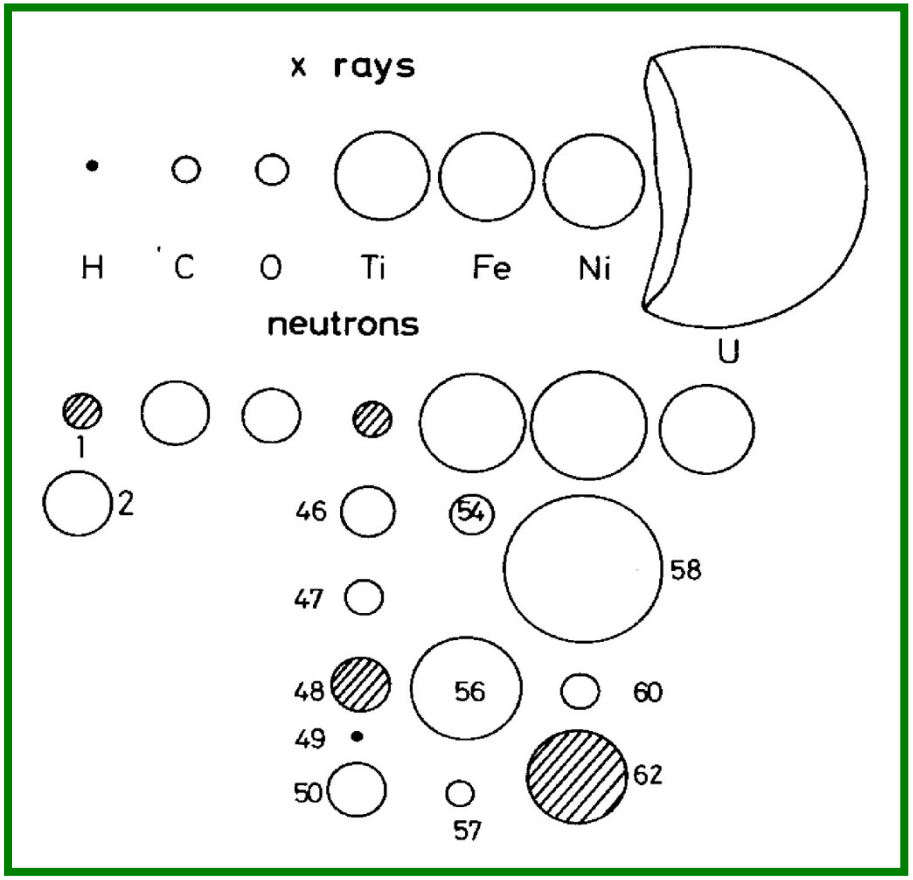
M_i: mass number

Neutrons

nuclear: **magnetic:**

$\rho \sum c_i b_i$ $\rho \sum c_i M_i^{\perp}$

b_i: scattering length $M_i^{\perp}$: magnetization



-radii of the circles are proportional to the scattering length

-negative values are indicated by cross-hatched shading

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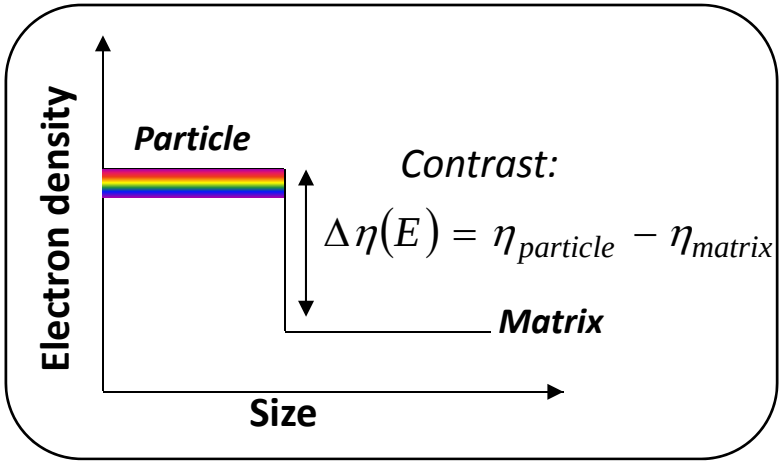
➢ Scattering Intensity

$$I(q, E) = \int_0^\infty N(r) V_p(r)^2 \left|F(q, r, \Delta\eta(E))\right|^2 S(q, r)\, dr$$

Size distribution — *Volume* — *Form factor* — *Structure factor*

- *Sc. Amplitude for a homogenous sphere of radius R:*

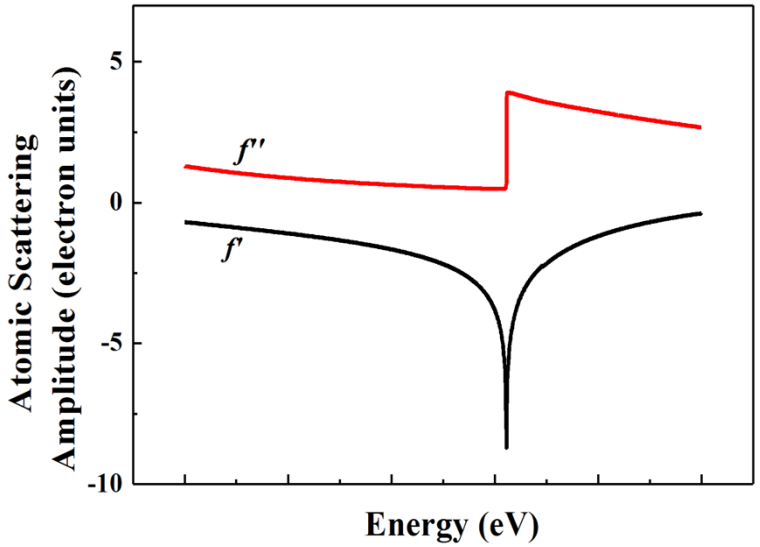
$$\mathrm{F(q, R, \Delta\eta(E))} = \Delta\eta(E)\, 3\, \frac{\sin(qR) - (qR)\cos(qR)}{(qR)^3}$$



effective electron *density*

$$\eta(E) = \frac{N_A D \sum_i c_i f_i(E)}{M_C}$$

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



- *ASAXS: Energy dependency of the atomic scattering amplitudes*

Anomalous Small Angle X-ray Scattering (ASAXS)

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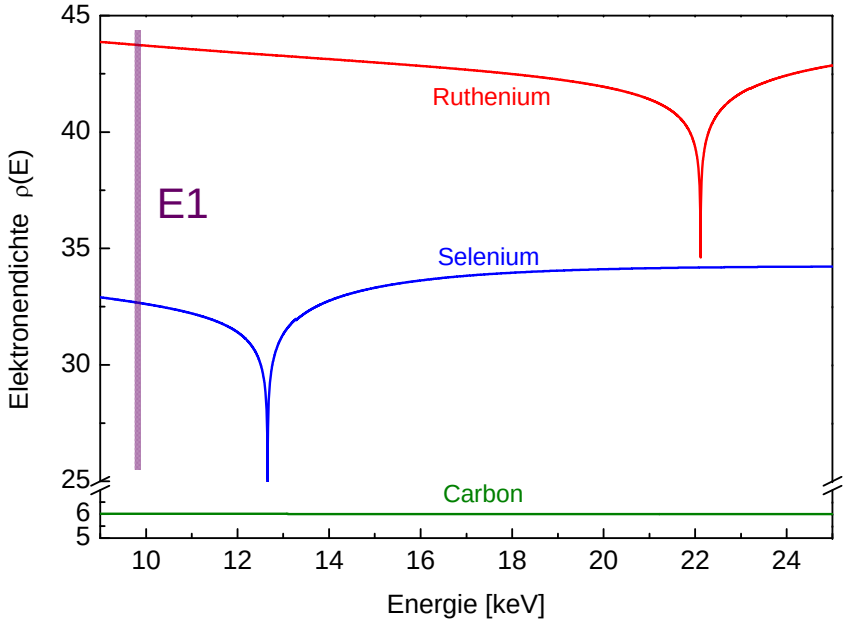
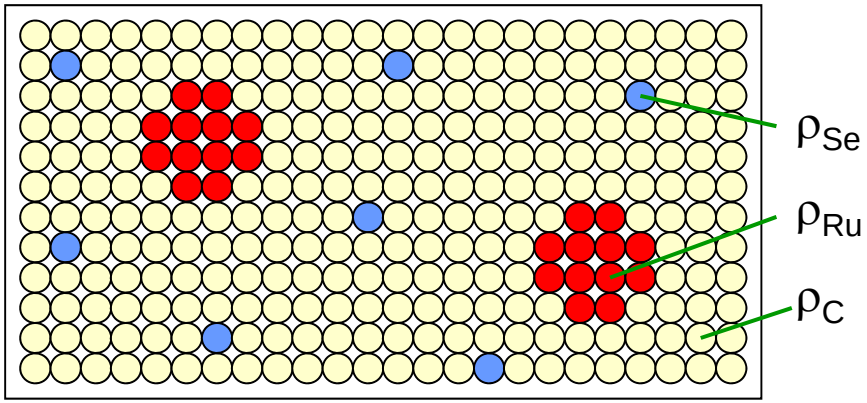
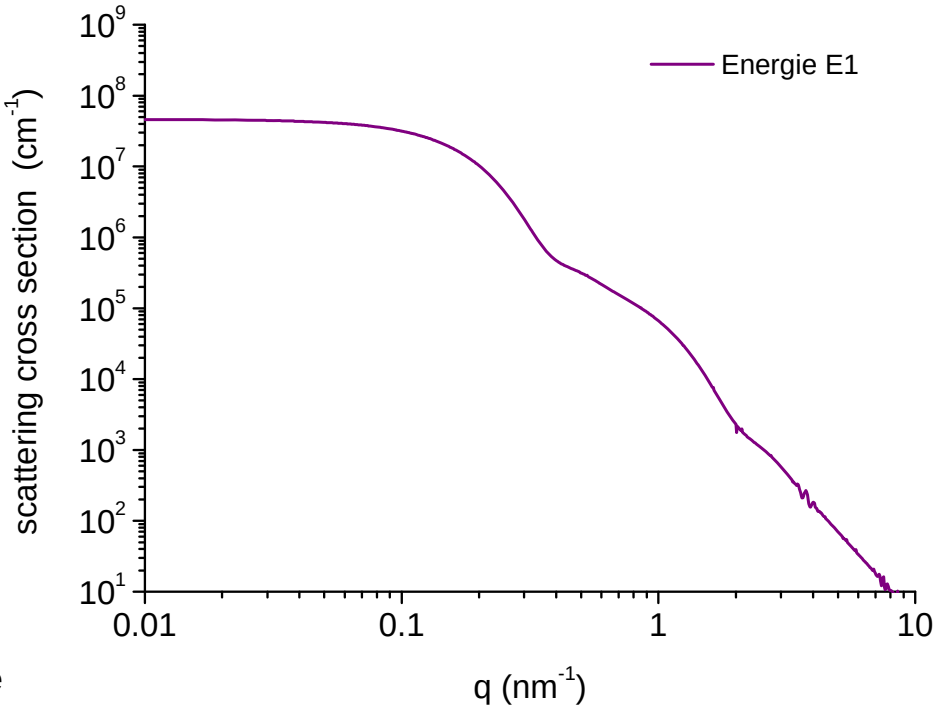
- effective “electron density” becomes energy dependent.







Anomalous Small Angle X-ray Scattering (ASAXS)

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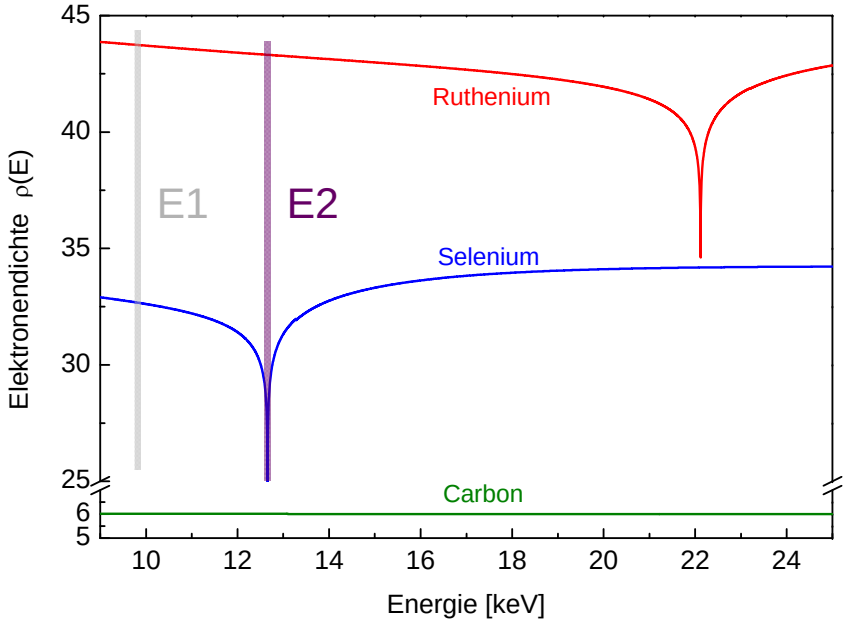
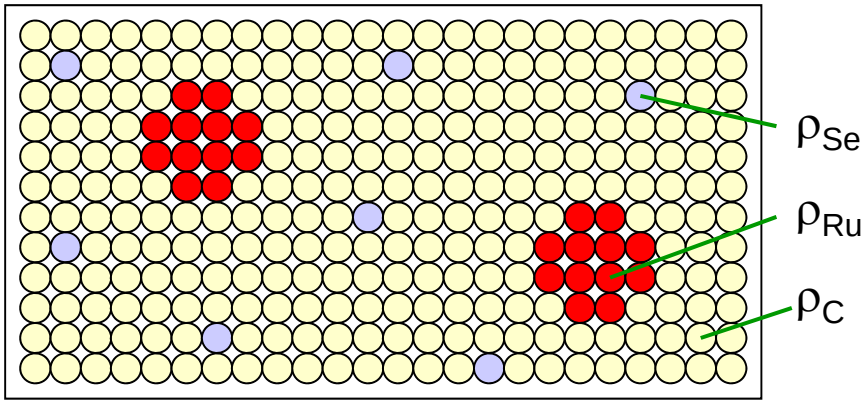
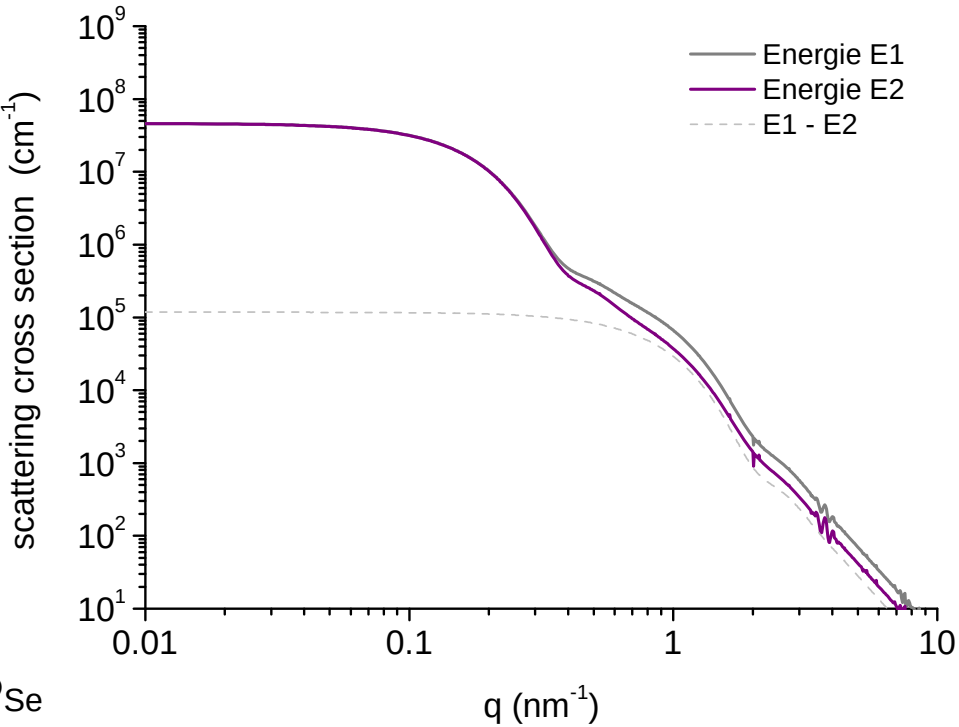
- effective “electron density” becomes energy dependent.



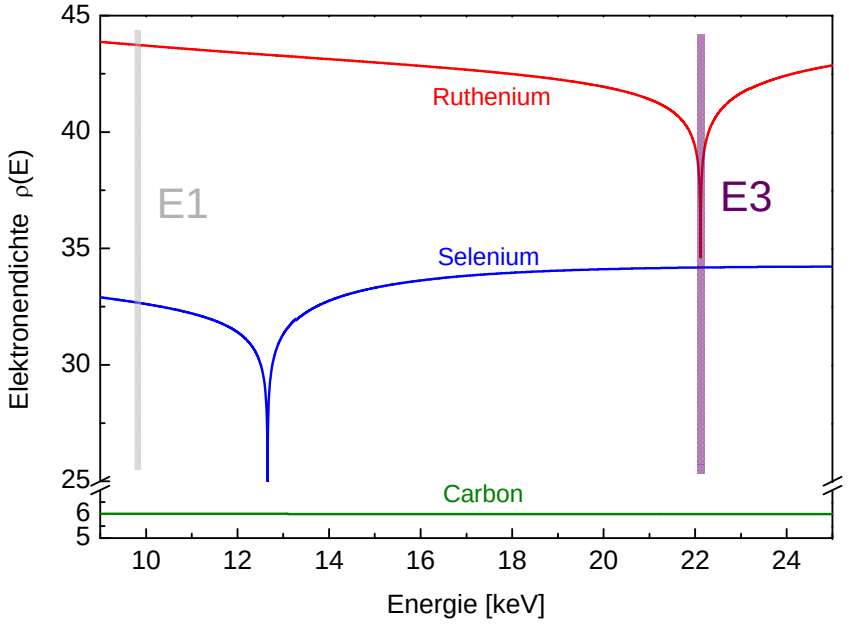


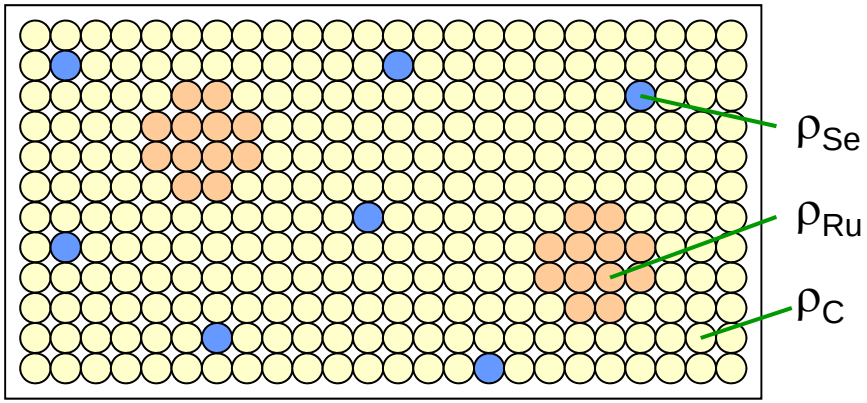


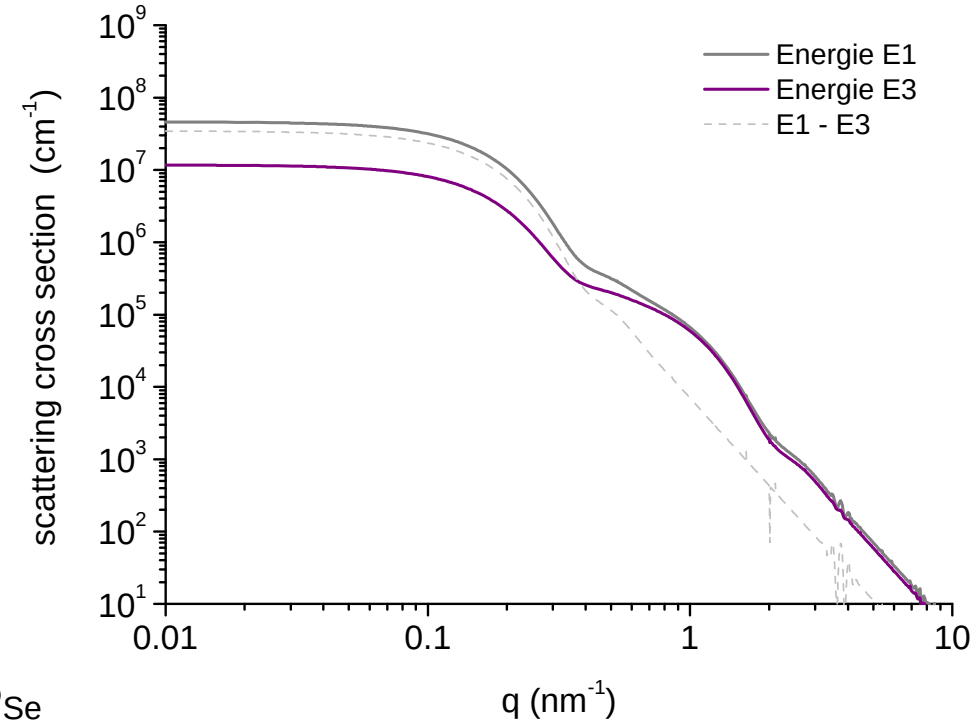
Anomalous Small Angle X-ray Scattering (ASAXS)

HZB Helmholtz Zentrum Berlin

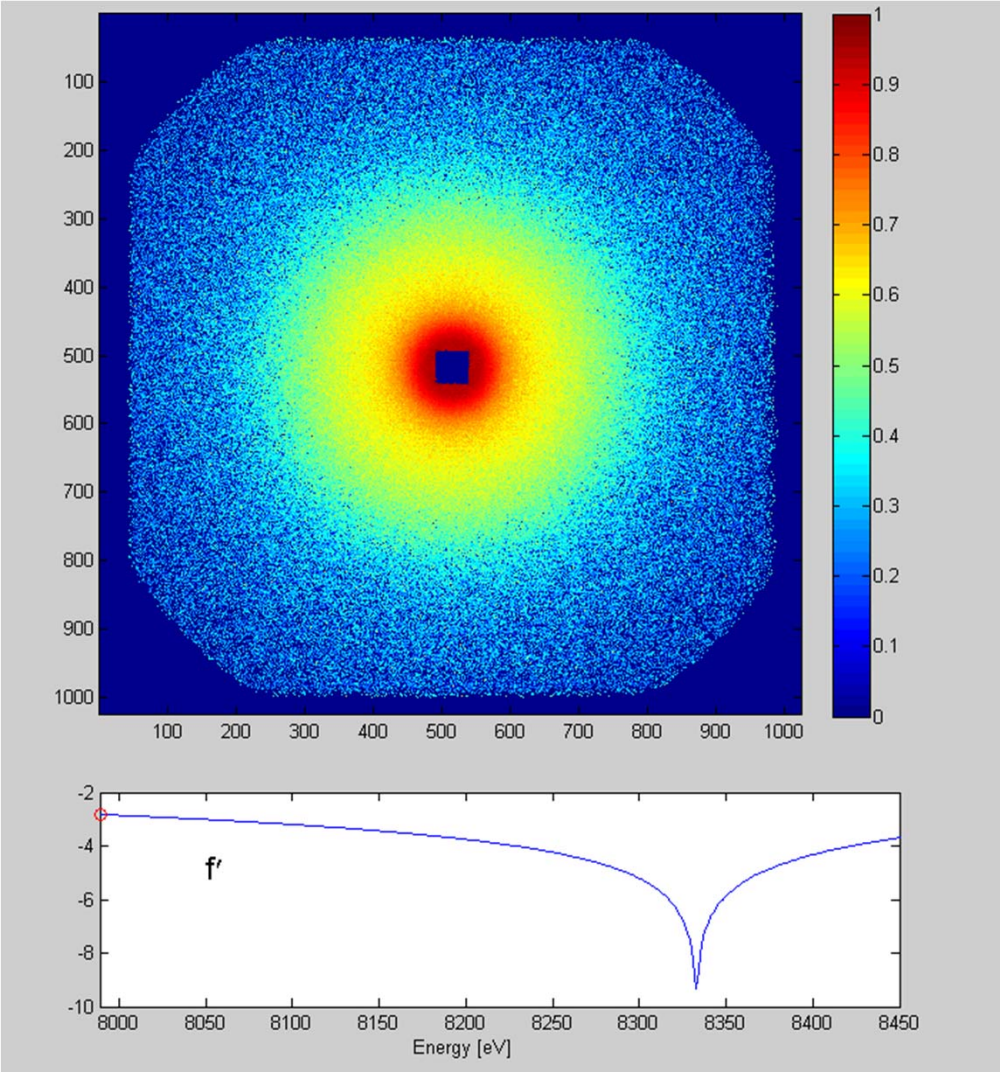
➢ effective “electron density” becomes energy dependent.







ASAXS Movie: $Al_{89}Ni_6La_5$ around Ni-K edge



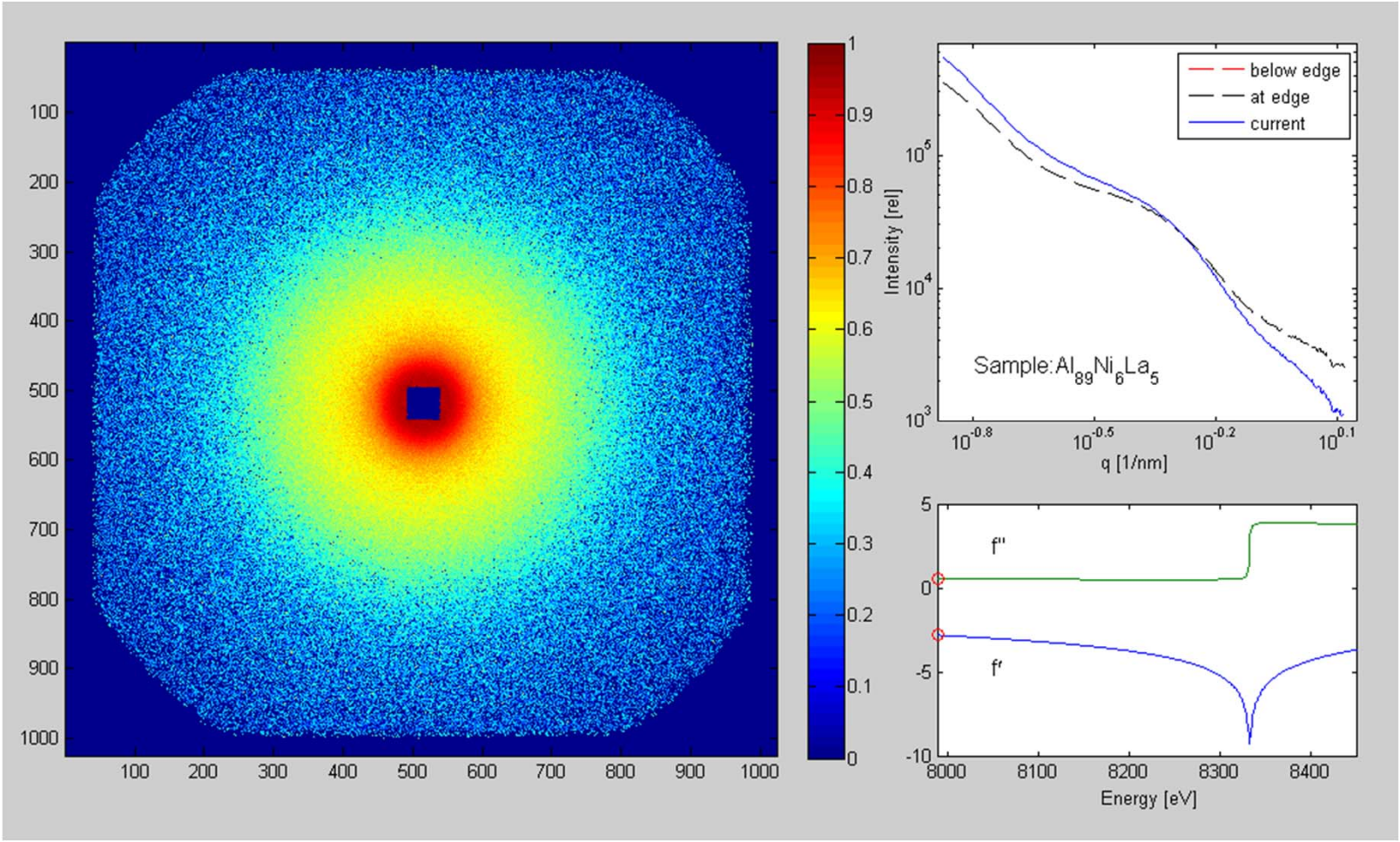
measured:
- 8000eV – 8450eV
- ΔE = 2.25eV
- 201 energy steps
- constant q-range on 2D gas detector

2D gas detector:

corrected by deadtime, monitor, transmission, detector sensitivity, solid angle distorsion, projection of detector surface on a sphere, and background subtraction

Instrument: SAXS @ BESSY

ASAXS Movie: $Al_{89}Ni_6La_5$ around Ni-K edge

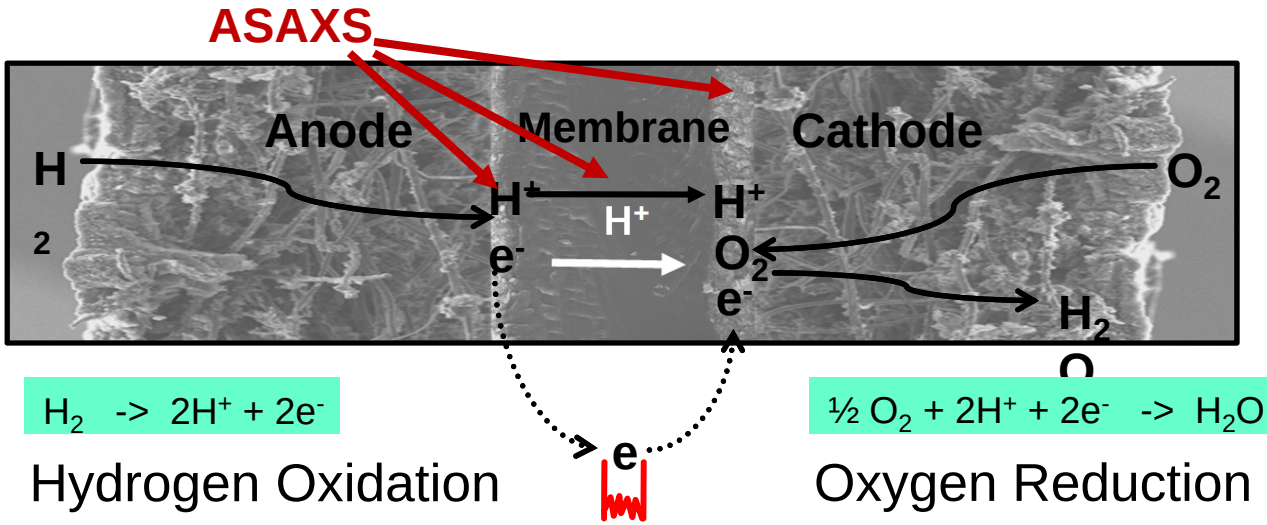


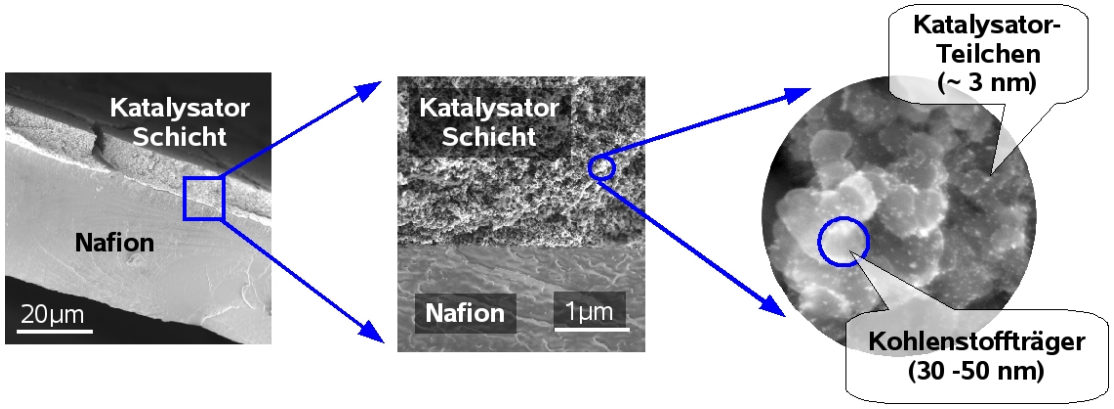
scattering curves are extracted from the corrected 2-dim. detector pictures

Example 1: RuSe Nanoparticle for fuel cell applications

Example 2: In situ study of the degradation of $PtNi_3$ alloys

Catalysts for polymer electrolyte membran fuel cells





Ru-Se Catalyst for fuel cells

Slow electrode kinetics,

Cost of catalyst,

Catalyst degradation…

…are the most critical issues in fuel cell research

Anomalous Small Angle X-Ray Scattering (ASAXS)

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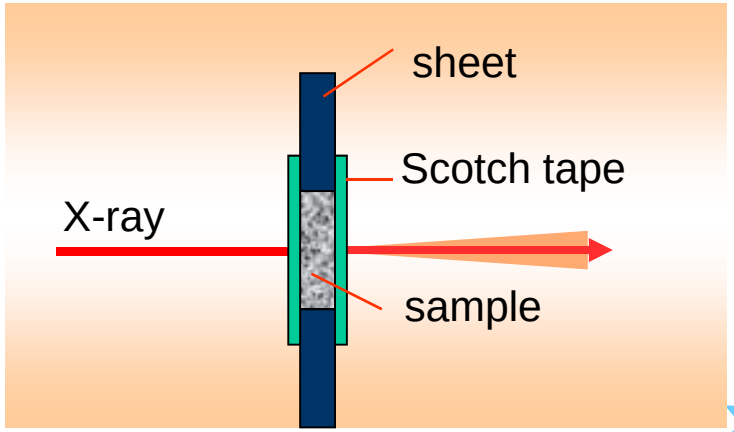
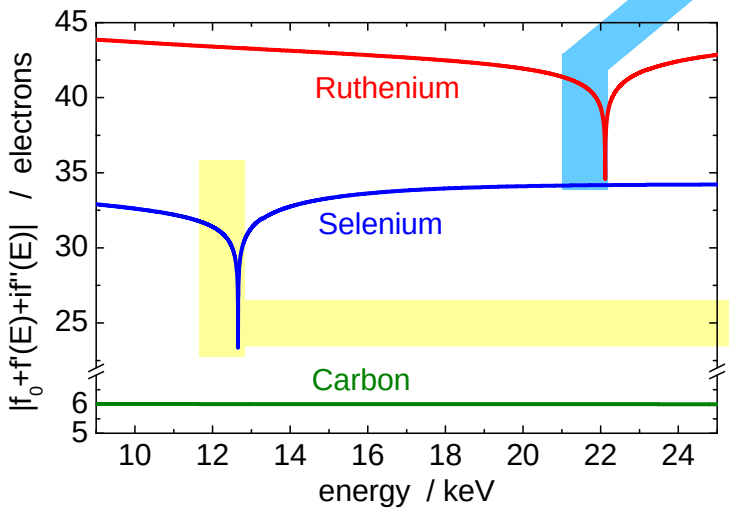
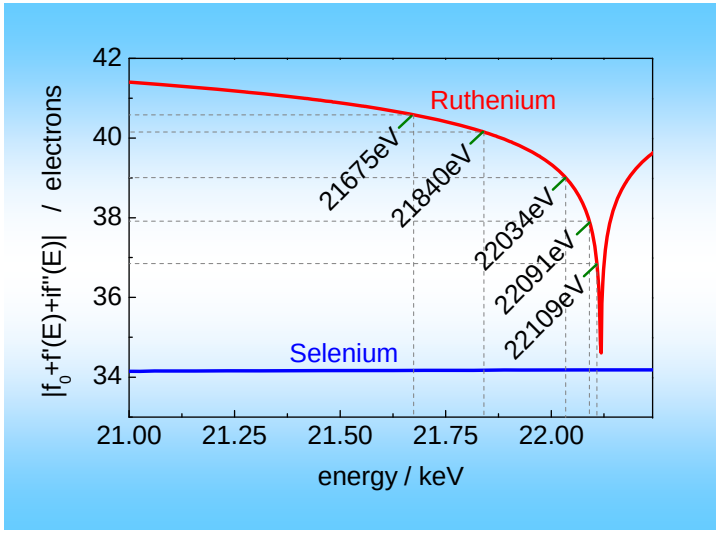
$$f(E) = f_o + f'(E) + if''(E)$$

Sample preparation

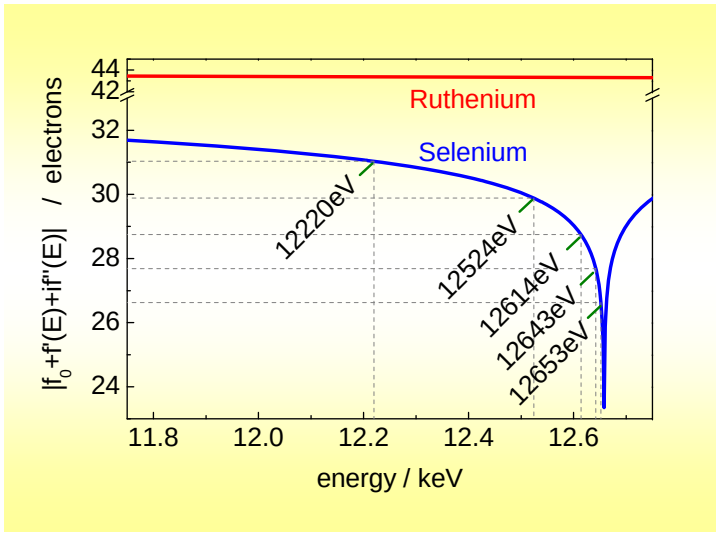


Atomic scattering amplitudes





Ru K edge
- 442 eV
- 277 eV
- 83 eV
- 26 eV
- 8 eV



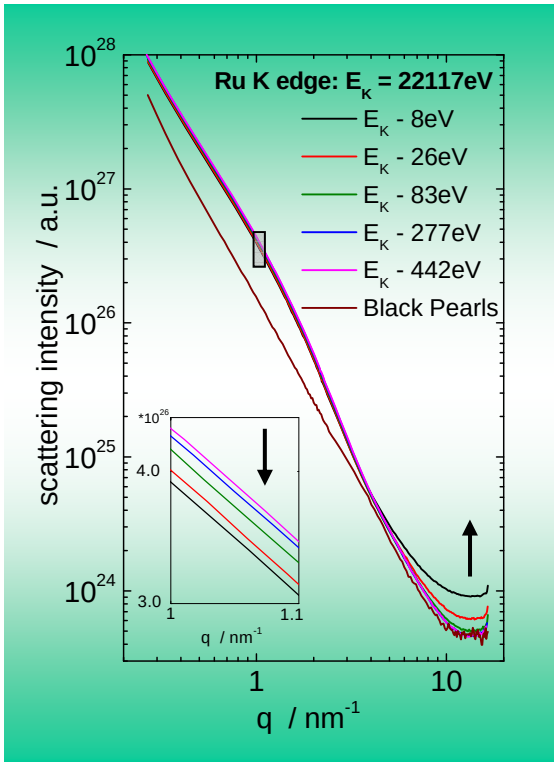
Se K edge
- 438 eV
- 134 eV
- 44 eV
- 15 eV
- 5 eV

ASAXS curves obtained at the:

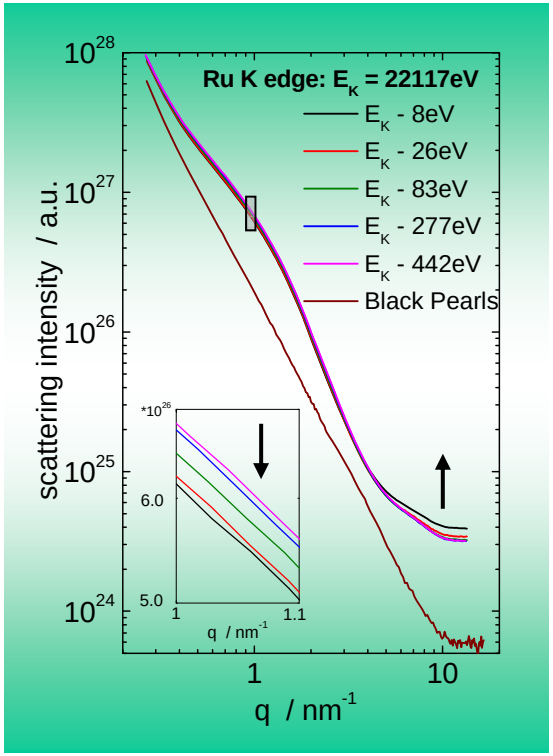
HZB Helmholtz Zentrum Berlin

Ru-K-edge (22117eV)

Ru on Black Pearls



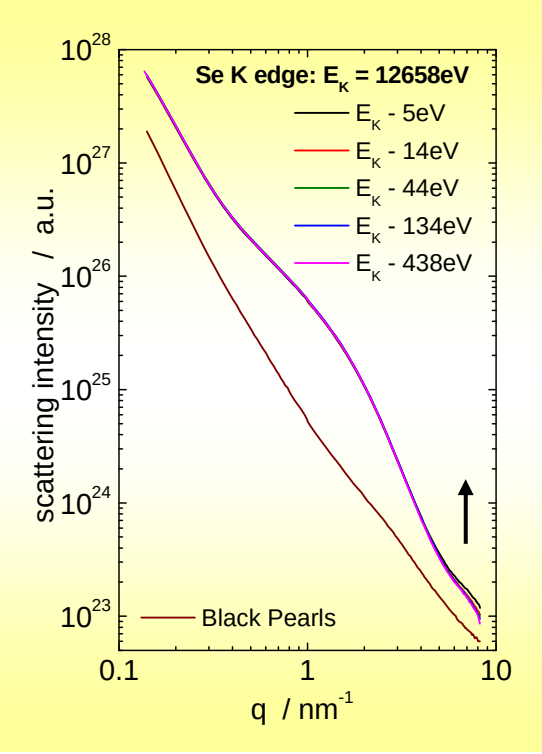
RuSe$_x$ on Black Pearls



→ clear anomalous effect

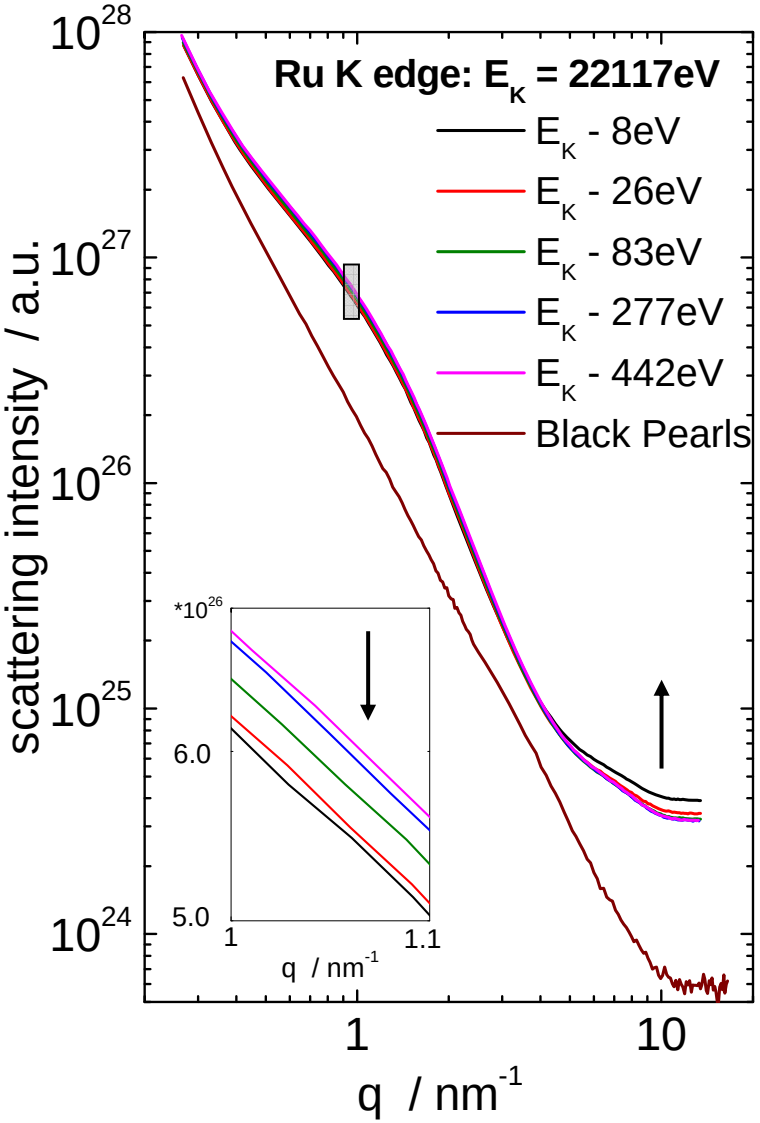
Se-K-edge (12658eV)

RuSe$_x$ on Black Pearls

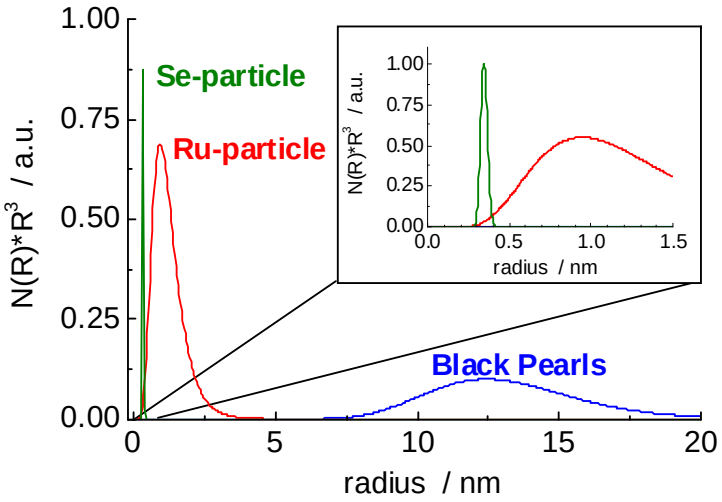


→ **no** anomalous effect

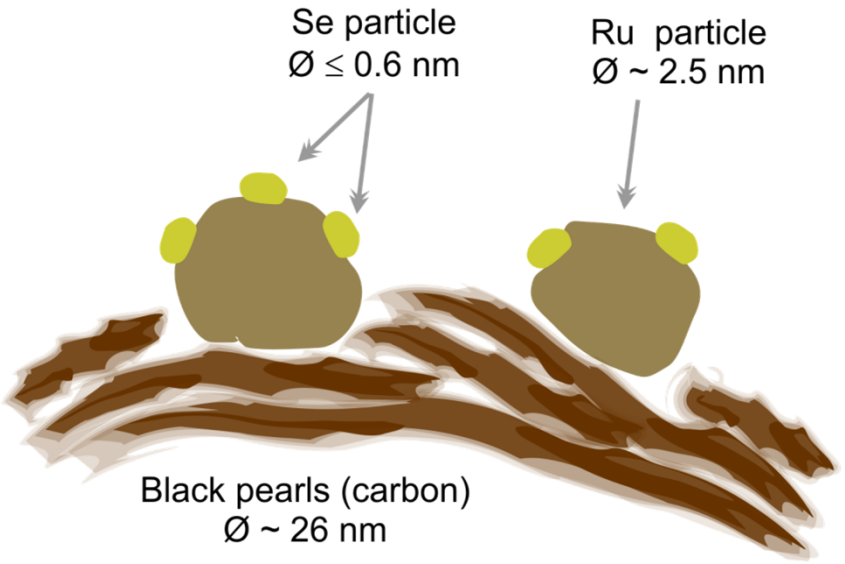
ASAXS: $RuSe_x/C$



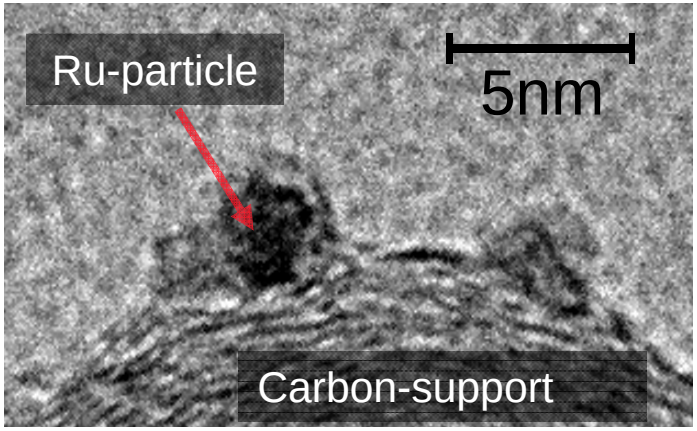
Volume weighted size distribution



Structural model for the Ru-Se based catalyst



TEM



G. Zehl, G. Schmithals, A. Hoell, S. Haas, C. Hartnig, I. Dorbandt, P. Bogdanoff, and S. Fiechter, *Angew. Chem. Int. Ed.* 2007, **46**, 7311 –7314

Example 1: RuSe Nanoparticle for fuel cell applications

Example 2: In situ study of the degradation of $PtNi_3$ alloys

Experimental setup for in situ ASAXS at BESSY II

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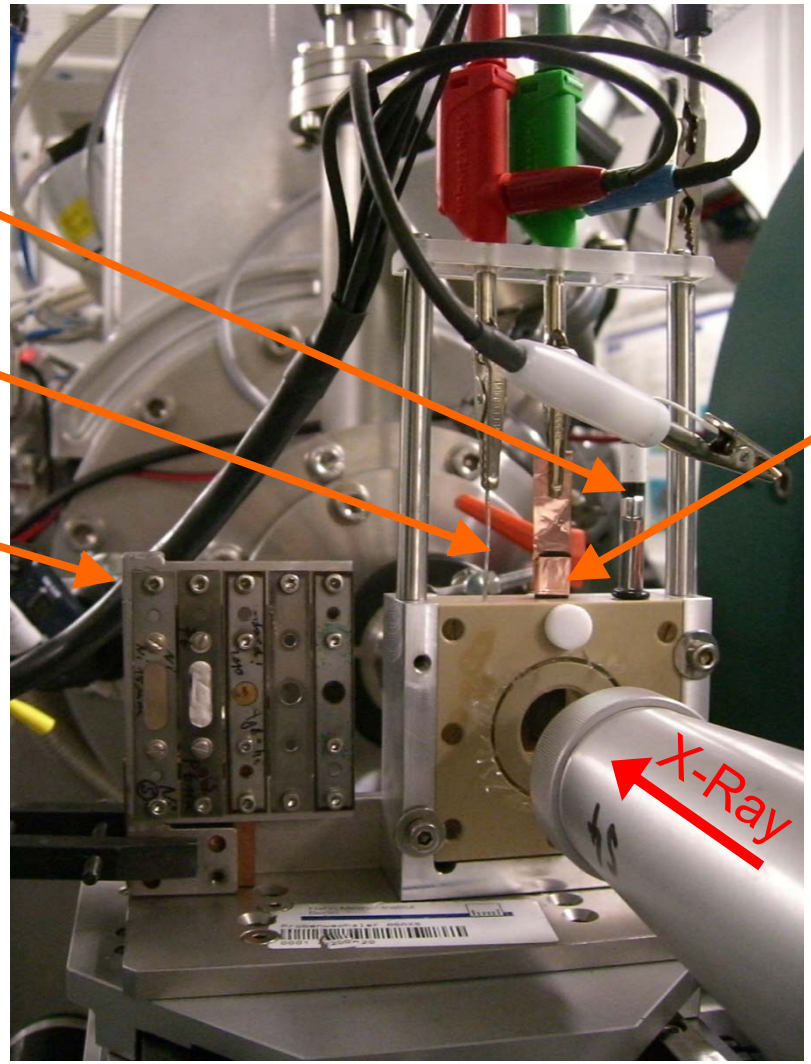
Reference electrode

Counter electrode

Reference samples for ASAXS



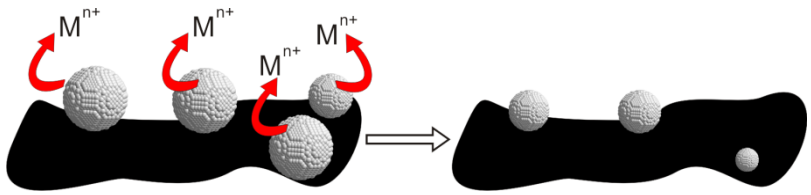
Working electrode

Catalyst ink droplet

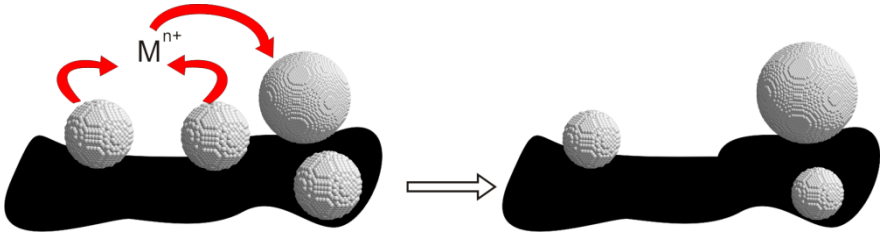
HZB Helmholtz Zentrum Berlin

SAXS is capable to distinguish the mechanism of particle surface area loss

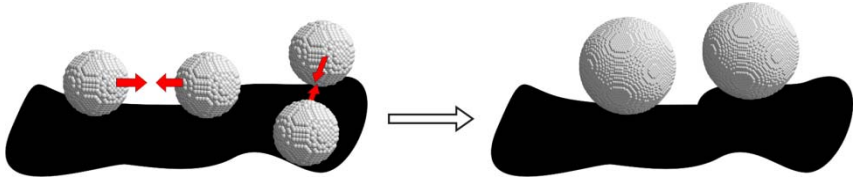
1. Dissolution



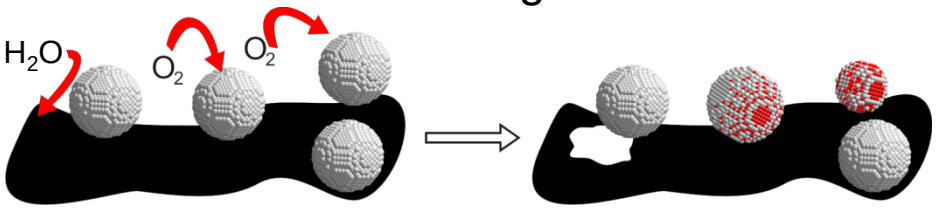
2. Ostwald Ripening



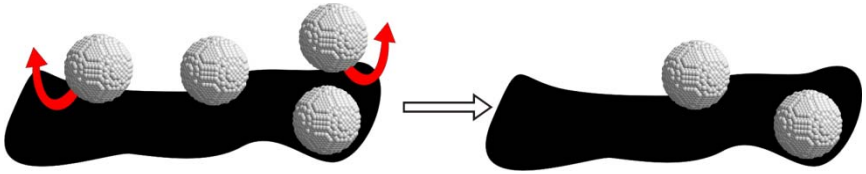
3. Coalescence



4. Oxidation/Poisoning

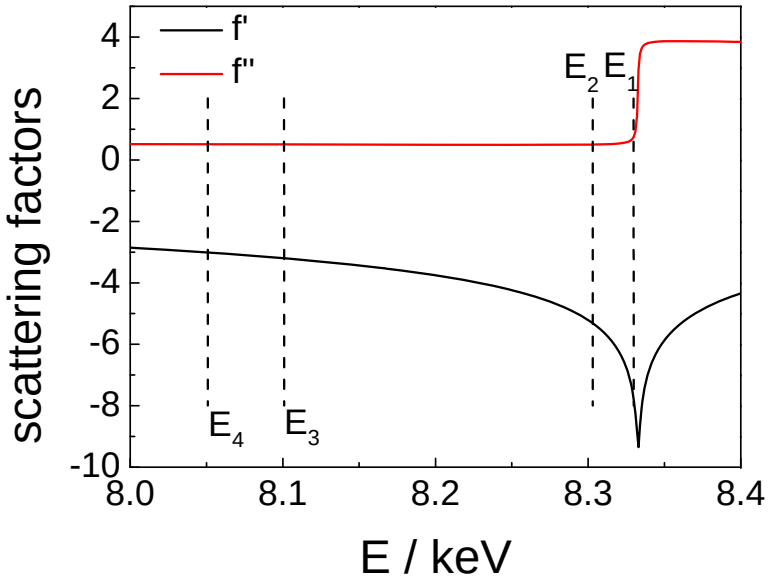


5. Mechanical detachment from conductive support

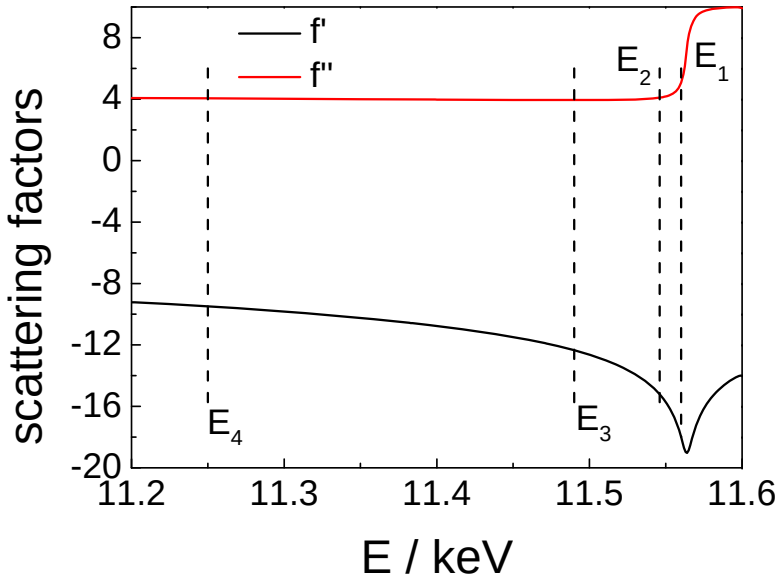


ASAXS: Selected Energies at Ni-K and Pt-L_3 edges

For Ni-resonant scattering



For Pt-resonant scattering

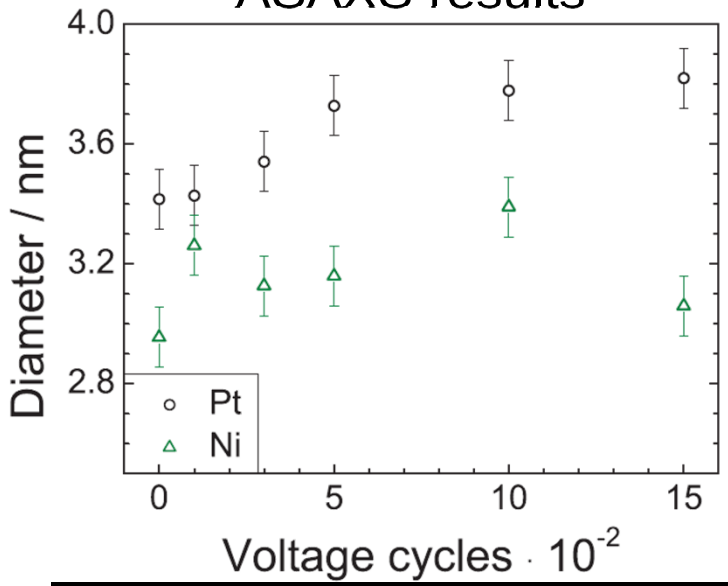


The protocol was kept the same as for the electrochemical characterization.

ASAXS was monitored during a chronoamperometry at 0.5 V after a certain number of stress cycles (0.5 – 1.1 V)

$PtNi_3$, in-situ ASAXS and SAXS

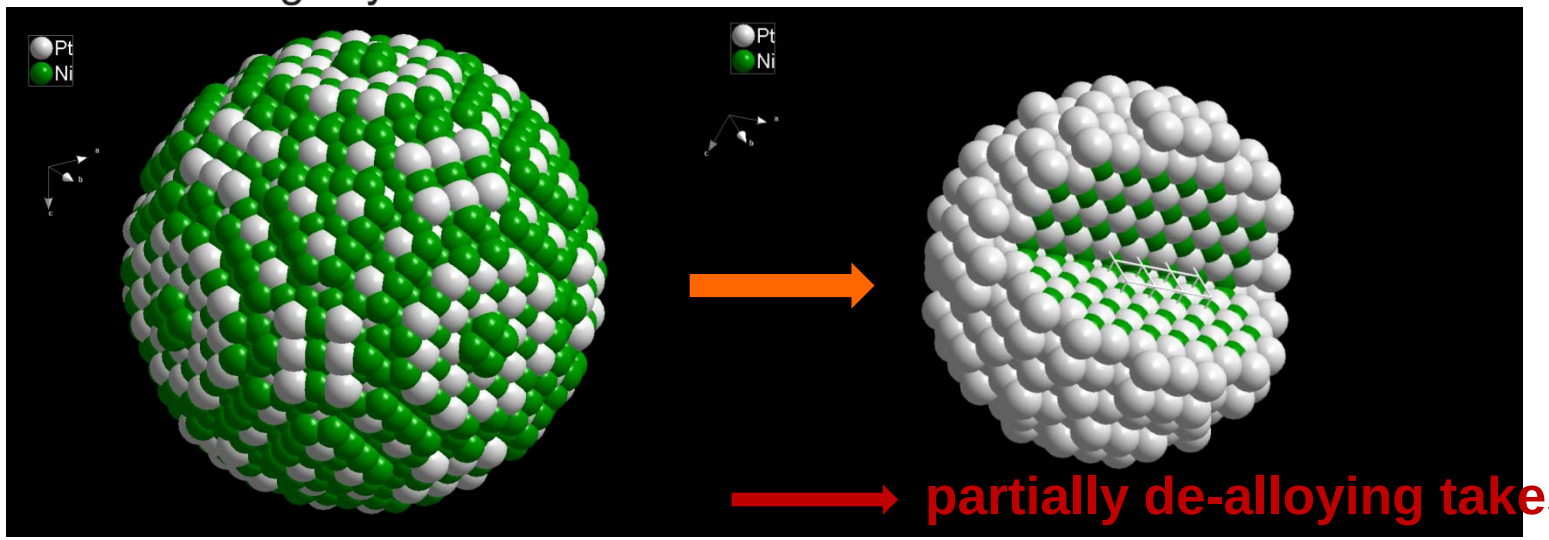
ASAXS results



HE-XRD: PDF-analysis

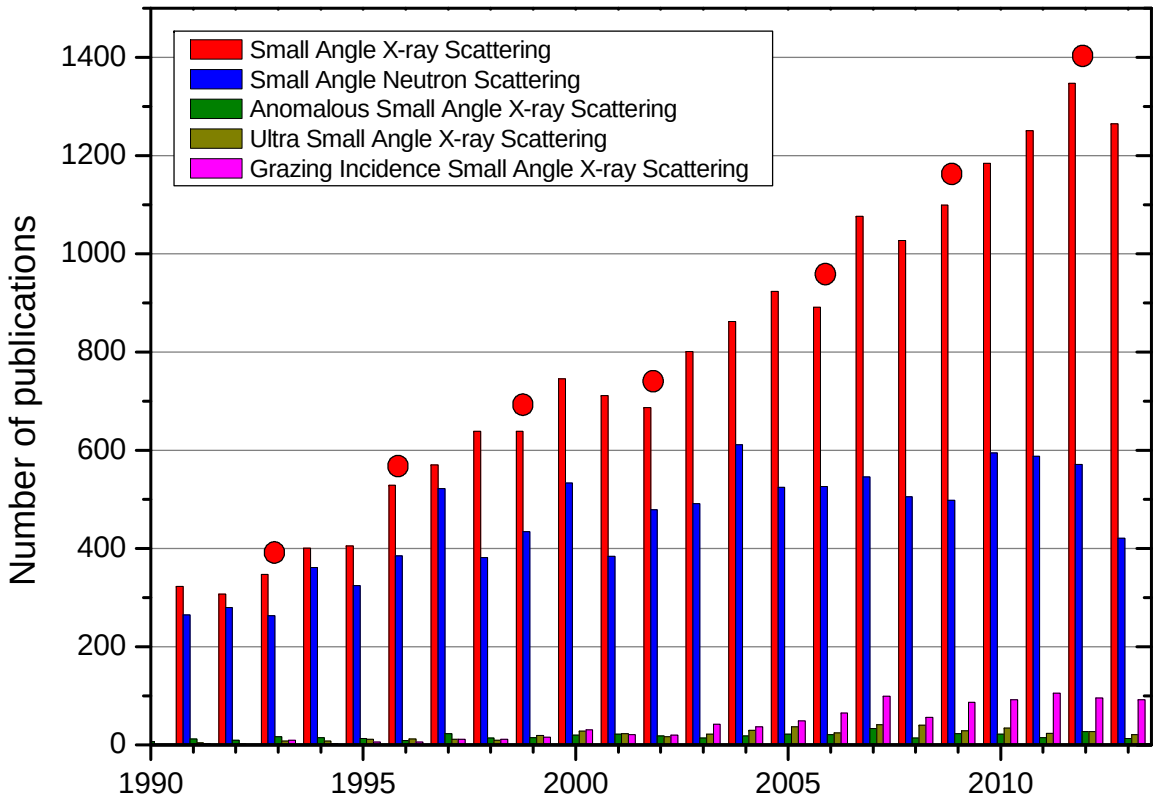
Pristine particles: partially chemically ordered $PtNi_3$ single phase.

Stressed particles: predominant $PtNi_3$ phase and Ni phases.



Tuaev, X.; Rudi S.; Petkov V.; Hoell A.; Strasser, P. *ACS Nano,* **2013**, *7(7)*, 5666-5674.

Popularity of Small-Angle Scattering / Publications



Year of an international SAS conference

Next international Conference on Small-Angle Scattering:
13. – 18. September 2015, TU Berlin (about 500 participants expected)

HZB Helmholtz Zentrum Berlin

Thank You!