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# Methoden moderner Röntgenphysik II: Streuung und Abbildung

## Lecture 7

Vorlesung zum Haupt/Masterstudiengang Physik

SS 2014

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Location: Hörs AP, Physik, Jungiusstrasse

Tuesdays 12.45 – 14.15

Thursdays 8:30 – 10.00

# Methoden moderner Röntgenphysik II: 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, ..

Coherent Scattering
Spatial coherence, second order coherence,..

Applications of coherent Scattering
Imaging and Correlation spectroscopy,..

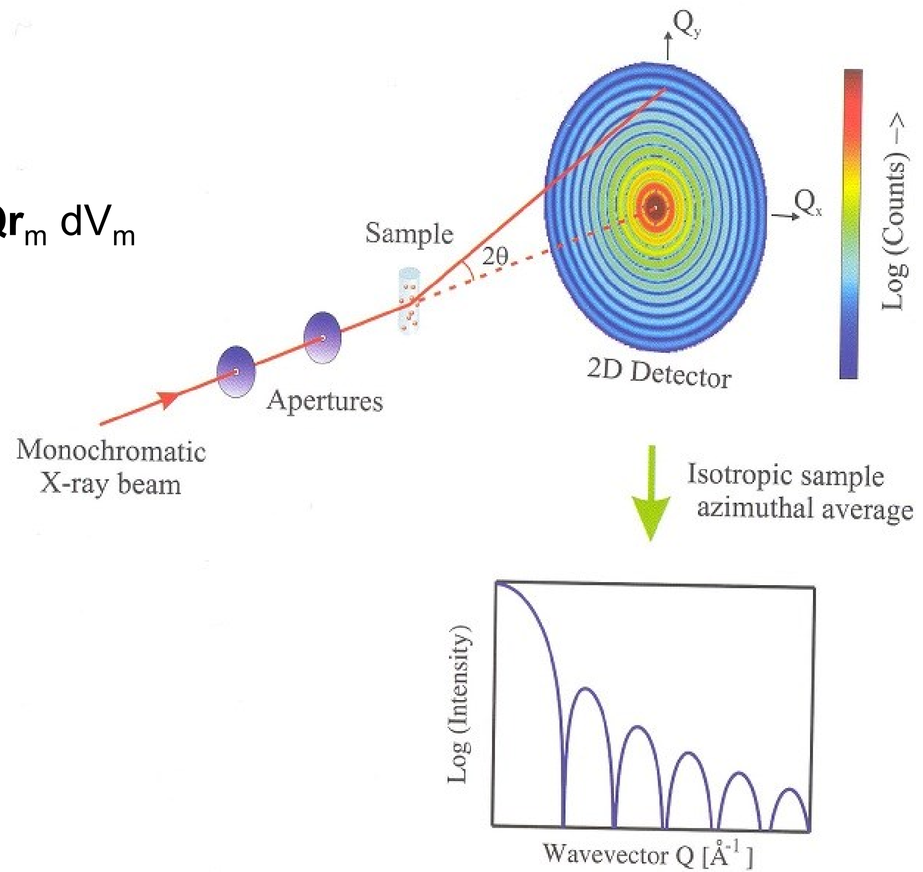
# Small Angle X-ray Scattering (SAXS)

From Eq. (**)

$I_{SAXS}(Q) = f^2{}_n\Sigma\, {}_V\!\int \rho_{at} \exp i\mathbf{Q}(\mathbf{r}_n-\mathbf{r}_m)\, dV_m$

$= f^2{}_n\Sigma \exp i\mathbf{Q}\mathbf{r}_n\; {}_V\!\int \rho_{at} \exp -i\mathbf{Q}\mathbf{r}_m\, dV_m$

$= f^2{}_V\!\int \rho_{at} \exp i\mathbf{Q}\mathbf{r}_n\, dV_n\; {}_V\!\int \rho_{at} \exp -i\mathbf{Q}\mathbf{r}_m\, dV_m$

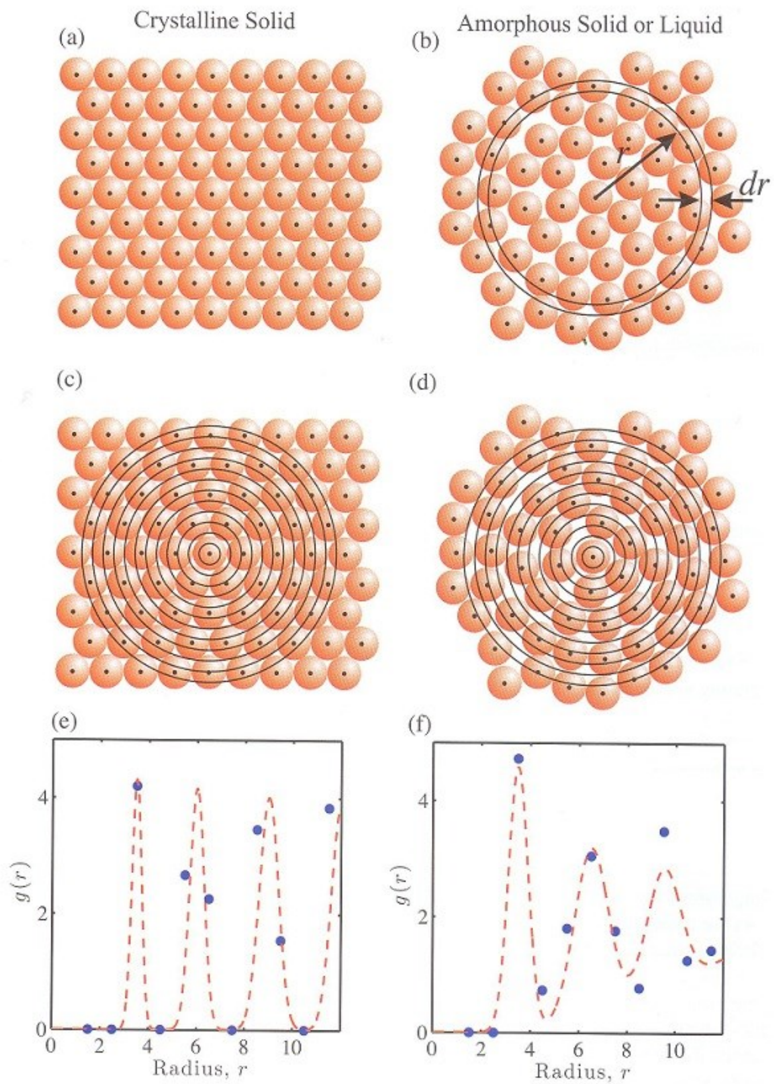



$\Rightarrow$

$I_{SAXS}(Q) = |\, {}_V\!\int \rho_{sl} \exp i\mathbf{Q}\mathbf{r}\, dV\, |^2$

with $\rho_s = f\, \rho_s$

# Scattering from liquids and glasses




The positions of atoms in non-crystalline materials changes over a wide range of timescales (from nanoseconds in the case of liquids to millennia or more in the case of glasses.

X-rays are a fast probe delivering snapshots of the structure as shown schematically in the figure.

Radial density: $\rho(r) = N(r) / (2\pi r dr)$

$N(r)$ number of atoms in annulus $r+dr$
with $2\pi r dr$ being the annulus' area

Radial distribution function: $g(r) = \rho(r)/\rho_{at}$

$\rho_{at}$ average areal number density

The radial distribution function of a non-crystalline material damps and broadens as a function of r with g(r) tending to unity.

# The liquid structure factor

Consider mono-atomic or mono-molecular system:

$$I(\mathbf{Q}) = f(\mathbf{Q})^2 \; {}_n\Sigma \exp(i\mathbf{Q}\mathbf{r}_n) \; {}_m\Sigma \exp(i\mathbf{Q}\mathbf{r}_m) = f(\mathbf{Q})^2 \; {}_n\Sigma_m\Sigma \exp i\mathbf{Q}(\mathbf{r}_n-\mathbf{r}_m)$$

with $f(\mathbf{Q})$ formfactor

separate summations

$$I(\mathbf{Q}) = Nf(\mathbf{Q})^2 + f(\mathbf{Q})^2 \; {}_n\Sigma_{m\neq n}\Sigma \exp i\mathbf{Q}(\mathbf{r}_n-\mathbf{r}_m)$$

Replace $m\neq n$ sum by integral and separate out average density $\rho_{at}$:

$$I(\mathbf{Q}) = \underbrace{Nf(\mathbf{Q})^2 + f(\mathbf{Q})^2 \; {}_n\Sigma \; {}_V\!\int [\, \rho_n(\mathbf{r}_{nm})-\rho_{at})\exp i\mathbf{Q}(\mathbf{r}_n-\mathbf{r}_m)dV_m}_{I_{SRO}(Q)} + \underbrace{f(\mathbf{Q})^2 \rho_{at} \; {}_n\Sigma \; {}_V\!\int \exp i\mathbf{Q}(\mathbf{r}_n-\mathbf{r}_m)\, dV_m}_{I_{SAXS}(Q)}$$

$I_{SRO}$ (Q)

measures short-range order 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 $Q \rightarrow 0$
(otherwise oscillates to zero)

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

# SAXS (Form Factor)

The form factor of isolated particles

$$I_{SAXS}(Q) = (\rho_{sl,p} - \rho_{sl,0})^2 \quad | {}_V\!\int \exp i\mathbf{Qr} \, dVp |^2$$

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

$$F(\mathbf{Q}) = 1/V_p \; {}_{Vp}\!\int \exp i\mathbf{Qr} \, dVp$$

one finds

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

The formfactor 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:

$$F(Q) = 1/V_p \; {}_0\!\int^R {}_0\!\int^{2\pi} {}_0\!\int^{\pi} \exp iQr\cos(\theta) \, r^2 \sin\theta \, d\theta d\phi dr = 1/V_p \; {}_0\!\int^R 4\pi \sin(Qr)/QR \, r^2 \, dr$$

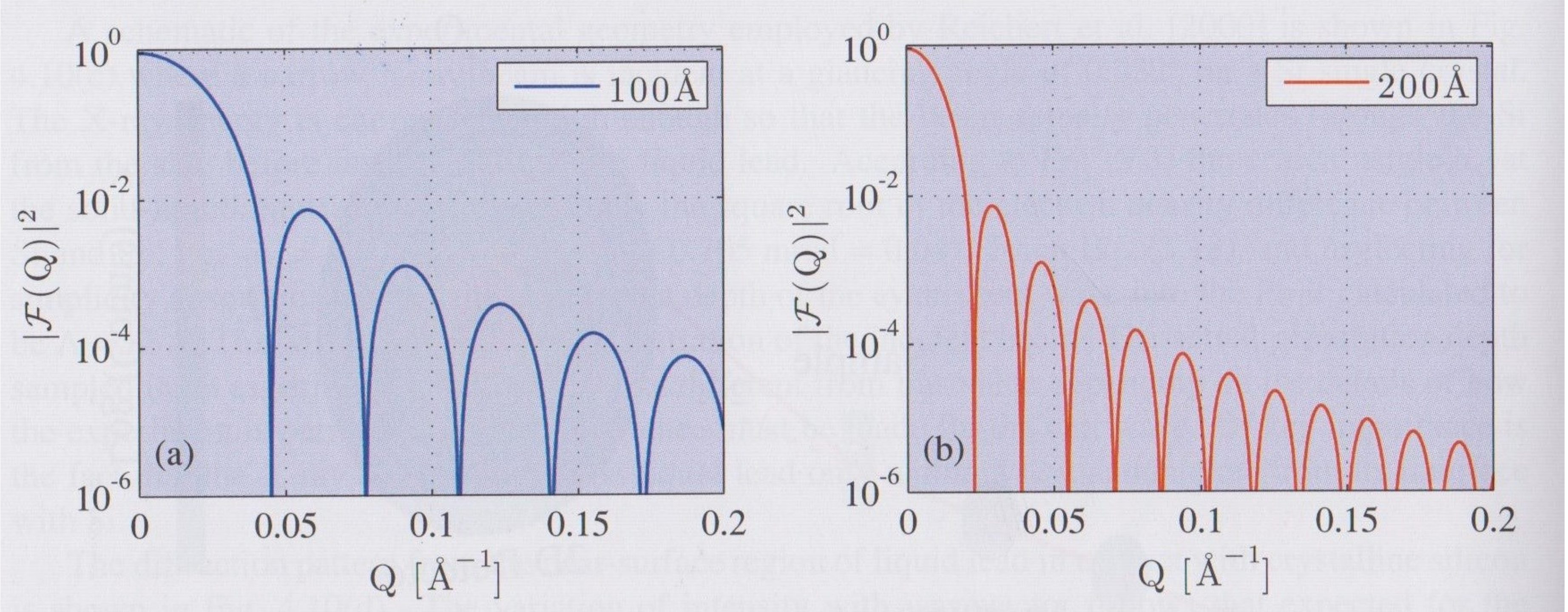
$$= 3\,[\sin(QR) - Qr\cos(QR)] \,/\, [(QR)^3] = 3\, J_1(QR) \,/\, QR$$

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

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

# Form Factor for monodisperse spheres

Monodisperse speres of radius 10nm and 20 nm

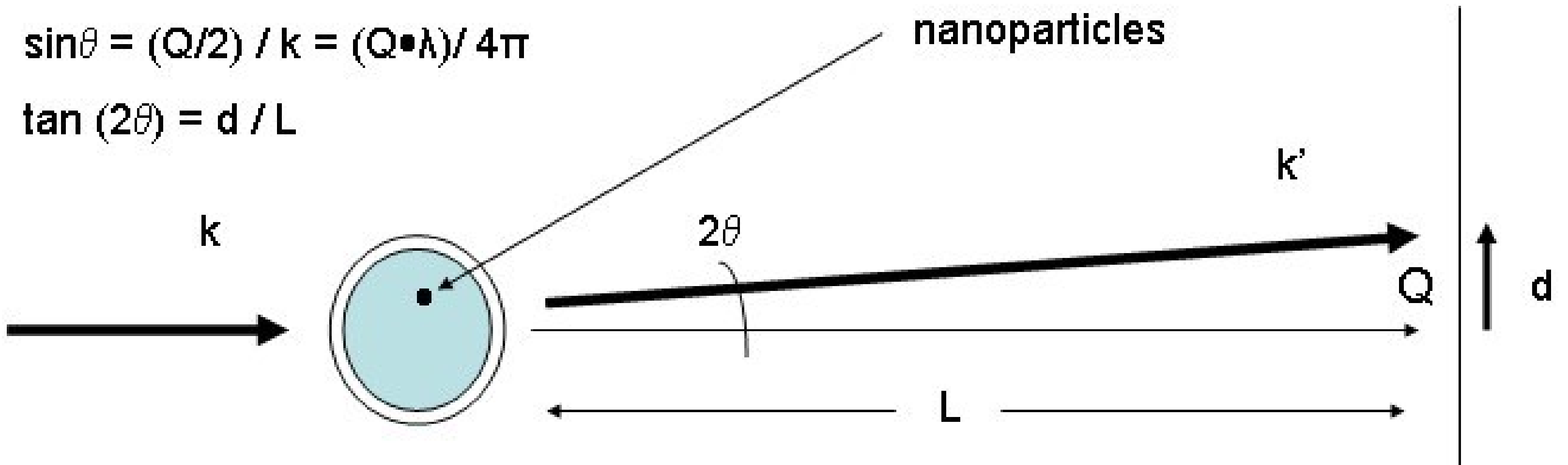


# Experimental Set-up (SAXS)

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

$\sin\theta = (Q/2) / k = (Q \bullet \lambda) / 4\pi$

$\tan(2\theta) = d / L$




$Q \approx \xi = 2\pi/d_{Particle} = 2\pi / 628Å = 0.01\ Å^{-1}$

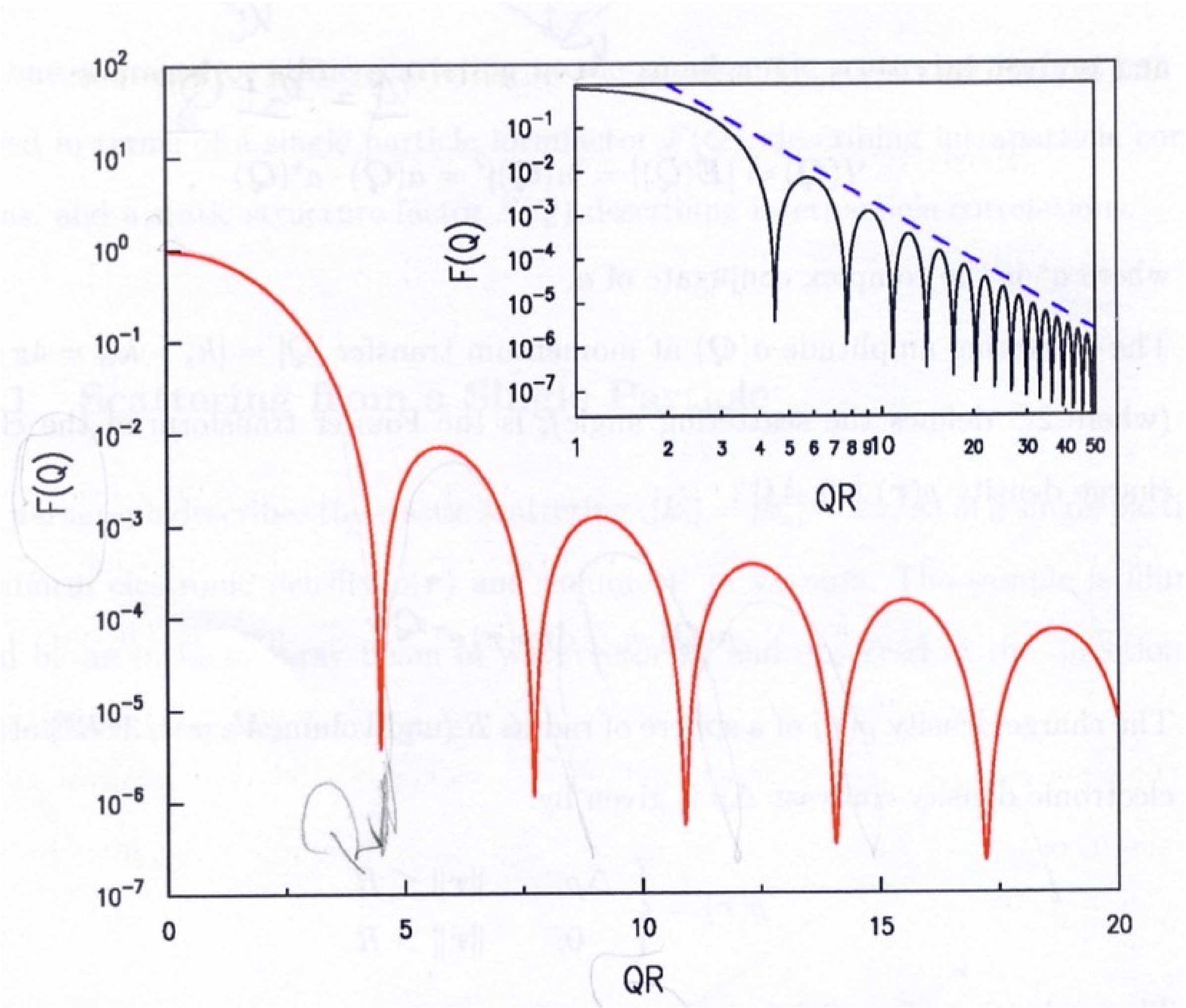
$\theta = \sin^{-1}(Q \bullet \lambda/4\pi) = \sin^{-1}(0.01Å^{-1} \bullet 1Å / 4\pi) \approx 0.0456\ \text{deg}$

$d = L \bullet \tan(2\theta) = 2\ \text{m} \bullet 1.58 {*} 10^{-3} = 3.183\ \text{mm}$

screen

2-D detector

# Form Factor for monodisperse spheres



# The small Q limit: Guinier Regime

For $QR \rightarrow 0$:

$F(Q) \approx 3/(QR)^3 \;\; [QR - (QR)^3/6 + (QR)^5/120 - \ldots \;\; -QR(1-(QR)^2/2 + (QR)^4/24 - \ldots)]$

$\approx 1 - (QR)^2/10$

Thus:

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

Thus the $QR \rightarrow 0$ limit can be used to determine the particle radius R via:

$I_{SAXS}(Q) \approx \Delta\rho^2 \, V^2{}_p \, \exp \; (-(QR)^2/5)$ $\qquad QR \ll 1 \qquad [\exp(-x) = 1-x]$

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

# The large Q limit: Porod Regime

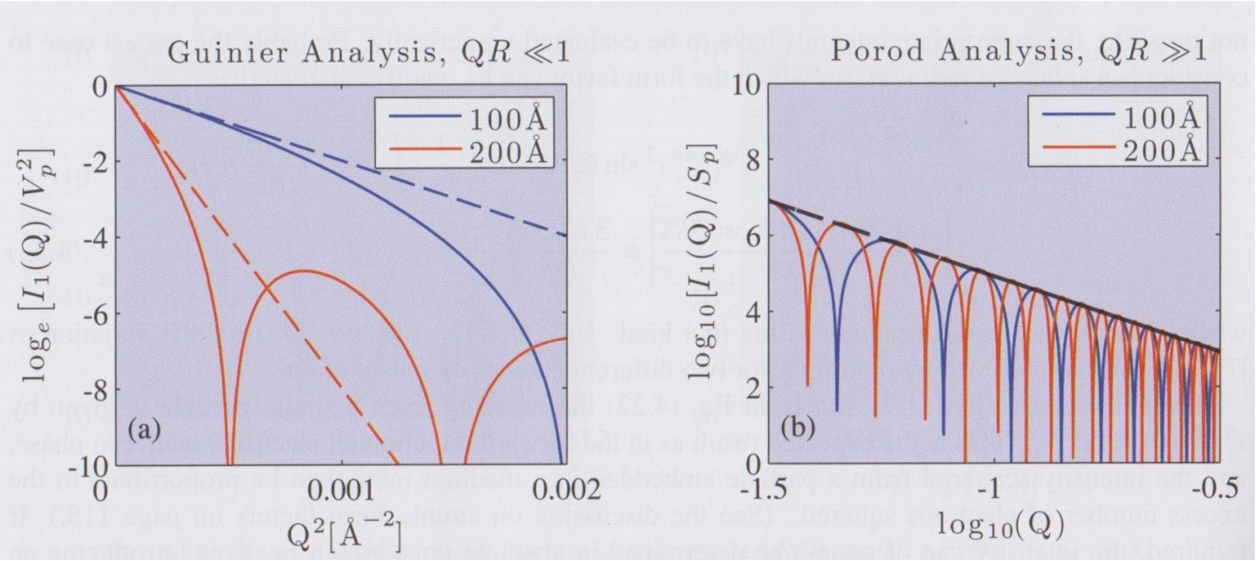
For QR >> 1: wavelength small compared to particle size

$F(Q) \approx 3/[\sin(QR)/(QR)^3 - \cos(QR) / (QR)^2)] \approx 3 [-\cos(QR) / (QR)^2 ]$

When QR >> 1, $\cos^2(x)$ oscillates towards ½ and

$$I_{SAXS}(Q) = 9\Delta\rho^2 V^2_p <\cos^2(QR)> /(QR)^4 = 9\Delta\rho^2 V^2_p / 2(QR)^4$$

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



# Radius of Gyration

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

$$R_G = 1/V_p \,_{Vp}\!\int r^2 \, dV_p$$

$$R_G^2 = {}_{Vp}\!\int \rho_{sl,p}(r)\, r^2 \, dV_p \; / \; {}_{Vp}\!\int \rho_{sl,p}(r)\, dV_p$$

For uniform spheres: $R_G^2 = 3/5\, R^2$

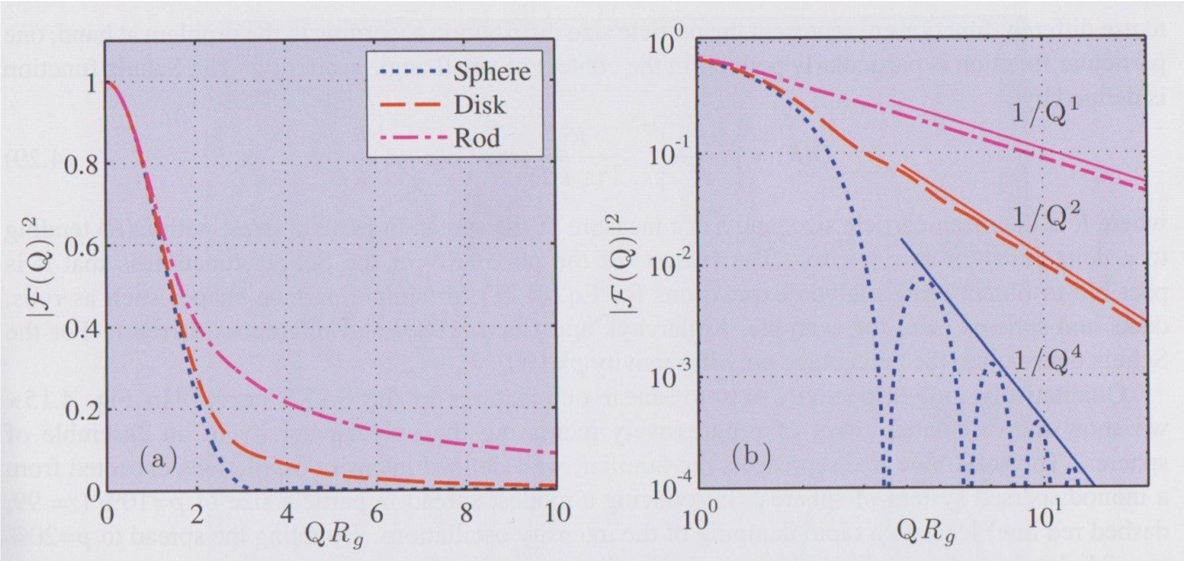
$$I_{SAXS}(Q) \approx \Delta\rho^2 \, V^2_p \, \exp\,(-\, QR_G)^2/3$$

# Formfactor and Particle Shape

$F(\mathbf{Q}) = 1/V_p \ {}_{Vp}\!\int \exp i\mathbf{Qr} \, dVp$

| | $\|F(Q)\|^2$ | RG | Porod Exp |
|---|---|---|---|
| Sphere (d=3) | $(3J_1(QR)/QR)^2$ | sqrt(3/5)R | -4 |
| Disc (d=2) | $2/(QR)2x(1-J_1(2QR)/QR)$ | sqrt(1/2)R | -2 |
| Rod (d=1) | $2\,Si(QL)/QL-4\sin^2(QL/2)/(QL)^2$ | sqrt(1/12)L | -1 |

with: $Si(x)\ {}_0\!\int^x \sin t/t\, dt$



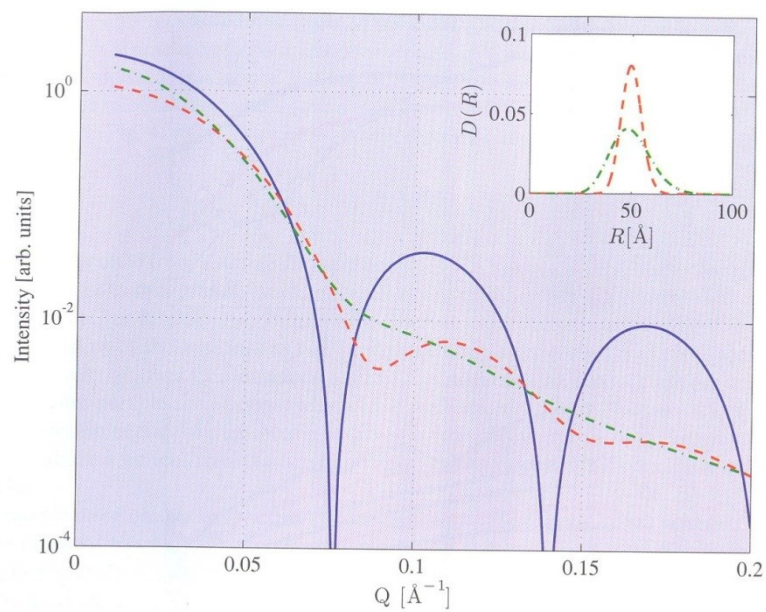
# Polydispersity

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

$$I_{SAXS}(Q) = \Delta\rho^2 \, {}_0\!\int^\infty D(R)\, V^2{}_p \, |F(Q,R)|^2 \, dR$$

with ${}_0\!\int^\infty D(R)\, dR = 1$. A frequently used distribution function is the so-called Schultz function, where z is a measure of the polydispersity:

$$D(R) = [(z+1)/\langle R\rangle]^{z+1} R^z/(\Gamma(z+1) \exp( -(z+1)R/\langle R\rangle)$$



# Structure Factor

Interparticle interactions:

S(Q): structure factor

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

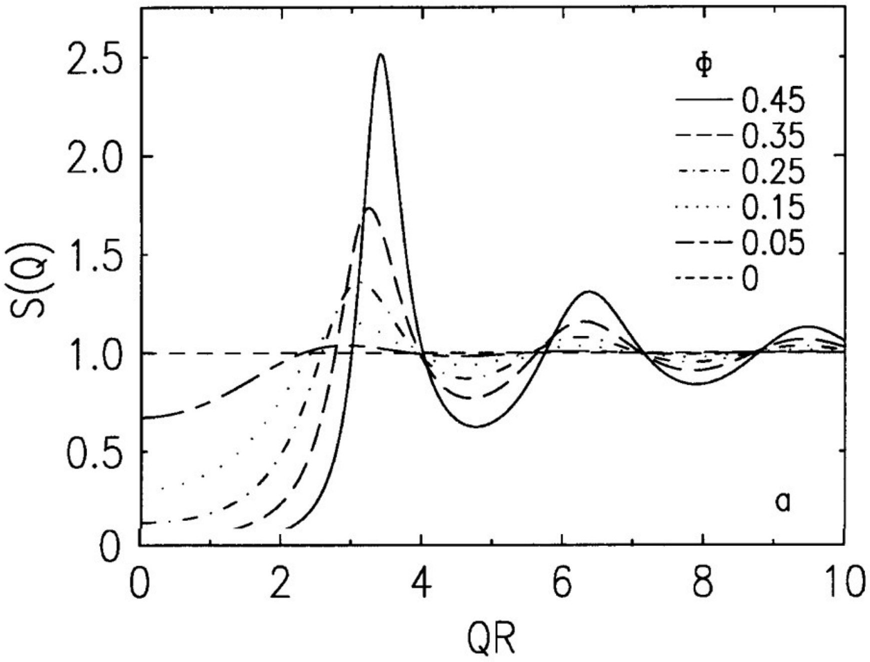
$S(Q) = 1/nN < \sum_{i,j}^{N} \exp(i\mathbf{Q}(R_i - R_j)) >$

$= \int d^3r \exp(iQr) \cdot g(r)$

<u>Hard sphere structure factor:</u>

$V(r) = 0$ for $r \geq d$

$V(r) = \infty$ for $r < d$



# SAXS experiment

- measure I(Q)
- modell F(Q)
- for spherical particles I(Q)=F(Q)•S(Q)
- get and modell S(Q)