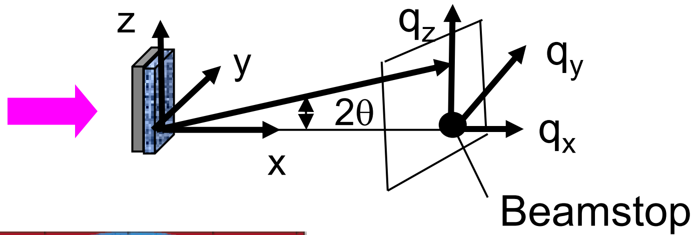
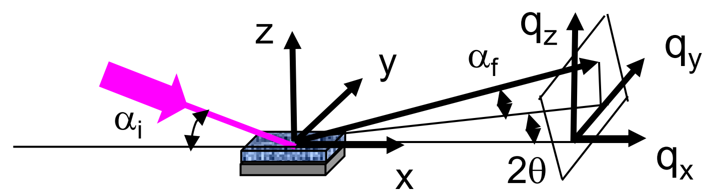
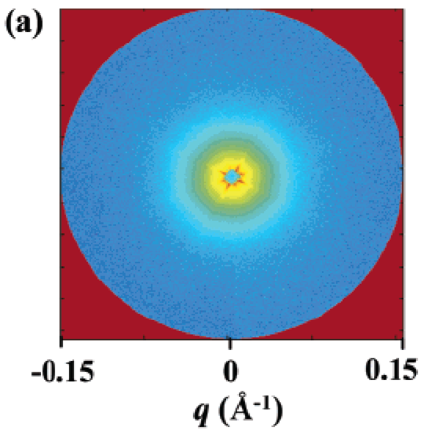
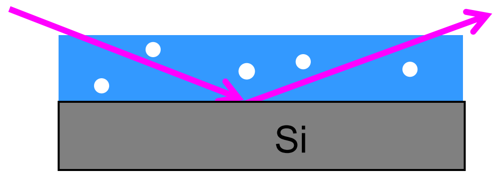
- 31.05. : Small-Angle X-ray Scattering (SAXS)
- 02.06. : Applications &
  A short excursion into Polymeric materials
- 04.06. : Grazing incidence SAXS (GISAXS)

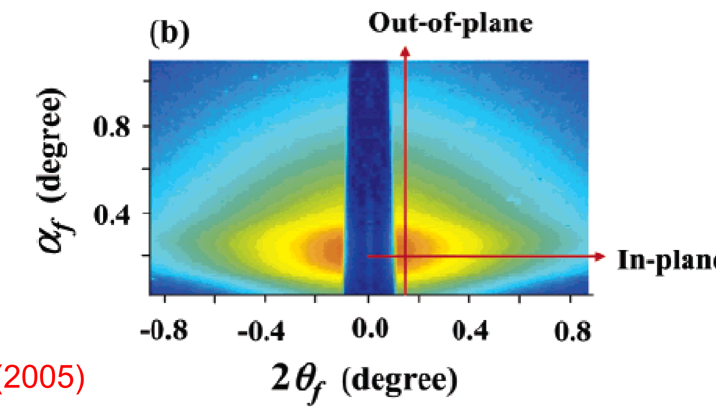
T-SAXS vs GISAXS











Lee et al., Macromolecules, 38, 8991 (2005)

- Easy measurement
- Easy analysis
- In-plane information (q_y,q_z)

- Any possible scattering from substrate
- Transparency of substrate
- High energy

- Strong intensity
- Easy preparation of samples
- Full information (q_x,q_y,q_z)

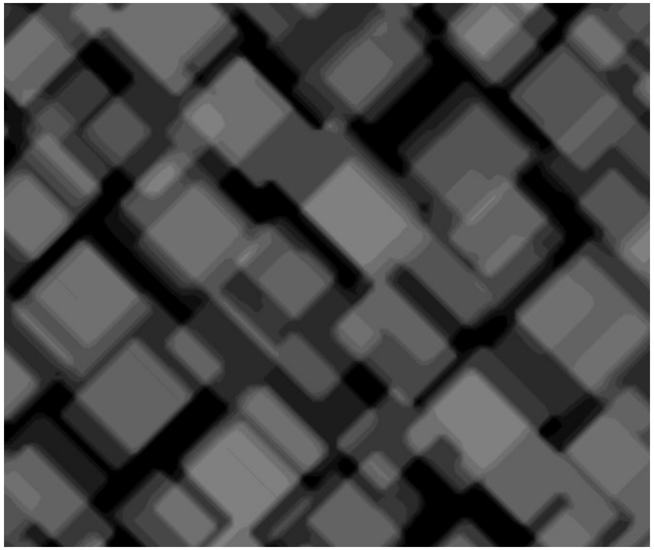
- Scattering from surface / internal structure
- Scattering from reflected AND transmitted beam
- Refraction effects (DWBA)
- Special setup

Aim

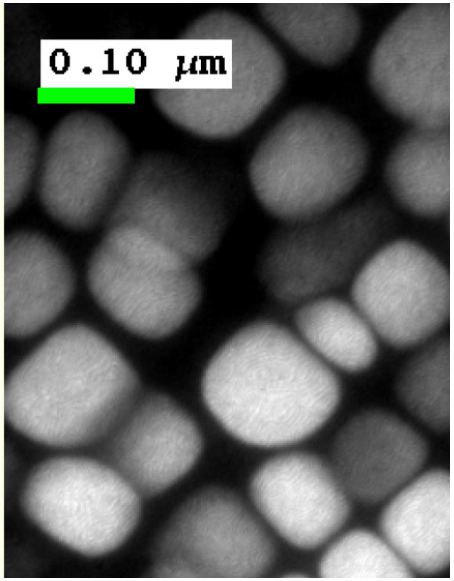
> To understand the **structure – property relation** of **materials** on **multiple length scales**

- **q-resolution**
- Maximum q-value
- **Beam size**

- Real pieces & materials
- Model systems
- Nanotechnology



Courtesy: R. Gilles (TUM)



http://news.thomasnet.com/companystory/GE-Gas-Turbine-Technology-Selected-for-Pearl-GTL-Project-in-Qatar-495497

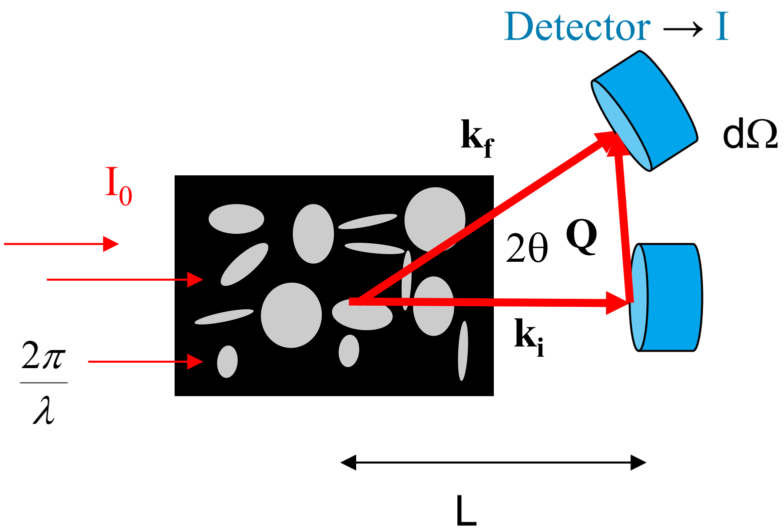
Outline II - Today

- SAXS – Introduction
- Instrumentation
  - P03/MiNaXS @ PETRA III
- Bulk materials ➔ Transmission U/SAXS:
  - Porous materials
  - Ni-base superalloys
  - Droplet drying

Neutrons, X-rays and Light: Scattering Methods Applied to Soft Condensed Matter.
Eds: P. Lindner, Th. Zemb. North Holland Delta Series, Elsevier, Amsterdam (2002)
ISBN: 0-444-51122-9

Cross Section

- Differential cross section



$$d\sigma = \frac{I}{I_0}(L^2 d\Omega)$$

$$\frac{d\sigma}{d\Omega} = \frac{I}{I_0}(L^2) \quad \Rightarrow \quad \frac{d\Sigma}{d\Omega} = \frac{1}{V}\frac{d\sigma}{d\Omega}$$

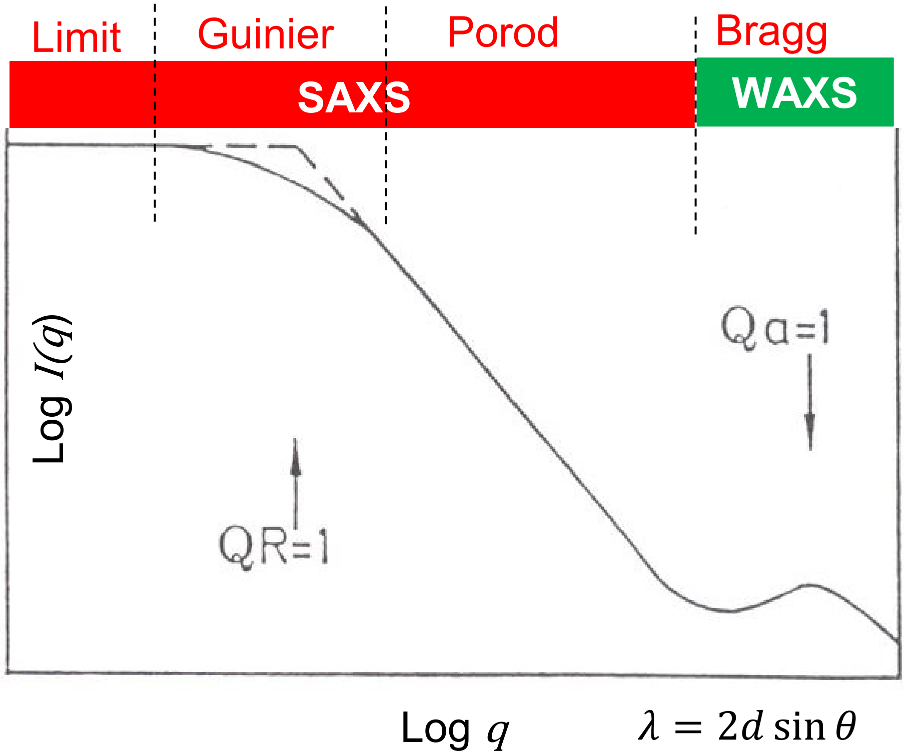
V = Sample volume

$$\vec{q} = \overrightarrow{k_f} - \overrightarrow{k_i} \qquad |\vec{k}_f| = |\vec{k}_i| = \frac{2\pi}{\lambda} \qquad |\vec{q}| = 2\frac{2\pi}{\lambda}\sin(\theta)$$

- Scattering occurs due to density differences

WAX, SAX, GISAX

Source: Streumethoden zur Untersuchung kondensierter Materie
1996; ISBN 978-3-89336-180-9



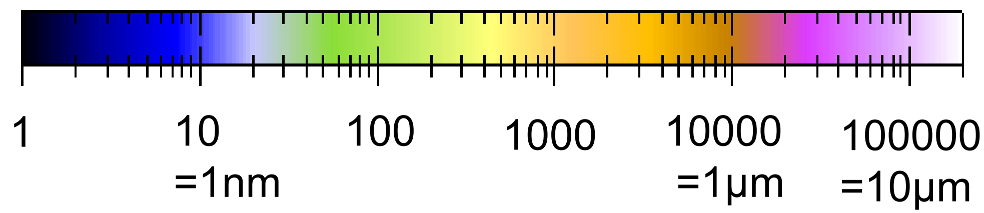
$$\lambda = 2d \sin\theta$$

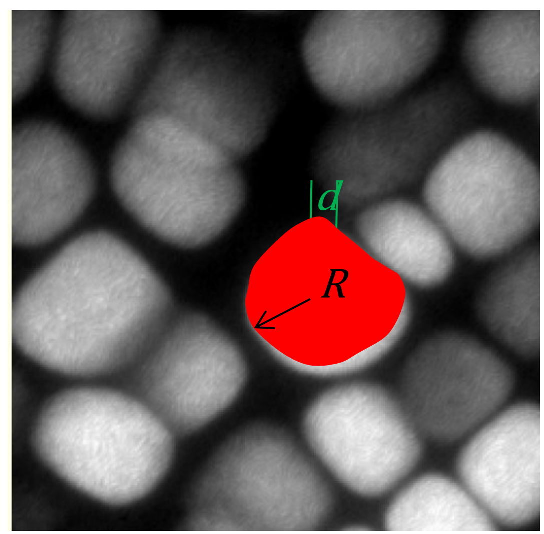
$$\lambda = 1.54\text{Å}$$

d / resolution [Å]

WAXS: Crystal structure

SAXS/GISAXS: density fluctuations, precipitates

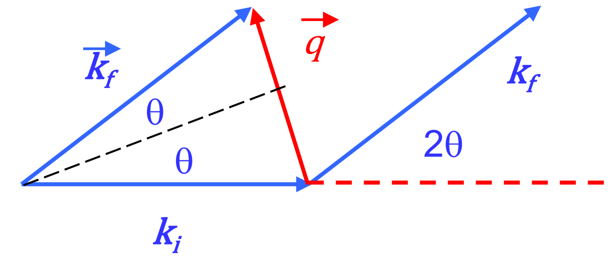




- R~particles “radius“
- d~interatomic distance
- SAXS: $\theta < 5°$

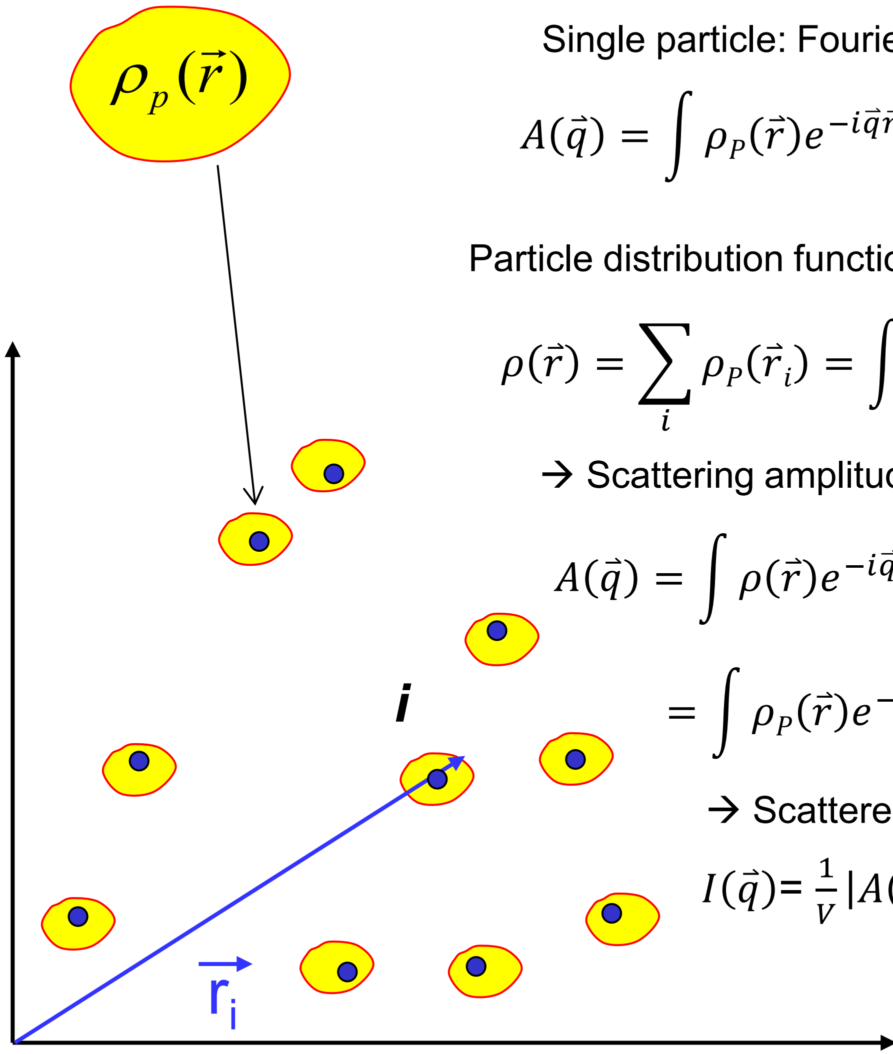
Scattering Amplitude

- Interference in far field



- Phase difference: $\Delta\varphi_i = \left(\vec{k_f} - \vec{k_i}\right) \cdot \vec{r}_i = \vec{q} \cdot \vec{r}_i$
- Scattering amplitude: $A(\vec{q}) = \int \rho(\vec{r}) e^{-i\vec{q}\vec{r}} dV = \int \rho(\vec{r}) e^{-i\vec{q}\vec{r}} d^3\vec{r}$
- Intensity: $I\left(\vec{q}\right) = \frac{1}{V} \left| A\left(\vec{q}\right) \right|^2$

Form factor and structure factor: Fourier transform



Single particle: Fourier transformation

$$A(\vec{q}) = \int \rho_P(\vec{r}) e^{-i\vec{q}\vec{r}} dV = \int \rho_P(\vec{r}) e^{-i\vec{q}\vec{r}} d^3\vec{r}$$

Particle distribution function G(**r**) → Electron density distribution

$$\rho(\vec{r}) = \sum_i \rho_P(\vec{r}_i) = \int \rho_P(\vec{r}\,') G(\vec{r} - \vec{r}\,') d^3r' = \rho_P(\vec{r}) * G(\vec{r})$$

→ Scattering amplitudes of the whole arrangement

$$A(\vec{q}) = \int \rho(\vec{r}) e^{-i\vec{q}\vec{r}} dV = \int [\rho_P(\vec{r}) * G(\vec{r})\,] e^{-i\vec{q}\vec{r}} d^3\vec{r}$$

$$= \int \rho_P(\vec{r}) e^{-i\vec{q}\vec{r}} dV \cdot \int G(\vec{r}) e^{-i\vec{q}\vec{r}} dV$$

→ Scattered Intensity

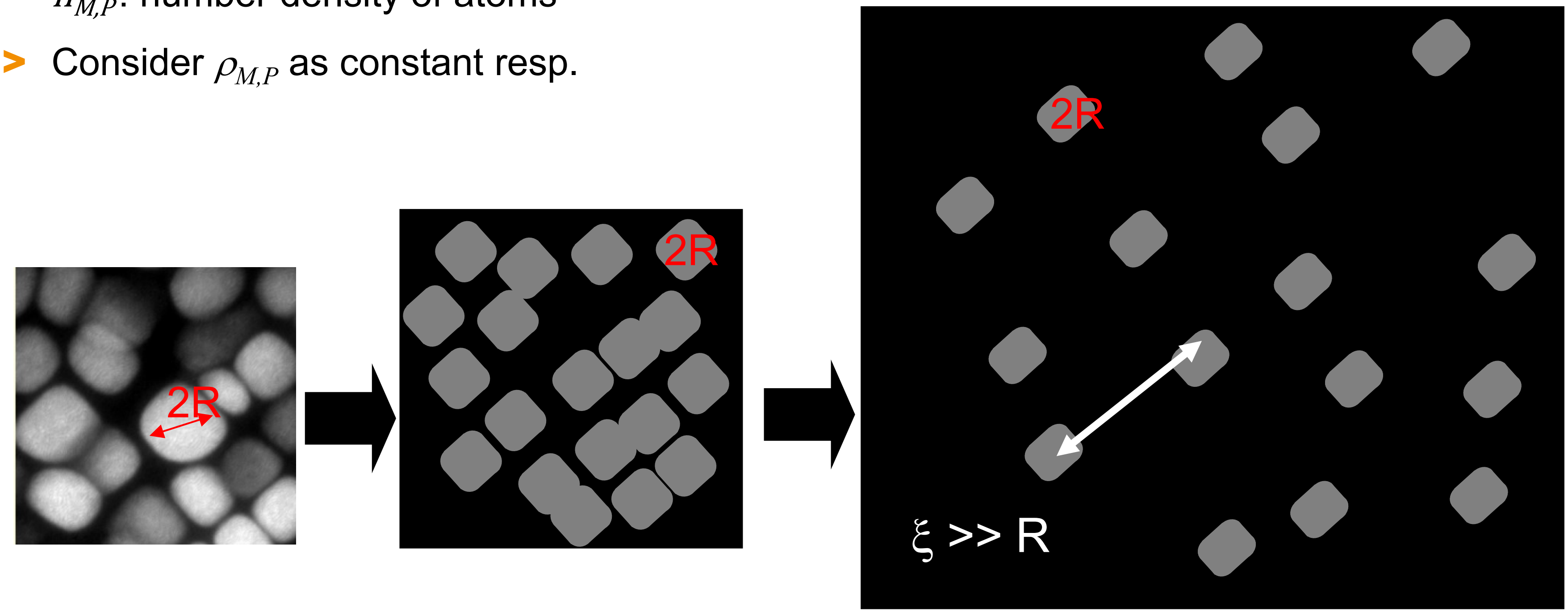
$$I(\vec{q}) = \frac{1}{V} |A(\vec{q})|^2 = P(\vec{q}) S(\vec{q})$$

Form factor Structure factor

Two phase Model: Dilute systems

- Only form of particle relevant
- Matrix M, volume fraction Φ
  Particles P, volume fraction (1-Φ)
  Electron density: $\rho_{M,P}=n_{M,P}*f_{M,P}$
  $f_{M,P}$: atomic form factor („extension of the electron cloud“, resonances)
  $n_{M,P}$: number density of atoms
- Consider $\rho_{M,P}$ as constant resp.

ASAX



Two phase Model

- Scattering amplitude:

$A(\vec{q}) = \int \rho(\vec{r}) e^{-i\vec{q}\vec{r}} d^3\vec{r} = \int_{\Phi V} \rho_M(\vec{r}) e^{-i\vec{q}\vec{r}} d^3\vec{r} + \int_{(1-\Phi)V} \rho_P(\vec{r}) e^{-i\vec{q}\vec{r}} d^3\vec{r}$

$$A(\vec{q}) = (\rho_M - \rho_P) \int_{\Phi V} e^{-i\vec{q}\vec{r}} d^3\vec{r}$$

$A(\vec{q}) = \Delta\rho \int_{\Phi V} e^{-i\vec{q}\vec{r}} d^3\vec{r}$

- $I(\vec{q}) = \frac{1}{V} |A(\vec{q})|^2 \sim \Delta\rho^2$

- Porod Invariant Q (Porod, 1982):
  $Q = \int I(\vec{q}) d^3\vec{q} = 4\pi\Phi(1-\Phi)\Delta\rho^2$

- Only dependent on density contrast $\Delta\rho$

Ableiten!
Mittelung <..> erklären S.25, S.51

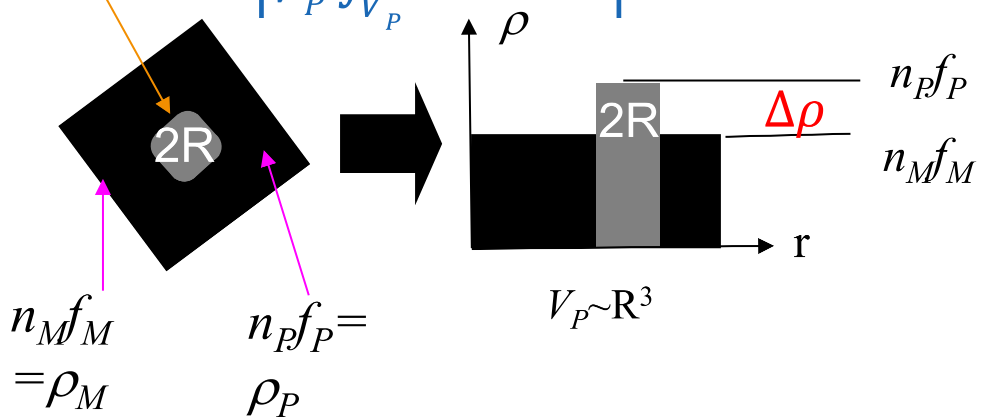
Herleitung Porod-Invariante

- Siehe Handzettel und Übung
- Q-Berechnung Übung

Two phase Model – single particle approximation

- Amplitude: $A(\vec{q}) = \Delta\rho \int_{\Phi V} e^{-i\vec{q}\vec{r}} d^3\vec{r}$
- Intensity: $I(\vec{q}) = \frac{1}{V} |A(\vec{q})|^2$
- Closer look at $I(q)$ for dilute systems: N_P independent scatterers
- Incoherent sum of intensities:

$$I(\vec{q}) \sim NP\ V_P{}^2\ \Delta\rho^2 \left| \frac{1}{V_P} \int_{V_P} e^{-i\vec{q}\vec{r}}\, d^3r \right|^2$$



Two phase Model – single particle approximation

- Amplitude: $A(\vec{q}) = \Delta\rho \int_{\Phi V} e^{-i\vec{q}\vec{r}} d^3\vec{r}$
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- Closer look at $I(q)$ for dilute systems: N_P independent scatterers
- Incoherent sum of intensities:

$$I_m(\vec{q}) \sim NP\ V_P{}^2\ \Delta\rho^2 \left| \frac{1}{V_P} \int_{V_P} e^{-i\vec{q}\vec{r}}\, d^3r \right|^2$$

$$P(q) = \left| 3\,\frac{\sin(qR) - qR\cos(qR)}{(qR)^3} \right|^2$$

- Form factor of a **sphere of radius *R***
- Isotropic scattering

Colloid: homogeneous sphere of radius R

A simple, but important calculation:

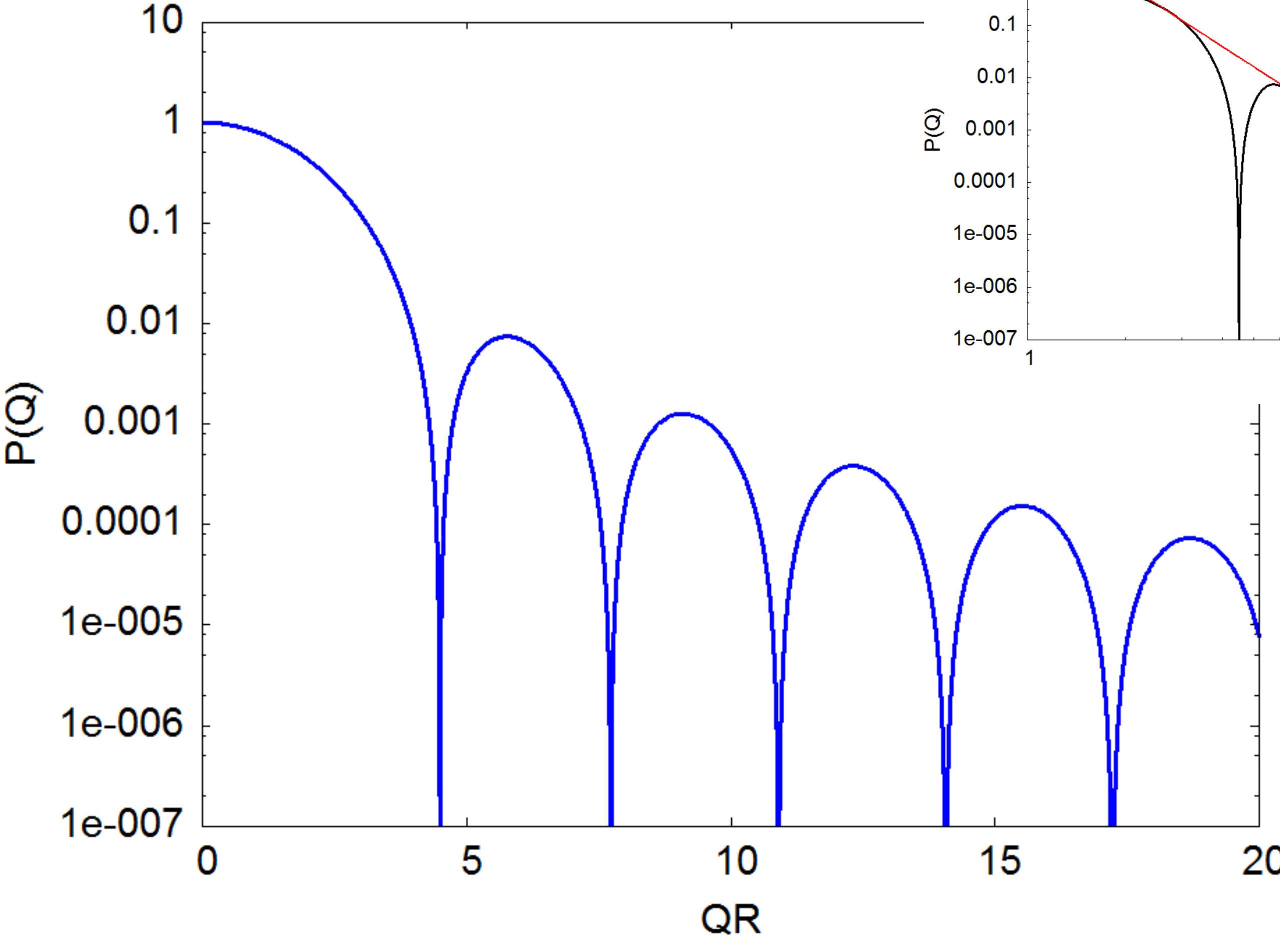
$$F(\vec{q}) = \int_{V=particleVolume} \rho(\vec{r}) \cdot e^{-i\vec{q}\vec{r}} \cdot d^3r = \int_0^R \int_0^{2\pi} \int_0^{\pi} \rho_0 \cdot e^{-i\vec{q}\vec{r}} r^2 \sin(\theta) d\theta d\varphi dr$$

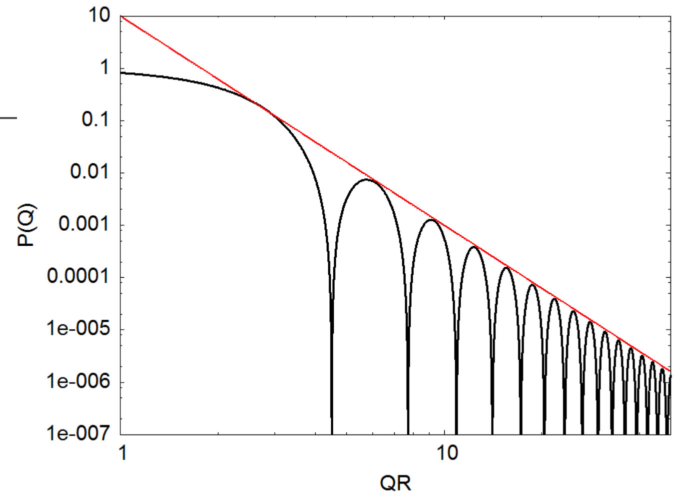
$$F(\vec{q}) = \rho_0 2\pi \int_0^R \int_0^{\pi} e^{-iqr\cos(\theta)} r^2 \sin(\theta) d\theta d\varphi dr = \rho_0 2\pi \int_0^R \frac{e^{iqr} - e^{-iqr}}{qr} r^2 \sin(\theta) dr$$

$$F(\vec{q}) = \rho_0 2\pi \cdot \frac{2}{q} \int_0^R \sin(qr) r \; dr = \frac{4\pi\rho_0}{q} \left[- \frac{r\cos(qr)}{q} \Bigg|_0^R + \int_0^R \frac{\cos(qr)}{q} dr \right]$$

$$F(\vec{q}) = \frac{4\pi\rho_0}{q} \left[- \frac{R\cos(qR)}{q} + \frac{\sin(qR)}{q^2} \right] = 4\pi R^3 \rho_0 \frac{\left(\sin(qR) - qR\cos(qR)\right)}{(qR)^3}$$

Colloid:homogeneous sphere of radius R





Guinier radius

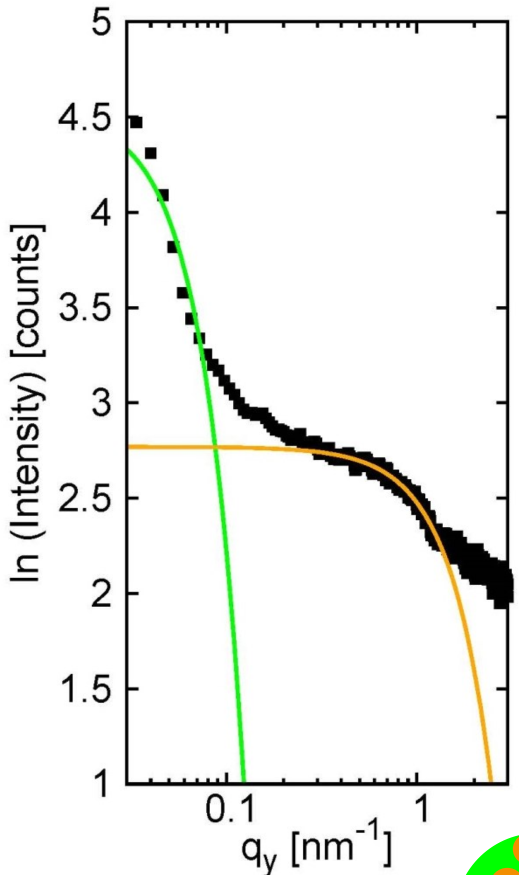
- $Q \rightarrow 0$
- Homogenous sphere of radius R

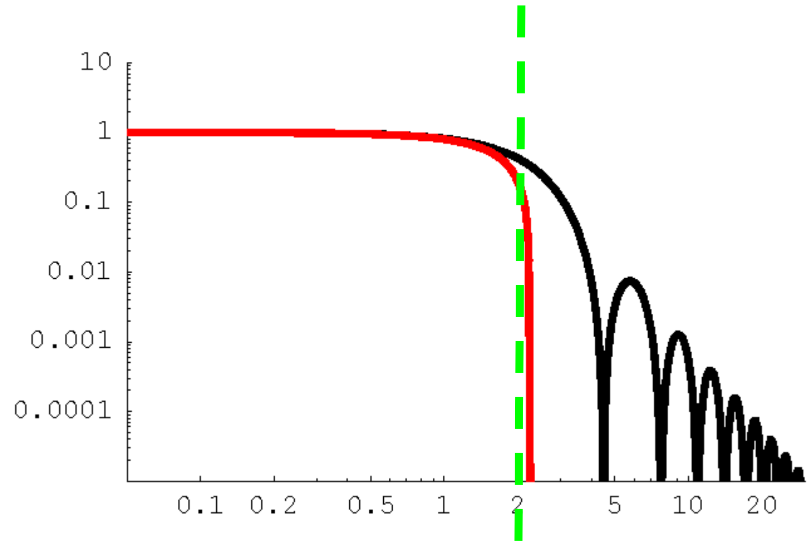
$$P(q) = \left|3\frac{\sin(qR) - qRcos(qR)}{(qR)^3}\right|^2 \sim 1 - \frac{1}{5}q^2R^2 \sim \exp(-\frac{1}{5}q^2R^2)$$

Ableiten

- Radius of gyration:
  replace homogenous sphere by shell of same moment of intertia: R_g
- $R_g = \sqrt{3/_5}\,R$
- $P(q) \sim \exp(-\frac{1}{3}q^2{R_g}^2)$ general form of Guinier law [Guinier (1955)]
- Independent of particle form

Guinier Approximation





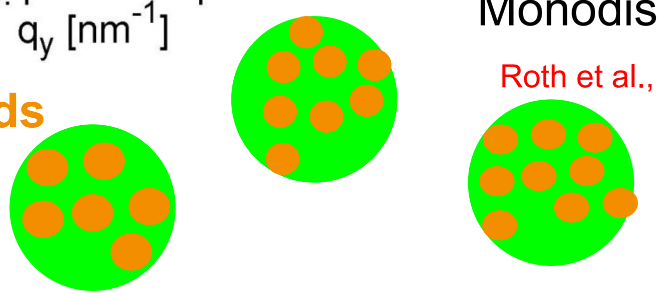
$$\lim_{q \to 0} I(q) = \Delta\rho^2 \cdot V^2 \cdot \exp(-q^2 \cdot \frac{R_g^2}{3})$$

Radius of Gyration R_g

Monodisperse spheres of radius R: $R_g = \sqrt{3/5} \cdot R$

Roth et al., Appl. Phys. Lett. **91**, 091915 (2007)

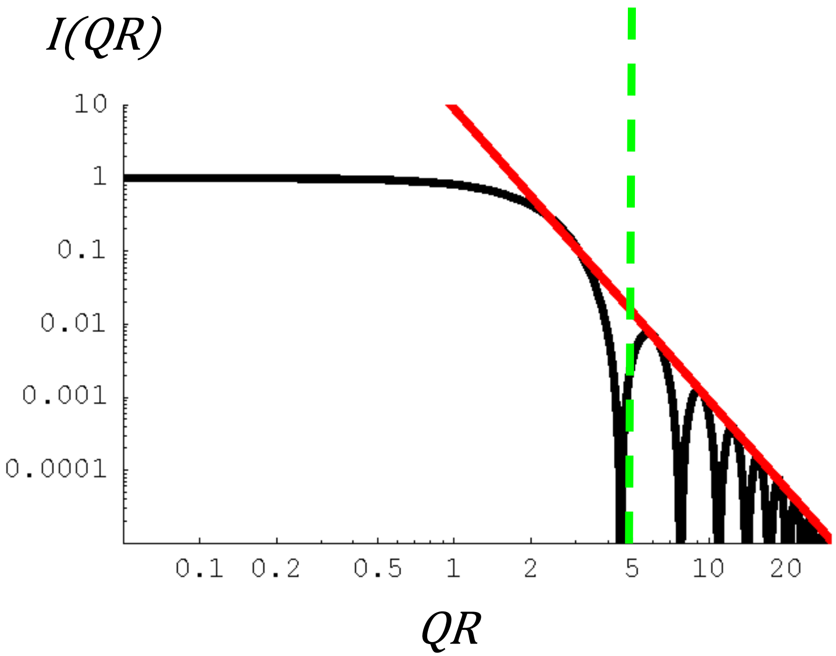
2nm Colloids
domains



Porod´s law: large q

Scattered intensity: $\sim \left| 4\pi R^3 \rho_0 \frac{(\sin(qR) - qR\cos(qR))}{(qR)^3} \right|^2$

Look at maxima of form factor



$$\sim \left| 4\pi \rho_0 \frac{(\sin(qR) - qR\cos(qR))}{(qR)^3} \right|^2$$

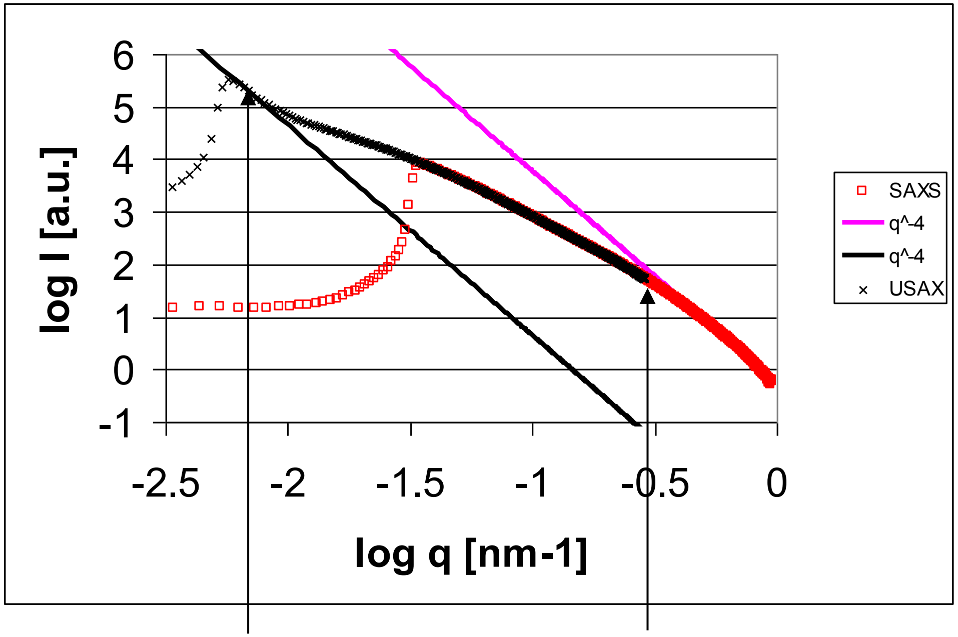
$$\leq \left(4\pi \rho_0 \frac{|\sin(qR)| + qR|\cos(qR)|}{(qR)^3} \right)^2$$

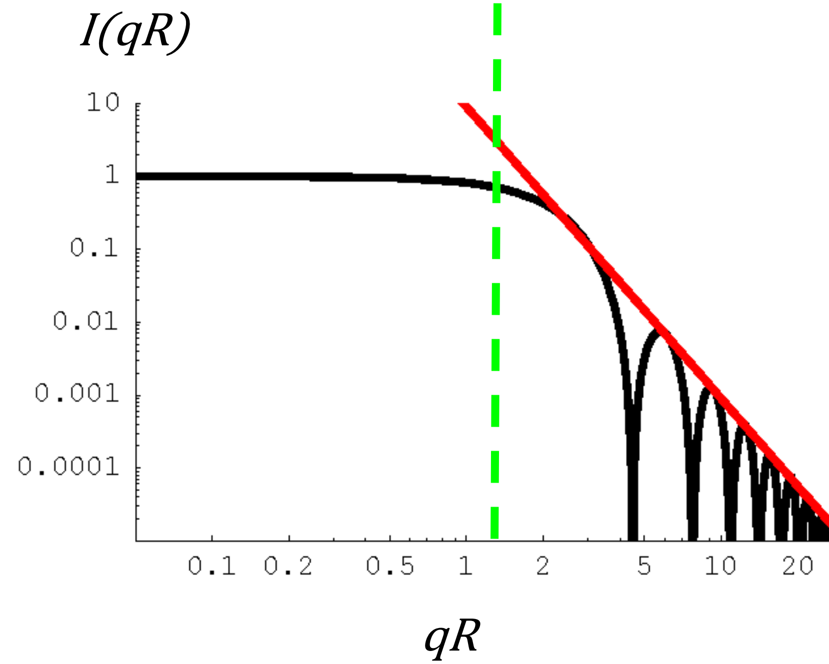
$$\sim \left(4\pi \rho_0 \frac{1 + qR}{(qR)^3} \right)^2 \sim \left(4\pi \rho_0 \frac{qR}{(qR)^3} \right)^2$$

$$\sim \frac{1}{(q)^4} \frac{R^2}{R^6} \sim \frac{S}{V_P{}^2} q^{-4}$$

Surface of sphere

Porod´s Law





R>1µm *R*~18nm

$$P(qR > 4.5) = 2\pi\left(\frac{S}{V_P{}^2}\right)q^{-4}$$

- Depends only on Surface and particle Volume
- No shape dependance

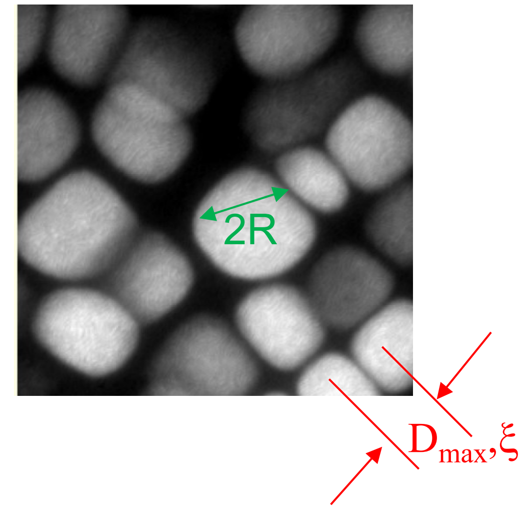
The structure factor – many particle, close distance

- Real systems: not dilute, many particles…
- Generalisation of Bragg's Law in crystallography:
  $I(q) = c\,P(q)\,S(q)$

Form factor ($P(q)$)

Structure factor ($S(q)$)

Interference due to assembly of particles



- Periodic ordering with periodicity d,ξ in the electron density :
- $I(q)$ shows a corresponding maximum at $q=2\pi/(D_{max}, \xi)$

$$S(q) \propto \frac{1 - \exp(-2\sigma_D^2 q^2)}{1 - 2\exp(-\sigma_D^2 q^2)\cos(qD_{max}) + \exp(-2\sigma_D^2 q^2)}$$

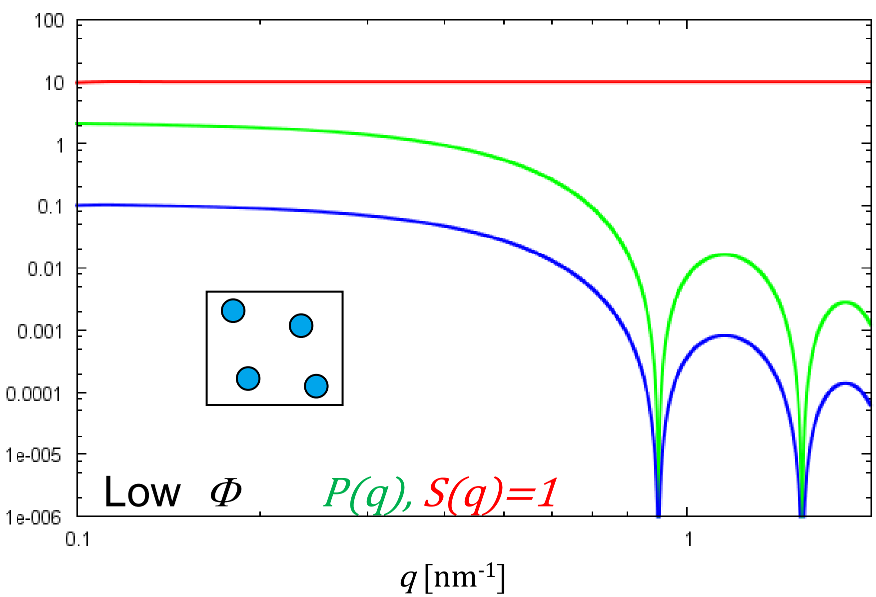
Smearing (σ_D)

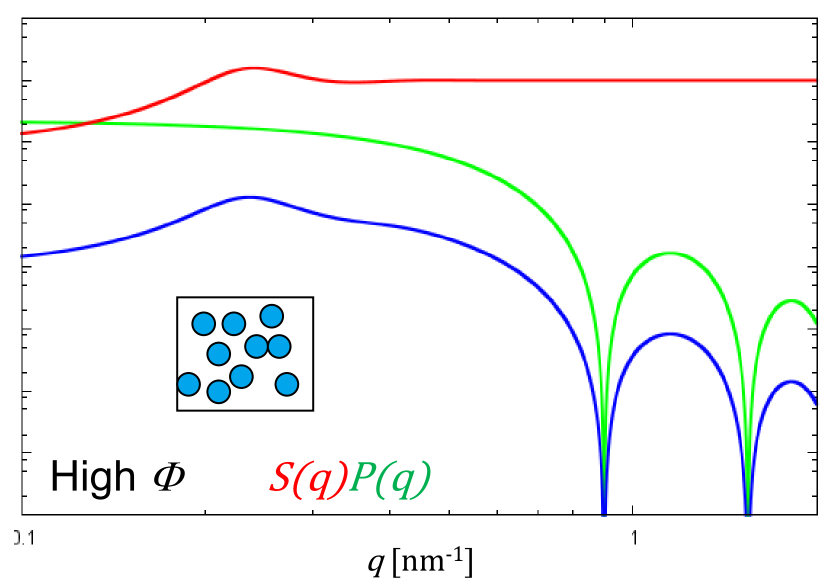
Distance of particles (D_{max})

Lode (1998)
Roth et al., J. Appl. Cryst. **36**, 684 (2003)

The Structure factor – many particle, close distance

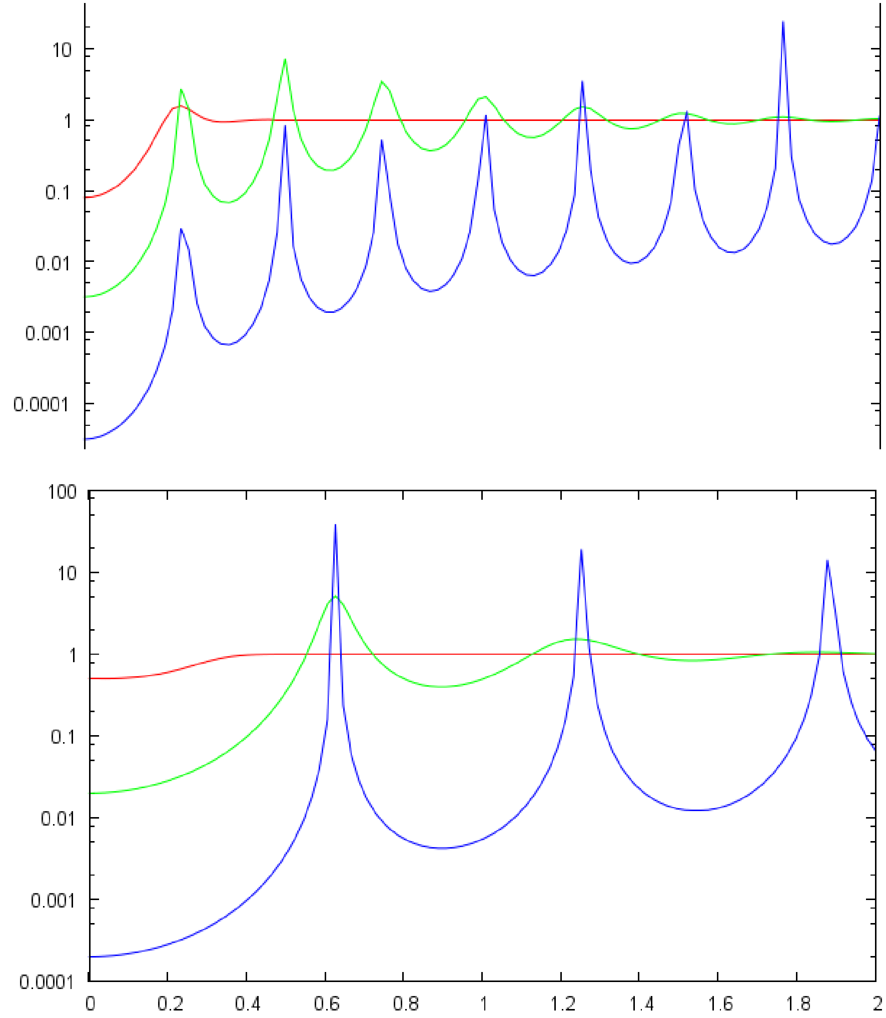
- Real systems: not dilute, many particles…
- Generalisation of Bragg's Law in crystallography:
  $I(q) = c\,P(q)\,S(q)$
- Examples: R=5nm, D_{max}=100nm, 25nm, $\sigma D/D_{max}$=25%





Structure factor and form factor

- D_{max}=25nm
  D_{max}=10nm
- σ_D= 5nm, 1nm, 0.1nm
- $S(q) \rightarrow 1 \quad q \rightarrow \infty$
  well separated particles



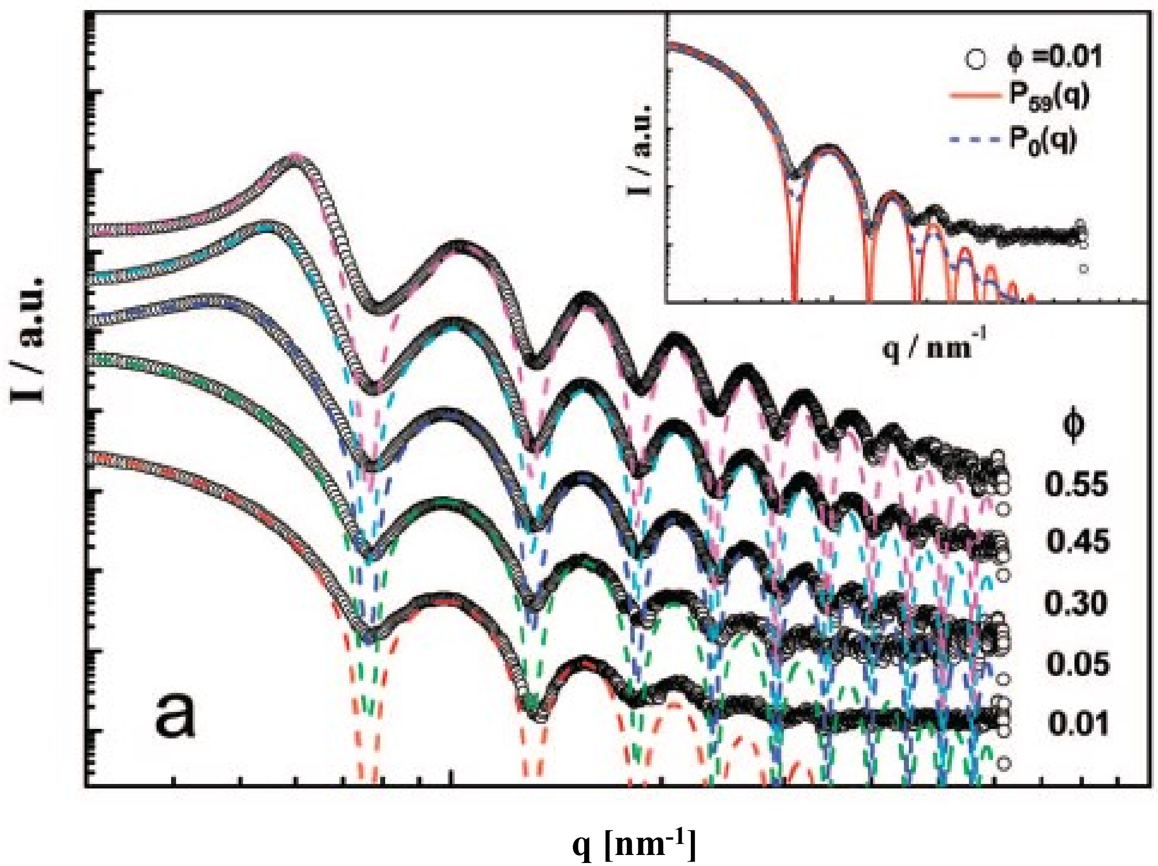
Colloidal System

> Latex spheres in water

$I(q) = c\,P(q)\,S(q)$

Low Φ — $P(q)$, $S(q)=1$

High Φ — $S(q)P(q)$



> Gaussian distribution of particle sizes

> Shift in maximum: Decreasing distance

Hu et al., Macromolecules, 41, 5073 (2008)