Small-angle X-ray scattering – a (mostly) theoretical introduction to the basics

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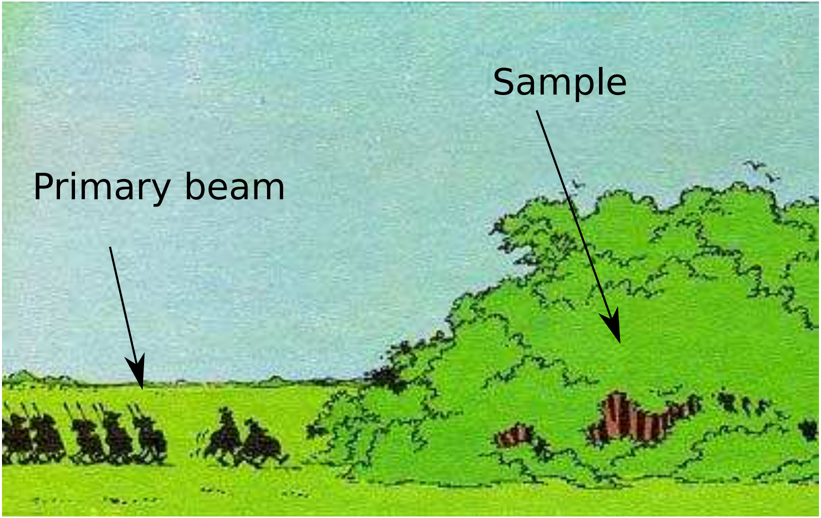
History of (small-angle) scattering

- “Even the ancient greeks. . . ”
- Scattering: XVII-XIX. century (Huygens, Newton, Young, Fresnel. . .)
- X-rays: 1895 (Wilhelm Konrad Röntgen)
- X-ray diffraction on crystals: W.H. és W.L. Bragg (1912), M. von Laue, P. Debye, P. Scherrer. . . (-1930)
- First observation of small-angle scattering: P. Krishnamurti, B.E. Warren (kb. 1930)
- Mathematical formalism and theory of small-angle scattering: André Guinier, Peter Debye, Otto Kratky, Günther Porod, Rolf Hosemann, Vittorio Luzzati (1940-1960)

The principle of scattering



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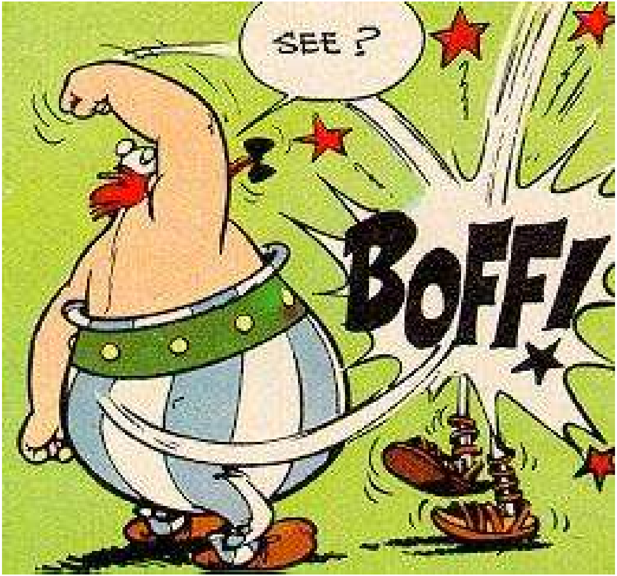
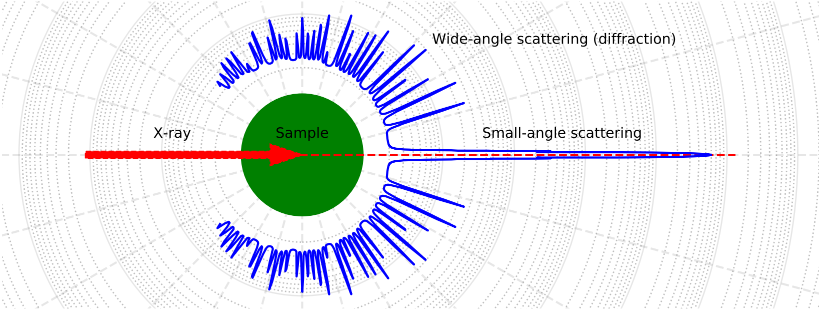


SAXS vs. WAXS

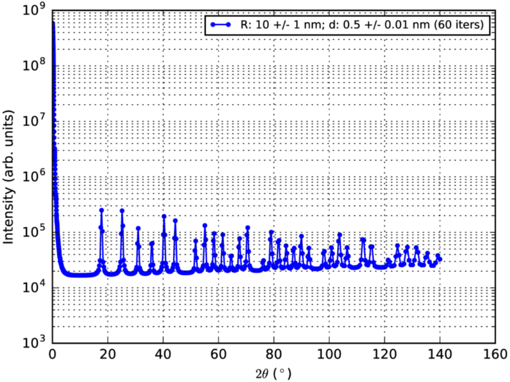
- Principle of scattering: probe particles → interaction with the structure → deflection → detection → structure determination



- Measurement: the “intensity” of radiation deflected in different directions
- Strong forward scattering (logarithmic scale!)
- Wide-angle scattering: Bragg equation (cf. previous lecture)
- Small-angle scattering: . . .

Small- and wide-angle X-ray scattering

Scattering of a spherical nanocrystallite (simple cubic lattice)



- Wide-angle scattering: crystal structure

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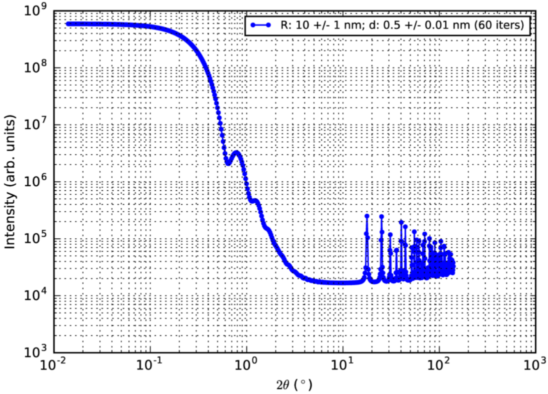

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- Small-angle scattering: the overall size of the crystallite

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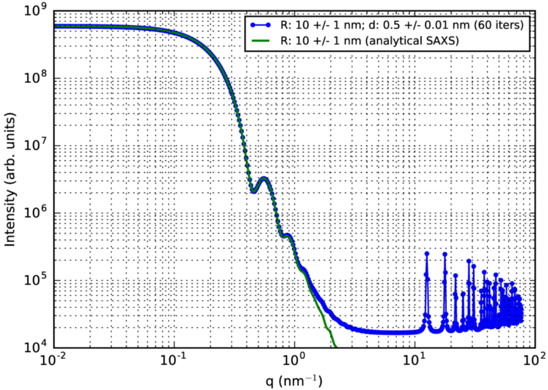
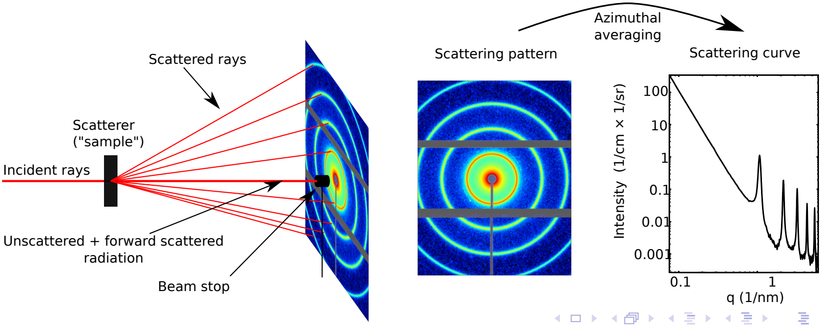


- Wide-angle scattering: crystal structure
- Small-angle scattering: the overall size of the crystallite
- Small-angle scattering is blind on the atomic level: equivalence of homogeneous and discrete atomic structures

Small-angle scattering

- Small-Angle X-ray Scattering – SAXS
- *Elastic* scattering of X-rays on electrons
- Measurement: “intensity” versus the scattering angle
- Results: electron-density inhomogeneities on the 1-100 length scale
- But: indirect results, difficult to interpret (☹)
- Typical experimental conditions:
  - Transmission geometry
  - High intensity, nearly point-collimated beam
  - Two-dimensional position sensitive detector



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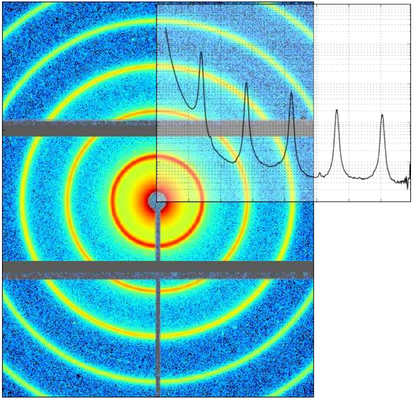
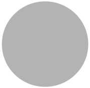
Scattering pattern – scattering curve



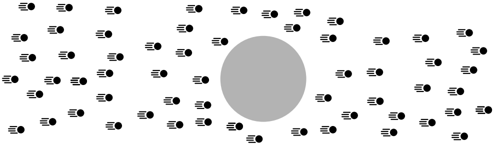
- Scattering pattern: matrix of incidence counts
  - Numerical values in the pixels: the number of the photons received
  - Each pixel has a corresponding scattering angle
- Scattering curve
  - The same information in a more tractable form
  - Obtained by azimuthally averaging the scattering pattern:
    1. Grouping of pixels corresponding to the same scattering angle
    2. Averaging of the intensities
  - Dependent variable: intensity (“count rate”)
  - Independent variable: scattering variable (“distance from the center”)

Scattering cross-section



- The sample under investigation (scatterer)

Scattering cross-section



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- Incident particle current density: $j_{in} = N_{in}/(A \cdot t)$ $[\mathrm{cm}^{-2}\ \mathrm{s}^{-1}]$

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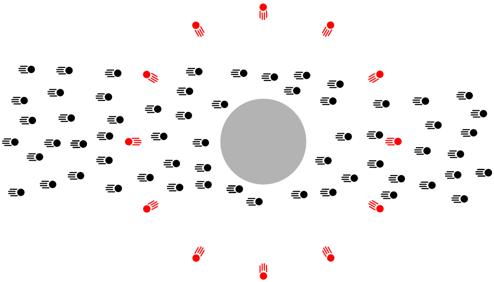

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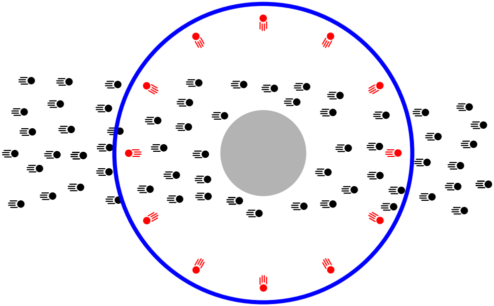

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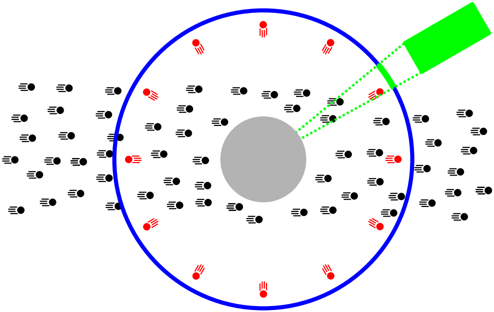

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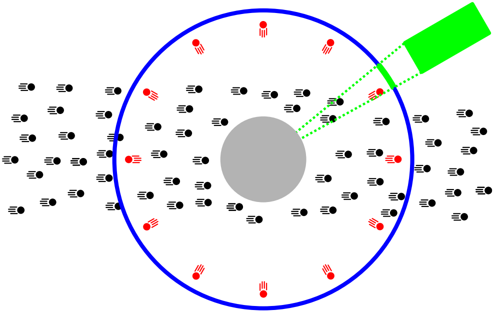

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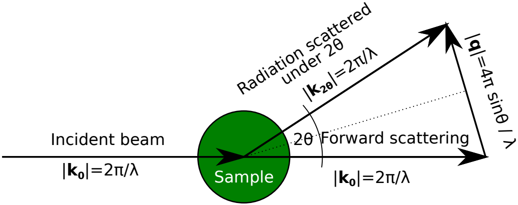
- *differential scattering cross-section*: $d\Sigma/d\Omega$ $[\mathrm{cm}^{2}\ \mathrm{sr}^{-1}]$
- **Normalized to unit sample volume:** $\frac{d\sigma}{d\Omega} \equiv \frac{1}{V}\frac{d\Sigma}{d\Omega}$ $[\mathrm{cm}^{-1}\ \mathrm{sr}^{-1}]$

The scattering variable

- The natural variable of the intensity is the scattering vector:

$$\vec{q} \equiv \vec{k}_{2\theta} - \vec{k}_0 \qquad \left[\vec{s} \equiv \vec{S}_{2\theta} - \vec{S}_0 = \vec{q}/(2\pi)\right]$$

  i.e. the vectorial difference of the wave vectors of the scattered and the incident radiation
- [Wave vector: points in the direction of wave propagation, magnitude is $2\pi/\lambda$]
- Physical meaning: the momentum acquired by the photon upon scattering ($\rightarrow$ "momentum transfer")



- Magnitude: $q = |\vec{q}| = 4\pi\frac{\sin\theta}{\lambda} \underset{\text{small angles}}{\approx} 4\pi\theta/\lambda \qquad [s = 2\sin\theta/\lambda])$
- Bragg-equation: $q = 2\pi n/d \quad n \in \mathbb{Z} \qquad [s = n/d]$

The scattering contrast

- X-rays are scattered by electrons
- Scattering contrast = relative electron density with respect to the average
- Only the relative electron density counts!
- Small contrast: weak scattering signal
  - Water: 333.3 e^-/nm^3 (homework to calculate)
  - SiO_2 nanoparticles: 660-800 e^-/nm^3
  - Proteins: 400-450 e^-/nm^3
- Determined by:
  - Mass density of the matter (e.g. solid copolimers)
  - Presence of elements with high atomic numbers
  - Choice of solvent (mean electron density)

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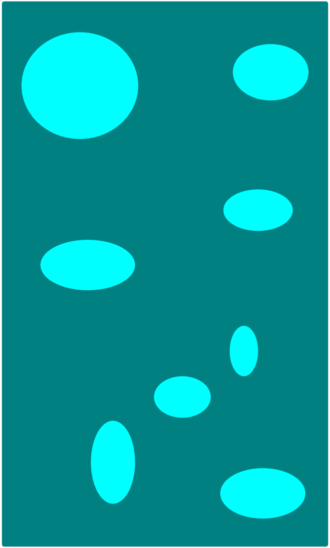

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Recapitulation of the basic quantities

Intensity: or differential scattering cross-section

- the proportion of the particles. . .
- . . . incoming in a unit cross section. . .
- . . . over unit time. . .
- . . . onto a sample of unit volume. . .
- . . . which is scattered in a given direction. . .
- . . . under unit solid angle.

Scattering variable (q): or momentum transfer: characterizing the angle dependence.

- Magnitude $\propto \sin\theta \approx \theta$
- $\hbar\vec{q}$: the momentum acquired by the photon due to the interaction with the sample

Scattering contrast: scattering potential of given part of the sample in comparison with its environment

- This is the relative electron density in case of X-ray scattering

Contents

Connection between structure and scattering

- Scattering on the inhomogeneities of the electron density ⇒ characterization of the structure with the relative electron density function:

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

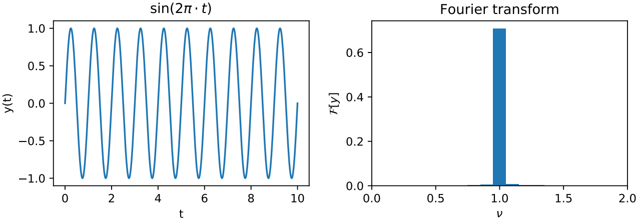
  (in the following we omit Δ!)
- The amplitude of the scattered radiation:

  $$A(\vec{q}) = \iiint\limits_V \rho(\vec{r}) e^{-i\vec{q}\vec{r}} \mathrm{d}^3\vec{r}$$

  which is formally the Fourier transform of the electron density.
- Only the intensity can be measured: $I = |A|^2$

Detour: Fourier transform

Basic question: what is the frequency of a given periodic signal?



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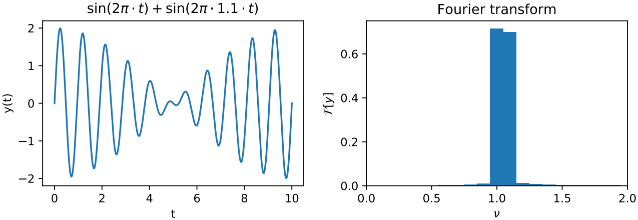

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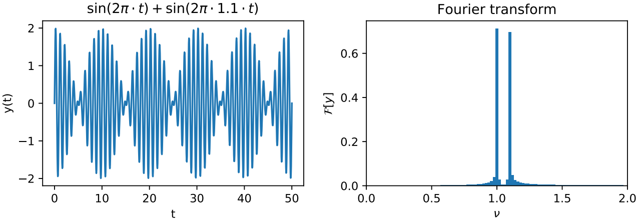

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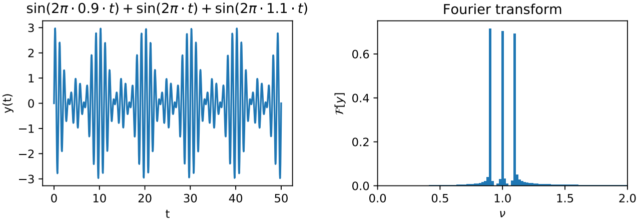

$\sin(2\pi \cdot 0.9 \cdot t) + \sin(2\pi \cdot t) + \sin(2\pi \cdot 1.1 \cdot t)$

Fourier transform

- Fourier transformation: determination of the frequency components
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- Even more frequency components

Detour: Fourier transform

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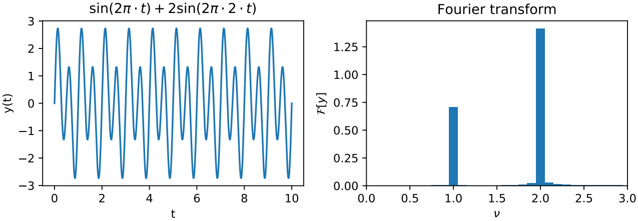

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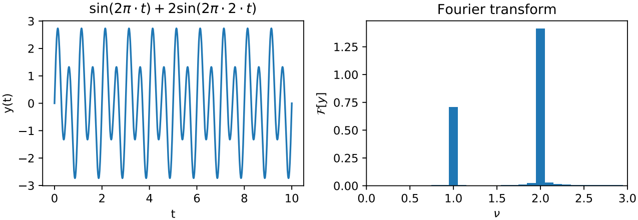

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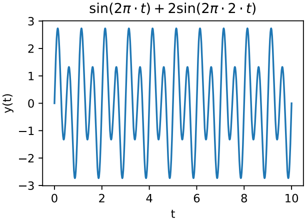
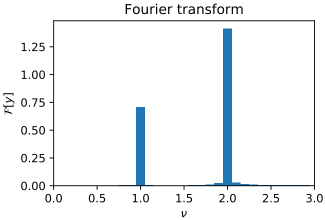

$\sin(2\pi \cdot t) + 2\sin(2\pi \cdot 2 \cdot t)$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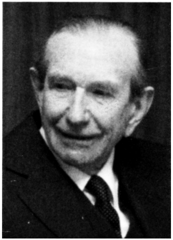
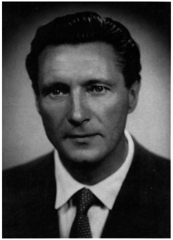
- Even more frequency components
- The relative weights of the frequency components is also given
- "Inside the black box": $F(\nu) = \int f(t) e^{-i\nu t} dt$
- Can be inverted (although...): $f(t) = \frac{1}{2\pi} \int F(\nu) e^{it\nu} d\nu$

The phase problem

- The Fourier transform is invertible (?!): the amplitude unambiguously describes the scattering structure
- Complex quantities:
$$z = a + bi = Ae^{i\phi}$$
- Absolute square (this is how we get the intensity):
$$|z|^2 = z \cdot z^* = Ae^{i\phi} \cdot Ae^{-i\phi} = A^2$$
- Where did the ϕ phase go?!
- Because the scattered amplitude cannot be measured, there is no chance to fully recover the structure just from scattering.
- Another problem: the intensity can only be measured in a subspace of the $\vec{q}$ space: only an incomplete inversion of the Fourier transform can be done.

How big is this problem?





Idea from Saldin et. al. J. Phys.: Condens. Matter 13 (2001) 10689-10707

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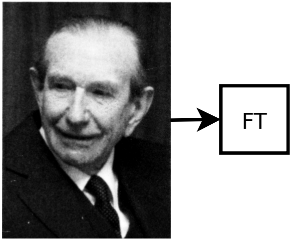

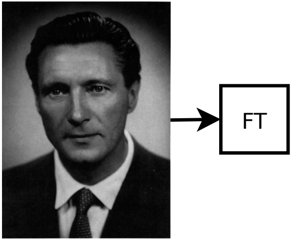

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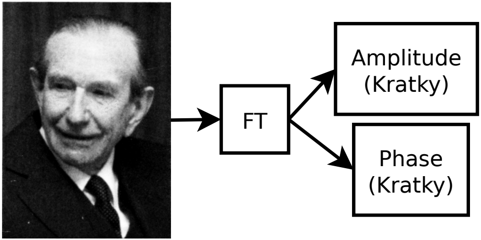
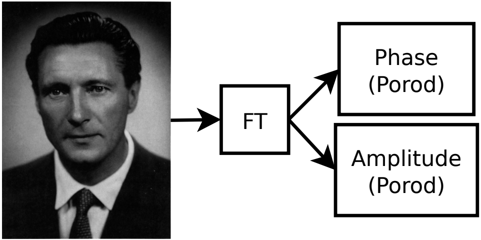


FT

Amplitude (Kratky)

Phase (Kratky)



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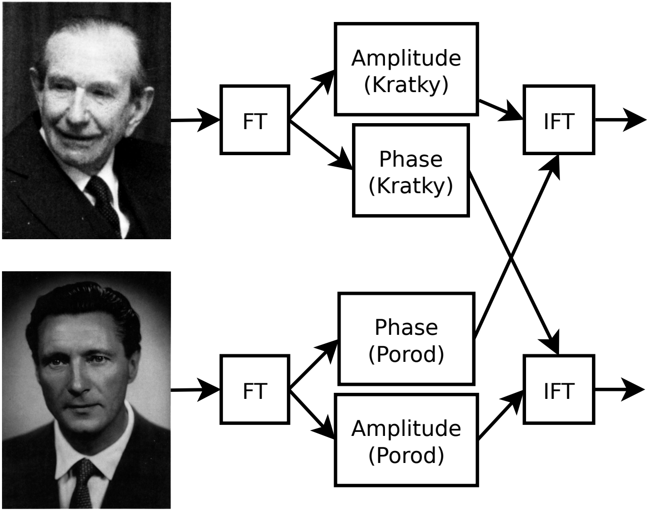

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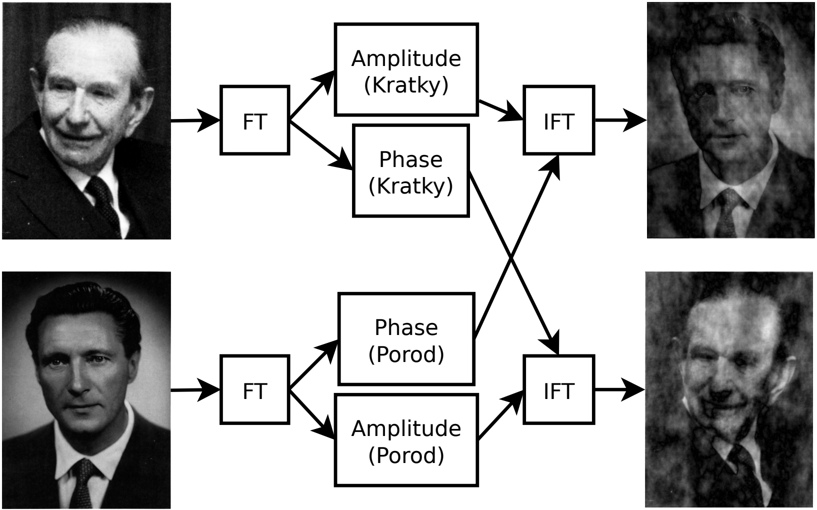

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- The phase carries most of the information!

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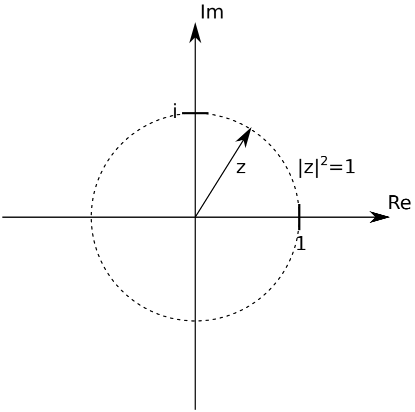
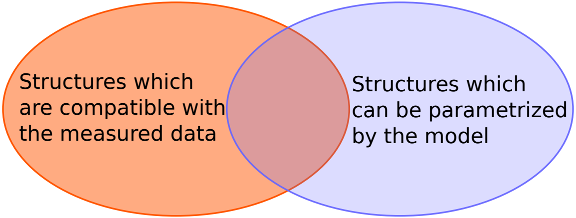


- The phase carries most of the information!
- The operation of taking the square root is ambiguous over the complex plane (there are ∞ complex numbers with $|z| = 1$)!

What can be done / Is this really a problem?

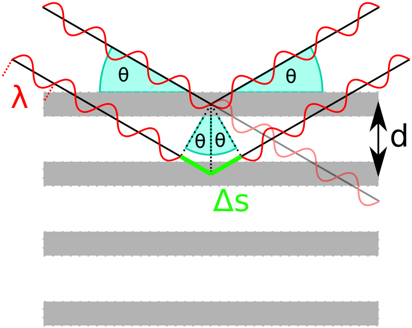
The scattering of vastly different structures can be undiscernible

1. Solution: determination of “robust” parameters (see later)
    - Guinier radius
    - Power-law exponent
    - Porod-volume
    - ...
2. Solution: model fitting
    - Choosing the specimen from a model-specimen described by given parameters which best fits the scattering curve
    - If the model ensemble is narrow enough, the $\rho(\vec{r}) \leftrightarrow I(\vec{q})$ mapping can be unique
    - *A priori* knowledge, results of other experiments are indispensable!
3. “Guessing” the phase (crystallography) or measuring it (holography)



Bragg's law: a special case

- The sample is periodic (d repeat distance)
- θ: incidence and exit angle
- Constructive interference in the detector: the rays reflected from neighbouring planes reach the detector in phase
- Path difference: $\Delta s = n\lambda$ where $n \in \mathbb{N}$
- From simple geometry: $\Delta s = 2d \sin\theta$
- $2d \sin\theta = n\lambda$
- $\frac{4\pi}{\lambda} \sin\theta = \frac{2\pi}{d} n$
- $\boxed{q = \frac{2\pi}{d} n}$



Detour/recap: spherical coordinates

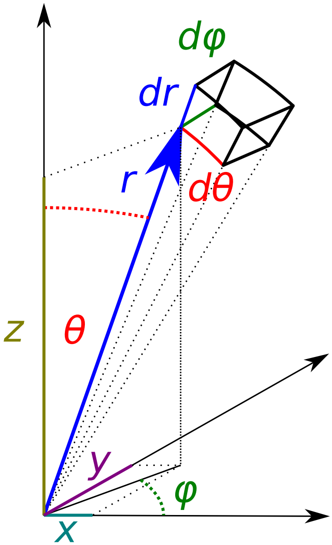
- Descartes: x, y, z
- Spherical:
  - $x = r \sin\theta \cos\varphi$,
  - $y = r \sin\theta \sin\varphi$,
  - $z = r \cos\theta$
- Infinitesimal volume:

$$dx\, dy\, dz = dV = r^2 \sin\theta\, dr\, d\theta\, d\varphi$$

- Integral:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(x,y,z) dx\, dy\, dz =$$

$$= \int_{0}^{2\pi}\int_{0}^{\pi}\int_{0}^{\infty} f(r,\theta,\varphi) r^2 \sin\theta dr\, d\theta\, d\varphi$$



Small-angle scattering of a sphere (I)

General formula of the scattered intensity:

$$I(\vec{q}) = \left| \iiint \rho\left(\vec{r}\right) e^{-i\vec{q}\vec{r}} \mathrm{d}^3\vec{r} \right|^2$$

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Let us derive the (small-angle) scattering intensity of a sphere which has a radius R and ρ_0 homogeneous electron density inside!

Small-angle scattering of a sphere (I)

General formula of the scattered intensity:

$$I(\vec{q}) = \left| \iiint \rho\left(\vec{r}\right) e^{-i\vec{q}\vec{r}} \mathrm{d}^3\vec{r} \right|^2$$

Let us derive the (small-angle) scattering intensity of a sphere which has a radius R and ρ_0 homogeneous electron density inside!
Electron-density function of an isotropic object: $\rho(\vec{r}) = \rho(|\vec{r}|) = \rho(r)$.
The integral can be simpified in spherical coordinates:

$$I(\vec{q}) = \left| \int_0^{2\pi} \mathrm{d}\phi \int_0^{\infty} \mathrm{d}r\, r^2 \rho(r) \int_0^{\pi} \sin\theta \, \mathrm{d}\theta \, e^{-i|\vec{q}|\cdot|\vec{r}|\cos\theta} \right|^2$$

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Substitution of $u = \cos\theta$:

$$I(\vec{q}) = \left| \underbrace{\int_0^{2\pi} \mathrm{d}\phi}_{2\pi} \int_0^{\infty} r^2 \rho(r) \mathrm{d}r \int_{-1}^{1} \mathrm{d}u \, e^{-iqru} \right|^2$$

Small-angle scattering of a sphere (II)

The innermost integral can be readily evaluated:

$$\int_{-1}^{1} \mathrm{d}u \, e^{-iqru} = \left[\frac{1}{-iqr} e^{-iqru} \right]_{-1}^{1}$$

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$$\boxed{I(\vec{q}) = I(q) = (4\pi)^2 \left| \int_0^R \rho(r) r^2 \frac{\sin(qr)}{qr} \mathrm{d}r \right|^2}.$$

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- The scattering intensity of an isotropic system is also isotropic: depends only on $|\vec{q}|$
- The scattering amplitude of an isotropic system (more precisely where $\rho(\vec{r}) = \rho(-\vec{r})$) is real

Small-angle scattering of a sphere (III)

The electron-density function of a homogeneous sphere is:

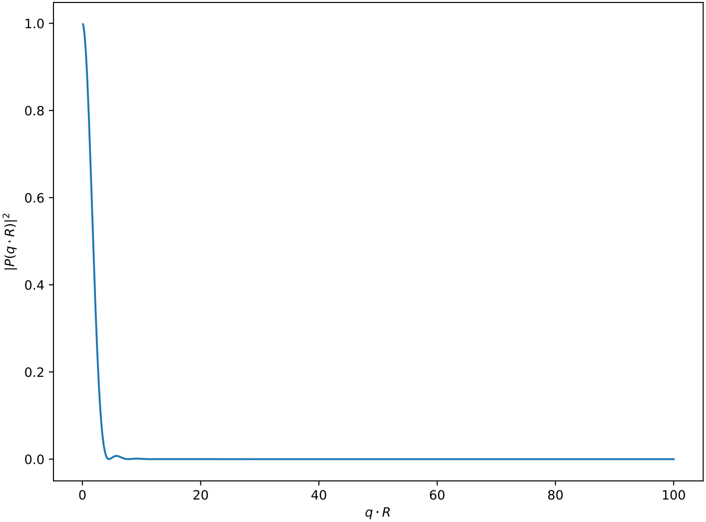
$$\rho(\vec{r}) = \begin{cases} \rho_0 & \text{if } |\vec{r}| \leq R \\ 0 & \text{otherwise.} \end{cases}$$

Evaluating the previous integral:

$$\begin{aligned} I_{\mathrm{g}}(q) &= \left(\frac{4\pi\rho_0}{q^3} \left(\sin(qR) - qR\cos(qR) \right) \right)^2 \\ &= \rho_0^2 \left(\underbrace{\frac{4\pi R^3}{3}}_{V} \underbrace{\frac{3}{q^3 R^3} \left(\sin(qR) - qR\cos(qR) \right)}_{P_g(qR)} \right)^2 \end{aligned}$$

- The scattered intensity scales with the 6th power of the linear size ($I \propto V^2 \propto R^6$)

Small-angle scattering of a sphere (IV)



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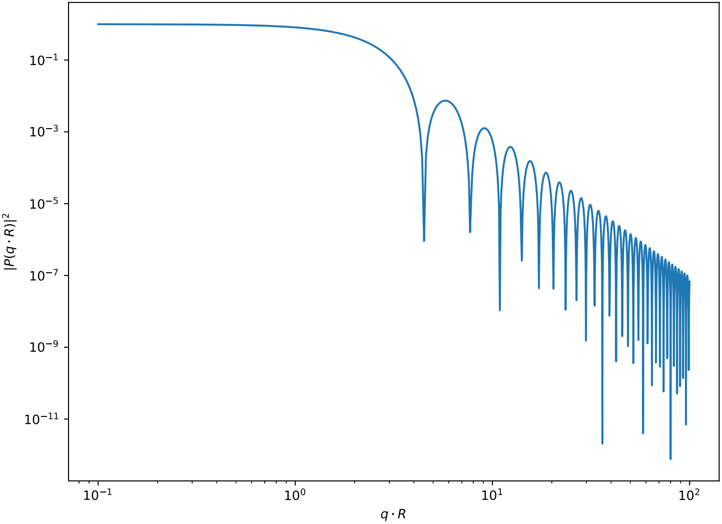
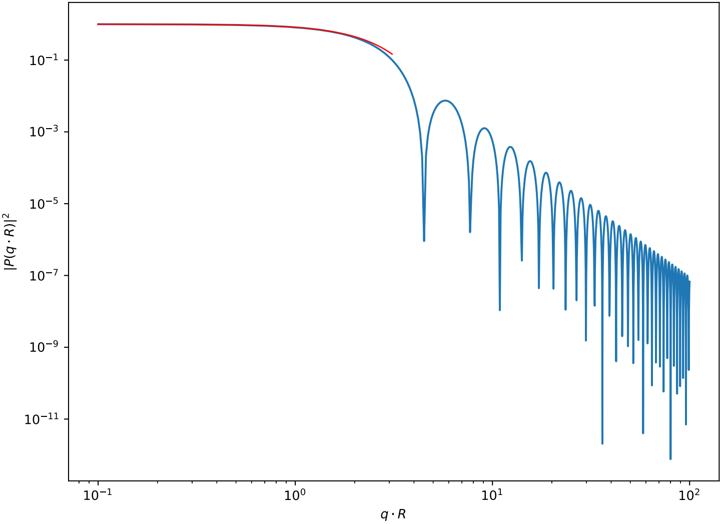


- Log-log plotting is good ☺

Small-angle scattering of a sphere (IV)



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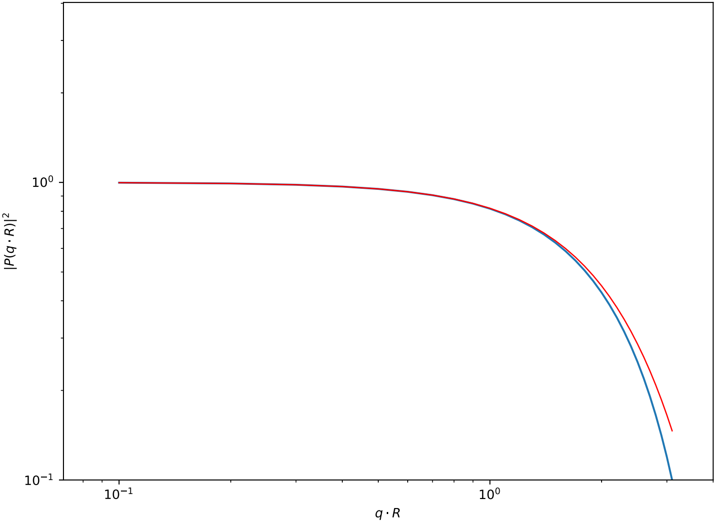

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The Guinier approximation

- André Guinier: the low-q scattering of dilute nanoparticle suspensions follows a Gaussian curve
- Generally:

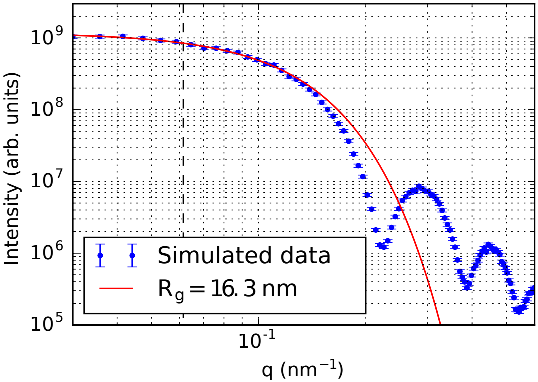
$$I(q \approx 0) = I_0 e^{-\frac{q^2 R_g^2}{3}}$$

- Radius of gyration (or Guinier radius): describes the linear size of a scattering object. By definition:

$$R_g \equiv \sqrt{\frac{\iiint_V r^2 \rho(\vec{r}) \mathrm{d}^3\vec{r}}{\iiint_V \rho(\vec{r}) \mathrm{d}^3\vec{r}}}$$

- Connection between the shape parameters and R_g:
  - sphere: $R_g = \sqrt{3/5}R$
  - spherical shell: $R_g = R$
  - cylinder: $\sqrt{\frac{R^2}{2} + \frac{L^2}{12}}$
  - linear polymer chain: $Nb^2/6$
  - ...

Guinier plot



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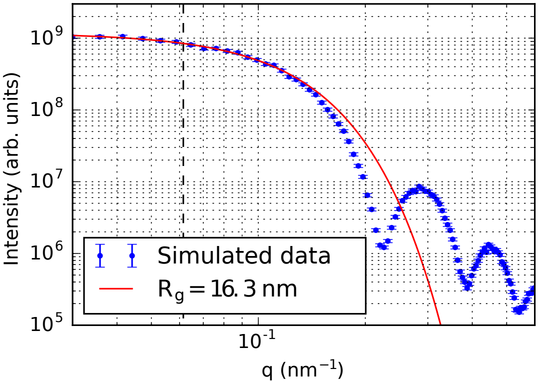
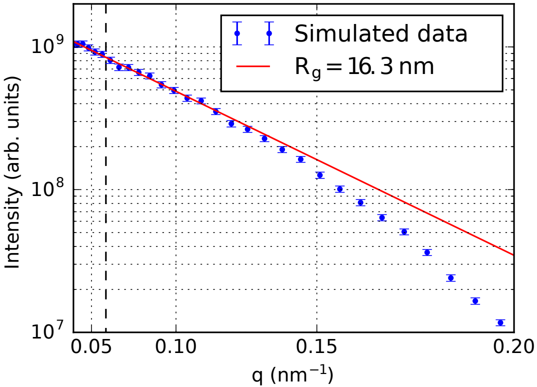
Guinier plot



- $I \approx I_0 e^{-\frac{q^2 R_g^2}{3}}$
- $\ln I \approx \ln I_0 - \frac{R_g^2}{3} q^2$

Guinier plot



- $I \approx I_0 e^{-\frac{q^2 R_g^2}{3}}$
- $\ln I \approx \ln I_0 - \frac{R_g^2}{3} q^2$
- $\ln I$ - q^2: first order polynomial
- Visual check on the validity of the Guinier approximation

The validity of the Guinier approximation

- The Guinier approximation holds for *nearly monodisperse* particulate systems too (see next slides)
- Nearly spherical particles: $qR_g \lessapprox 3$
- Anisotropic particles: $qR_g \lessapprox 0.7$
- Upturn at small q ("smiling Guinier"): attraction between the particles (aggregation)
- Downturn at small q ("frowning Guinier"): repulsive interaction between the particles
- More details will be given for protein scattering later...

André Guinier (1911 - 2000)

The effect of polydispersity

Multi-particle system:

$$\rho(\vec{r}) = \sum_j \rho_j(\vec{r} - \vec{R}_j)$$

Scattering amplitude:

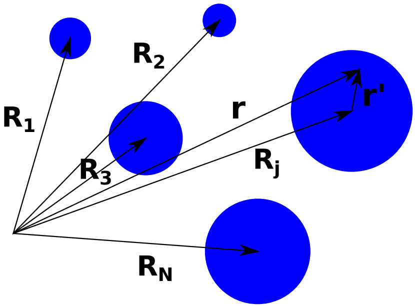
$$\begin{aligned} A(\vec{q}) &= \sum_j A_j(\vec{q}) \\ &= \sum_j A_{j,0}(\vec{q}) e^{-i\vec{q}\vec{R}_j} \end{aligned}$$

Intensity:

$$\begin{aligned} I(\vec{q}) &= A(\vec{q})A^*(\vec{q}) \\ &= \sum_j \sum_k A_j(\vec{q}) A_k^*(\vec{q}) e^{i\vec{q}(\vec{R}_k - \vec{R}_j)} \end{aligned}$$

Shifting of the electron density function by $\vec{R}$:

$$A_{\text{shifted}}(\vec{q}) = A_0(\vec{q}) e^{-i\vec{q}\vec{R}}$$



Multi-particle system

$$I(\vec{q}) = \sum_j \sum_k A_j(\vec{q}) A_k^*(\vec{q}) e^{i\vec{q}(\vec{R}_k - \vec{R}_j)} = \underbrace{\sum_j I_j(\vec{q})}_{\text{incoherent}} + \underbrace{\sum_j \sum_{k \neq j} A_j(\vec{q}) A_k^*(\vec{q}) e^{i\vec{q}(\vec{R}_k - \vec{R}_j)}}_{\text{interference term}}$$

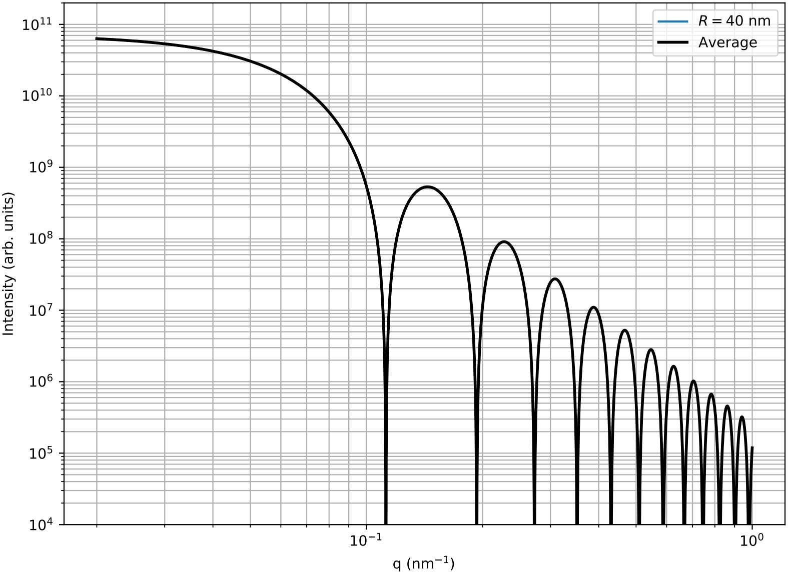
- Incoherent sum: the *intensity* of the distinct particles is summarized
- Cross-terms: interference from the correlated *relative* positions of the particles
- Special case: identical, spherically symmetric particles

$$I(q) = \rho_0^2 V^2 P_g(qR)^2 N \underbrace{\left\{ 1 + \frac{2}{N} \sum_j \sum_{k>j} \cos\left(\vec{q}(\vec{R}_k - \vec{R}_j) \right) \right\}}_{S(q)}$$

- Structure factor: depends only on the relative positions of the distinct particles but not on their shape
- Uncorrelated system: $S(q) = 1$. Otherwise the Guinier region is distorted!

Size distribution

There's no such thing as a fully monodisperse system.



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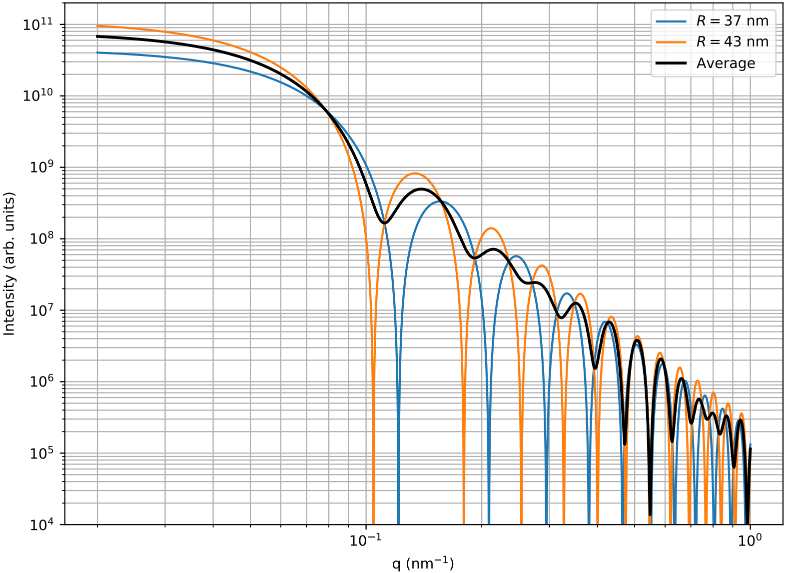

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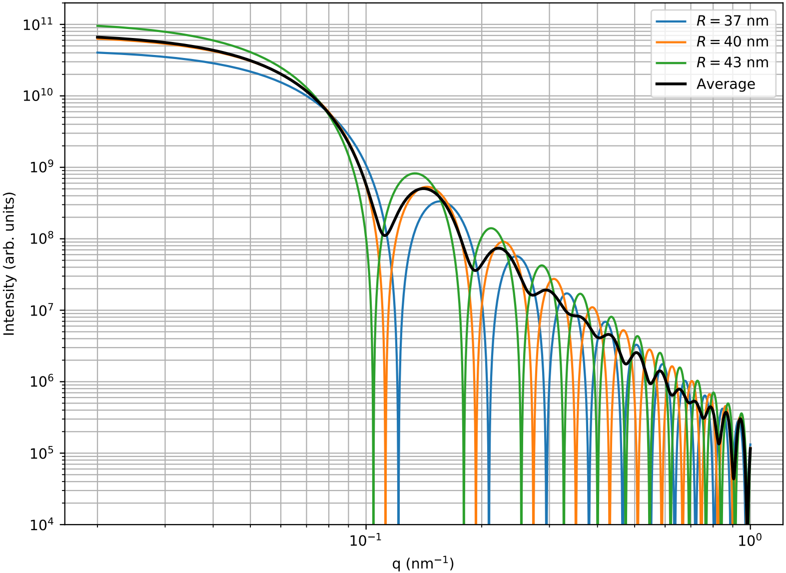

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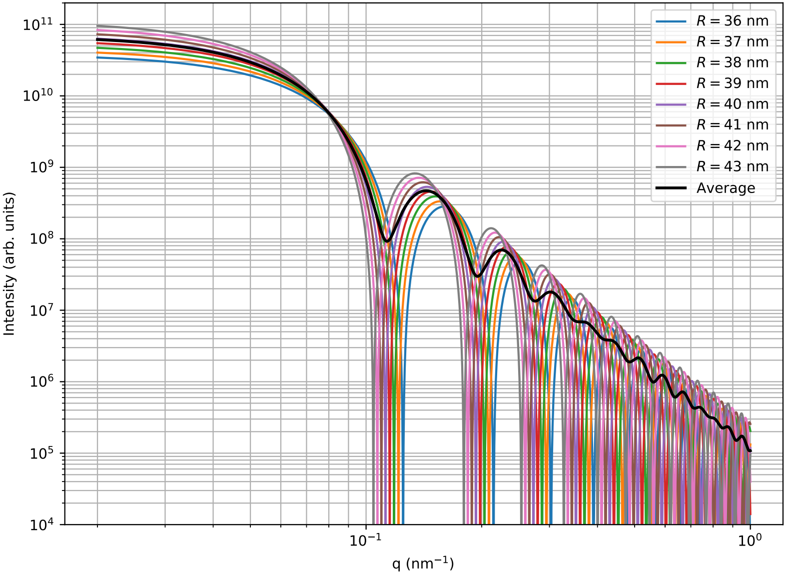
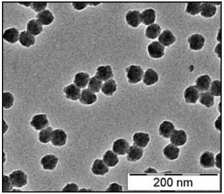


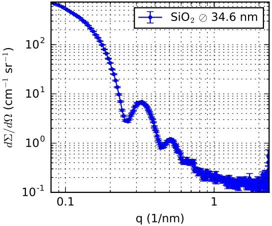
Scattering of a slightly polydisperse suspension of nanoparticles

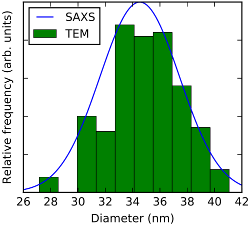
- Scattering of a dilute nanoparticle suspension:

$$I(q) = \underbrace{P^2(qR)}_{\text{form factor}}$$

- If the shape of the particles is known, the size distribution can be determined by fitting the scattering curve.







- Statistically significant ($\approx 10^9$ particles in 1 mm^3)
- Accurate sizes with well-defined uncertainties (SI "traceability")

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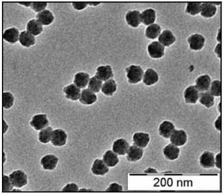

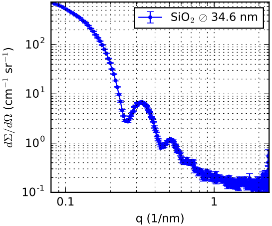

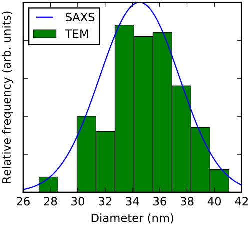

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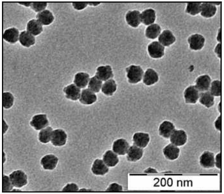

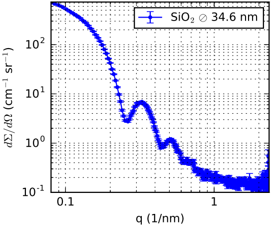

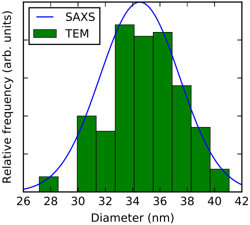

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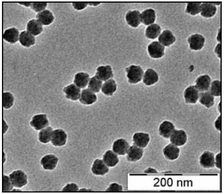

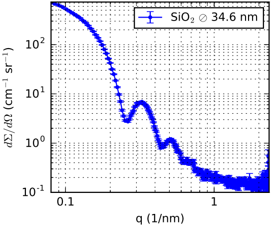

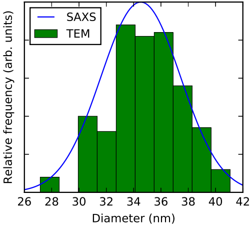

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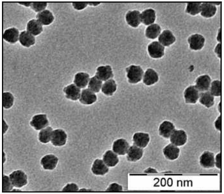

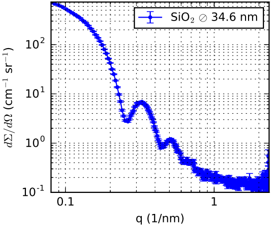

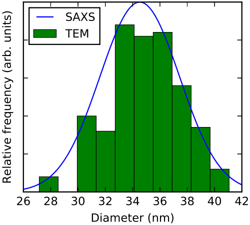

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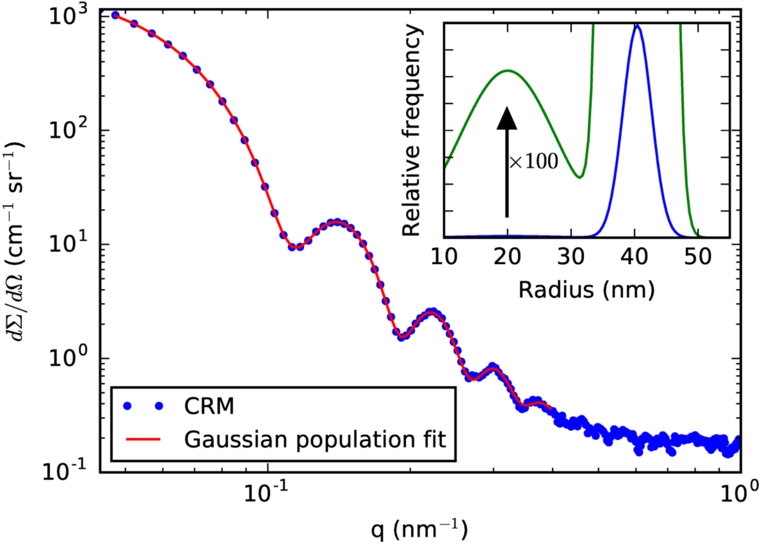
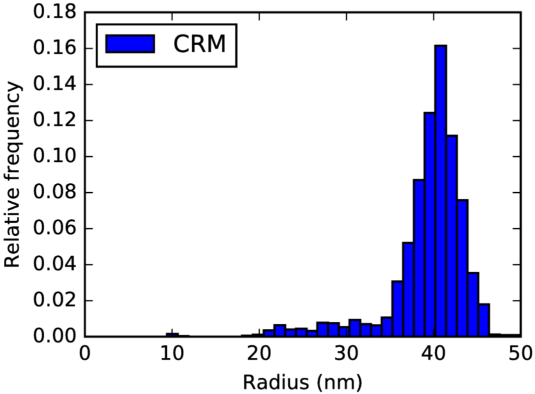
Bimodal nanoparticle distribution

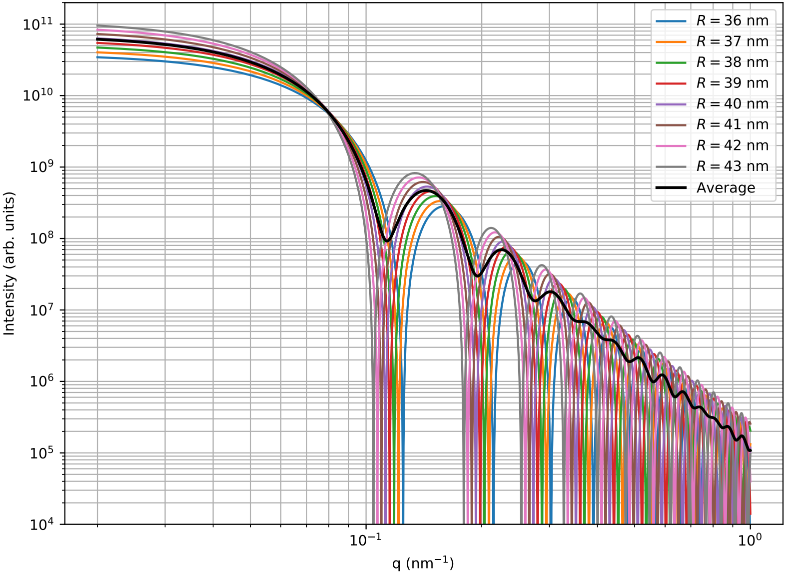


Model-independent approach

- The $\mathcal{P}(R)$ size distribution function is obtained in a histogram form.
- Large number of model parameters $\Rightarrow$ danger of “overfitting”



Power-law behaviour



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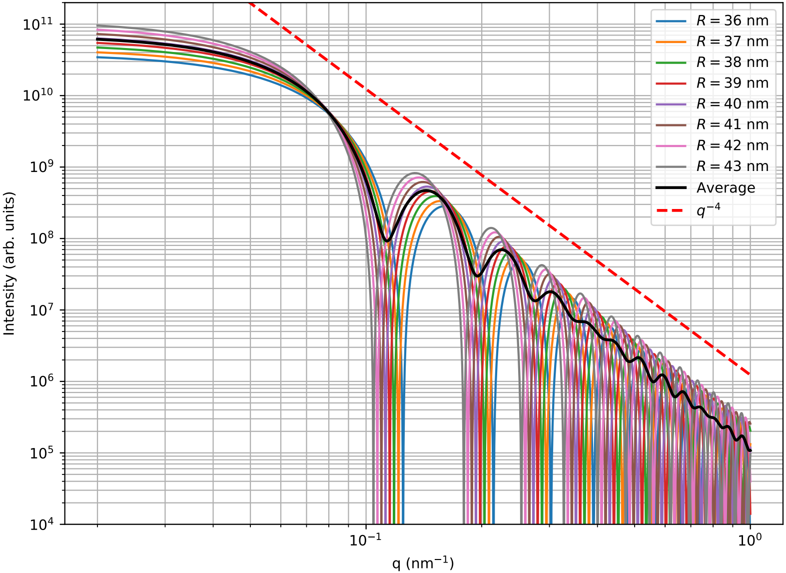


The Porod region

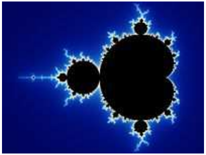
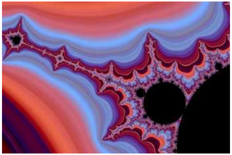
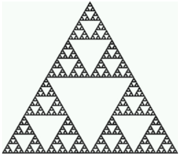
- Power-law decreases are frequently found in scattering curves: $I \propto q^{-\alpha}$.
- Particles with smooth surfaces: $I(q \to \infty) \propto \frac{S}{V} q^{-4}$: specific surface!
- Solutions of unbranched polymers:
  - Ideal solvent (Θ-solution): random walk following Gaussian statistics: $I(q) \propto q^{-2}$
  - Bad solvent: self-attracting random walk: $I(q) \propto q^{-3}$
  - Good solvent: self-avoiding random walk: $I(q) \propto q^{-3/5}$
- Surface and mass fractals. . .

Günther Porod (1919 - 1984)

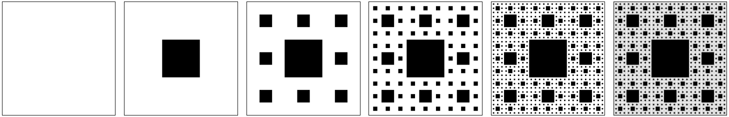
Detour: fractals

- Self-similar systems: showing the same shapes even in different magnifications
- Nanosystems with fractal properties:
  - Activated carbon
  - Porous minerals
  - Uneven surfaces
- Characterization: Hausdorff-dimension (fractal dimension)



Fractal dimension



- Measure the area of the Sierpińsky carpet with different unit lengths
- Connection between the unit length and the required unit areas to cover the carpet:

Length unit	1	1/3	1/9	...	3^{-n}
Required unit areas	1	8	64	...	8^n

- A Hausdorff dimension: how the number of required unit areas (A) scales with the unit length (a)?

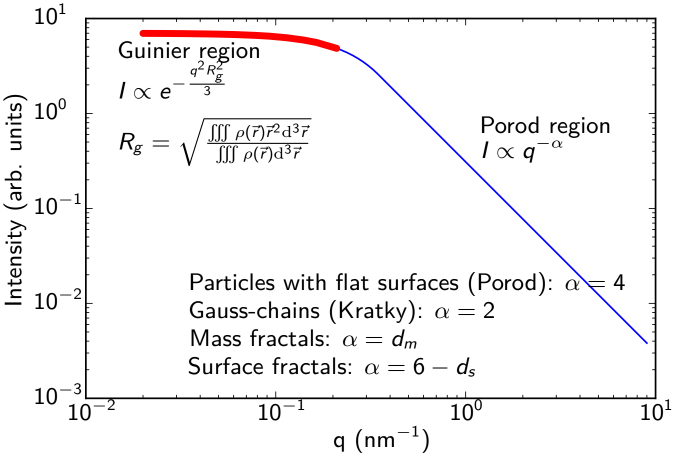
$$a = 1/3^n \to n = -\log_3 a$$

$$A = 8^n = 8^{-\log_3 a} = 8^{-\frac{\log_8 a}{\log_8 3}} = a^{\log_8 3} = a^{\frac{\ln 3}{\ln 8}} = a^{-d}$$

- The fractal dimension of the Sierpińsky carpet is $\ln 8/\ln 3 \approx 1.8928 < 2$
- For a simple square:

  $A = a^{-2}$, i.e. the fractal dimension is the same as the Euclidean

Fractal dimension on the scattering curve



Guinier region

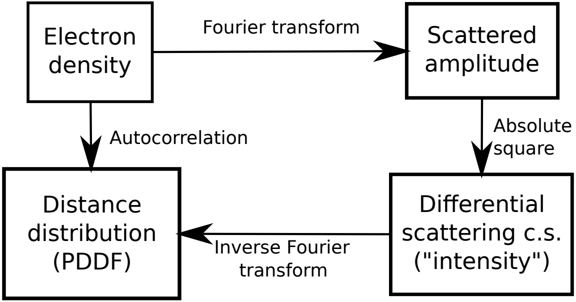
$I \propto e^{-\frac{q^2 R_g^2}{3}}$

$R_g = \sqrt{\frac{\iiint \rho(\vec{r})\vec{r}^2 \mathrm{d}^3\vec{r}}{\iiint \rho(\vec{r})\mathrm{d}^3\vec{r}}}$

Porod region
$I \propto q^{-\alpha}$

Particles with flat surfaces (Porod): $\alpha = 4$
Gauss-chains (Kratky): $\alpha = 2$
Mass fractals: $\alpha = d_m$
Surface fractals: $\alpha = 6 - d_s$

The pair density distribution function – back to the real space



Electron density

Fourier transform

Scattered amplitude

Autocorrelation

Absolute square

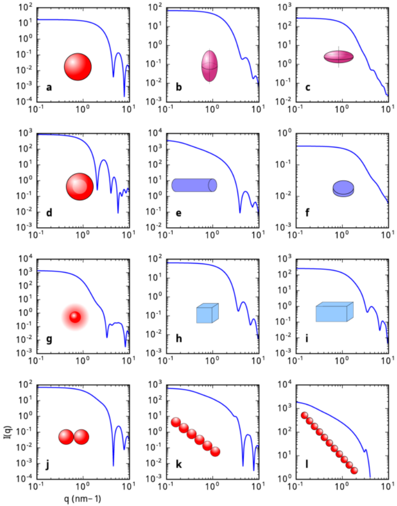
Distance distribution (PDDF)

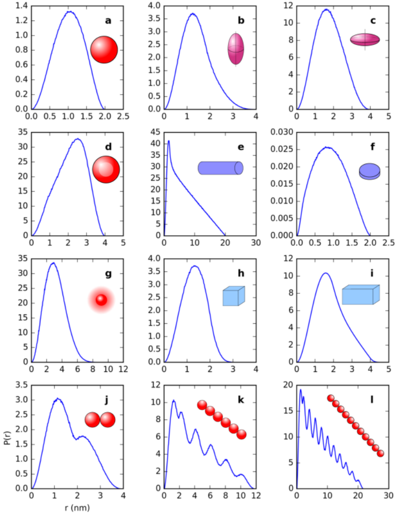
Inverse Fourier transform

Differential scattering c.s. ("intensity")

- There is another route connecting the electron density and the scattered intensity
- The $p(r)$ pair density distribution function (PDDF) is the self-correlation of the electron density.
- $p(r) = \mathcal{F}^{-1}\left[I(q)\right]$ real space information.
- Physical meaning: find all the possible point pairs inside the particle and make a histogram from their distances

The PDDFs of some geometrical shapes





Contents

Summary – Pros and cons of scattering experiments

Advantages

- Statistically significant average results
- Simple measurement principle
- Separation of length scales (SAXS is blind for atomic sizes)
- Accurate quantitative results, traceable to the definitions of the SI units of measurement

Disadvantages

- Nonintuitive, indirect measurement results → difficult interpretation
- Cannot be used on too complex systems
- Possible ambiguity of the determined structure (phase problem)
- Measures mean values: no means for getting results on structural forms present in low concentrations

Summary, outlook

Summary

- Structure determination by scattering
- Intensity, momentum transfer, scattering pattern, scattering curve
- Fourier transform, absolute square, phase problem
- Scattering of a homogeneous sphere, Guinier and Porod limits
- Size distribution of nanoparticles

In the following weeks:

- How to measure SAXS: instrumentation, practicalities
- Different material systems: periodic samples, self-assembling lipid systems (micelles, bilayers), proteins, polymer solutions, phase separated polymers: based on actual measurement data

Thank you for your attention!