Vorlesung zum Haupt/Masterstudiengang Physik

Methoden Moderner Röntgenphysik II: Struktur und Dynamik Kondensierter Materie

Surfaces	(OHS)
Applications in Soft Matter	(MMAK / SVR)

Mottakin M. Abul Kashem / Stephan V. Roth (SVR)

Applications in Soft Matter

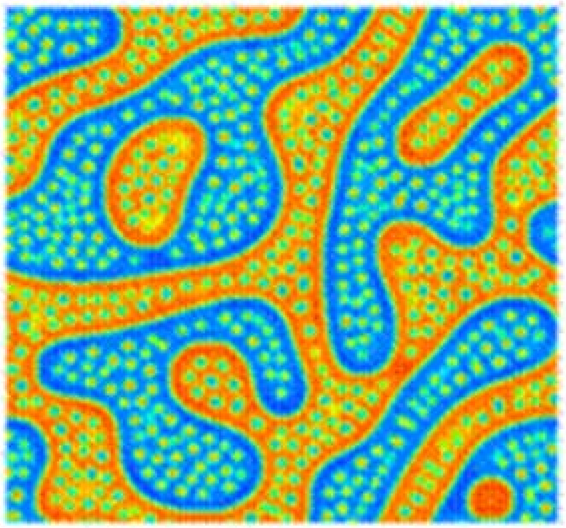
20.04.2010 An Introduction to Polymer Physics

22.04.2010 Small-Angle X-ray Scattering and its Applications

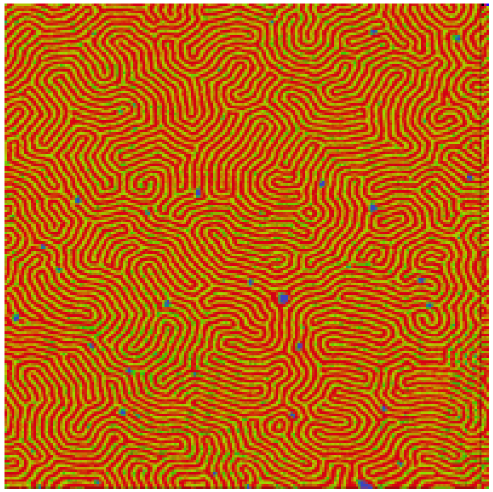
27.04.2010 Polymer, Colloidal and Nanocomposite Surfaces I

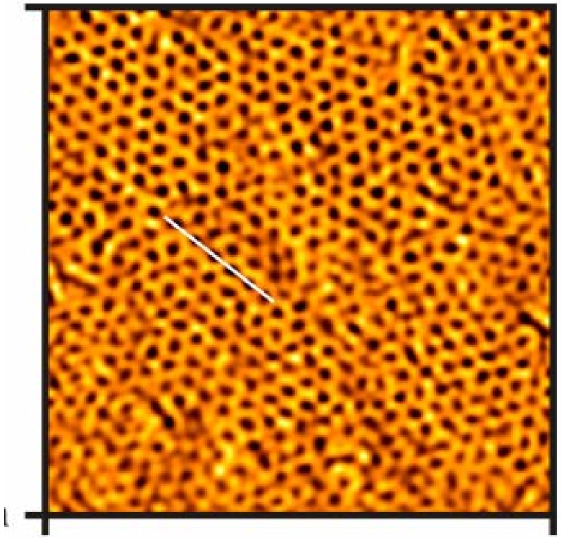
29.04.2010 Polymer, Colloidal and Nanocomposite Surfaces II

Summary last lecture



A blend of PS/PB





P(S-b-MMA)

Questions?

Small-angle X-ray scattering

- Introduction – Theory of SAXS
- Form factor
- Approximations
- Structure factor
- Beamlines
  - USAXS
  - Microfocus & nanofocus x-ray beams
- Application to polymer systems
  - Thick colloidal films
  - Deformation
  - Cracks & crazes
  - Tomography (3D-reconstruction)

Following [Lindner] and R. Gehrke, „SAXS“, Summer student lectures 2008

Small-angle X-ray scattering

A Note in advance

There are many formulas and derivations inside this lecture!

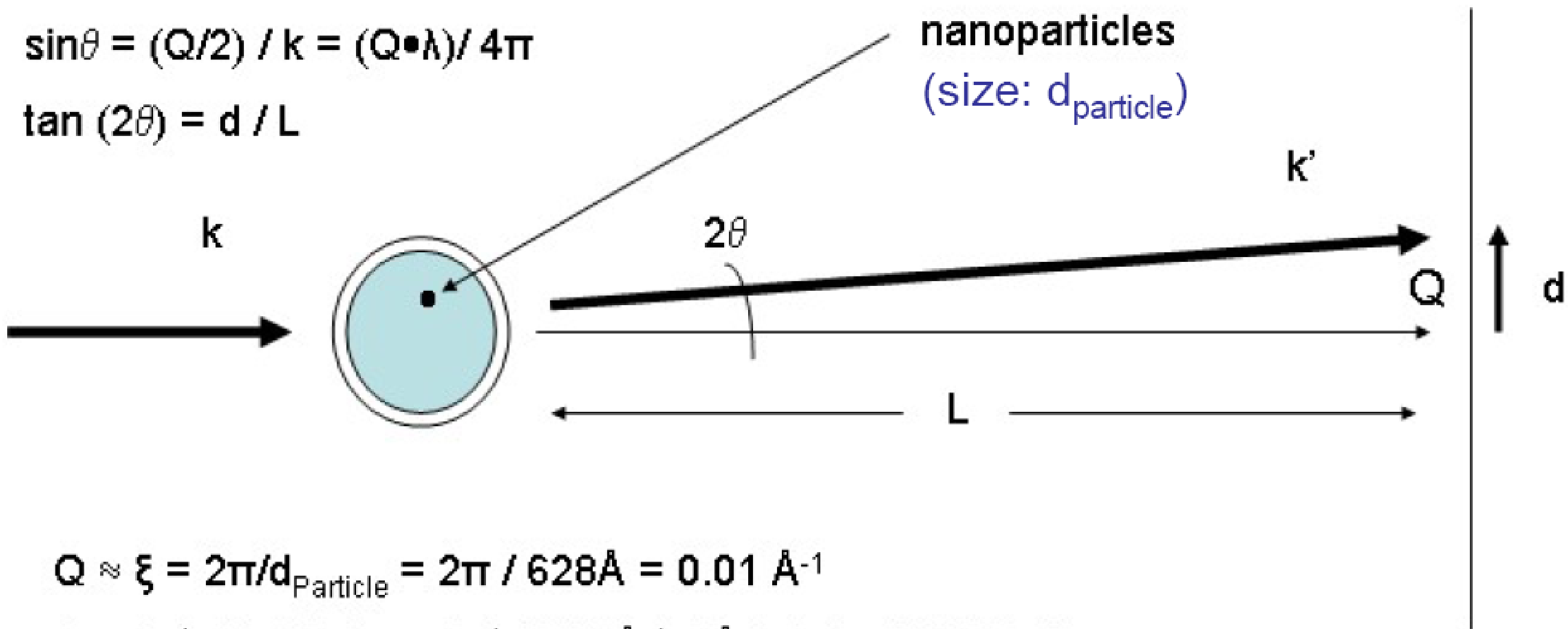
Our aim is NOT to follow in every detail the derivations etc., but more to explain the significance and practical application of these formulas!

SAXS – rep. from lecture GG

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

Scattering geometry

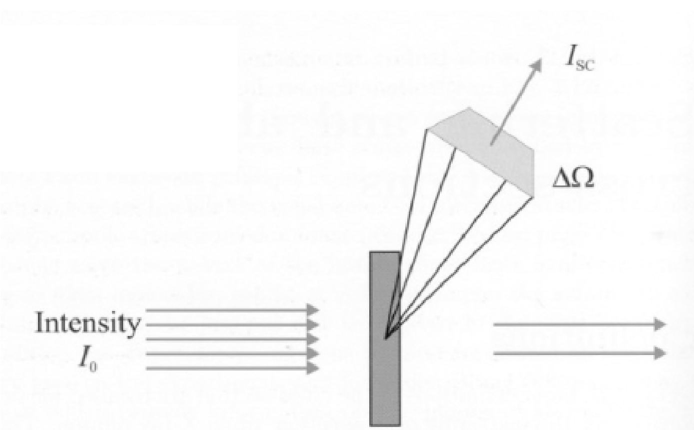
$I_{scattered} = Io\ N\ \Delta\Omega\ (d\sigma/d\Omega)$

Io: incident intensity

N: number objects

$\Delta\Omega$: solid angle

$(d\sigma/d\Omega)$: differential cross section



$(d\sigma/d\Omega)/V = r_o^2\ n\ (\rho_p-\rho_s)^2\ v^2\ F(Q)\ S(Q)$

n: volume fraction
ρ: electron density
v: particle volume

F(Q) formfactor

$F(Q) = \int d^3r\ \exp(i\mathbf{qr})\ \rho(\mathbf{r})$

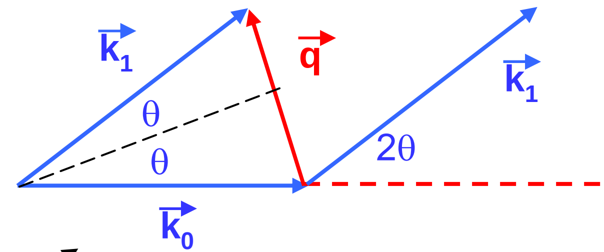
Important approximations for Form factor

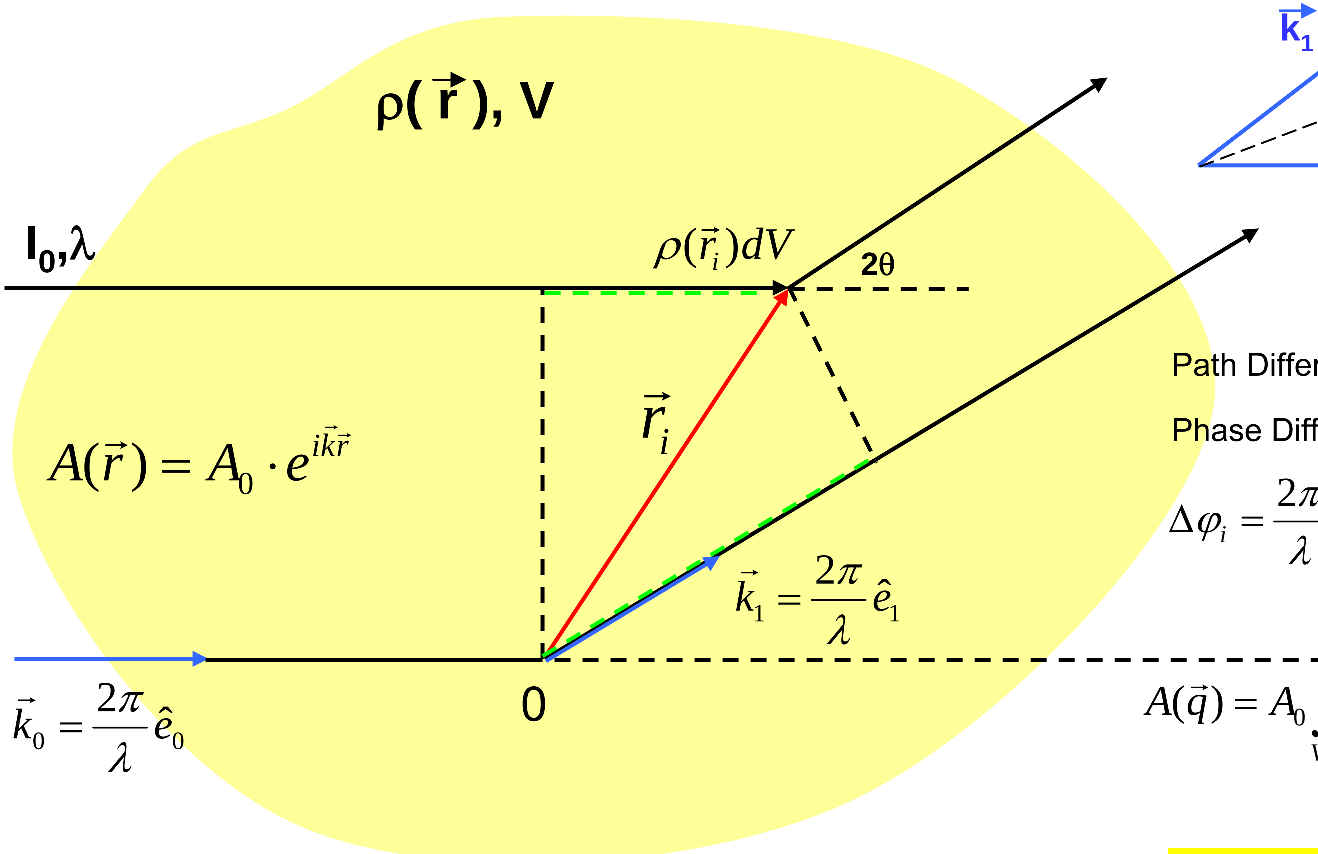
We will derive them, as they are frequently used:

-Guinier approximation

-Porod approximation

Single particle scattering, dilute Systems





Path Difference: $\Delta d = \hat{e}_1 \cdot \vec{r}_i - \hat{e}_0 \cdot \vec{r}_i$

Phase Difference:

$$\Delta\varphi_i = \frac{2\pi}{\lambda}(\hat{e}_1 - \hat{e}_0)\cdot\vec{r}_i = (\vec{k}_1 - \vec{k}_0)\cdot\vec{r}_i \equiv \vec{q}\cdot\vec{r}_i$$

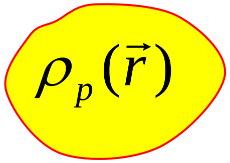
$$A(\vec{q}) = A_0 \int_V \rho(\vec{r}) \cdot e^{-i\vec{q}\vec{r}} \cdot d^3 r \equiv F\{\rho(\vec{r})\}$$

$$I(\vec{q}) = |A(\vec{q})|^2$$

$$|\vec{q}| = \frac{4\pi}{\lambda}\cdot\sin(\theta) \approx \frac{4\pi}{\lambda}\cdot\theta$$

Form factor and structure factor

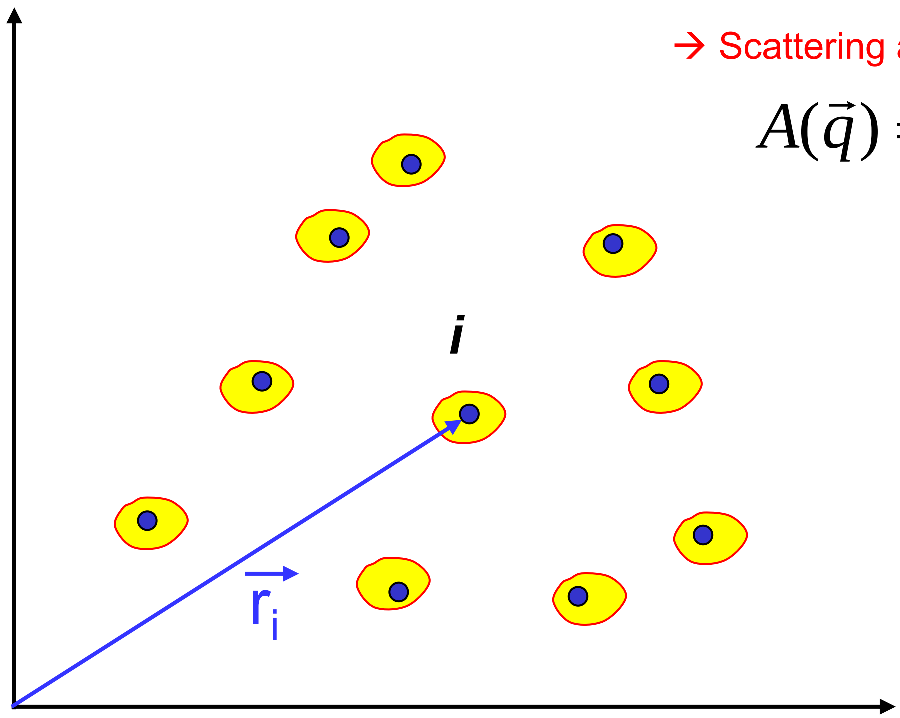
Single particle



$$A(\vec{q}) = A_0 \int_V \rho(\vec{r}) \cdot e^{i\vec{q}\vec{r}} \cdot d^3r = F\{\rho(\vec{r})\} \equiv F(\vec{q})$$

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

$$\rho(\vec{r}) = \sum_i \rho_p(\vec{r}_i) = \int \rho_p(\vec{r}) \cdot P(\vec{r} - \vec{r}\,') \cdot d^3r' \equiv \rho_p(\vec{r}) * P(\vec{r})$$



→ Scattering amplitudes of the whole arrangement

$$\begin{aligned} A(\vec{q}) &= F\{\rho(\vec{r})\} \\ &= F\{\rho_p(\vec{r}) * P(\vec{r})\} \\ &= F\{\rho_p(\vec{r})\} \cdot F\{P(\vec{r})\} \equiv F(\vec{q}) \cdot S(\vec{q}) \end{aligned}$$

→ Scattered Intensity

$$I(\vec{q}) = |A(\vec{q})|^2 = |F(\vec{q})|^2 \cdot |S(\vec{q})|^2$$

Formfactor Structurefactor

Now let's take a closer look into F(q)

Single Particle Scattering in Dilute Systems

$\boxed{I_s = N\langle|F(\mathbf{q})|^2\rangle}$ with $F(\vec{q}) = \int_{V=particleVolume} \rho(\vec{r}) \cdot e^{-i\vec{q}\vec{r}} \cdot d^3r$

Incoherent superposition of single particle scattering (S=1)

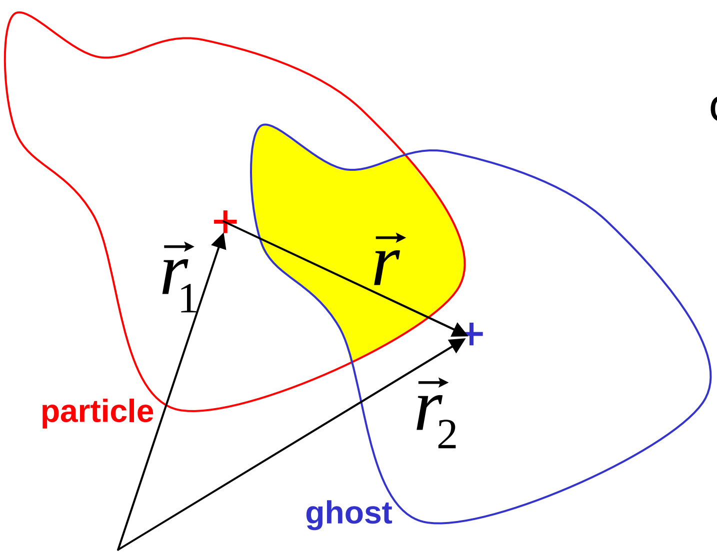
$$\left|F(\vec{q})\right|^2 = F(\vec{q}) \cdot F^*(\vec{q}) = \iint_V \rho(\vec{r}_1)\rho(\vec{r}_2)e^{-i\vec{q}(\vec{r}_1-\vec{r}_2)}d\vec{r}_1 d\vec{r}_2$$

substitute $\mathbf{r}_1 - \mathbf{r}_2 = \mathbf{r}$

$$= \iint \underbrace{\rho(\vec{r}_1 - \vec{r}\,)\rho(\vec{r}_1)d\vec{r}_1}e^{-i\vec{q}\vec{r}}\, d\vec{r}$$

$$\gamma(\vec{r}) \equiv \int_V \rho(\vec{r}_1)\rho(\vec{r}_1 - \vec{r}\,)d\vec{r}_1$$

convolution square of the density distribution



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

$$= \int \gamma(\vec{r})e^{-iqr\cos(\theta)}r^2\sin(\theta)d\theta d\varphi dr$$

$$= \int \gamma(r)\frac{e^{iqr} - e^{-iqr}}{iqr}r^2 dr \cdot 2\pi$$

$$2\frac{\sin(qr)}{qr}$$

Colloid: homogeneous sphere of radius R

A simple, but important calculation:

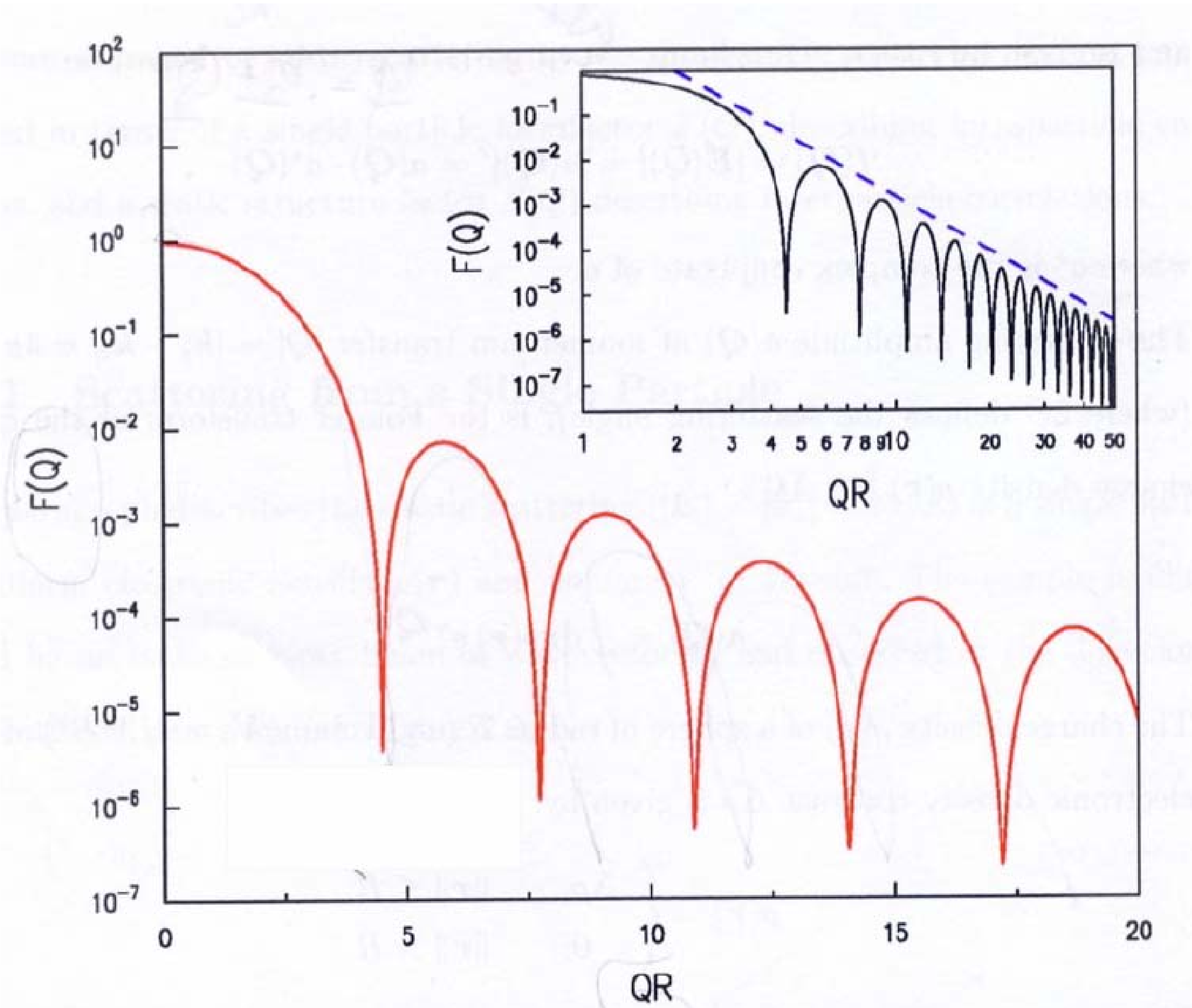
$$F(\vec{q}) = \int_{V=particleVolume} \rho(\vec{r}) \cdot e^{-i\vec{q}\vec{r}} \cdot d^3r = \int_0^R \int_0^{2\pi} \int_0^{\pi} \rho_0 \cdot e^{-i\vec{q}\vec{r}} r^2 \sin(\theta) d\theta d\varphi dr$$

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

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

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

Colloid: homogeneous sphere of radius R



See lecture 4 of GG

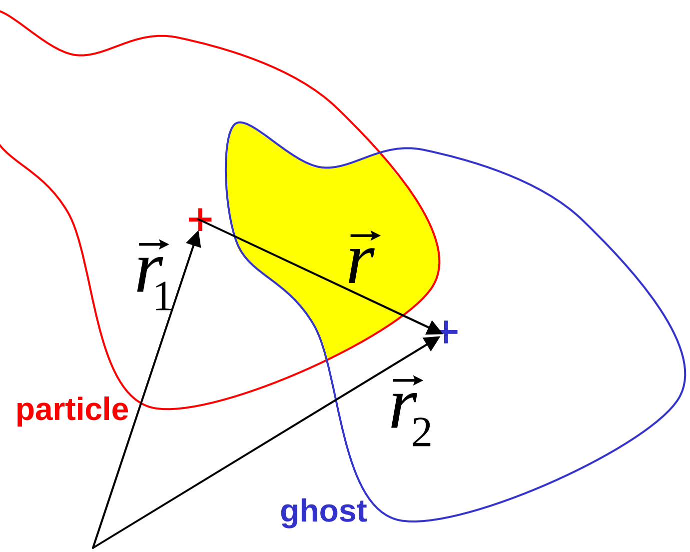
Single Particle Scattering in Dilute Systems

For homogeneous particles $\gamma(\mathbf{r})$ is just the overlapping volume

Average over all directions for a given $r = |\mathbf{r}|$

$$I(q) = \left\langle \left| F(\vec{q}) \right|^2 \right\rangle = 4\pi \int_0^\infty \gamma(r) \cdot r^2 \cdot \frac{\sin(qr)}{qr} \cdot dr$$

$\gamma(r) \cdot r^2 \equiv p(r) \equiv$ Pair Distance Distribution Function



Guinier-Approximation

Two derivations:
1) From the formulas
2) For polymer systems

$$I(q) = \left\langle \left| F(\vec{q}) \right|^2 \right\rangle = 4\pi \int_0^\infty \gamma(r) \cdot r^2 \cdot \frac{\sin(qr)}{qr} \cdot dr \qquad q \to 0$$

Forward scattering

We use: $$\frac{\sin(qr)}{qr} = \frac{qr - \frac{1}{6}(qr)^3 + \ldots}{qr} = 1 - \frac{1}{6}(qr)^2 + O\left((qr)^4\right)$$

Taylor series expansion for qr→0 or q << 1/r !

$$I(q) \approx 4\pi \int_0^\infty \gamma(r) \cdot r^2 \cdot \left(1 - \frac{1}{6}(qr)^2\right) \cdot dr = 4\pi \left(\int_0^\infty \gamma(r) \cdot r^2 dr - \int_0^\infty \gamma(r) \cdot r^2 \frac{1}{6}(qr)^2 dr \right)$$

$$I(q) = 4\pi \int_0^\infty \gamma(r) \cdot r^2 dr - 4\pi \frac{1}{3} q^2 \int_0^\infty \gamma(r) \cdot r^2 \frac{1}{2} r^2 dr = 4\pi \int_0^\infty \gamma(r) \cdot r^2 dr \cdot \left(1 - \frac{q^2 {R_G}^2}{3}\right)$$

I(q=0)

$$R_G^2 \equiv \frac{1}{2} \int_0^\infty \gamma(r) r^4 dr \Big/ \int_0^\infty \gamma(r) r^2 dr$$

$$I(q) = I(0) \cdot \left(1 - \frac{q^2 {R_G}^2}{3}\right) \approx I(0) \cdot e^{-\frac{q^2 {R_G}^2}{3}}$$

Radius of Gyration

$$R_G = \sqrt{\frac{1}{M} \sum_1^N \left\langle m_i \vec{r}_i^{\,2} \right\rangle}$$

Guinier-Approximation – for polymer systems

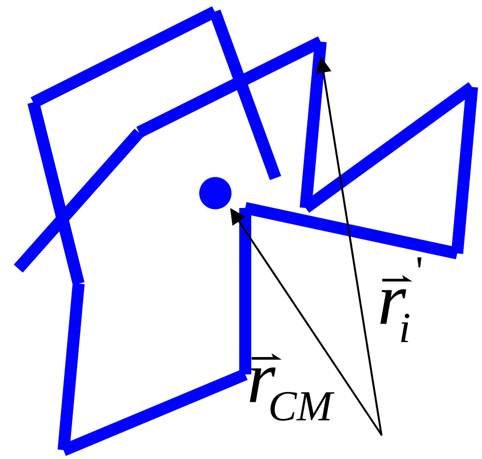
$$R_G = \sqrt{\frac{1}{M}\sum_1^N \left\langle m_i \vec{r}_i^{\,2} \right\rangle}$$

Say M=N M$_0$ $\quad R_G^{\,2} = \frac{1}{N}\sum_1^N \left\langle \vec{r}_i^{\,2} \right\rangle = \frac{1}{N}\sum_1^N \left\langle \left(\vec{r}\,'_i - \vec{r}_{CM}\right)^2 \right\rangle$

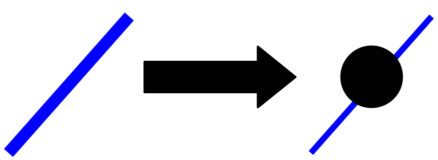
$$\vec{r}_{CM} = \frac{1}{N}\sum_1^N \left\langle \vec{r}_i \right\rangle \Rightarrow R_G^{\,2} = \frac{1}{N}\sum_{i=1}^N \left\langle \left(\vec{r}\,'_i - \sum_{j=0}^{N} \vec{r}\,'_j \right)^2 \right\rangle$$

$$\Rightarrow R_G^{\,2} = \frac{1}{2N^2}\sum_{j,i=1}^N \underbrace{\left\langle \left(\vec{r}\,'_i - \vec{r}\,'_j\right)^2 \right\rangle}_{|j-i|a^2}$$

a~mean length



Point-like colloid=segment, δ-scatterers, N segments



$$\left\langle \left|F(\vec{q})\right|^2 \right\rangle = \iint_V \rho(\vec{r}_1)\rho(\vec{r}_2)e^{-i\vec{q}(\vec{r}_1-\vec{r}_2)}d\vec{r}_1 d\vec{r}_2$$

Replace integral by discrete sum: $\left\langle \left|F(\vec{q})\right|^2 \right\rangle = \frac{1}{N}\sum_{j,k=1}^{N} \left\langle e^{-i\vec{q}(\vec{r}_j-\vec{r}_k)} \right\rangle$

Guinier-Approximation – for polymer systems

$$\left\langle \left|F(\vec{q})\right|^2 \right\rangle = \frac{1}{N}\sum_{j,k=1}^{N}\left\langle e^{-i\vec{q}(\vec{r}_j-\vec{r}_k)}\right\rangle \approx \frac{1}{N}\sum_{j,k=1}^{N}\left\langle\left(1-\underbrace{i\vec{q}(\vec{r}_j-\vec{r}_k)}_{\langle\ldots\rangle\to 0}-\frac{1}{2}\left|\vec{q}(\vec{r}_j-\vec{r}_k)\right|^2\right)\right\rangle$$

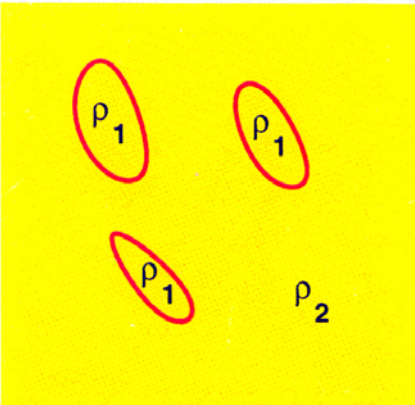
$$\left\langle \left|\vec{q}(\vec{r}_j-\vec{r}_k)\right|^2 \right\rangle = \left|q^2\right|\left\langle \underbrace{\left|\vec{r}_j-\vec{r}_k\right|^2}_{\text{Only r-dependence, no }\theta\text{-dependence}}\cos(\theta)^2\right\rangle = \frac{1}{3}q^2\left\langle\left|\vec{r}_j-\vec{r}_k\right|^2\right\rangle$$

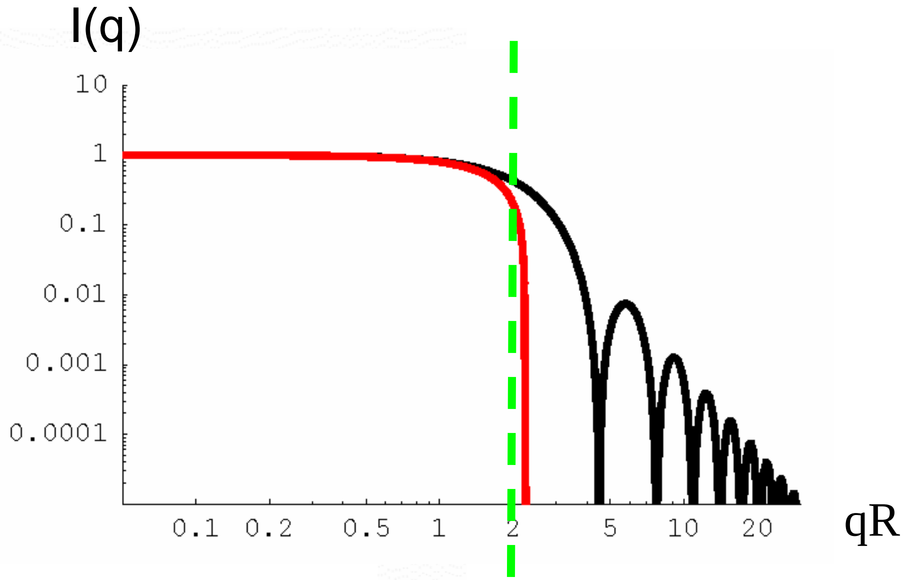
$$\left\langle \left|F(\vec{q})\right|^2 \right\rangle = \frac{1}{N}\sum_{j,k=1}^{N}\left(1-\frac{1}{6}q^2\left\langle\left|(\vec{r}_j-\vec{r}_k)\right|^2\right\rangle\right)$$

$$= \frac{1}{N}\left(N^2-\frac{1}{3}q^2\frac{1}{2}\sum_{j,k=1}^{N}\left\langle\left|(\vec{r}_j-\vec{r}_k)\right|^2\right\rangle\right)$$

$$\boxed{\left\langle \left|F(\vec{q})\right|^2 \right\rangle = \underbrace{\frac{1}{N}}_{I(q=0)}N^2\left(1-\frac{1}{3}q^2\underbrace{\frac{1}{2N^2}\sum_{j,k=1}^{N}\left\langle\left|(\vec{r}_j-\vec{r}_k)\right|^2\right\rangle}_{R_G^{\;2}}\right)}$$

Guinier approximation - spheres





$$I(q) = I(0) \cdot \exp\left(-\frac{1}{3} R_G^2 q^2\right)$$

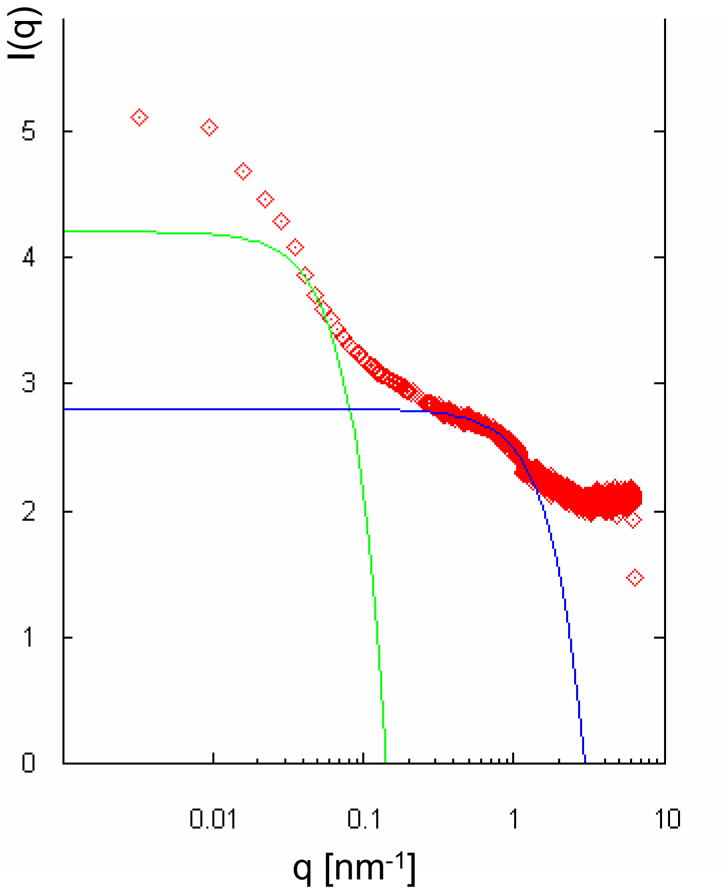
$$\ln(I) = \ln I(0) - \frac{1}{3} R_G^2 \cdot q^2$$

Radius of Gyration R_g

Monodisperse spheres of radius *R*:

$$R_g = \sqrt{3/5} \cdot R$$

Guinier Approximation

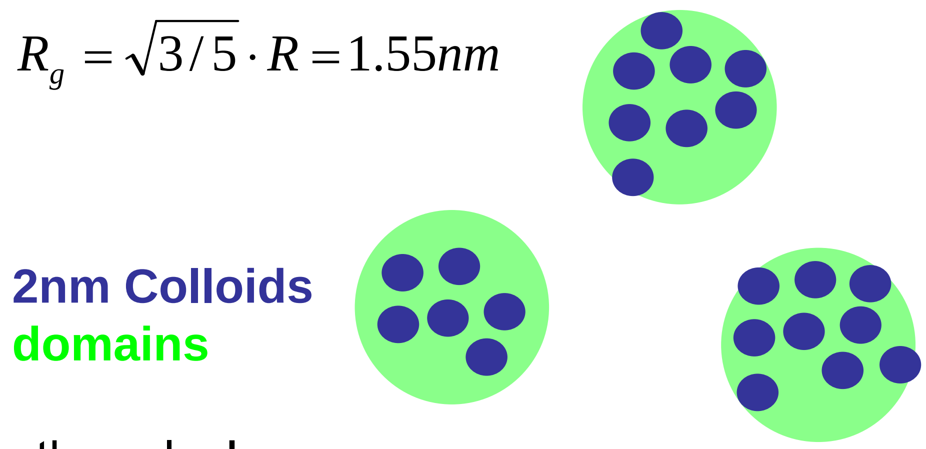


$$\lim_{q \to 0} I(q) = \Delta\rho^2 \cdot V^2 \cdot \exp(-q^2 \cdot \frac{R_g^2}{3})$$

Radius of Gyration R_g

Monodisperse spheres of radius R=2nm:

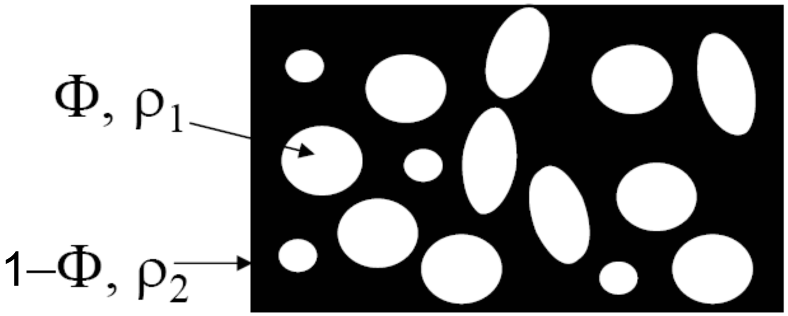
$$R_g = \sqrt{3/5} \cdot R = 1.55nm$$



Very useful to get a hand on length scales!
Sometimes only valid in limited q-range

Porod‘s Theorems - I:

Two-phase system



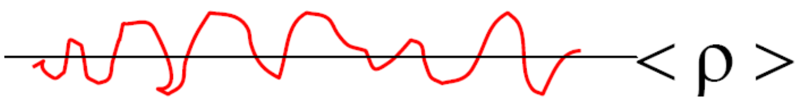
$\Delta\rho = \rho_1 - \rho_2 =$ contrast

$$F(\vec{q}) = \int_{\Phi V} \rho_1(\vec{r}) e^{-i\vec{q}\vec{r}} d^3r + \int_{(1-\Phi)V} \rho_2(\vec{r}) e^{-i\vec{q}\vec{r}} d^3r$$

$$F(\vec{q}) = \int_{\Phi V} (\rho_1 - \rho_2) e^{-i\vec{q}\vec{r}} d^3r + \rho_2 \int_V e^{-i\vec{q}\vec{r}} d^3r$$

$$F(\vec{q}) = \int_V \Delta\rho e^{-i\vec{q}\vec{r}} d^3r + \rho_2 \delta(\vec{q})$$

$$\eta(\vec{r}) = \rho(\vec{r}) - \langle \rho \rangle$$



$$\langle \eta^2 \rangle = \langle \rho^2 \rangle - \langle \rho \rangle^2$$

Only density fluctutation contribute to the measured signal at finite q:

$$I_m(\vec{q}) = I(\vec{q}) - \langle \rho \rangle^2 \delta(\vec{q})$$

$$Q \equiv \int I_m(\vec{q}) d^3q = (2\pi)^3 \langle \eta^2 \rangle$$

Isotropic:

$$Q = \int I(q) q^2 dq = 2\pi^2 \cdot \Phi \cdot (1 - \Phi) \cdot (\Delta\rho)^2$$

Q is called „invariant“ because it does not depend on the structure but only on volume fraction and contrast

Porod‘s Theorems - I: Derivation

Total intensity: $$\int I(\vec{q})d\vec{q} = \int \ d\vec{q}\int \gamma(\vec{r})e^{-i\vec{q}\vec{r}}d^3r = \int \gamma(\vec{r})\delta(\vec{r})d^3r = \gamma(0)$$

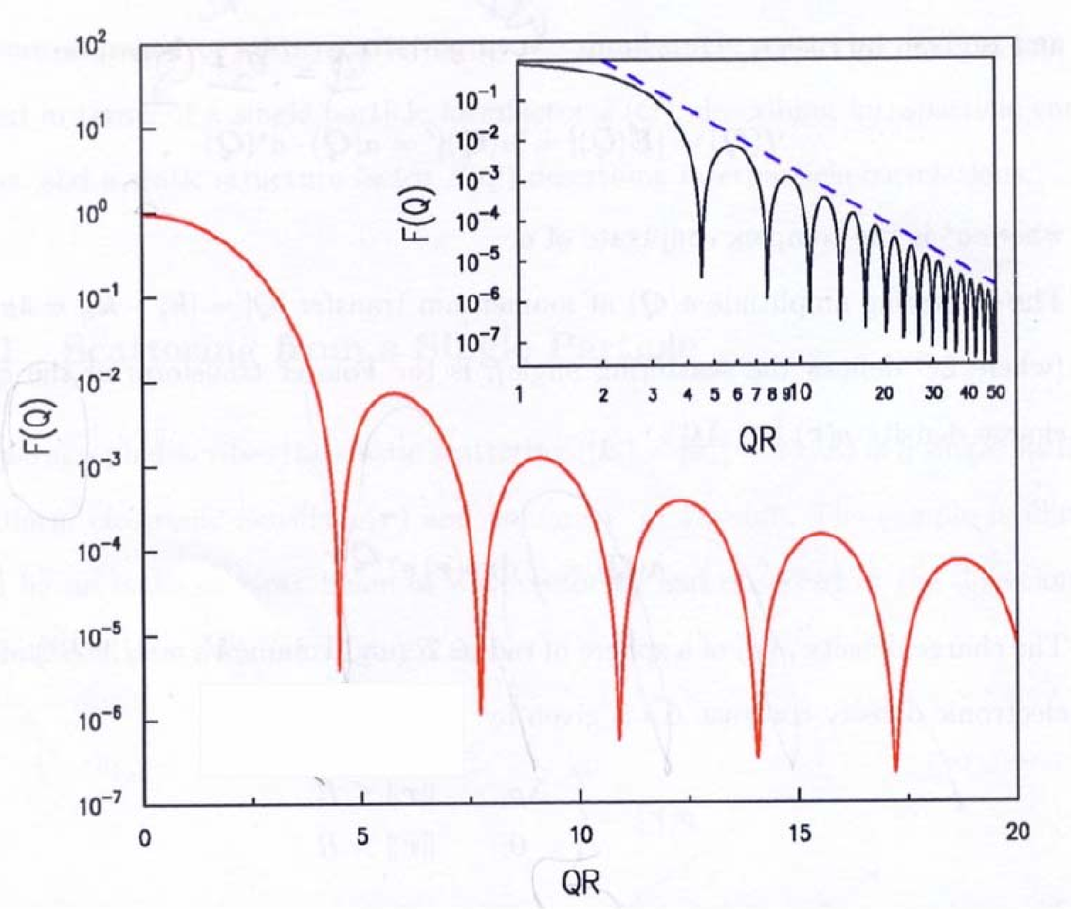
$$\int I_m(\vec{q})d\vec{q}I_m(\vec{q}) = \left\langle \rho^2 \right\rangle - \left\langle \rho \right\rangle^2$$

$$\gamma(0) \equiv \int_V \rho(\vec{r}_1)\rho(\vec{r}_1)d\vec{r}_1 = \left\langle \rho^2 \right\rangle$$

Porod's Theorems - II: large q

Scatterd 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



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

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

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

$$\sim \frac{R^2}{(q)^4}$$

Surface of sphere

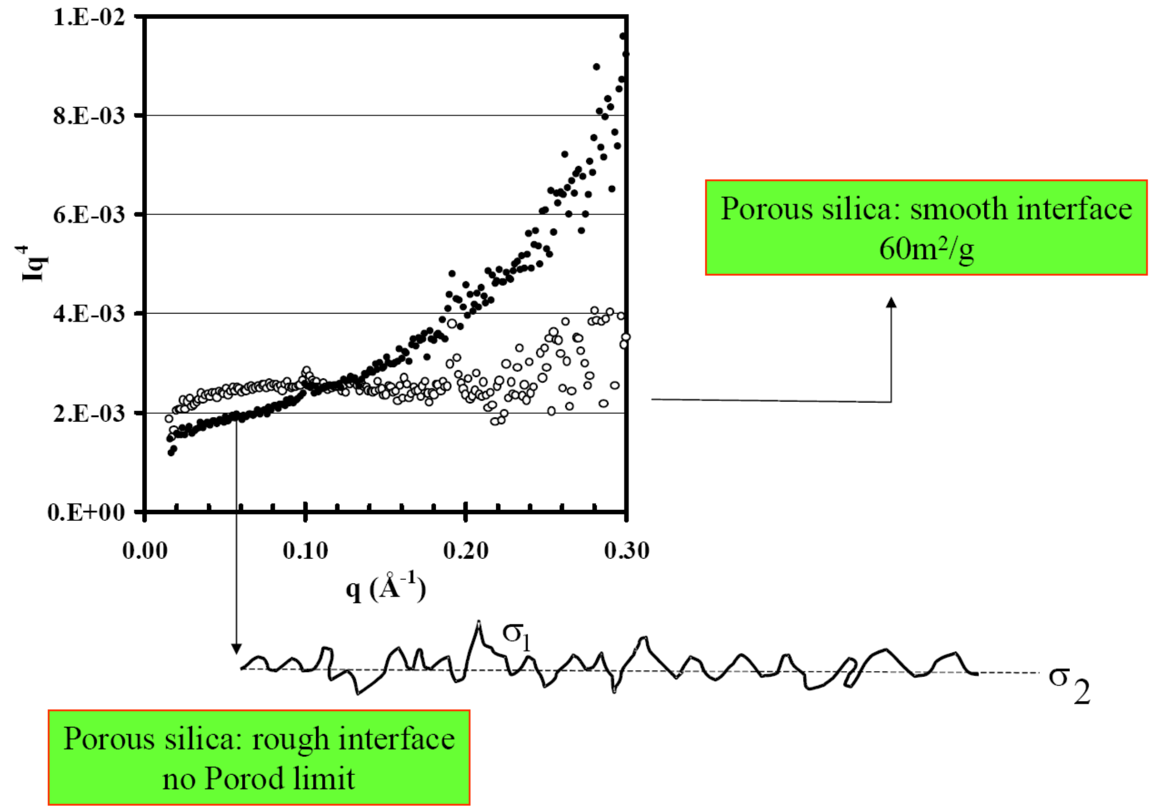
General

Two phases with sharp interface

$$\lim_{q\to\infty} I(q) = \frac{2\pi(\Delta\rho)^2}{q^4}\cdot\frac{\sigma}{V}$$

For large q intensity decreases with q^{-4}

Means to determine specific surface σ/V

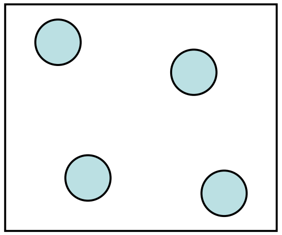


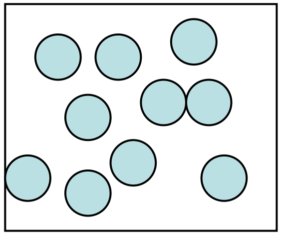
Structure factor

Latex spheres

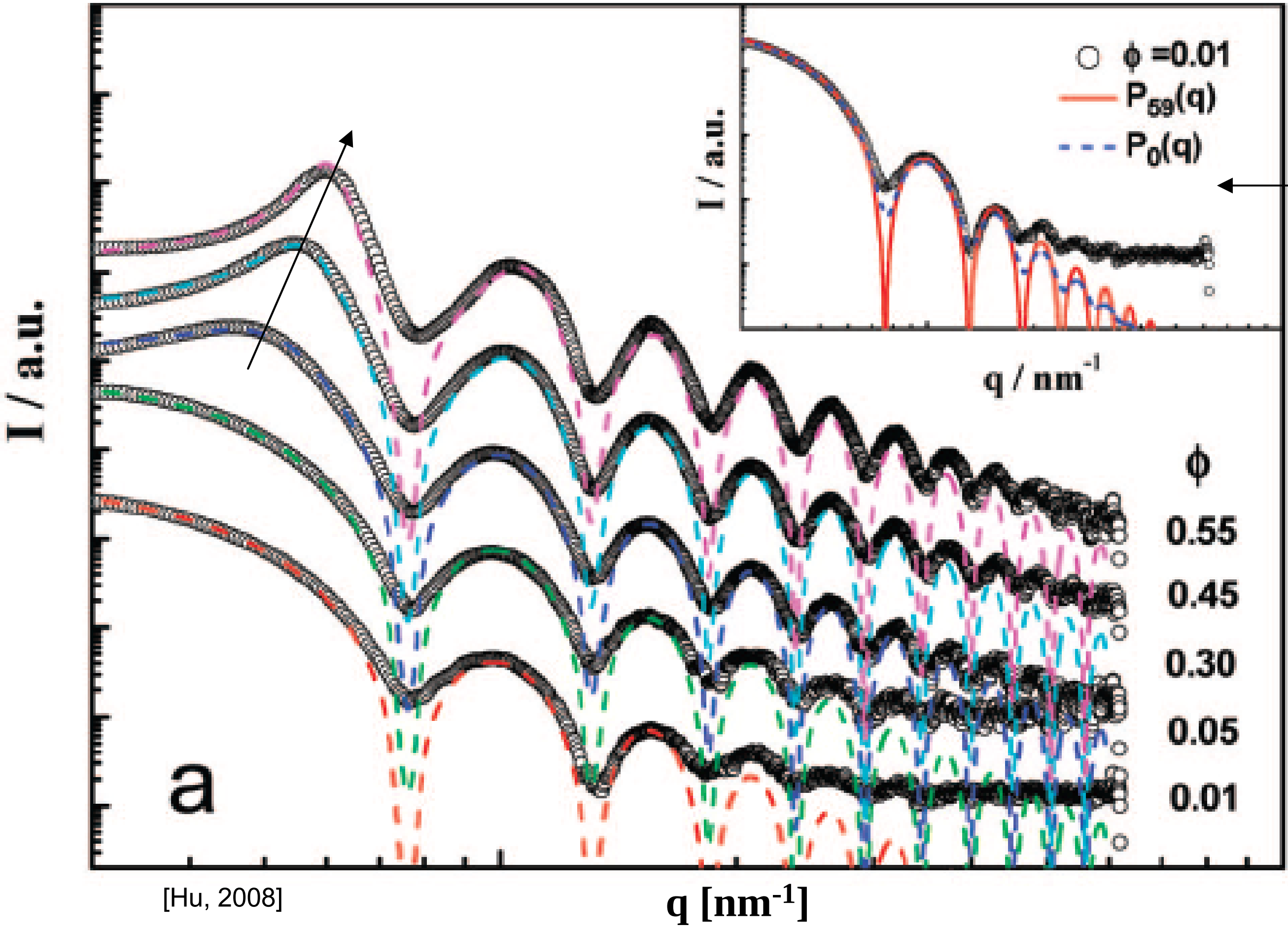
$$I(q) = S(q)P(q)$$

Low ϕ P(q)
High ϕ S(q)P(q)





Gaussian distribution of particle sizes



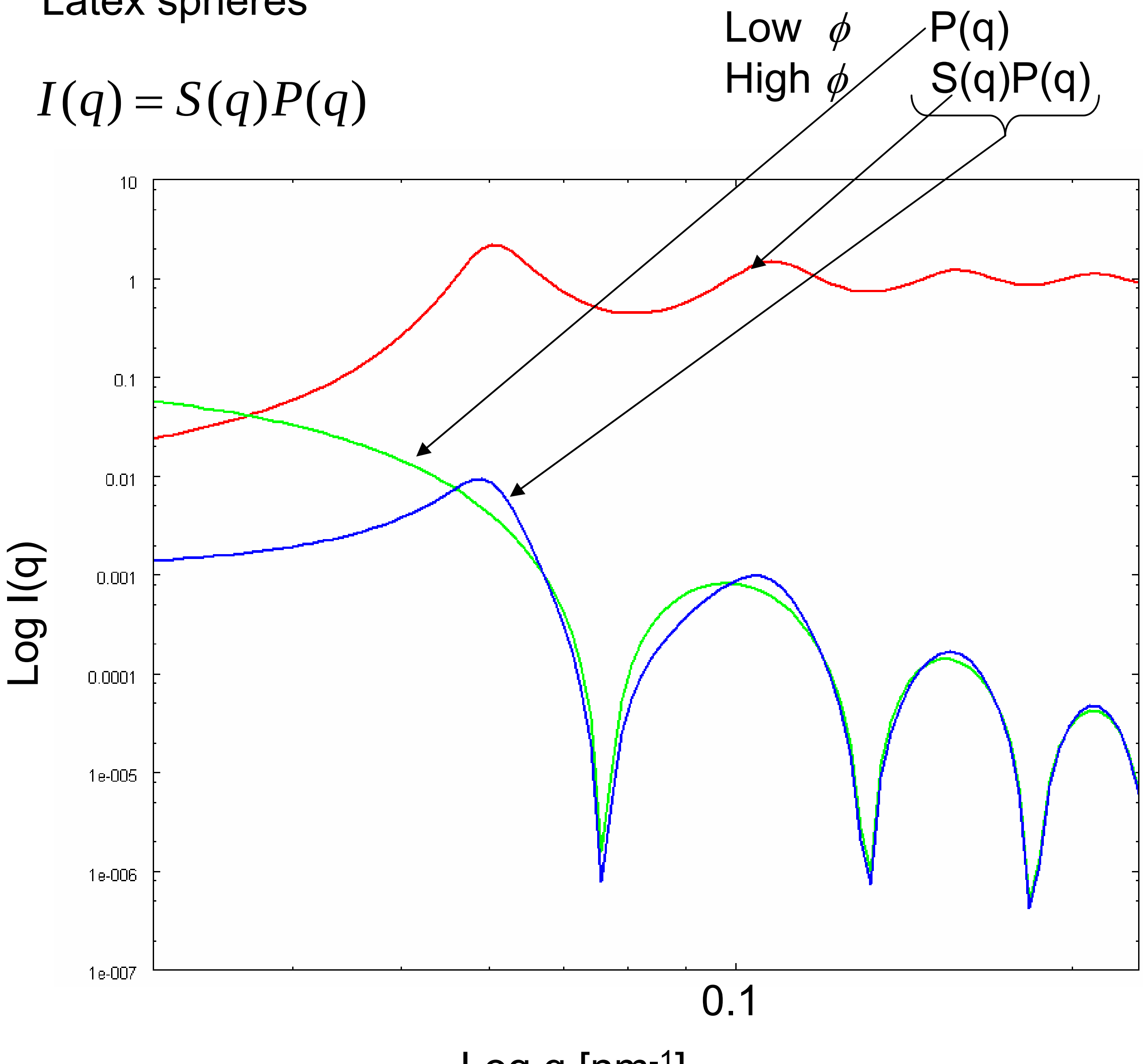
Shift in maximum: Decreasing distance

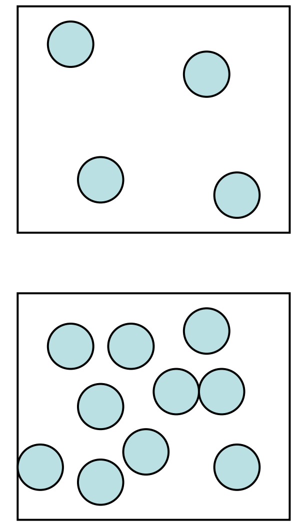
[Hu, 2008]

Structure factor

Latex spheres

$$I(q) = S(q)P(q)$$





Small-angle X-ray scattering

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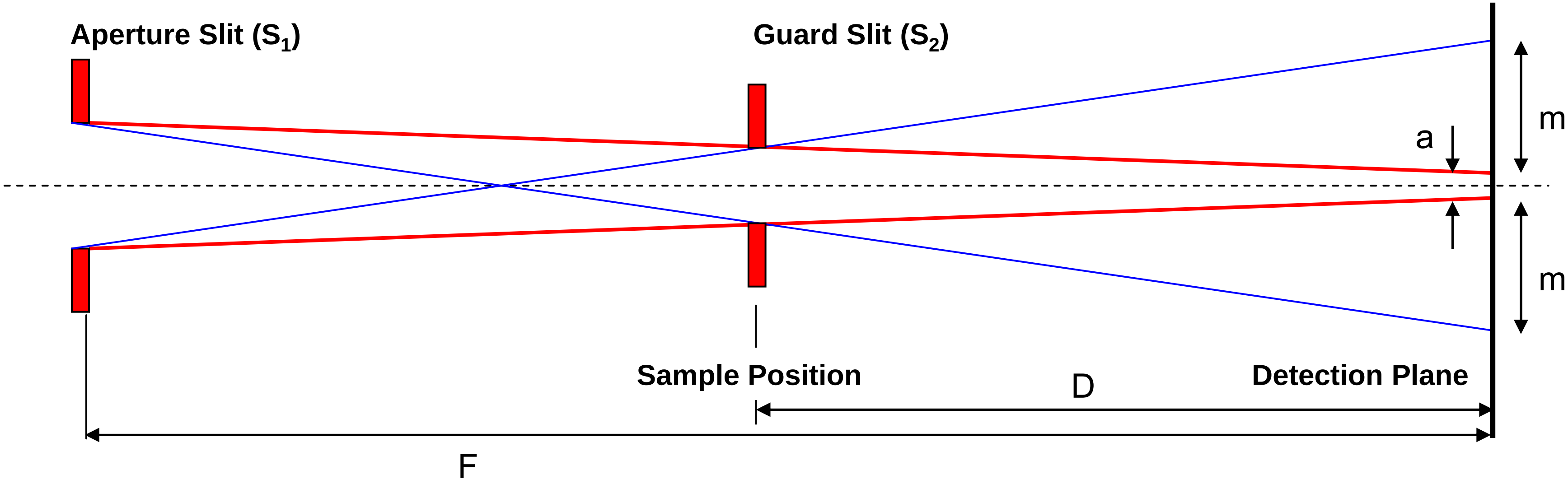
    - Cracks & crazes
    - Tomography (3D-reconstruction)

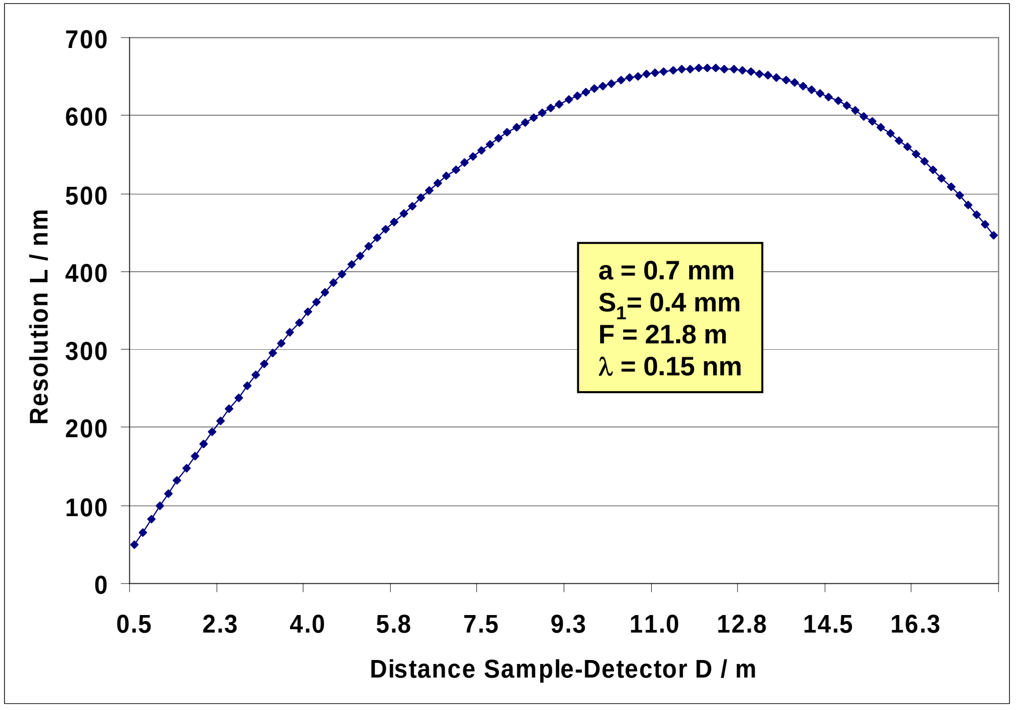
Resolution of a SAXS Instrument



$$S_2 = \frac{S_1 - a}{F} \cdot (D + a)$$

$$m = S_2 \cdot \left(\frac{1}{2} + \frac{D}{2} \cdot \frac{S_1 + S_2}{(F - D) \cdot S_2} \right)$$

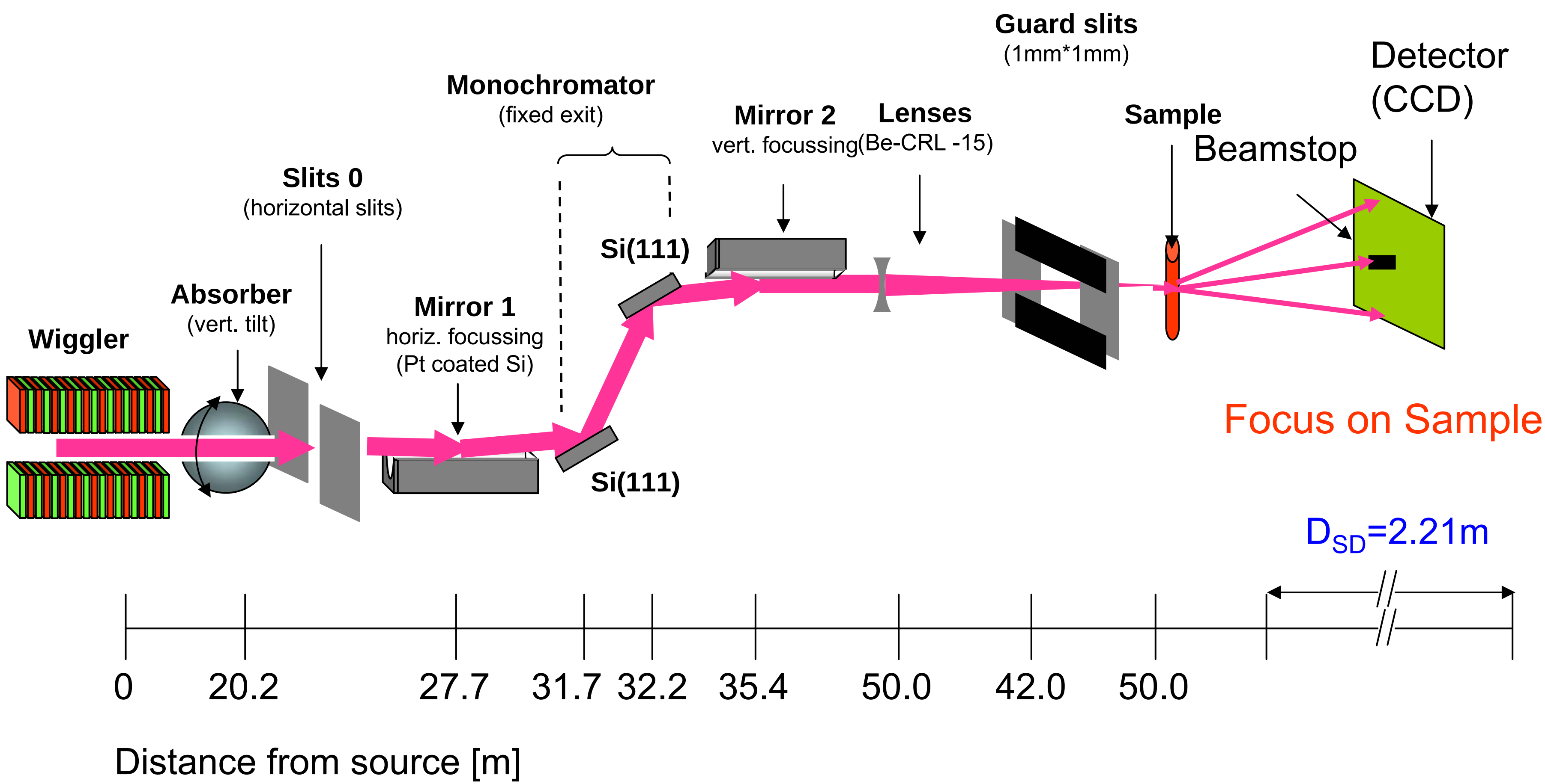
$$L_{res} = \frac{\lambda}{2 \cdot \sin\left(0.5 \cdot \tan^{-1} \frac{m}{D} \right)}$$



SAXS Instrument - Example BW4 - USAXS

Resolution (maximum observed correlation distances) depends on sample to detector distance: 90 nm to 700 nm, photon flux $5 \cdot 10^9$ sec^{-1} (monocromatic)

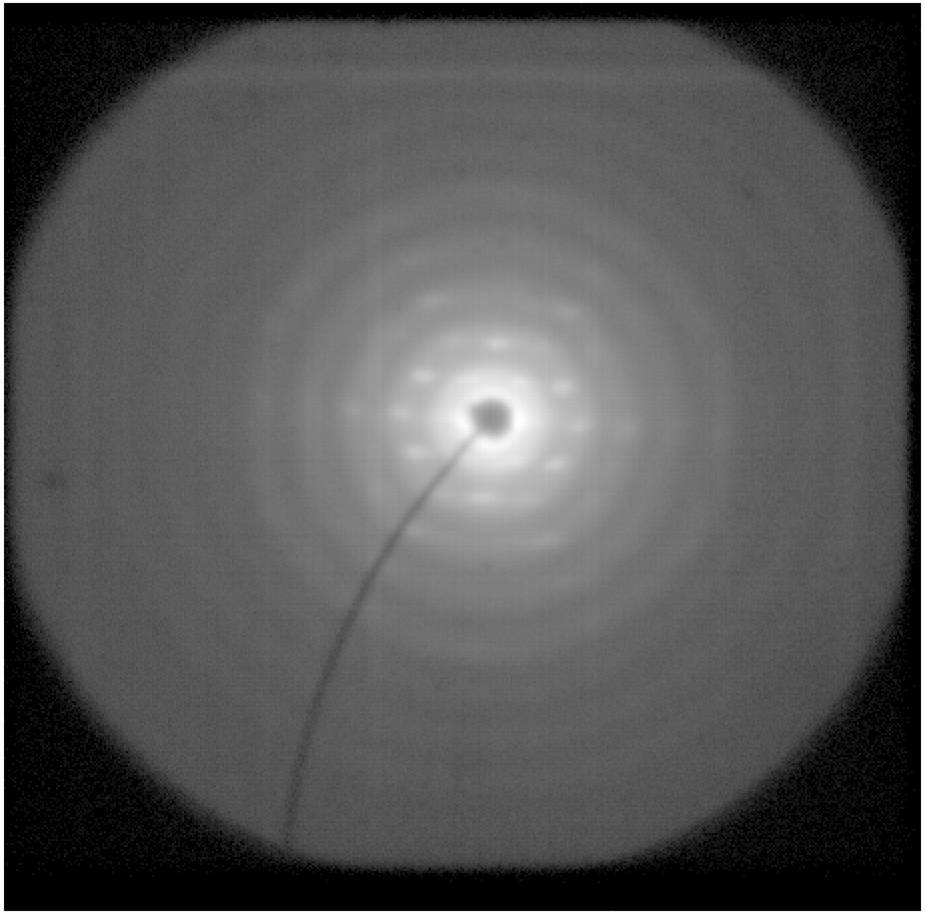
Microfocus @ BW4

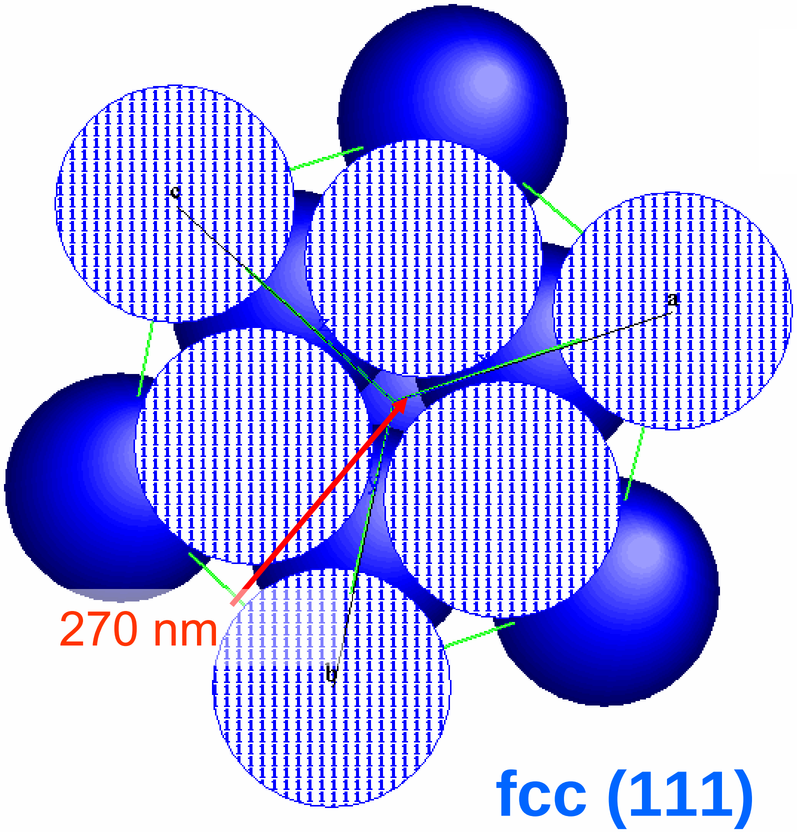


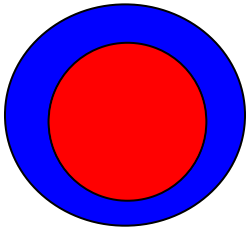
Small-angle X-ray scattering

- Introduction – Theory of SAXS
- Form factor
- Approximations
- Structure factor
- Beamlines
  - USAXS
  - Microfocus x-ray beams
- Application to polymer systems
  - Thick colloidal films
  - Deformation
  - Cracks & crazes
  - Tomography (3D-reconstruction)

SAXS at Polymeric Core-Shell Particles (Photonic Crystals)





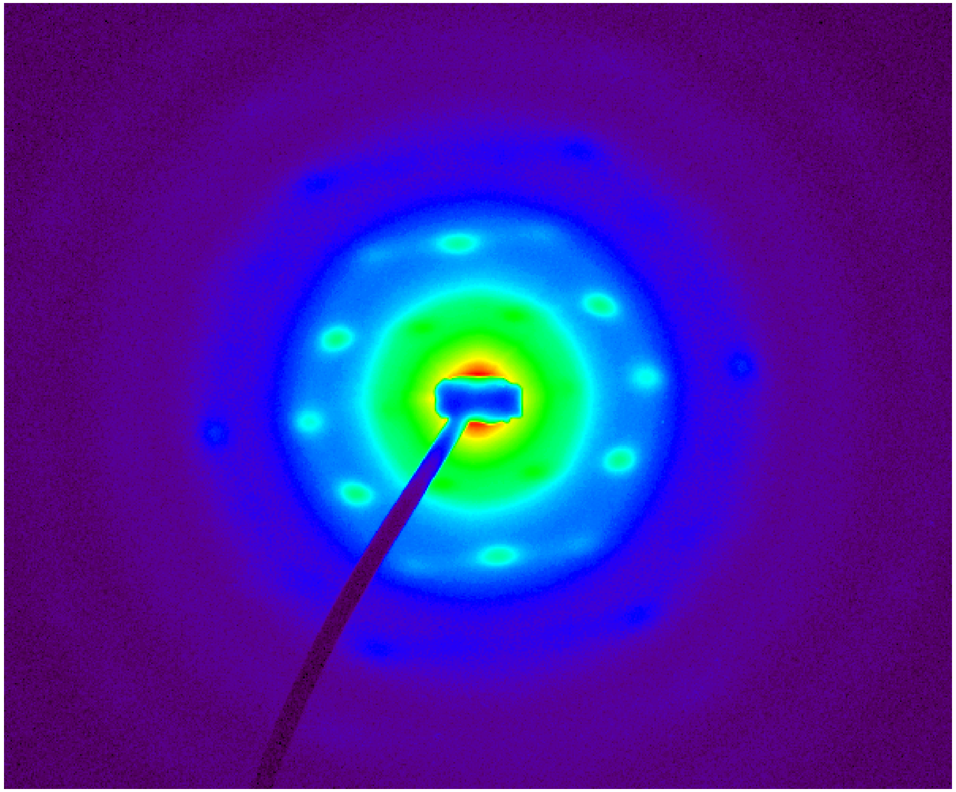


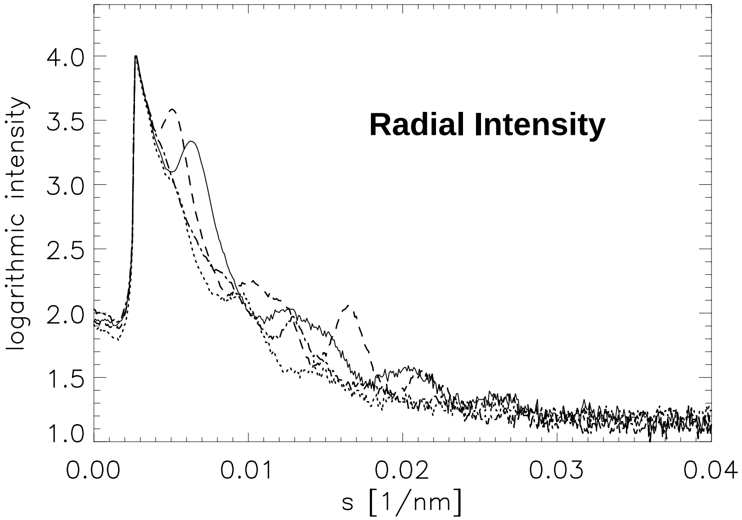
Core: PS (hard)
Shell: PMMA (soft)

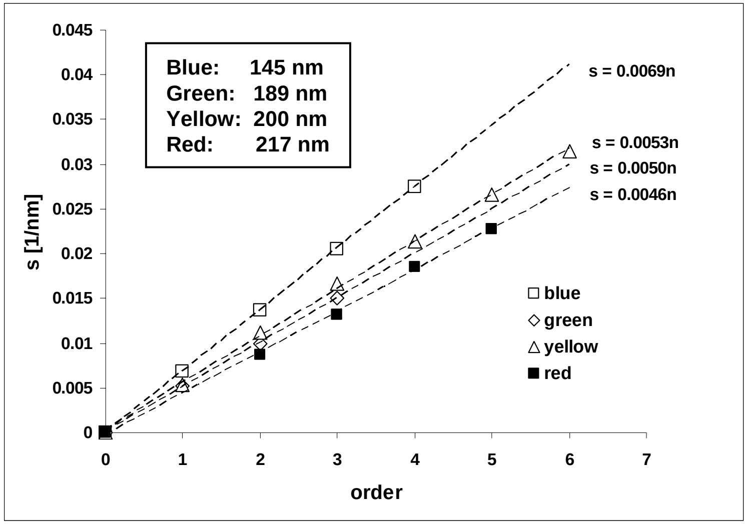
Colloidal Crystals in Latex Films

Core: Polystyrene
Shell: Polymethylmetacrylate - polyethylacrylate

Fcc lattice

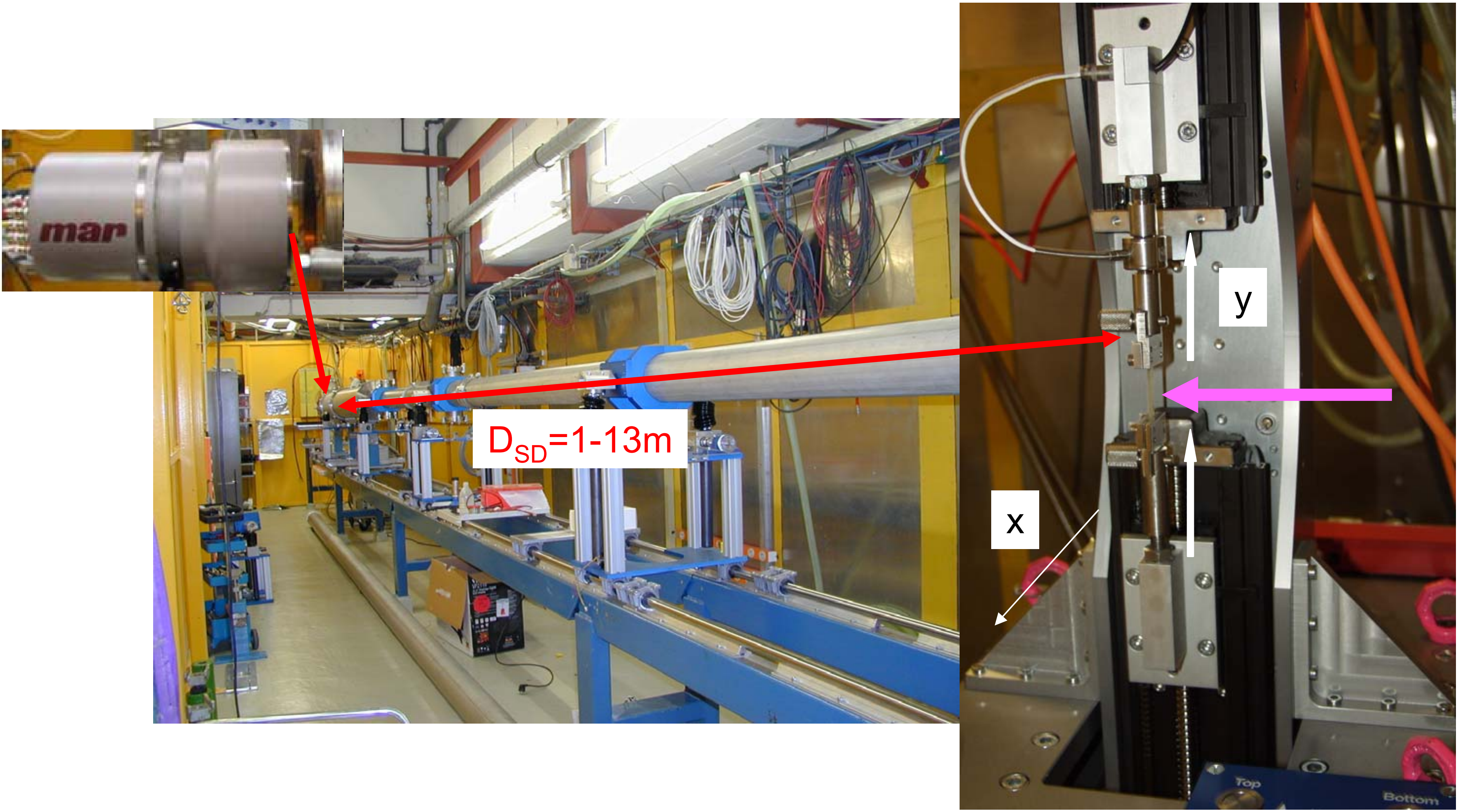




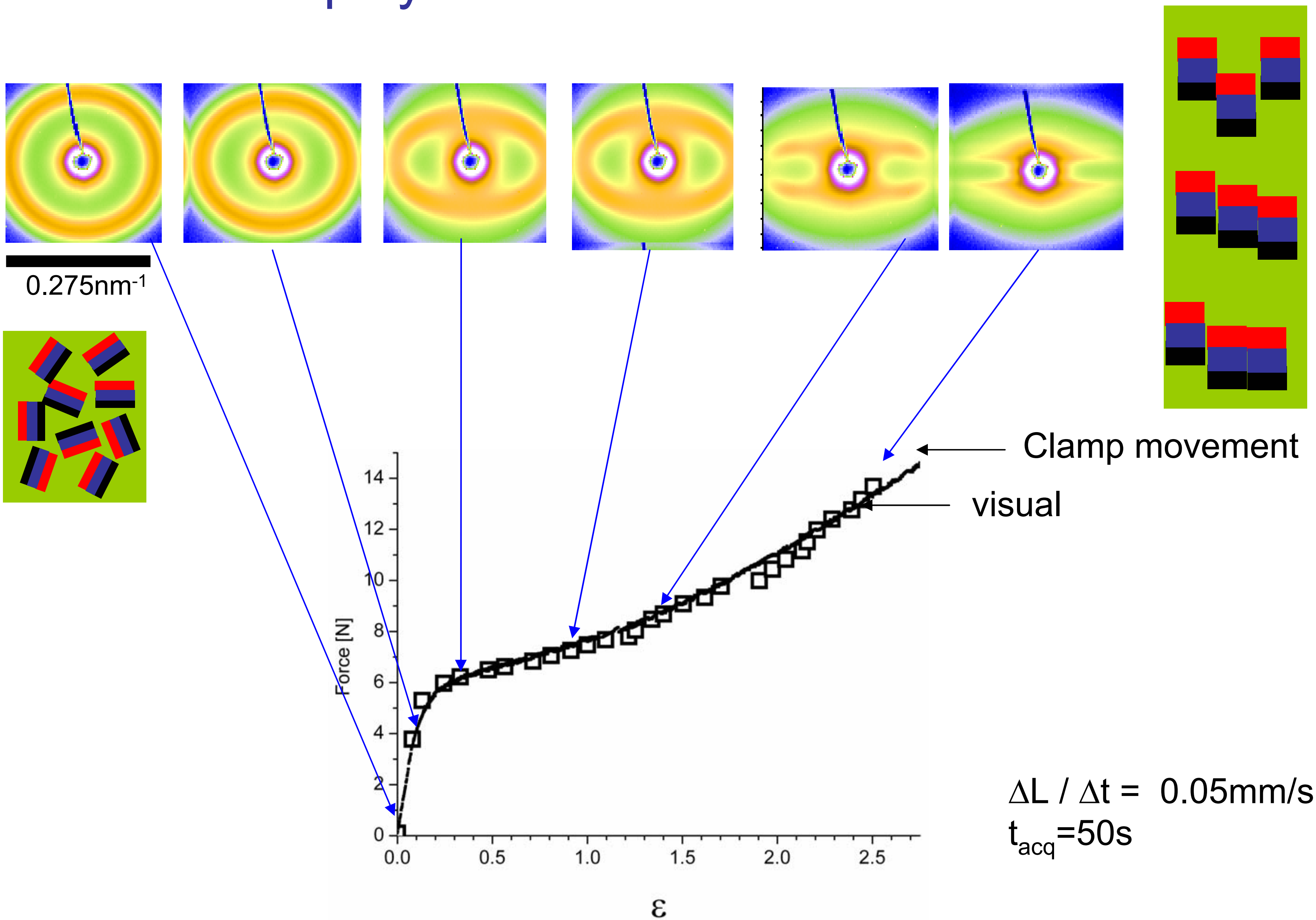


Deformation of polymers - SBS

Triblock-copolymer



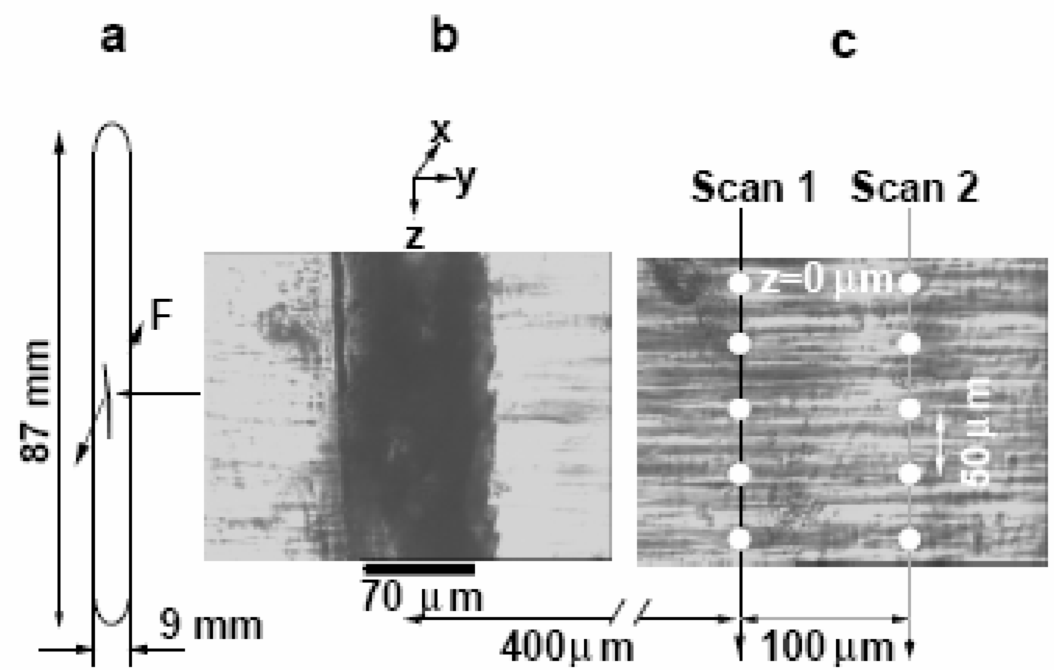
Deformation of polymers - SBS

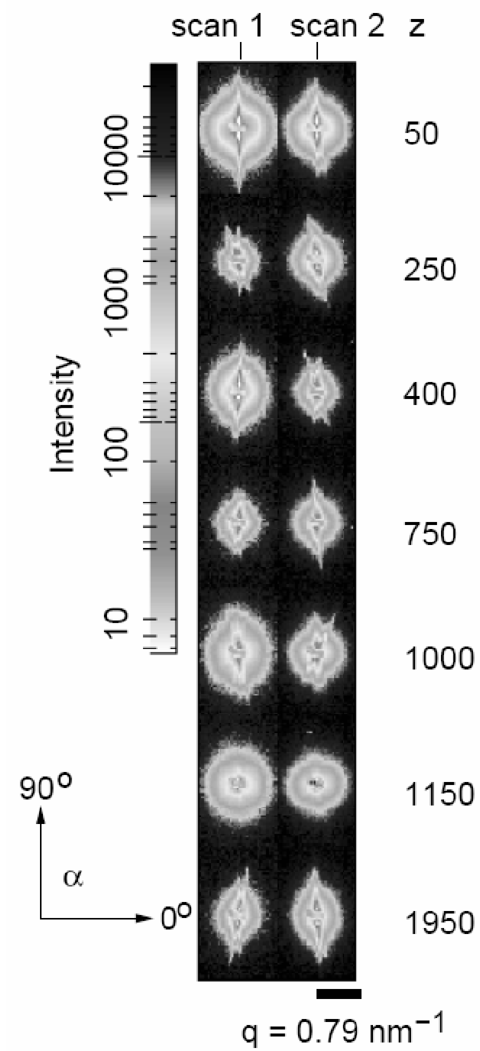


$\Delta L / \Delta t = 0.05 mm/s$

$t_{acq} = 50 s$

Deformation – cracks & crazes



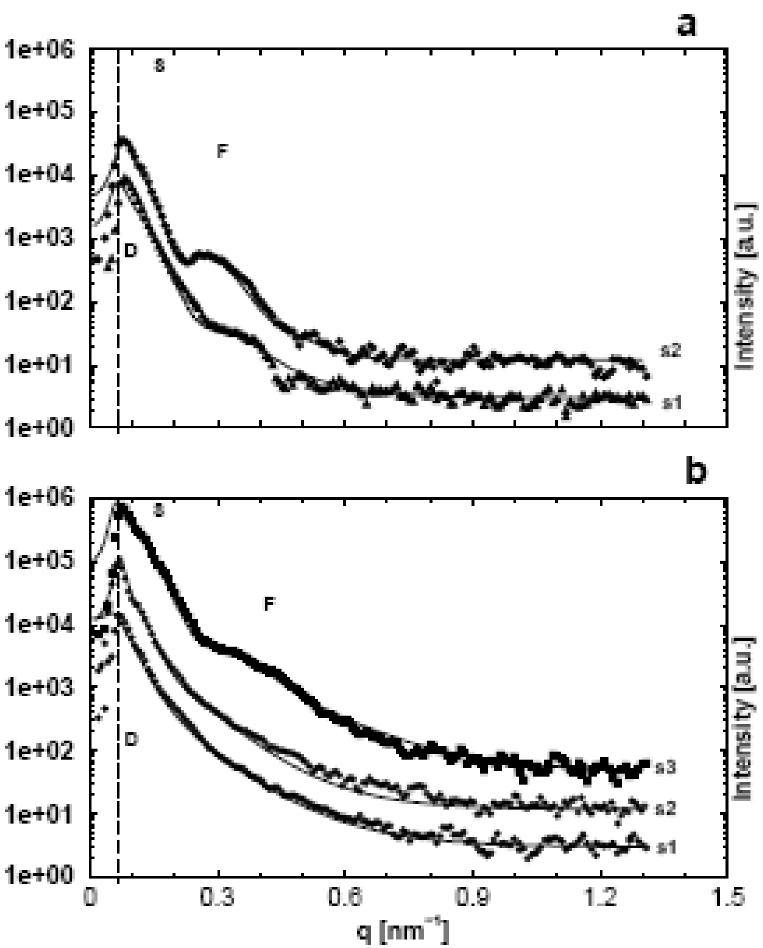


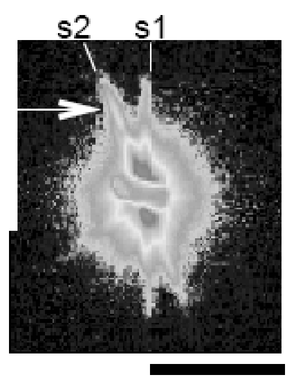
Roth et al., J. Appl. Cryst. 36, 684 (2003)

Strong overlap to materials science

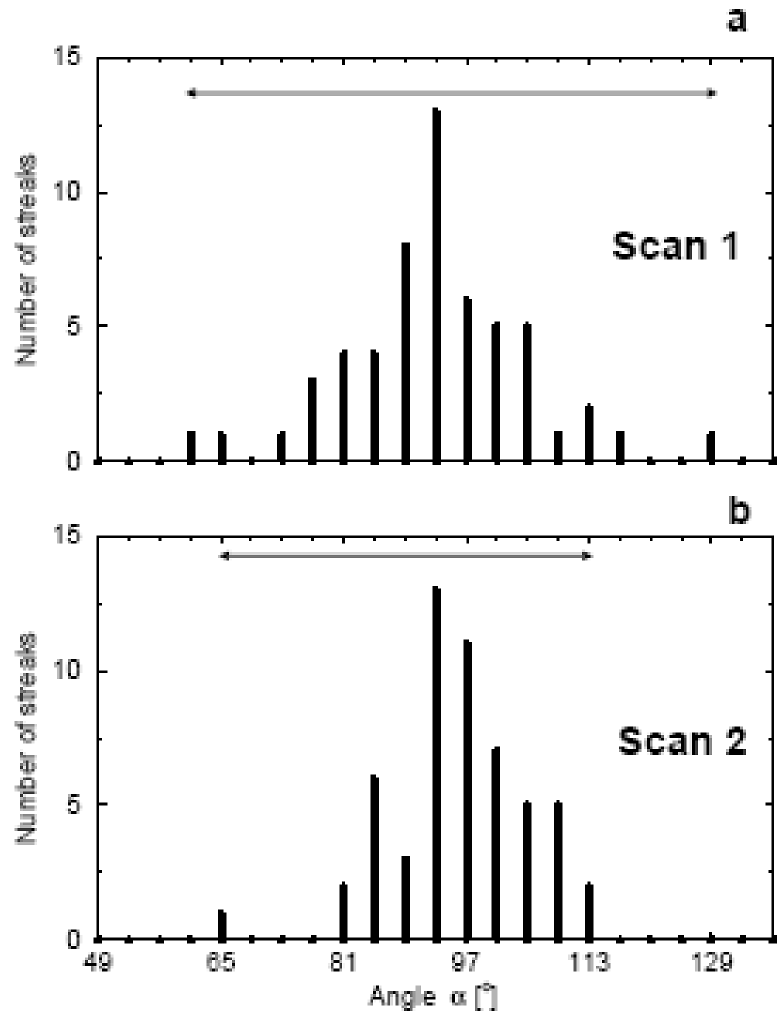
Deformation – cracks & crazes

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





q = 0.79 nm^{-1}



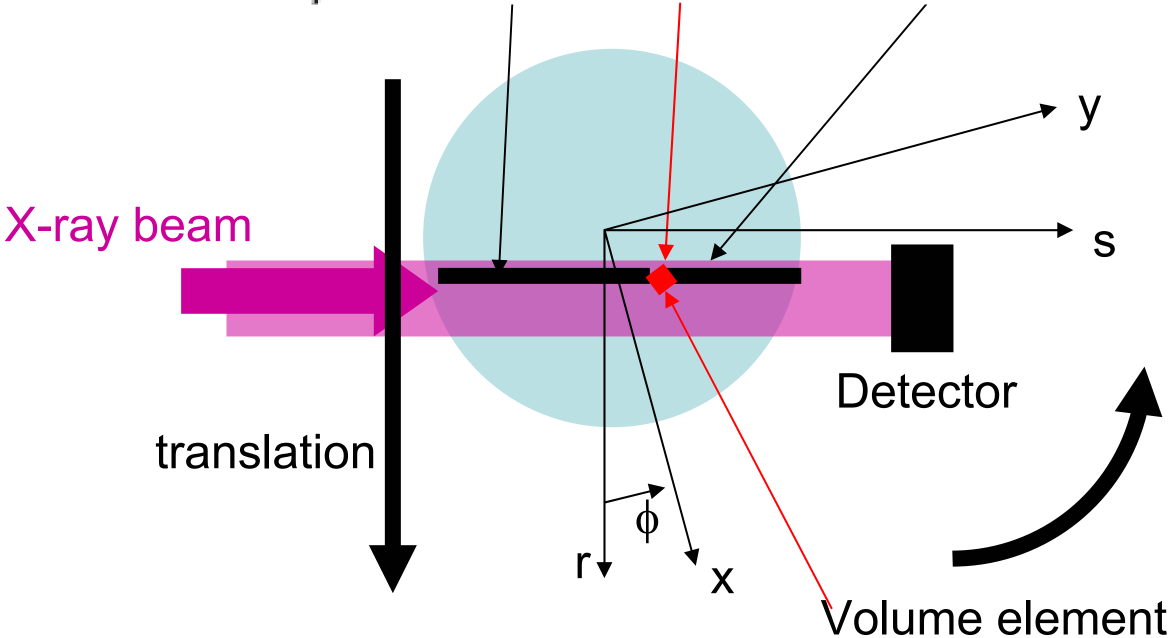
Statistics!

Thick sample

SAXS-Tomography

Tomography => 3D reconstruction of objects

$$I_{\mathbf{q}}(r,\phi) = I_0 \int ds f(\phi,s,r) p_{\mathbf{q},\phi}(x,y) g(\phi,s,r).$$



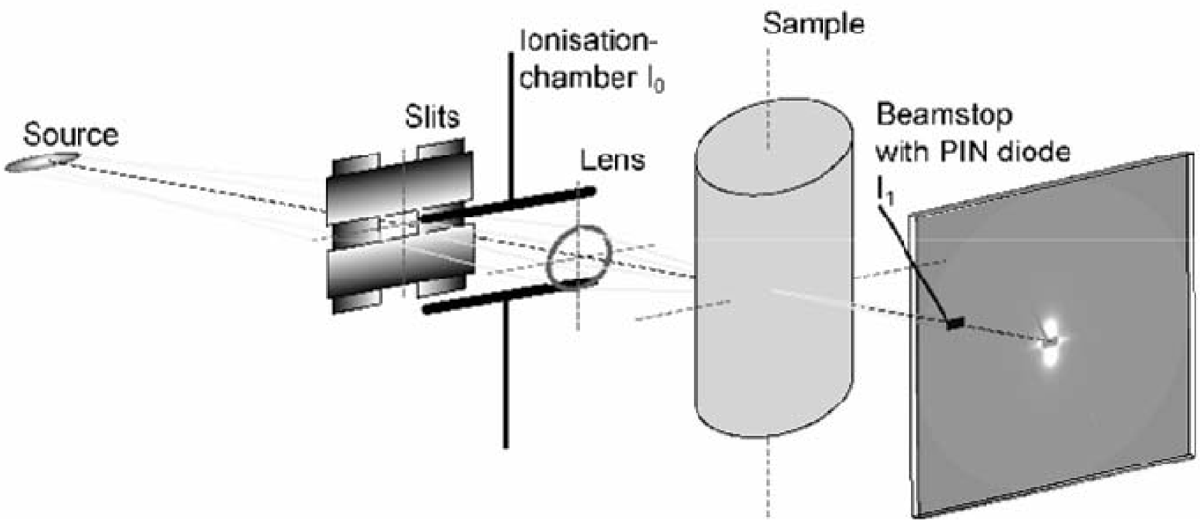
f,g: ~exp(-μL)
-> absorption coefficient μ

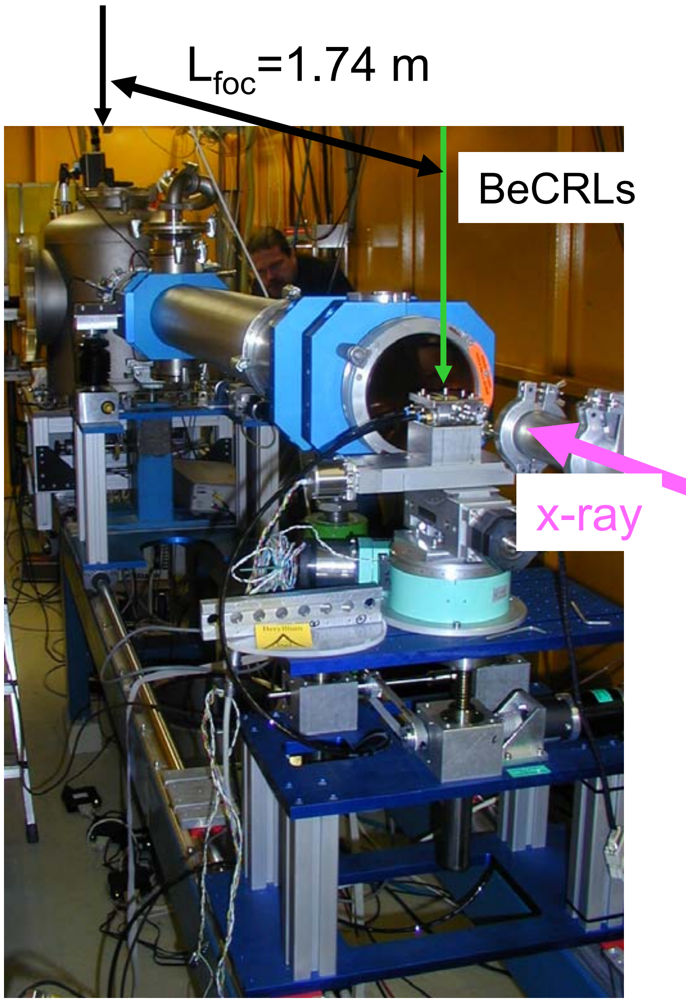
p~r(Vi)~S(q)*P(q)

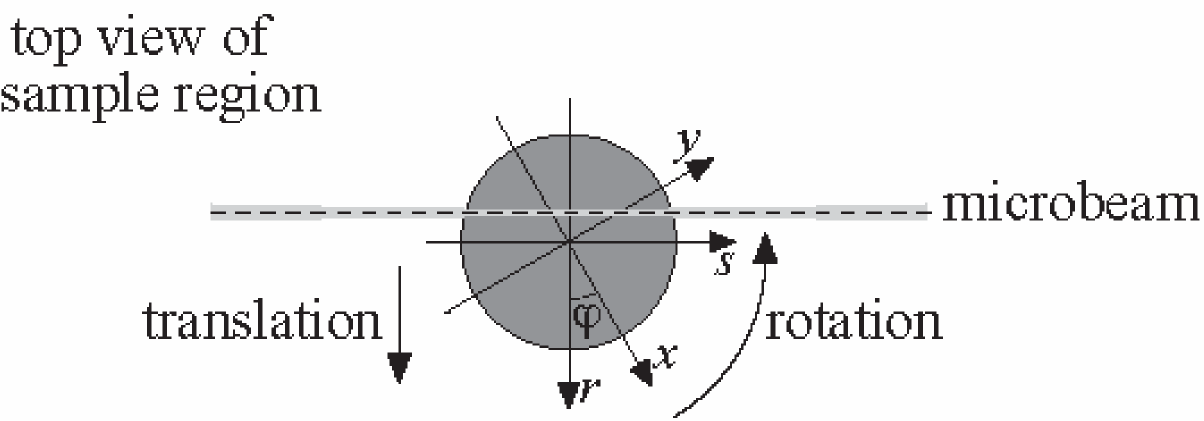
- Greek: *tomé* (cut) & *gráphein* (write, draw)
- Produce a virtual cut through object without actual slicing
- Mathematical technique for extracting a certain feature, e.g. absorption coefficient from the object, starting from integral of this feature.

Tomographic Reconstruction of µSAXS Pattern (BW4)

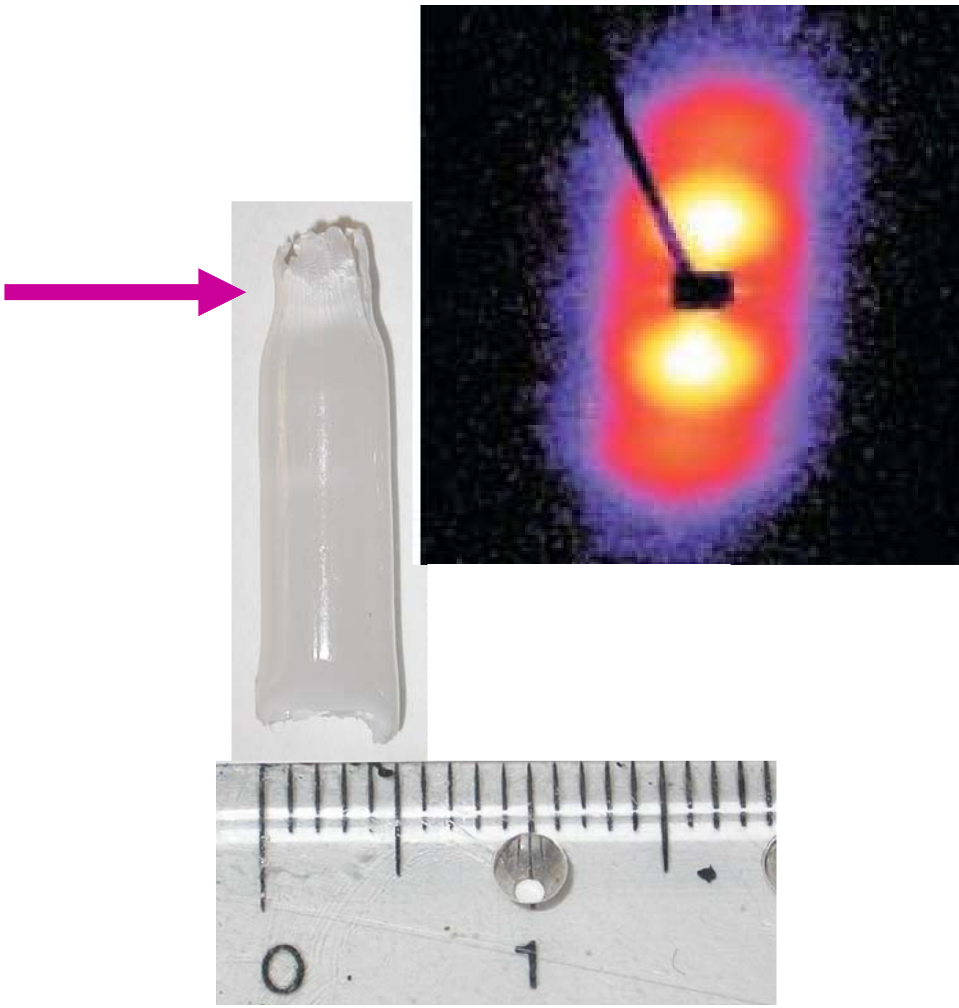
Irradiation direction of a volume element is varied step-by-step during the tomographic acquisition

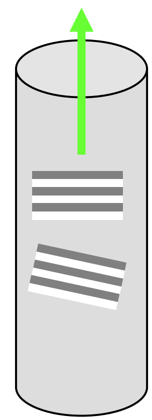






Tomographic Reconstruction of µSAXS Pattern (BW4)





Lupolen 6021D by BASF

Beam size 60x30µm^2

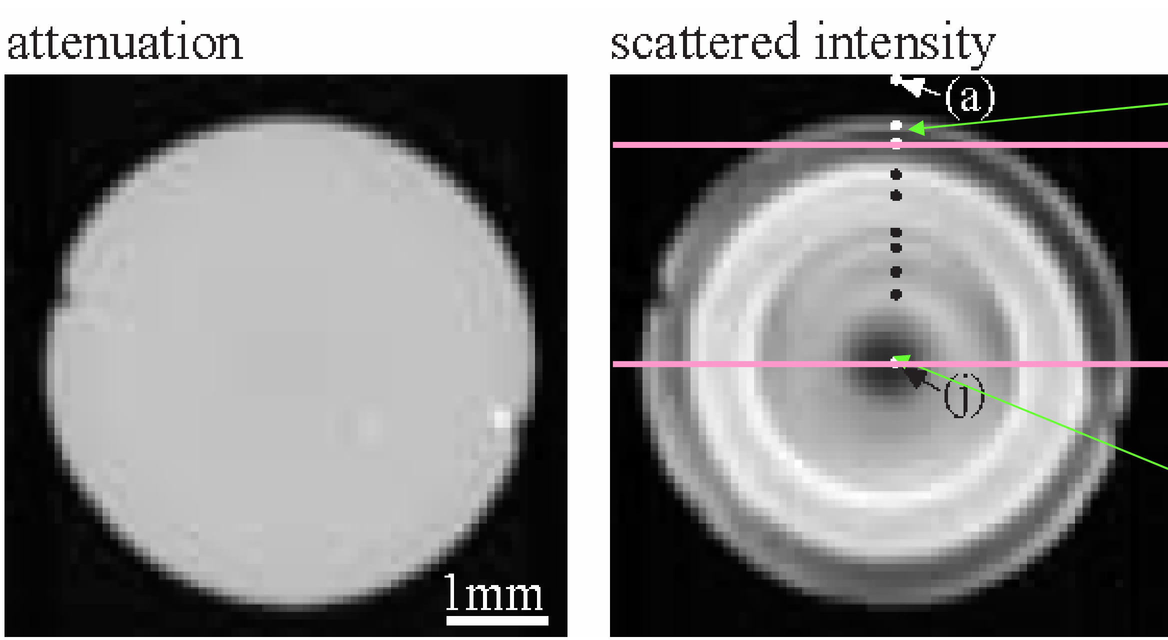
Results

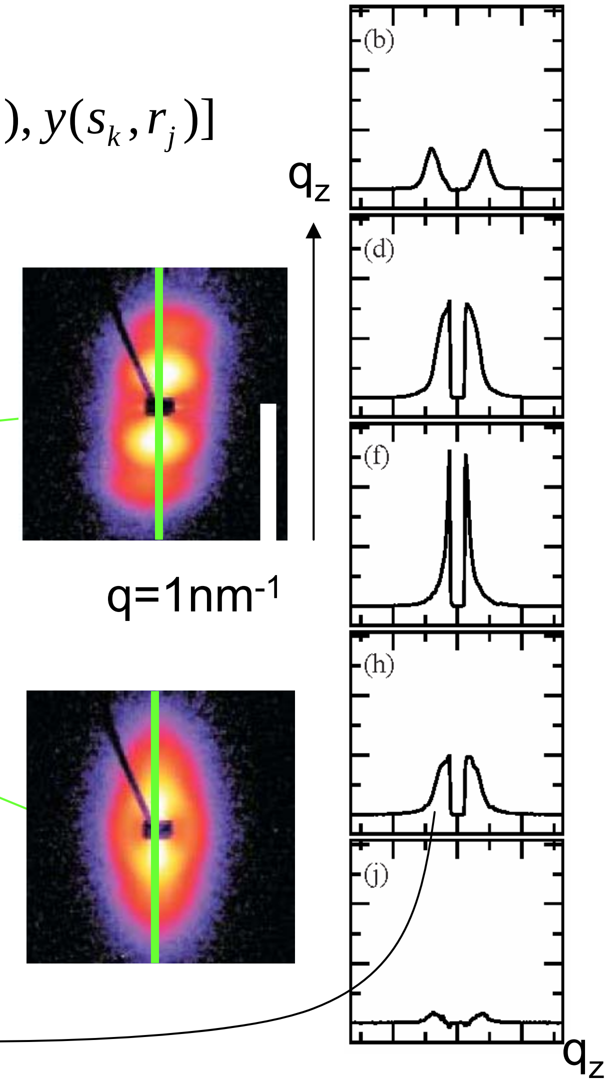
For each translation and rotation *(r,ϕ)* => one value for $I_q(r,\phi)$

Solve system of linear equations to extract $p_{q,\phi}$

$$I_{\mathbf{q}}(r,\phi) = I_1 \int ds p_{\mathbf{q},\phi}[x(s,r),y(s,r)] \sim \sum_k p_{q,\phi_j}[x(s_k,r_j),y(s_k,r_j)]$$

SAXS cross section





Integral of curve = grey scale

Results