Methoden moderner Röntgenphysik: Streuung und Abbildung

Lecture 7	Vorlesung zum Haupt- oder Masterstudiengang Physik, SoSe 2021		
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Location	online		
Date	Tuesdays	12:30 - 14:00	(starting 6.4.)
	Thursdays	8:30 - 10:00	(until 8.7.)

DESY

Methoden moderner Röntgenphysik: Online Info

Tuesday Zoom-Meeting
https://desy.zoom.us/j/92674682486
Meeting ID: 926 7468 2486
Passcode: 144456

Thursday Zoom-Meeting
https://desy.zoom.us/j/99738625981
Meeting ID: 997 3862 5981
Passcode: 841881

Tutorial Zoom-Meeting
https://desy.zoom.us/j/95288979489
Meeting ID: 952 8897 9489
Passcode: 832350

Literature

Basic concepts:

Moderne Röntgenbeugung
Röntgendiffraktometrie für
Materialwissenschaftler,
Physiker und Chemiker
Authors
(view affiliations)
Lothar Spieß
Robert Schwarzer
Herfried Behnken
Gerd Teichert
https://link.springer.com/book/10.1007/978-3-663-10831-3

Elements of Modern X-Ray Physics
J. A. Nielsen and D. McMorrow, J. Wiley&Sons (2001)

X-Ray Diffraction
B.E. Warren, DOVER Publications Inc., New York

Principles of Optics
M. Born and E. Wolf, Cambridge University Press, 7th ed.

Soft X-rays and Extreme Ultraviolet Radiation
D. Attwood, Cambridge University Press (2000)
http://www.coe.berkeley.edu/AST/sxreuv/

Physik der Teilchenbeschleuniger und Synchrotronstrahlungsquellen
K. Wille, Teubner Studienbücher 1996

Lecture Notes

https://photon-science.desy.de/research/research_teams/coherent_x_ray_scattering/teaching/index_eng.html

Methoden moderner Röntgenphysik: Streuung und Abbildung

Part I:

Basics of X-ray Physics

by Gerhard Grübel (GG)

Introduction
Overview, Introduction to X-ray Scattering

X-ray Scattering Primer & Sources of X-rays +Synchrotron Radiation
Elements of X-ray Scattering, Laboratory Sources, Accelerator Bases Sources

Reflection and Refraction from Interfaces
Snell's Law, Fresnel Equations

Kinematical Diffraction (I)
Diffraction from an Atom, a Molecule, from Liquids, Glasses, …

Kinematical Diffraction (II)
Diffraction from a Crystal, Reciprocal Lattice, Structure Factor, …

Methoden moderner Röntgenphysik: Streuung und Abbildung

Small Angle Scattering, and Soft Matter
Introduction, Form Factor, Structure Factor, Applications, ...

Anomalous Diffraction
Introduction into Anomalous Scattering, ...

Introduction into Coherence
Concept, First Order Coherence, Spatial Coherence, Second Order Coherence, ...

Coherent Scattering
Imaging and Correlation Spectroscopy, ...

The Liquid Structure Factor

Consider mono-atomic or mono-molecular systems:

$$I(\mathbf{Q}) = f(\mathbf{Q})^2 \sum_n e^{i\mathbf{Q}\mathbf{r}_n} \sum_m e^{i\mathbf{Q}\mathbf{r}_m} = f(\mathbf{Q})^2 \sum_n \sum_m e^{i\mathbf{Q}(\mathbf{r}_n - \mathbf{r}_m)}$$

with f(**Q**) form factor

separate summations

$$I(\mathbf{Q}) = Nf(\mathbf{Q})^2 + f(\mathbf{Q})^2 \sum_{n,\, m \neq n} e^{i\mathbf{Q}(\mathbf{r}_n - \mathbf{r}_m)}$$

Replace m≠n sum by integral and separate out average density ρ_{at}:

$$I(\mathbf{Q}) = \underbrace{Nf(\mathbf{Q})^2 + f(\mathbf{Q})^2 \sum_n \int_V [\rho_n(\mathbf{r}_{nm}) - \rho_{at}]\, e^{i\mathbf{Q}(\mathbf{r}_n - \mathbf{r}_m)} dV_m}_{I_{SRO}(Q)} + \underbrace{f(\mathbf{Q})^2 \rho_{at} \sum_n \int_V e^{i\mathbf{Q}(\mathbf{r}_n - \mathbf{r}_m)} dV_m}_{I_{SAXS}(Q)}$$

I_{SRO} (Q)

measures short-range order (SRO) since

$\rho_n(\mathbf{r}_{nm}) \rightarrow \rho_{at}$ after few atomic spacings

and the term oscillates then towards zero

I_{SAXS} (Q)

contributes only for Q → 0

(otherwise oscillates to zero)

where $\rho_n(\mathbf{r}_{nm})\, dV_m$ is the number of atoms in element dV_m located at $\mathbf{r}_m$ - $\mathbf{r}_n$ relative to $\mathbf{r}_n$.

Small Angle X-ray Scattering (SAXS)

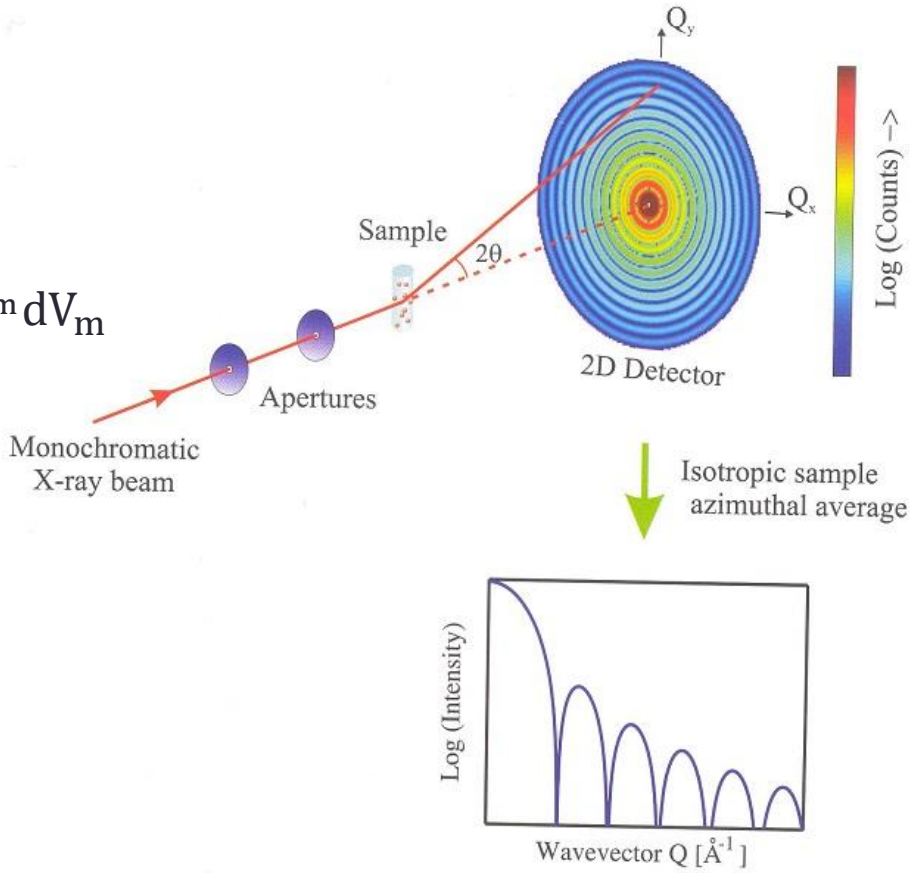
$$I_{SAXS}(Q) = f^2 \sum_n \int_V \rho_{at}\, e^{iQ(r_n - r_m)} dV_m$$

$$= f^2 \sum_n e^{iQr_n} \int_V \rho_{at}\, e^{-iQr_m}\, dV_m$$

$$= f^2 \int_V \rho_{at}\, e^{iQr_n} dV_n \int_V \rho_{at}\, e^{-iQr_m} dV_m$$

$$\Rightarrow I_{SAXS}(Q) = \left| \int_V \rho_{sl}\, e^{iQr} dV \right|^2$$

with $\rho_{sl} = f\,\rho_{at}$



SAXS (Form Factor)

The form factor of isolated particles

$$I_{SAXS}(Q) = (\rho_{sl,p} - \rho_{sI,0})^2 \left| \int_{Vp} e^{iQr} dV_p \right|^2$$

Where $\rho_{sl,p}$, $\rho_{sl,0}$ are the scattering length densities of the particle (p) and solvent (0) and V_p is the volume of the particle.

Using the particle form factor $$F(Q) = \frac{1}{V_p} \int_{Vp} e^{iQr} dV_p$$

one finds $I_{SAXS}(Q) = \Delta\rho^2 V^2_p |F(Q)|^2$ with $\Delta\rho = \rho_{sI,p} - \rho_{sI,0}$

The form factor depends on the morphology (size and shape of the particles) and can be evaluated analytically only in a few cases:

For a sphere with radius R one finds:

$$F(Q) = \frac{1}{V_p} \int_0^R \int_0^{2\pi} \int_0^{\pi} e^{iQr\cos(\theta)} r^2 \sin\theta \, d\theta d\phi dr = \frac{1}{V_p} \int_0^R 4\pi \frac{\sin(Qr)}{Qr} r^2 dr$$

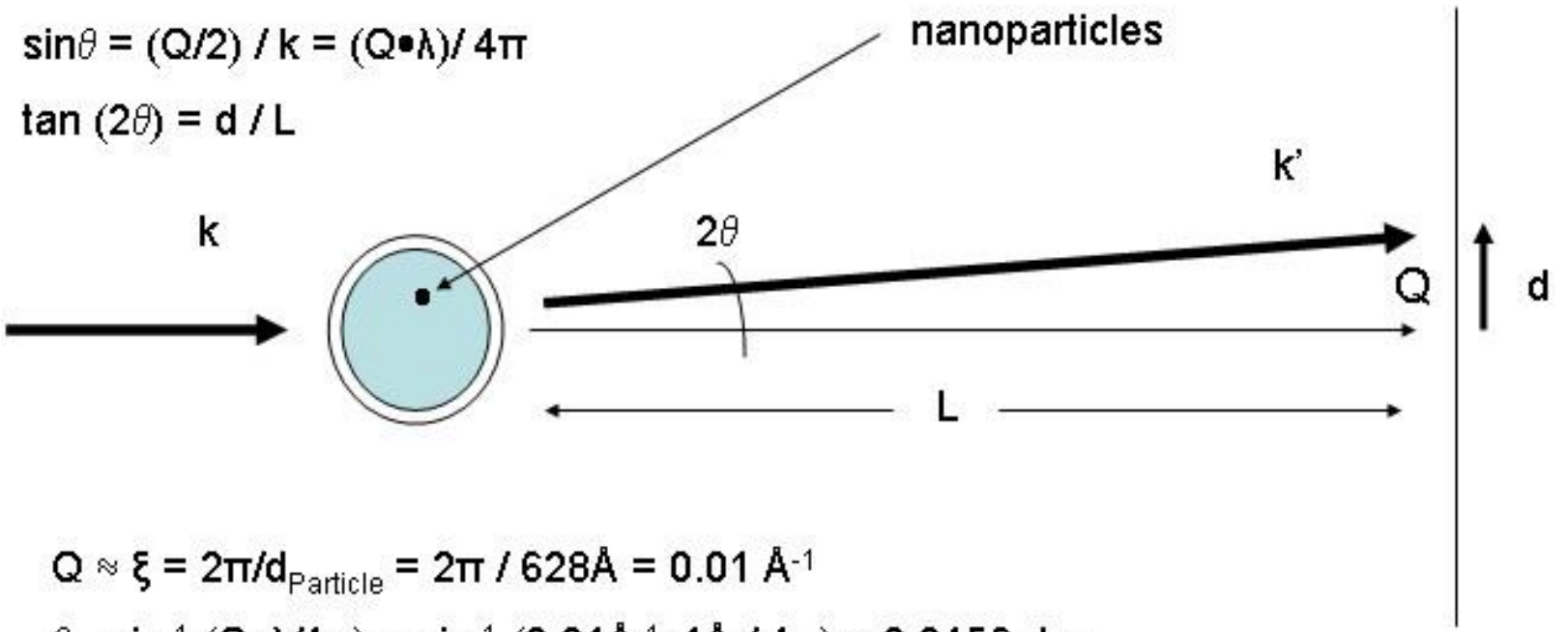
$$= 3\frac{\sin(QR) - Qr\cos(QR)}{(QR)^3} = 3\frac{J_1(QR)}{QR}$$

with $J_1(x)$: Bessel function of the first kind.

For Q→0: $|F(Q)|^2 = 1$ and $I_{SAXS}(Q=0) = \Delta\rho^2 V^2_p$

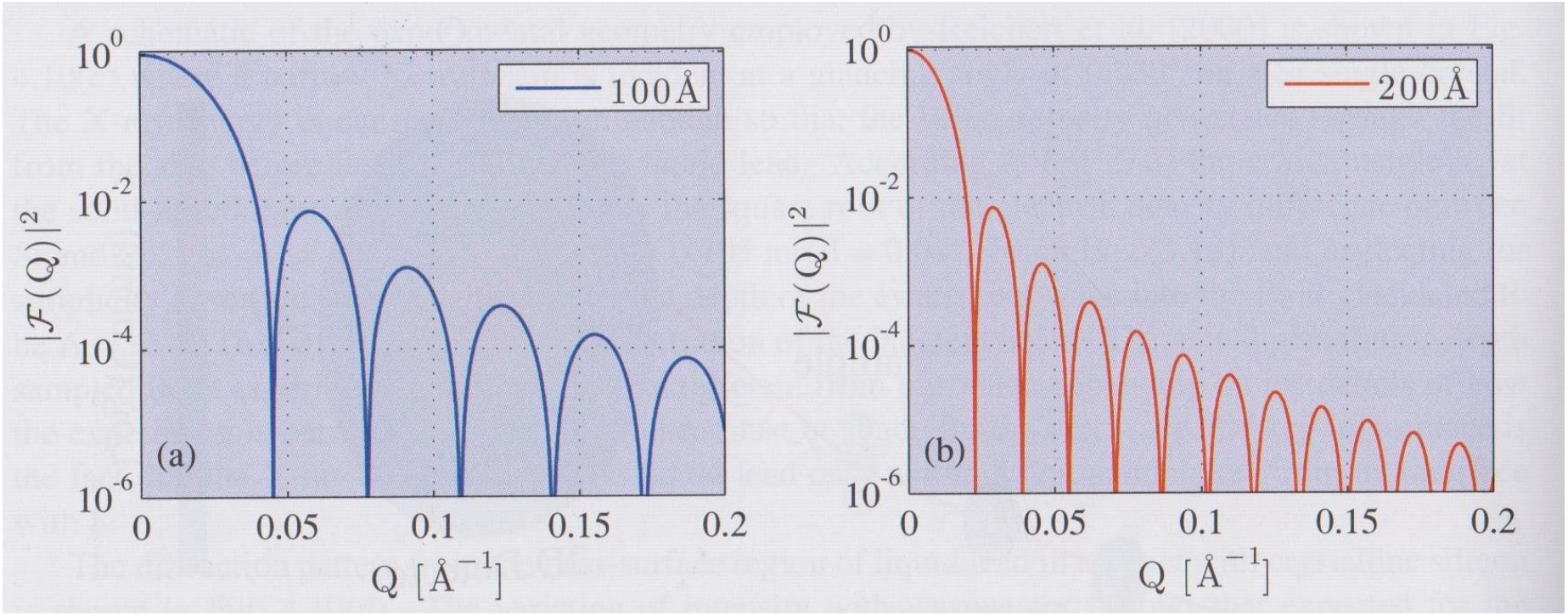
Experimental Set-up (SAXS)

Consider objects (nano-structures) of sub-µm size



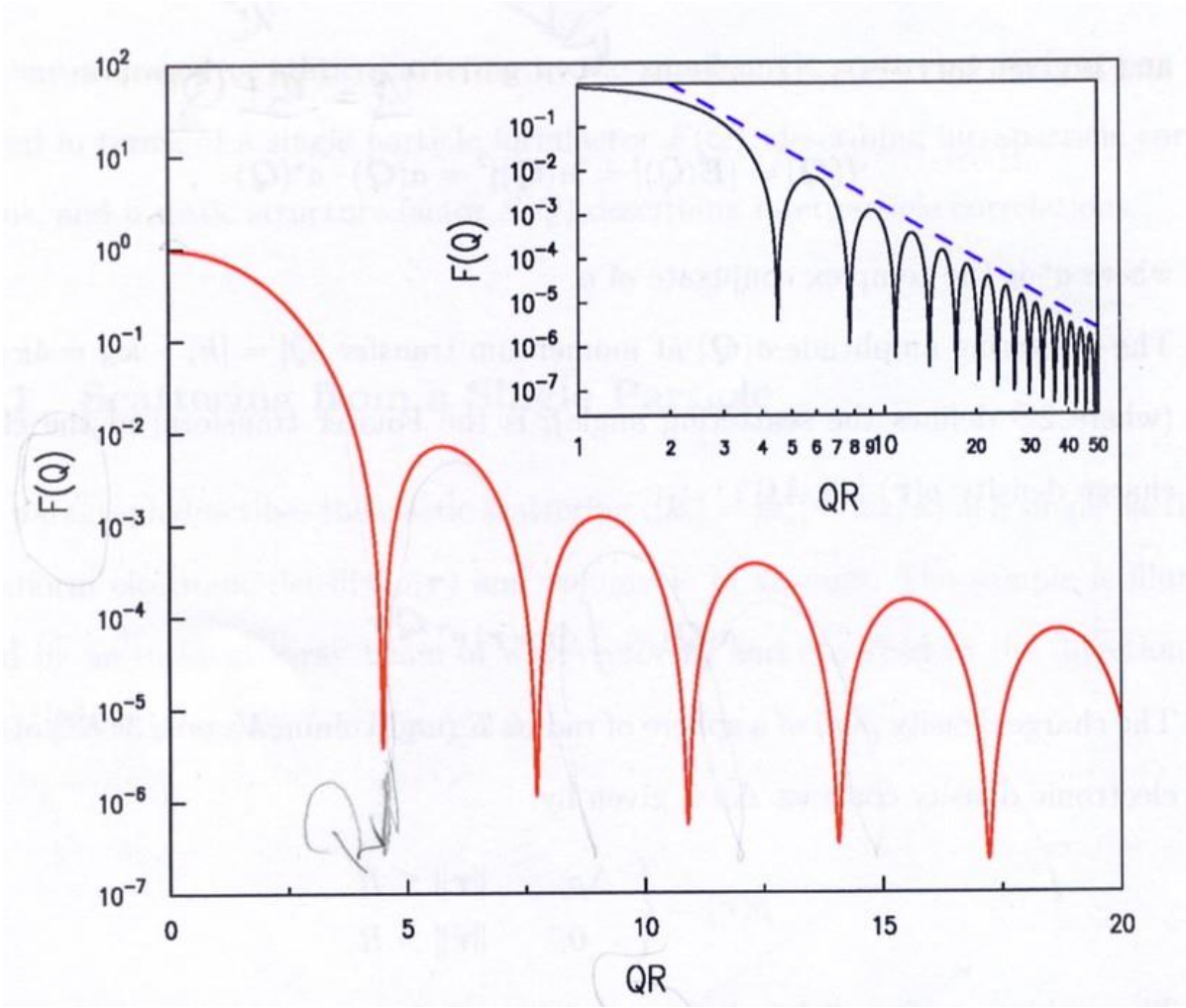
Form Factor for Monodisperse Spheres

Simulated monodisperse spheres of radius 10nm and 20 nm



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

Form Factor for Monodisperse Spheres



The Small Q Limit: Guinier Regime

For $QR \to 0$:

$$F(Q) \approx \frac{3}{(QR)^3}\left[QR - \frac{(QR)^3}{6} + \frac{(QR)^5}{120} - \cdots - QR\left(1 - \frac{(QR)^2}{2} + \frac{(QR)4}{24}\right)\right]$$

$$\approx 1 - \frac{(QR)^2}{10}$$

Thus:

$$I_{SAXS}(Q) \approx \Delta\rho^2\, V^2{}_p \left[1 - \frac{(QR)^2}{10}\right]^2 \approx \Delta\rho^2\, V^2{}_p \left[1 - \frac{(QR)^2}{5}\right]$$

Thus the QR → 0 limit can be used to determine the particle radius R via:

$$I_{SAXS}(Q) \approx \Delta\rho^2\, V^2{}_p \; e^{-\frac{(QR)^2}{5}}$$

Note: if $x << 1$
then $e^{-x} \approx 1 - x$

Thus: plotting ln $[I_{SAXS}(Q)]$ vs. Q^2 reveals a slope ~ $R^2/5$ $\Rightarrow$ R

The Large Q Limit: Porod Regime

For QR >> 1: wavelength small compared to particle size

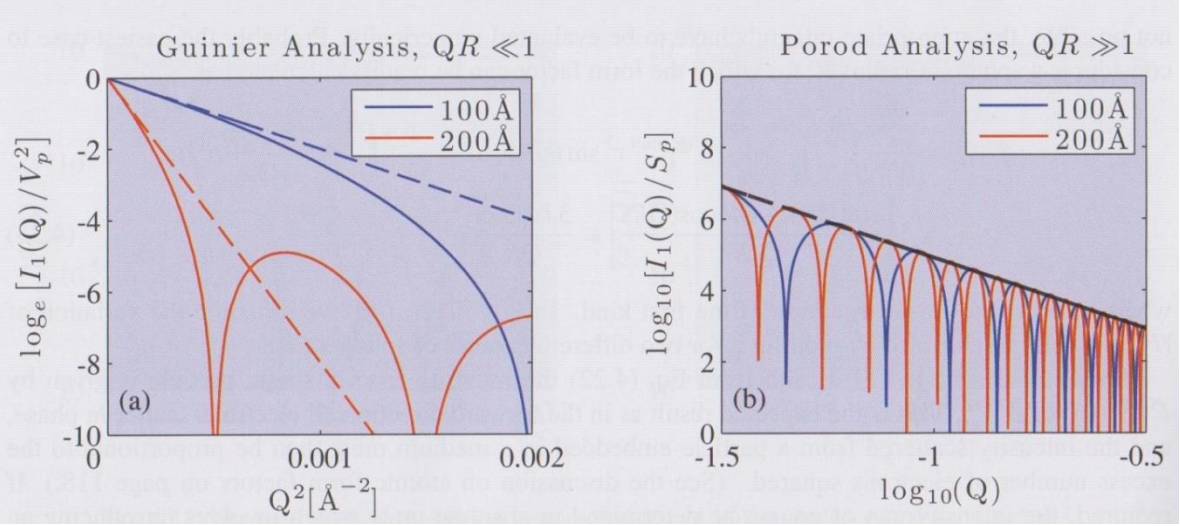
$$F(Q) = 3\left[\frac{\sin(QR)}{(QR)^3} - \frac{\cos(QR)}{(QR)^2}\right] \approx 3\left[-\frac{\cos(QR)}{(QR)^2}\right]$$

Note: $\lim_{x\to\infty} \frac{\sin(x)}{x} = 0$

$$I_{SAXS}(Q) = 9\Delta\rho^2 V_p^2 \frac{\langle\cos^2(QR)\rangle}{(QR)4} = \frac{9\Delta\rho^2 V_p^2}{2(QR)^4}$$

Note: $\lim_{x\to\infty} \cos^2(x) = 1/2$

Thus: $I_{SAXS}(Q) \sim \frac{1}{Q^4}$



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Radius of Gyration

Radius of gyration: root mean square distance from the particle's center

$$R_G^2 = \frac{1}{V_p} \int_{v_p} r^2 dV_p$$

Analytical solution for uniform spheres: $R^2{}_G = \frac{3}{5} R^2$

Remember: $I_{SAXS}(Q) \approx \Delta\rho^2 \, V^2{}_p \; e^{-\frac{(QR)^2}{5}}$ (Guinier Regime)

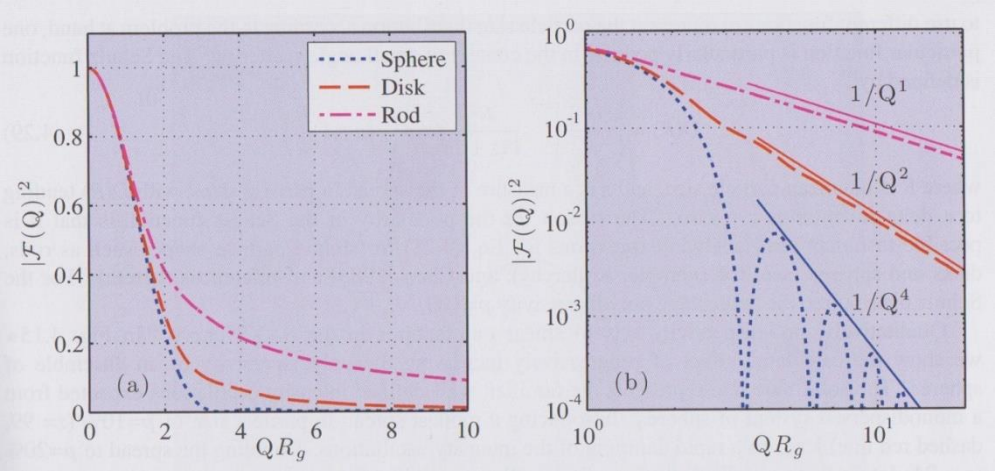
$$I^{SAXS}(Q) \approx \Delta\rho^2 \, V_P^2 \, e^{\frac{(-(QR_G)^2}{3}}$$

→ Now the radius of gyration can be extracted from the Guinier plot.

Form Factor and Particle Shape

$$F(Q) = \frac{1}{V_p}\int_{v_p} e^{iQr}\,dV_p$$

	$\lvert F(Q)\rvert^2$	R_G	Porod Exp.
Sphere (d=3)	$\left(\frac{3J_1(QR)}{QR}\right)^2$	$\sqrt{\frac{3}{5}}\,R$	-4
Disc (d=3)	$\frac{2}{(QR)^2}\left(1-\frac{J_1(2QR)}{QR}\right)$	$\sqrt{\frac{1}{2}}\,R$	-2
Rod (d=1)	$\frac{2Si(QL)}{QL}-\frac{4\sin^2(QR/2)}{(QL)^2}$	$\sqrt{\frac{1}{12}}\,L$	-1



with: $Si(x) \int_0^x \frac{\sin t}{t}\,dt$

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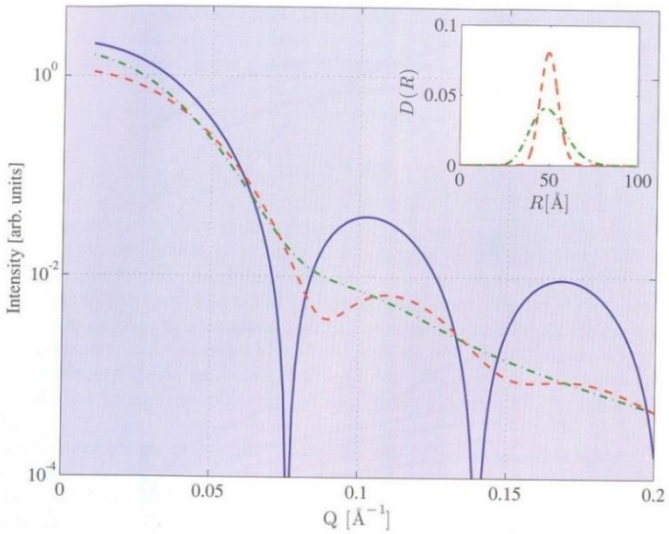
Polydispersity

Realistic ensembles of particles display a certain distribution of particle sizes that shall be distributed by a distribution function D(R). Thus the scattering intensity may be written as

$$I_{SAXS(Q)} = \Delta\rho^2 \int_0^\infty D(R)\, V_p(R)^2\, |F(Q,R)|^2 dR$$

with $\int_0^\infty D(R)\, dR = 1$. A frequently used distribution function is the so-called Schultz function:

$$D(R) = \left[\frac{z+1}{< R >}\right]^{z+1} \frac{R^z}{\Gamma(z+1)}\, e^{\left(-(z+1)\frac{R}{<R>}\right)}$$



<R> is the mean particle size

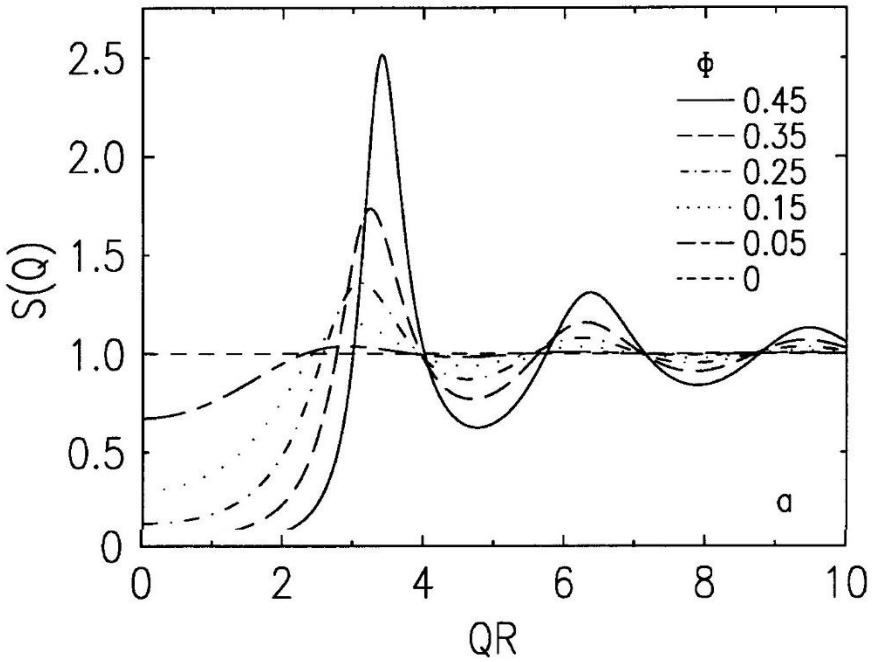
z is a measure of the polydispersity

Structure Factor

Interparticle interactions:

S(Q): structure factor

$$I_{SAXS}(Q) = \Delta\rho 2\, V_p^2\, |F(Q)|^2\, S(Q)$$



S(Q) can be modeled via Rescaled Mean Spherical Approximation (RMSA)

Input parameters for RMSA are:

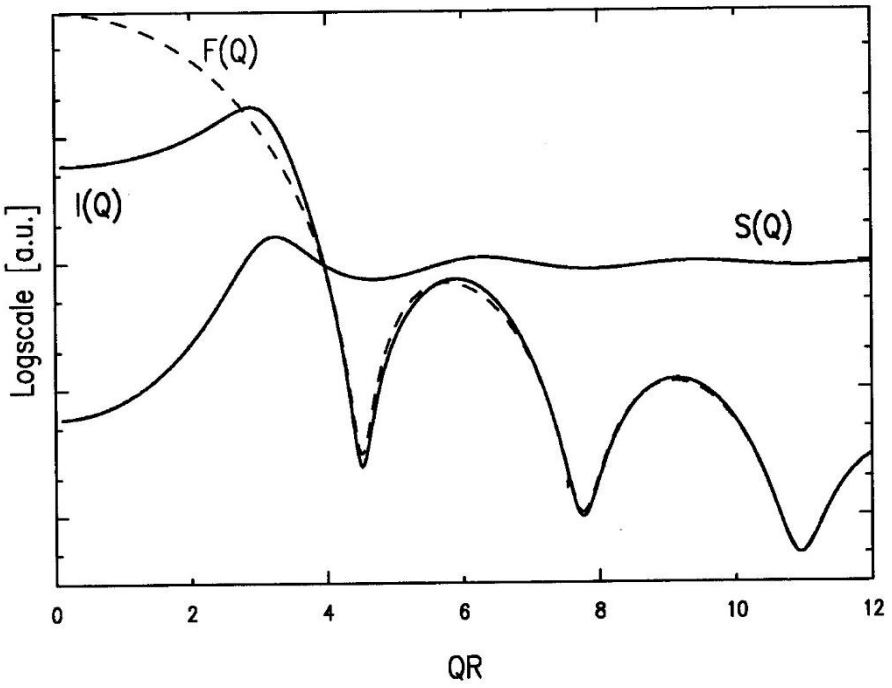
- Particle radius
- Volume fraction Φ
- Charge per particle
- Electrolyte (mol)
- Temperature
- Permittivity

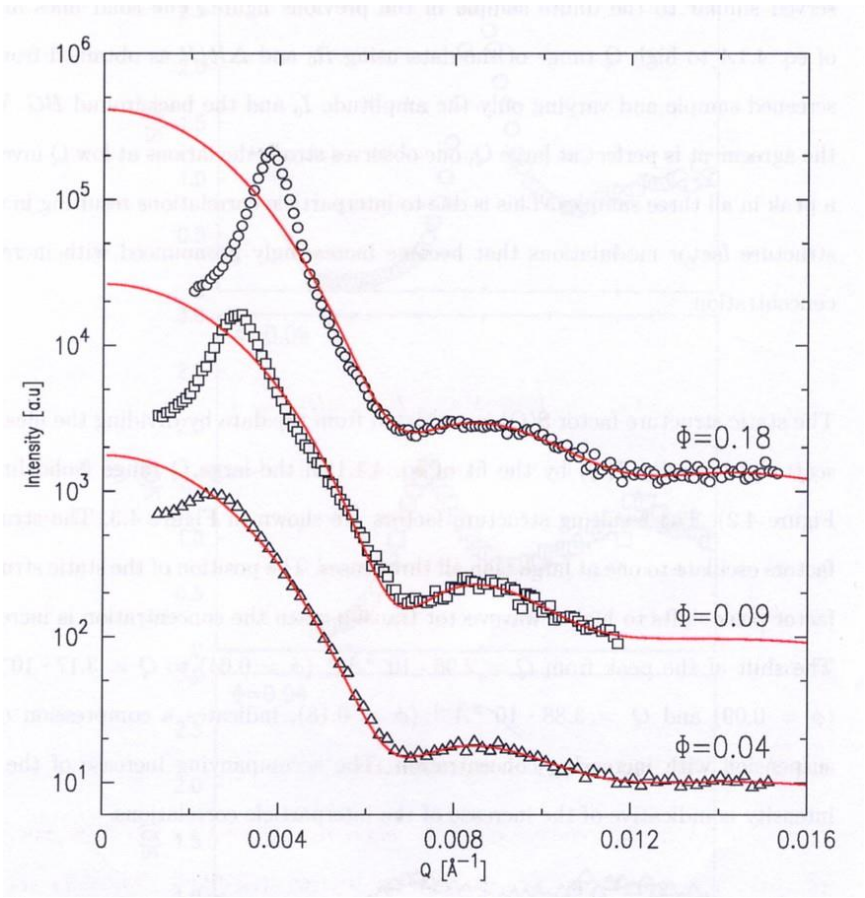
for Φ =0 (no interparticle interaction) → S(Q)=1

SAXS Experiment

for spherical particles: I(Q)=F(Q)•S(Q)

- measure I(Q)
- model F(Q)
- model S(Q)





Methoden moderner Röntgenphysik II: Streuung und Abbildung

Small Angle Scattering, and Soft Matter
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Coherent Scattering
Spatial Coherence, Second Order Coherence, ...

Applications of Coherent Scattering
Imaging and Correlation Spectroscopy, ...

Resonant Scattering (phasing, magnetism,..)

Scattering length of an atom: $- r_0 f^0(\mathbf{Q})$

$f^0(\mathbf{Q})$ atomic form factor (fourier transform of charge distribution)

r_0 thomson scattering length of single electron

in order to include absorption effects (f '') → a more elaborate model than the free electron gas is needed

⟶ Electrons are bound to atoms

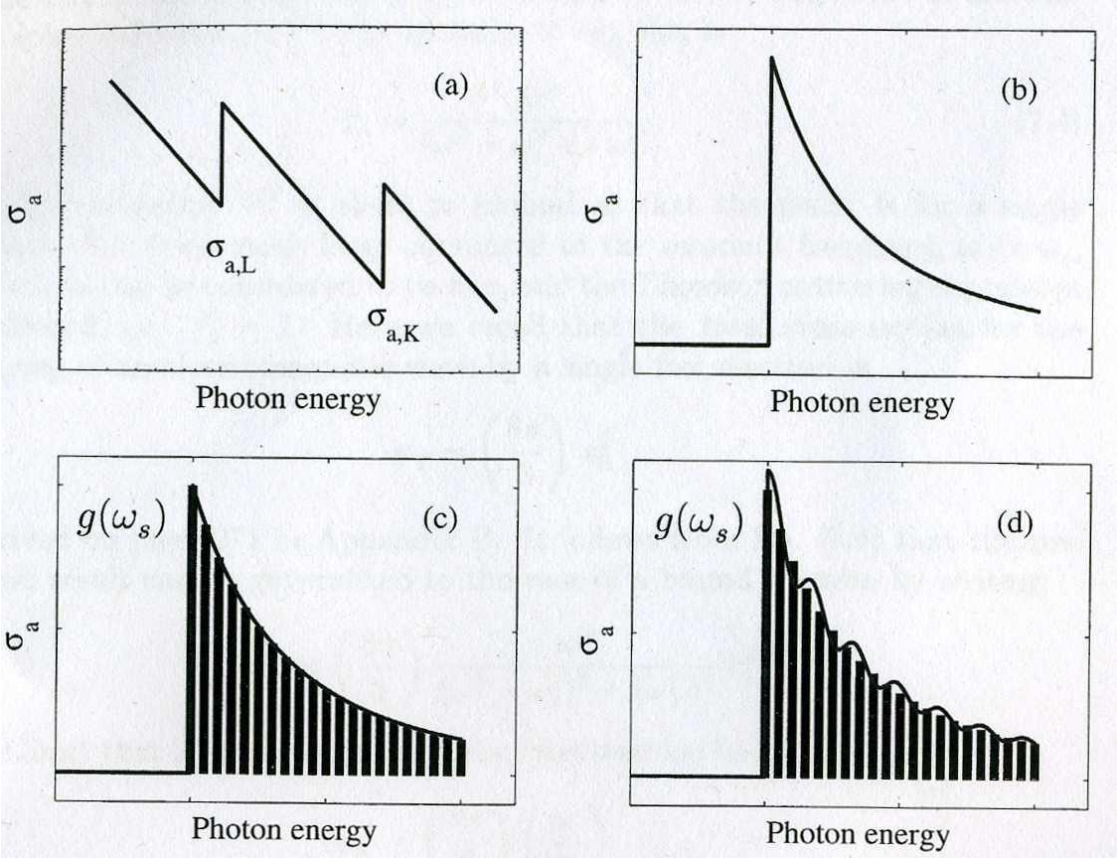
⟶ Forced oscillator modell with resonant frequency ω_s and damping constant Γ

include dispersion corrections (f', f''): [note: f'' = $(k/4\pi r_0)\ \sigma_a$]

$f(\mathbf{Q}, \omega) = f^0(\mathbf{Q}) + f'(\omega) + i f''(\omega)$ [in units of r_0]

Resonant Scattering

What can we measure?



The absorption cross-section σ_a as a function of the photon energy

Resonant Scattering

classical model of an electron bound in an atom in E field

$$\boldsymbol{E_{in}}(\mathbf{r},t) = \hat{\boldsymbol{x}}\, E_o \exp\{-i\omega t\}$$ ⟶ equation of motion of the electron

$$\ddot{x} + \Gamma \dot{x} + \omega_S^2 x = -\left(\frac{e E_0}{m}\right) \exp\{-i\omega t\}$$

Γ = damping

ω_s resonant frequency

Solution: $x(t) = x_0 \exp\{-i\omega t\}$ ⟶ $x_0 = -\left(\frac{e E_0}{m}\right) \frac{1}{(\omega_S^2 - \omega^2 - i\omega\Gamma)}$ (A)

radiated field strength at distance R and time t

$$E_{rad}(R,t) = \left(\frac{e}{4\pi \varepsilon_0 R c^2}\right) \ddot{x}(t - R/c) \quad \text{(B)}$$

acceleration at "earlier" time (t-R/c)

Resonant scattering

inserting $\ddot{x}(t - R/c) = \omega^2 x_0 \exp\{-i\omega t\} \exp\{i(\omega/c)R\}$ using (A) into (B):

$$E_{rad}(R,t) = \frac{\omega^2}{(\omega_S^2 - \omega^2 - i\omega\Gamma)} \left(\frac{e^2}{4\pi\,\varepsilon_0\, m\, c^2}\right) Eo \exp\{-i\omega t\} \left(\frac{\exp\{ikR\}}{R}\right)$$

or

$$\frac{E_{rad}(R,t)}{E_{in}} = - r_0 \frac{\omega^2}{(\omega_S^2 - \omega^2 + i\omega\Gamma)} \left(\frac{\exp\{ikR\}}{R}\right)$$

atomic scattering length f_s (in units of $-r_0$) for bound electron (C)
note: $f_s \rightarrow 1$ ($\omega >> \omega_s$)

<u>total cross-section:</u> $\sigma_T = (8\pi/3)\, r_o^2$ (free electron)

$$\sigma_T = \left(\frac{8\pi}{3}\right) \frac{\omega^4}{(\omega^2 - \omega_S^2)^2 + (\omega\Gamma)^2} r_0^2$$

<u>for $\Gamma = 0$ and $\omega << \omega_s$:</u> $\sigma_T = (8\pi/3) r_o^2 (\omega / \omega_S)^4$: "Rayleigh Scattering"

Resonant scattering

$$f_s = \frac{\omega^2}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}$$

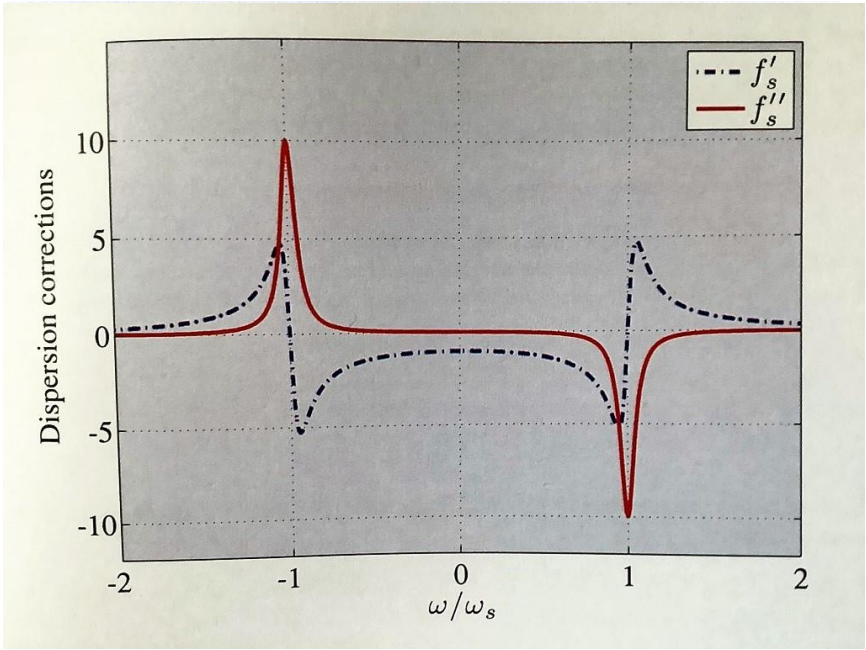
$$= \frac{\omega^2 - \omega_s^2 + i\omega\Gamma + \omega_s^2 - i\omega\Gamma}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}$$

$$= 1 + \frac{\omega_s^2 - i\omega\Gamma}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}$$

$$\approx 1 + \underbrace{\frac{\omega_s^2}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}}$$

dispersion correction $\chi(\omega)$

$$\chi(\omega) = f'_s + i f''_s = \frac{\omega_s^2}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}$$



with:

$$f'_s = \frac{\omega_s^2 (\omega^2 - \omega_s^2)}{(\omega^2 - \omega_s^2)^2 + (\omega\Gamma)^2}$$

$$f''_s = \frac{\omega_s^2 \omega \Gamma}{(\omega^2 - \omega_s^2)^2 + (\omega\Gamma)^2}$$

Resonant scattering

The absorption cross-section for a single oscillator model is given by

$f'' = -(k/4\pi r_0)\,\sigma_{a,s}$ (see J. A-N. & D. McM. p. 70)

$$\sigma_{a,s}(\omega) = 4\,\pi\, r_0\, c\, \frac{\omega_s^2\,\Gamma}{(\omega^2 - \omega_s^2)^2 + (\omega\Gamma)^2}$$

this function has:

- sharp peak at $\omega = \omega_s$
- $\Delta\omega_{FWHM} \approx \Gamma$

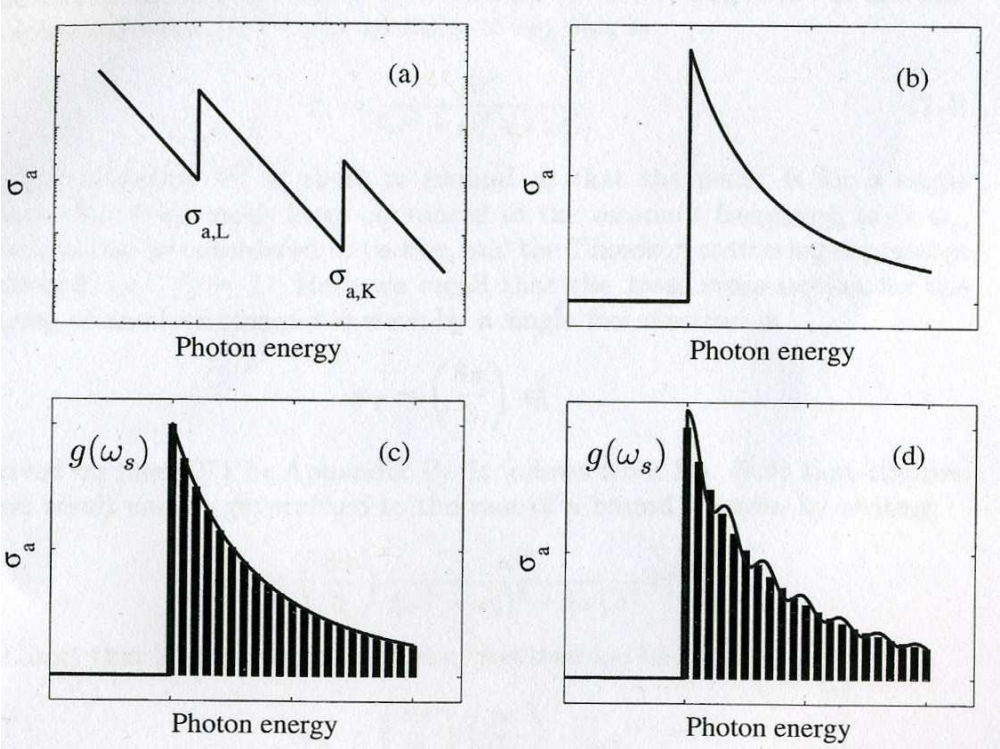
thus $\sigma_{a,s}$ may be written with help of a delta function:

$$\sigma_{a,s}(\omega) = 4\,\pi\, r_0\, c\, \frac{\pi}{2}\, \delta(\omega - \omega_s) \qquad (D)$$

Resonant scattering

The experimentally observed absorption cross-section is NOT a single line spectrum as suggested by (D).

There is a continuum of free states above an absorption edge that the electron can be excited into. This implies a series of different ω_s:



The absorption cross-section σ_a as a function of the photon energy

Resonant scattering

Absorption cross section for multiple harmonic oscillators:

$$\sigma_a(\omega) = 2\pi^2 r_0 c \sum_S g(\omega_S)\,\delta(\omega - \omega_S)$$

where $g(\omega_S)$ is the relative weight of each transition

The real part of the dispersion becomes:

$$f'(\omega) = \sum_S g(\omega_S)\, f'_S(\omega,\omega_S) \qquad (F)$$

(F) does not describe e.g. “white lines” or “EXAFS” oscillations (see figure) in the absorption cross section arising from the particular environement of the resonantly scattering atom.

Resonant scattering

measure absorption cross-section to obtain f ”:

$$f''(\omega) = -\left(\frac{\omega}{4\pi r_0 c}\right)\sigma_a(\omega) \qquad (E)$$

use Kramers-Kronig relations to obtain f ’:

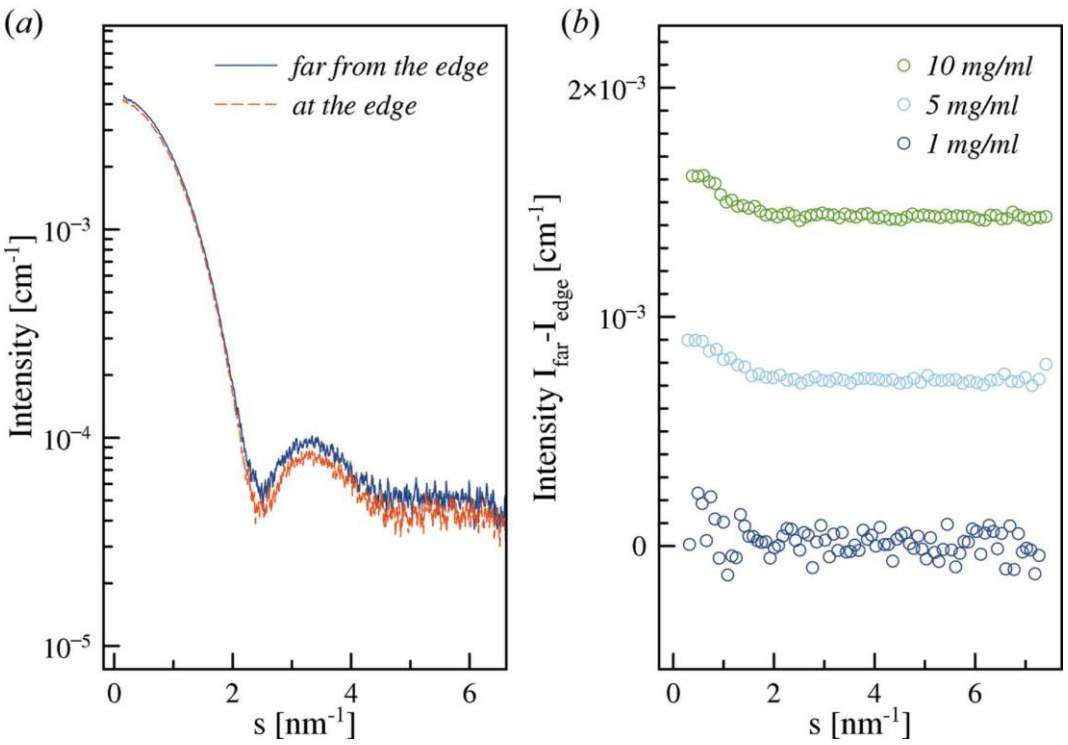
$$f'(\omega) = \frac{1}{\pi} P \int_{-\infty}^{+\infty} \frac{f''(\omega')}{(\omega' - \omega)}\, d\omega' = \frac{2}{\pi} P \int_{0}^{+\infty} \frac{\omega' f''(\omega')}{(\omega'^2 - \omega^2)}\, d\omega'$$

$$f''(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{+\infty} \frac{f'(\omega')}{(\omega' - \omega)}\, d\omega' = -\frac{2\omega}{\pi} P \int_{0}^{+\infty} \frac{f'(\omega')}{(\omega'^2 - \omega^2)}\, d\omega'$$

P stands for “principal value” (see also comments J. A-N & D. McM p. 242)

ASAXS- Anomalous SAXS

at P12 beamline EMBL Hamburg



(a) Computed curves far from the absorption edge and at the absorption edge from parvalbumin (PDB: 4cpv) with calcium atoms substituted by terbium (absorption edge 7514 eV) at a protein concentration of 10 mg ml^{-1}.

(b) Difference in the intensity between the computed curves far from the absorption edge and at the absorption edge from parvalbumin (PDB: 4cpv) with calcium atoms substituted by terbium (absorption edge 7514 eV) at different solute concentrations. The curves are shifted for the better representation.

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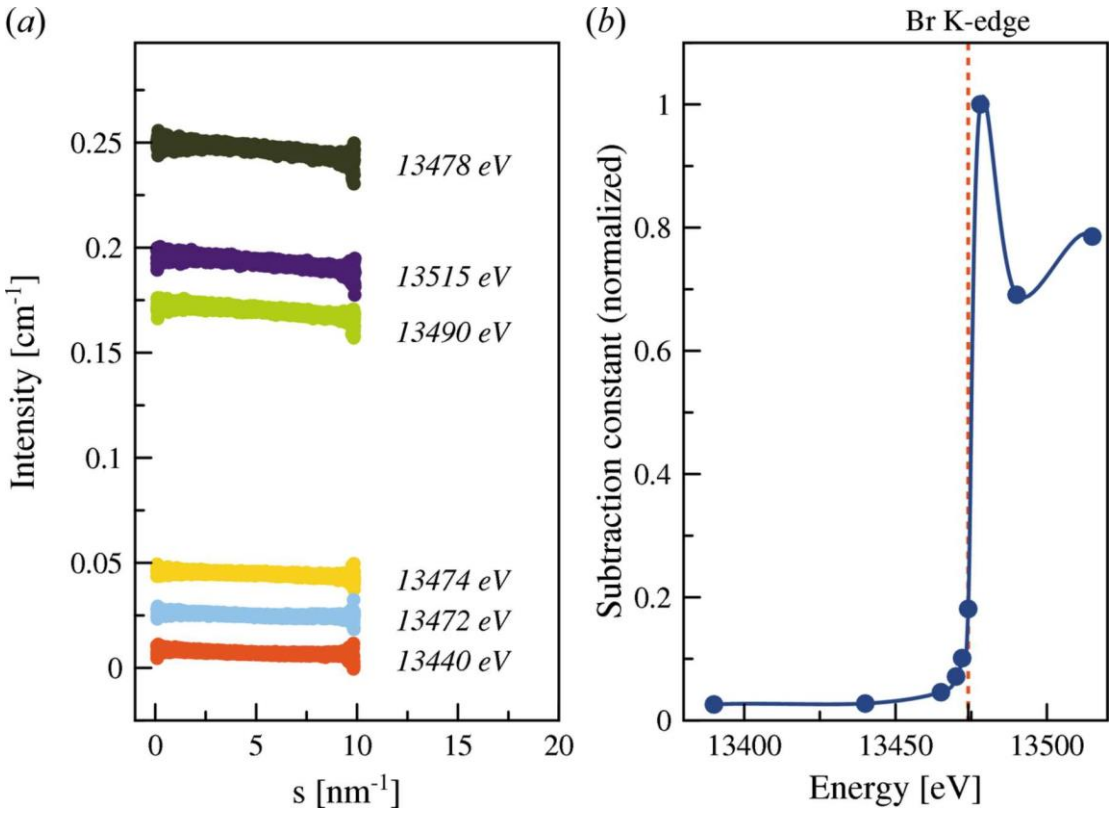
ASAXS- Anomalous SAXS



(a) SAXS scattering curves from potassium bromide solution in water measured at different energies.

(b) Normalized constant offset determined for each curve in (*a*) plotted against energy of incoming X-rays. The dashed line shows the position of the bromine *K*-edge.

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