Neutron Scattering

Part 1: Theory

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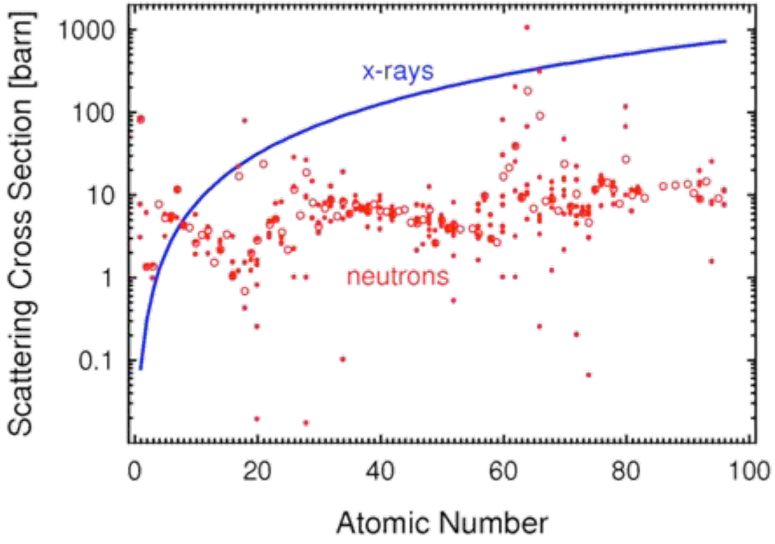
- Why neutrons?
- Static (elastic) scattering
- Dynamic (inelastic/quasielastic) scattering

Scattering probes: cross sections

	Neutrons	X-rays	Light
Wavelength λ	0.1…1 nm	0.05…0.2 nm	400…700 nm
Length scale *d*	0.05 nm…50 µm	0.03 nm…50 µm	200 nm…500 µm
Scattered by	nuclei	electrons	fluctuations of refractive index

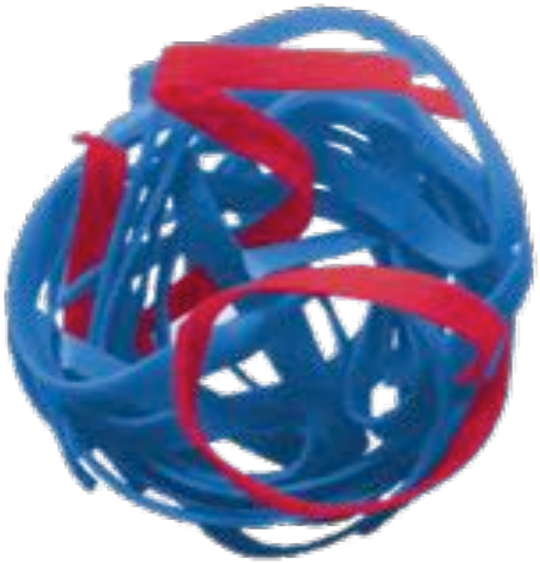


irregular dependence on isotope

preferential scattering by heavy atoms

SANS classical example

How can the structure of a single polymer chain in a melt be studied?

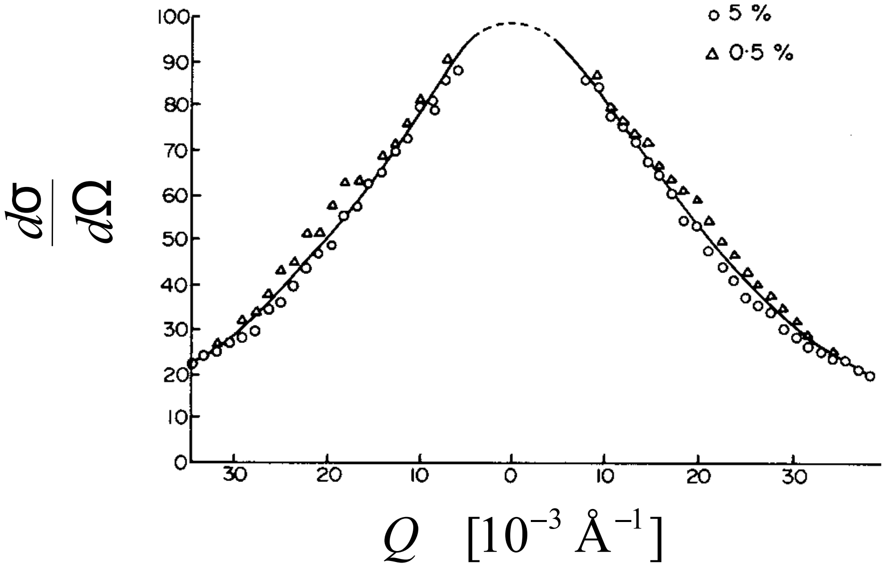


Isotopic Labelling:

$$b_\text{H} = -3.74\ \text{fm} \qquad b_\text{D} = +6.67\ \text{fm}$$

Scattering contrast with negligible chemical difference

Polystyrene: [Schelten et al. 1973]



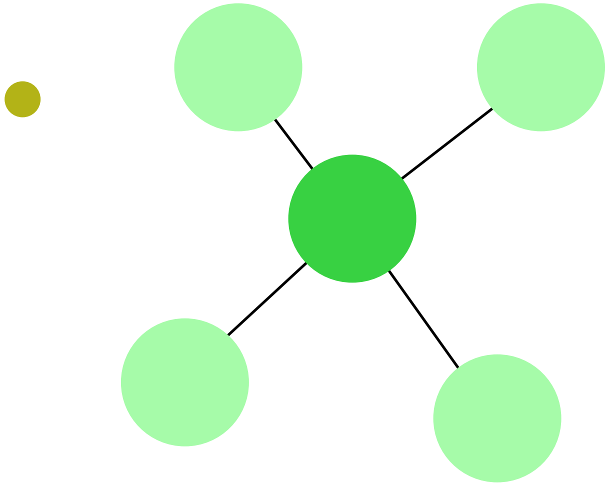
Fit with Debye function: Validity of Flory‘s theory

Elastic and inelastic scattering

What is the difference between elastic and inelastic scattering?

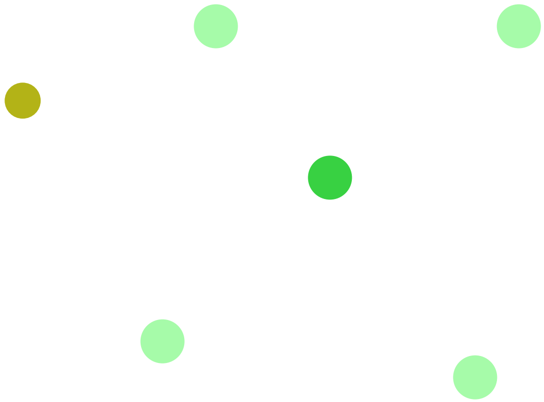
Elastic scattering

- scatterers are (assumed) fixed in space
- no energy transfer



Inelastic scattering

- scatterers are moving or moved by neutron
- energy transfer



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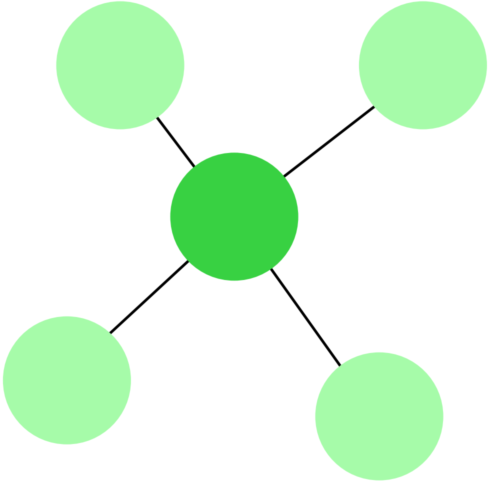
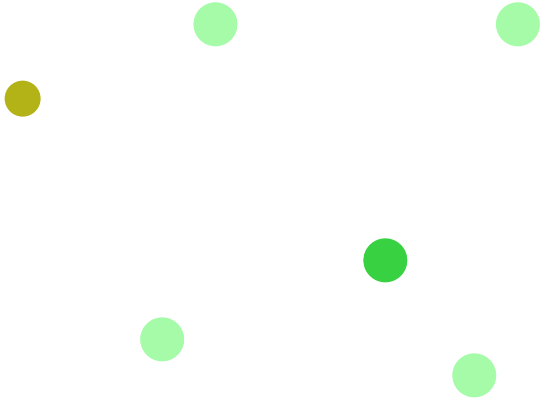


- Evidence:
  - high mass $m_{\mathrm{scatterer}} >> m_{\mathrm{n}}$
  - low temperature $k_{\mathrm{B}}T << E_{\mathrm{n}}$
  - crystal or glass

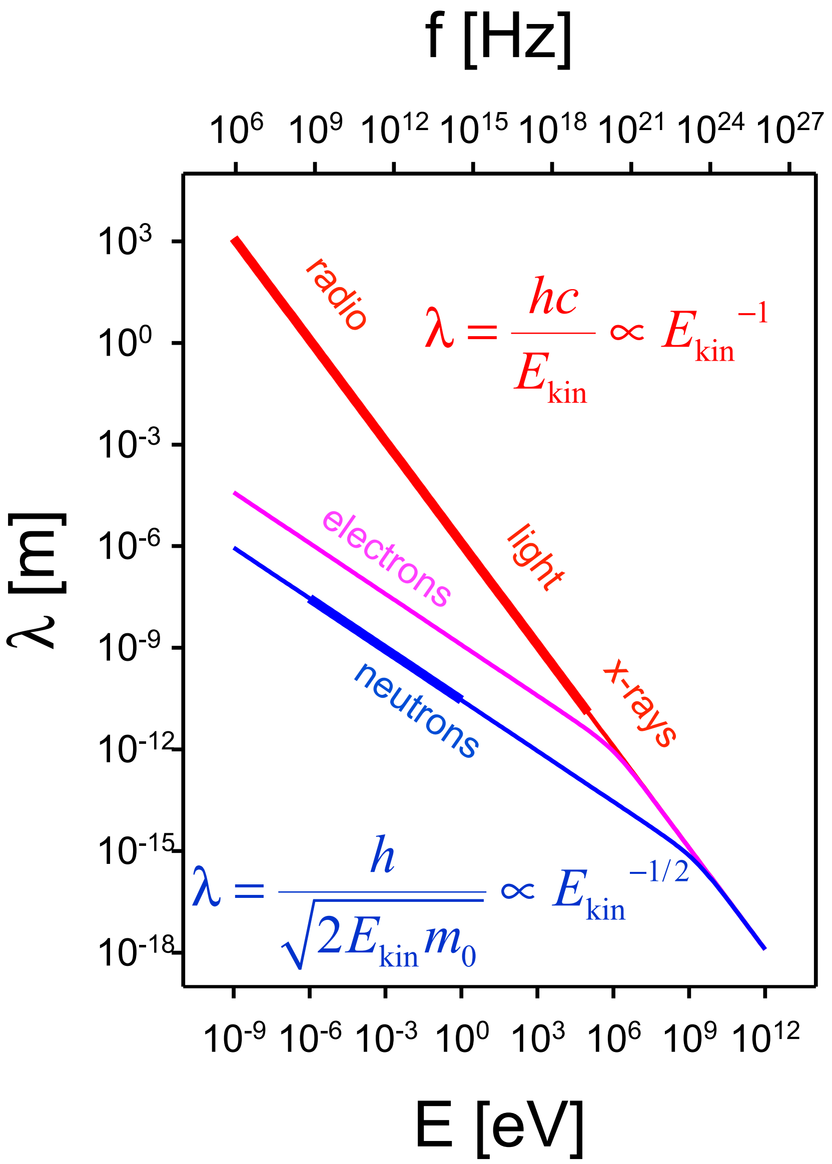
Inelastic scattering

- scatterers are moving or moved by neutron
- energy transfer



- Evidence:
  - low mass $m_{\mathrm{scatterer}} \approx m_{\mathrm{n}}$
  - high temperature $k_{\mathrm{B}}T \approx E_{\mathrm{n}}$
  - liquid or gas

Scattering probes: energies



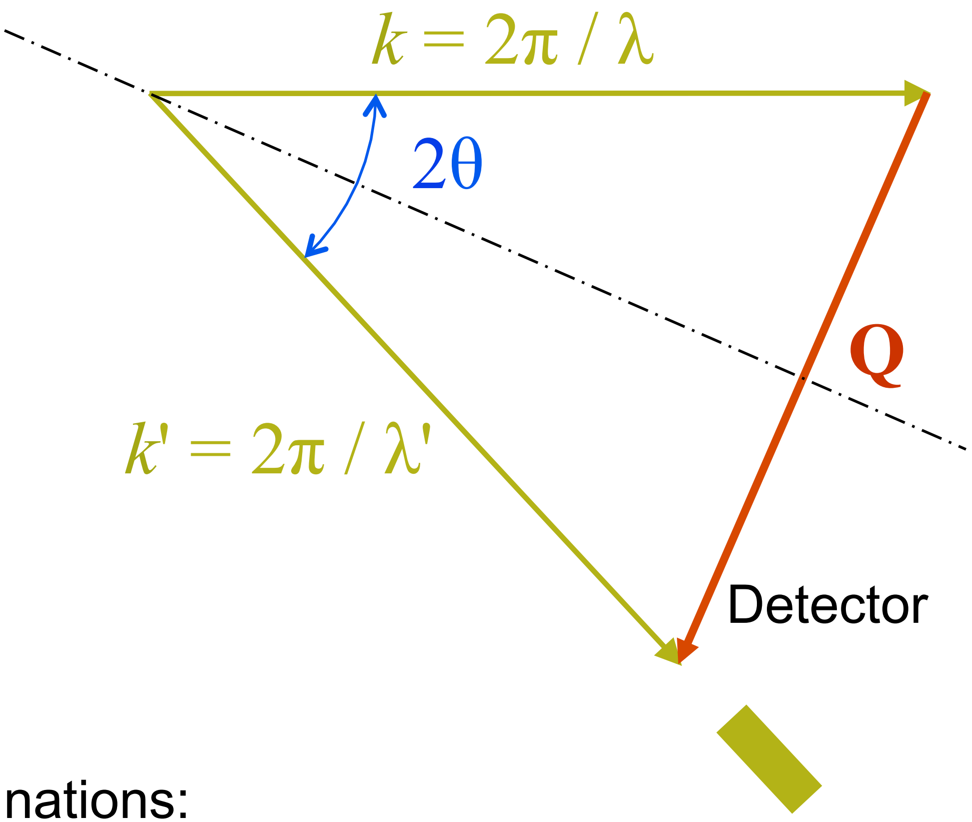
Energy of x-rays is often too high to detect inelastic scattering.

Neutron scattering from static systems (elastic scattering)

The scattering triangle (elastic scattering): Q vector

Elastic scattering ⇒ no energy transfer ⇒ $E' = E, \lambda' = \lambda, k' = k$

Source

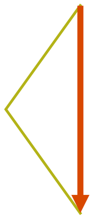


The scattering triangle is isosceles:

$$Q = 2k\sin\theta = \frac{4\pi}{\lambda}\sin\theta$$

Only difference $k' - k$ matters,
same Q with different λ-θ combinations:

large angle,
long wavelength:



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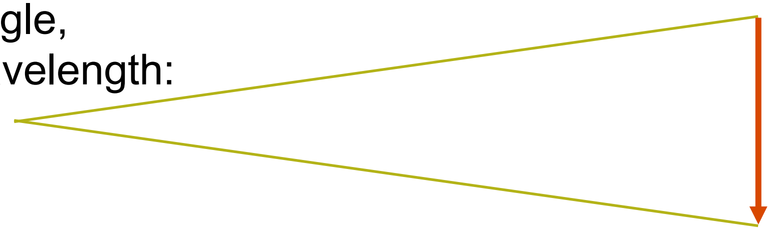
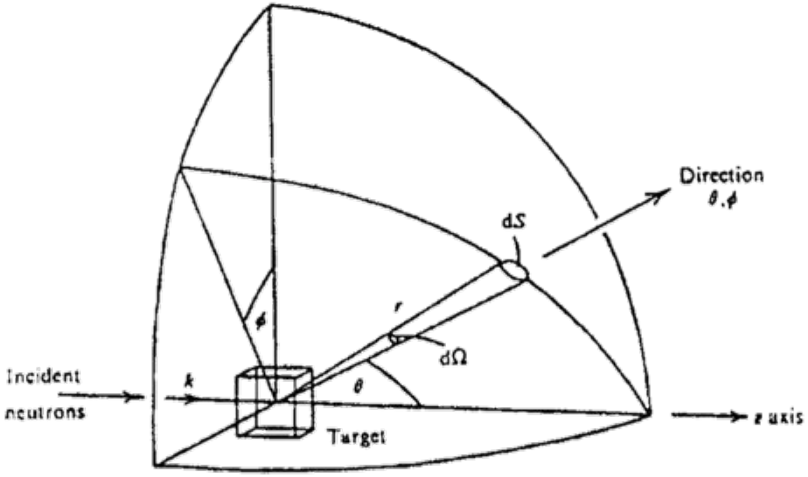
small angle,
short wavelength:



Structure factor

position of scatterer r_j → path length difference $Q \bullet r_j$ → phase shift $\exp(iQ \bullet r_j)$:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \left\langle \left| \sum_{j=1}^{N} b_j \exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}_j\right) \right|^2 \right\rangle$$



(Differential cross section)

Assume that all scatterers are identical (for neutrons: also isotope and spin-orientation identical):

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |b|^2 \left\langle \left| \sum_{j=1}^{N} \exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}_j\right) \right|^2 \right\rangle$$

N and b depend on the specific choice of the sample, the rest of the formula expresses the structure

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |b|^2 N \left\langle \frac{1}{N} \left| \sum_{j=1}^{N} \exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}_j\right) \right|^2 \right\rangle = |b|^2 N\, S(\mathbf{Q})$$

With $S(\mathbf{Q}) = \left\langle \frac{1}{N} \left| \sum_{j=1}^{N} \exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}_j\right) \right|^2 \right\rangle$ being the structure factor.

Continuum picture

How does the scattering look like for a scattering continuum? I.e. if

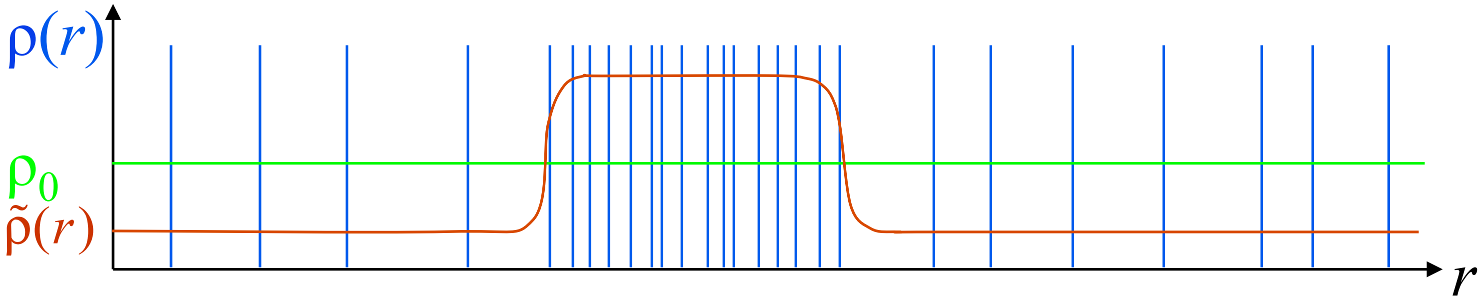
- the scatterer *is* continuous (magnetic moment of unpaired electrons)
- individual scatterers can not be resolved for given Q
  (SANS, SAXS: $Q \ll 2\pi /$ distance)

$$S(\mathbf{Q}) = \frac{1}{N} \left\langle \left| \int_V \mathrm{d}^3 r \exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}\right) \rho(\mathbf{r}) \right|^2 \right\rangle$$

Equivalence by $\rho(\mathbf{r}) = \sum_{j=1}^{N} \delta\left(\mathbf{r} - \mathbf{r}_j\right)$

Mesoscopic description, scattering length density

Is this good for anything in practice? If we know the position of each atom (crystal), no. But if we only have a ‚mesoscopic' description, yes:



This is an acceptable approximation if $Q \ll 2\pi /$ distance (small-angle scattering, reflectometry).

Generalisation to mixtures of scatterers:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \left\langle \left| \int_V \mathrm{d}^3 r \exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}\right)\rho_b(\mathbf{r}) \right|^2 \right\rangle \text{ with } \rho_b(\mathbf{r}) = \sum_{j=1}^{N} b_j \delta\left(\mathbf{r}-\mathbf{r}_j\right)$$

ρ_b is the scattering length density (dimension: m^{-2}).

The second way to derive the differential cross section

(not just a mathematical exercise but necessary if ρ($\mathbf{r}$) is not known)

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \left\langle \left| \sum_{i=1}^{N} b_j \exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}_i\right) \right|^2 \right\rangle = \left\langle \left(\sum_{i=1}^{N} b_i \exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}_i\right) \right)^* \left(\sum_{i=1}^{N} b_i \exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}_i\right) \right) \right\rangle =$$

$$= \left\langle \left(\sum_{i=1}^{N} b_i^* \exp\left(-\mathrm{i}\mathbf{Q}\cdot\mathbf{r}_i\right) \right) \left(\sum_{i=1}^{N} b_i \exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}_i\right) \right) \right\rangle = \left\langle \sum_{\boxed{i,j=1}}^{N} b_i^* b_j \exp\left(\mathrm{i}\mathbf{Q}\cdot\boxed{\left(\mathbf{r}_j - \mathbf{r}_i\right)}\right) \right\rangle$$

- The scattering originates from particle pairs (except for $i = j$).
- Only distances between particles matter, not their absolute positions.

Structure factor (identical particles):

$$S(\mathbf{Q}) = \left\langle \frac{1}{N} \sum_{i,j=1}^{N} \exp\left(\mathrm{i}\mathbf{Q}\cdot\left(\mathbf{r}_j - \mathbf{r}_i\right)\right) \right\rangle$$

Pair correlation function

How does the continuum picture look here?

Microscopic two-particle density:

$$\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) = \sum_{i,j=1}^{N} \delta(\mathbf{r}_1 - \mathbf{r}_i)\delta(\mathbf{r}_2 - \mathbf{r}_j)$$

The average is not just the average density squared:

$$\langle \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \rangle \neq \langle \rho(\mathbf{r}_1) \rangle \langle \rho(\mathbf{r}_2) \rangle = \rho_0{}^2$$

… but in homogeneous systems the ‚starting point‘ is arbitrary:

$$\langle \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \rangle = \langle \rho(\mathbf{0})\rho(\mathbf{r}_2 - \mathbf{r}_1) \rangle$$

Structure factor as Fourier transform of the pair correlation function:

$$S(\mathbf{Q}) = \left\langle \sum_{i,j=1}^{N} \exp\left(\mathrm{i}\,\mathbf{Q}\cdot(\mathbf{r}_j - \mathbf{r}_i)\right) \right\rangle = \frac{1}{\rho_0} \int_{V_d} d^3 r \exp(\mathrm{i}\,\mathbf{Q}\cdot\mathbf{r}) \langle \rho(\mathbf{0})\rho(\mathbf{r}) \rangle$$

Alternative definitions of the pair correlation function

$\left\langle \rho(\mathbf{0})\rho(\mathbf{r})\right\rangle = \rho_0 \left\langle \sum_{i,j=1}^{N} \delta\left(\mathbf{r}-\mathbf{r}_j+\mathbf{r}_i\right)\right\rangle$ has a delta function at $r=0$ which can be removed. Also it can be converted to a dimensionless quantity:

$$g(\mathbf{r}) = \frac{\left\langle \rho(\mathbf{0})\rho(\mathbf{r})\right\rangle}{\rho_0{}^2} - \frac{\delta(\mathbf{r})}{\rho_0}$$

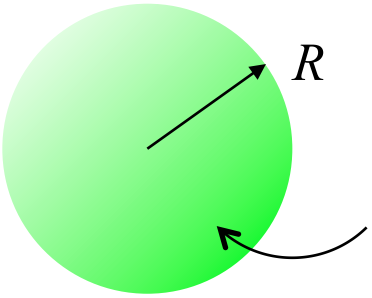
With this ‚literature standard‘ the final result is:

$$S(\mathbf{Q}) = \underbrace{1+}_{\text{compensates delta function in } g(\mathbf{r})} \rho_0 \int_{V_d} \mathrm{d}^3 r \exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}\right)\left(g(\mathbf{r}) \underbrace{-1}_{\text{avoids delta function in } S(\mathbf{Q})}\right)$$

Often isotropic materials, $g(\mathbf{r})$ does not depend on direction:

$$S(Q) = 1 + \frac{4\pi\rho_0}{Q}\int_0^\infty \left(g(r)-1\right)\sin(Qr)r\,\mathrm{d}r$$

Form factor of a sphere



N scatterers inside

$$P(\mathbf{Q})=\frac{1}{N^2}\left\langle\left|\int_V \mathrm{d}^3 r \exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}\right)\rho(\mathbf{r})\right|^2\right\rangle \quad \text{with } \rho(r)=\begin{cases}\tilde{\rho} \text{ for } r<R\\ 0 \text{ for } r>R\end{cases}$$

Fourier transform for spherical symmetry: $\int \mathrm{d}^3 r \exp(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}) f(\mathbf{r}) = \frac{4\pi}{Q}\int_0^\infty f(r) r \sin(Qr)\,\mathrm{d}r$

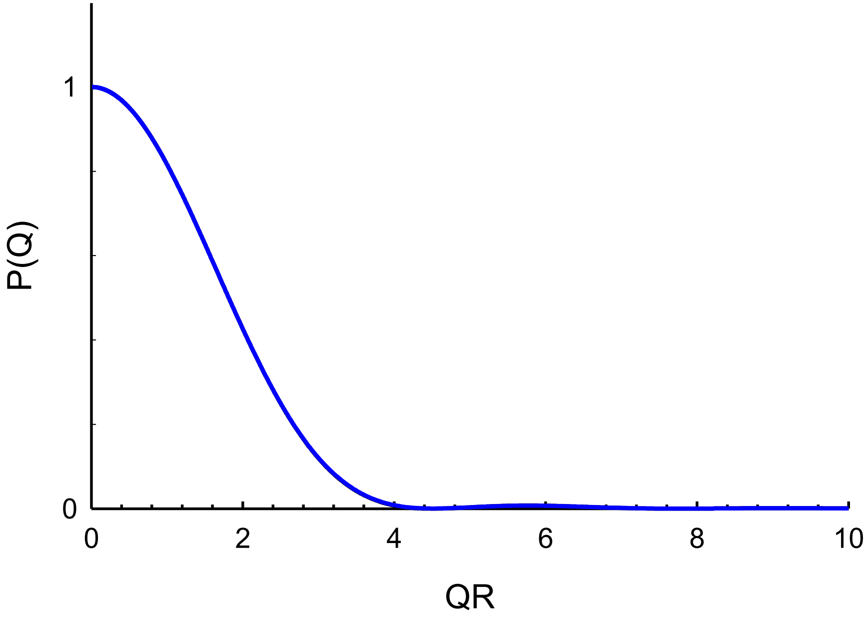
$$\int \mathrm{d}^3 r \exp(\mathrm{i}\mathbf{Q}\cdot\mathbf{r})\rho(\mathbf{r}) = \frac{4\pi}{Q}\int_0^R \tilde{\rho} r\sin(Qr)\,\mathrm{d}r \overset{x=Qr}{=} \frac{4\pi}{Q}\int_0^{QR}\tilde{\rho}\frac{x}{Q}\sin x\frac{\mathrm{d}x}{Q} = \frac{4\pi\tilde{\rho}}{Q^3}\int_0^{QR} x\sin x\,\mathrm{d}x =$$

$$= \frac{4\pi\tilde{\rho}}{Q^3}\left(\sin(QR) - QR\cos(QR)\right)$$

$$\tilde{\rho} = \frac{N}{V_{\text{sphere}}} = \frac{3N}{4\pi R^3} \quad \Rightarrow \quad \ldots = \frac{3N}{Q^3 R^3}\left(\sin(QR) - QR\cos(QR)\right)$$

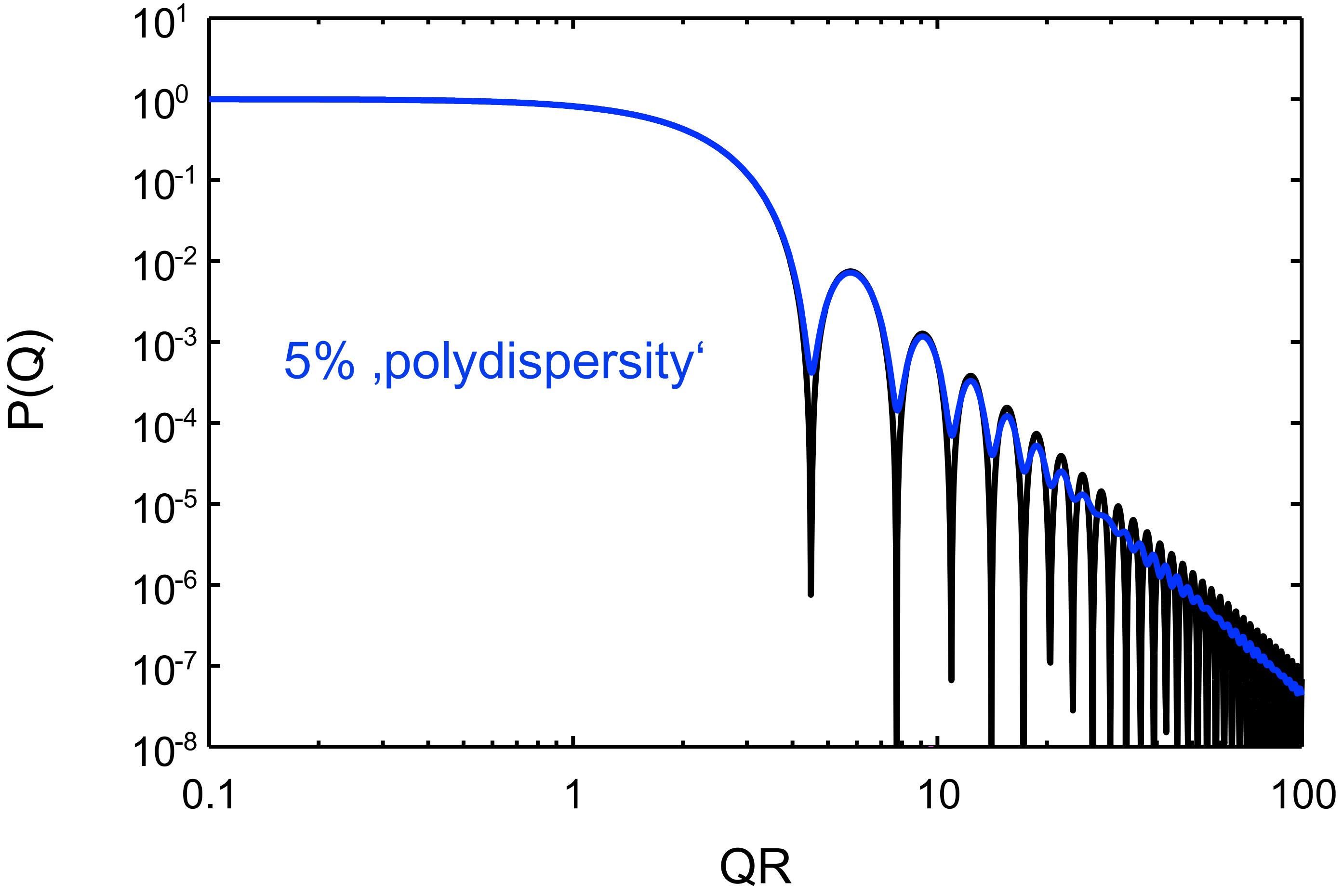
Form factor of a sphere

$$P(\mathbf{Q}) = \frac{1}{N^2}\left\langle \left| \int_V \mathrm{d}^3 r \exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}\right)\rho(\mathbf{r}) \right|^2 \right\rangle = \frac{9}{Q^6 R^6}\left(\sin(QR) - QR\cos(QR)\right)^2$$



Decays rapidly because of $1/Q^4$ term, better double-log plot!

Form factor of a sphere



Guinier approximation

The low Q form factor can be approximated as

$$P_{\text{Guinier}}(Q) = \exp\left(-\frac{Q^2 R_g{}^2}{3}\right) = 1 - \frac{Q^2 R_g{}^2}{3}\ldots$$

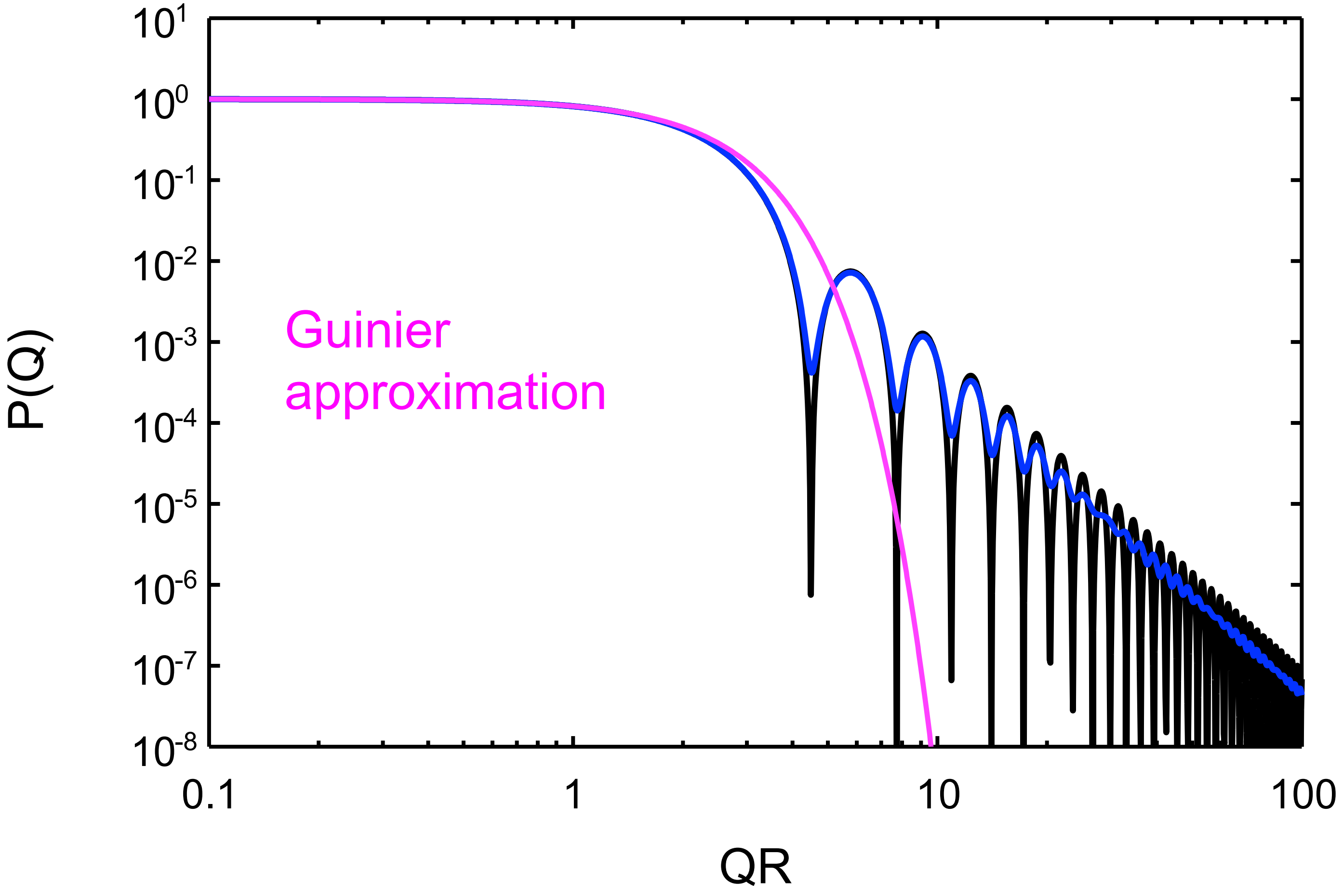
For any finite-size particle one can calculate the radius of gyration:

$$R_{\mathrm{g}}{}^2 = \frac{\int_V \rho(r) r^2 \,\mathrm{d}^3 r}{\int_V \rho(r)\,\mathrm{d}^3 r}$$

For the sphere:

$$R_{\mathrm{g}}{}^2 = \frac{\int_V \rho(r) r^2 \,\mathrm{d}^3 r}{\int_V \rho(r)\,\mathrm{d}^3 r} = \frac{\int_0^R \tilde{\rho} r^2 4\pi r^2 \,\mathrm{d}r}{\int_0^R \tilde{\rho} r^2 4\pi \,\mathrm{d}r} = \frac{4\pi\tilde{\rho}R^5/5}{4\pi\tilde{\rho}R^3/3} = \frac{3}{5}R^2$$

Form factor of a sphere



Porod law

High Q behaviour of the form factor:

$$\lim_{Q\to\infty} P(Q) = \frac{2\pi S_{\text{particle}}}{V_{\text{particle}}{}^{2}} \frac{1}{Q^4}$$

Valid for any compact particle with sharp boundaries.

For the sphere:

$$\frac{2\pi S_{\text{particle}}}{V_{\text{particle}}{}^{2}} \frac{1}{Q^4} = \frac{2\pi 4\pi R^2}{\left(4\pi R^3/3\right)^2} = \frac{9}{2R^4} \frac{1}{Q^4}$$