

Methoden moderner Röntgenphysik I: Struktur und Dynamik kondensierter Materie

Vorlesung zum Haupt/Masterstudiengang Physik
WS 2008/9
G. Grübel, M. Martins, E. Weckert et al.

Location: SemRm4, Physik, Jungiusstrasse
Thursdays 10.15 –11.45

G. Grübel (GG), A. Meents (AM), C. Gutt (CG), **S. Roth (SR)**

Soft Matter Applications

Stephan V. Roth

Introduction	(GG)
Modern Crystallography	(AM)
Coherence based techniques	(CG)
Soft matter applications	(SR)

22.01.2009 Basics, theory, preparation – a primer

➔ 29.01.2009 Small-angle X-ray scattering and its applications

03.02.2009 Polymer, colloidal and nanocomposite surfaces
(Note change Thursday (5.)-> Tuesday) (3.)

Aim: Overview over use of soft matter and x-ray scattering of soft matter

Summary last lecture

Polymers:

➤ Macromolecules, build up of a large number of molecular units

$$\bar{M}_n = \int p(M)M dM \quad \bar{M}_w = \frac{\int p(M)M \cdot M dM}{\int p(M)M dM}$$

➤ Radius of gyration $R_G = \sqrt{\frac{1}{M} \sum_0^N \langle m_i \bar{r}_i^2 \rangle}$

➤ Block copolymers: ..AAAABBBBBBAAAABBBBBB...

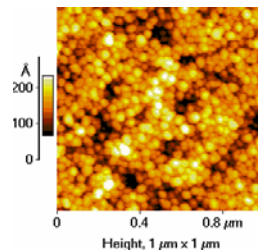
➤ Flory-Huggins-theory $\Delta G_{mix} = -T\Delta S_t + \Delta G_{loc}$

Mixing takes place, when $\Delta G_{mix} < 0$

Flory-Huggins-parameter χ

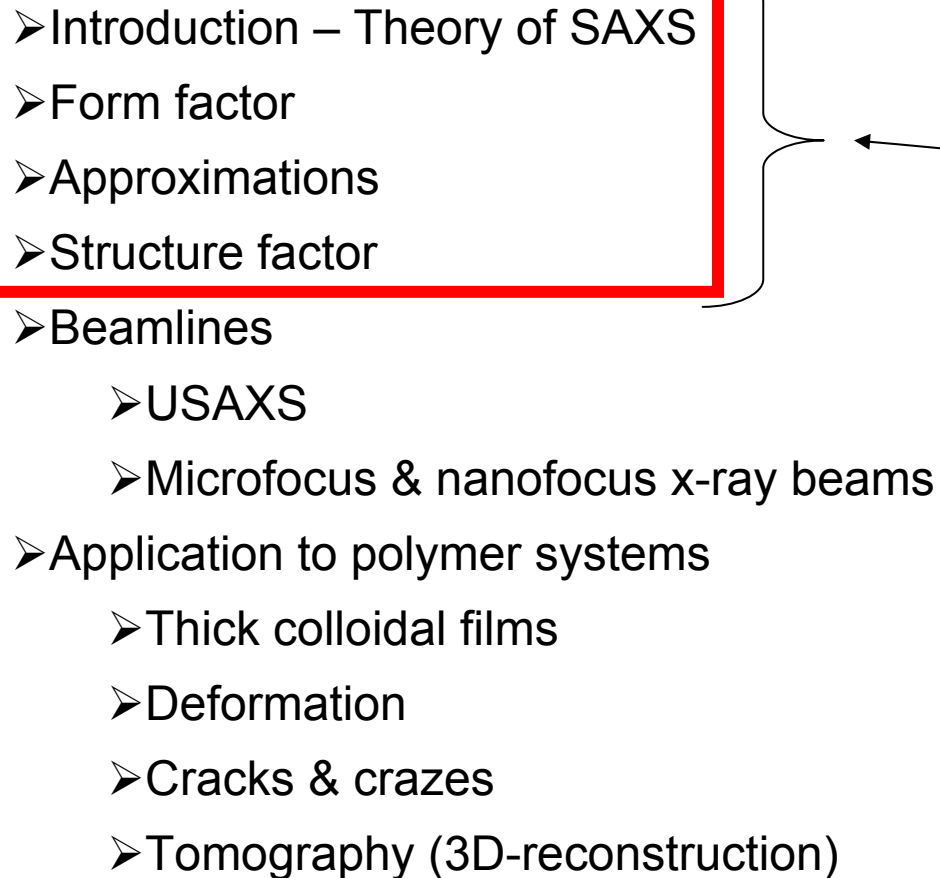
Colloids

Polymer-Metal nanocomposites



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

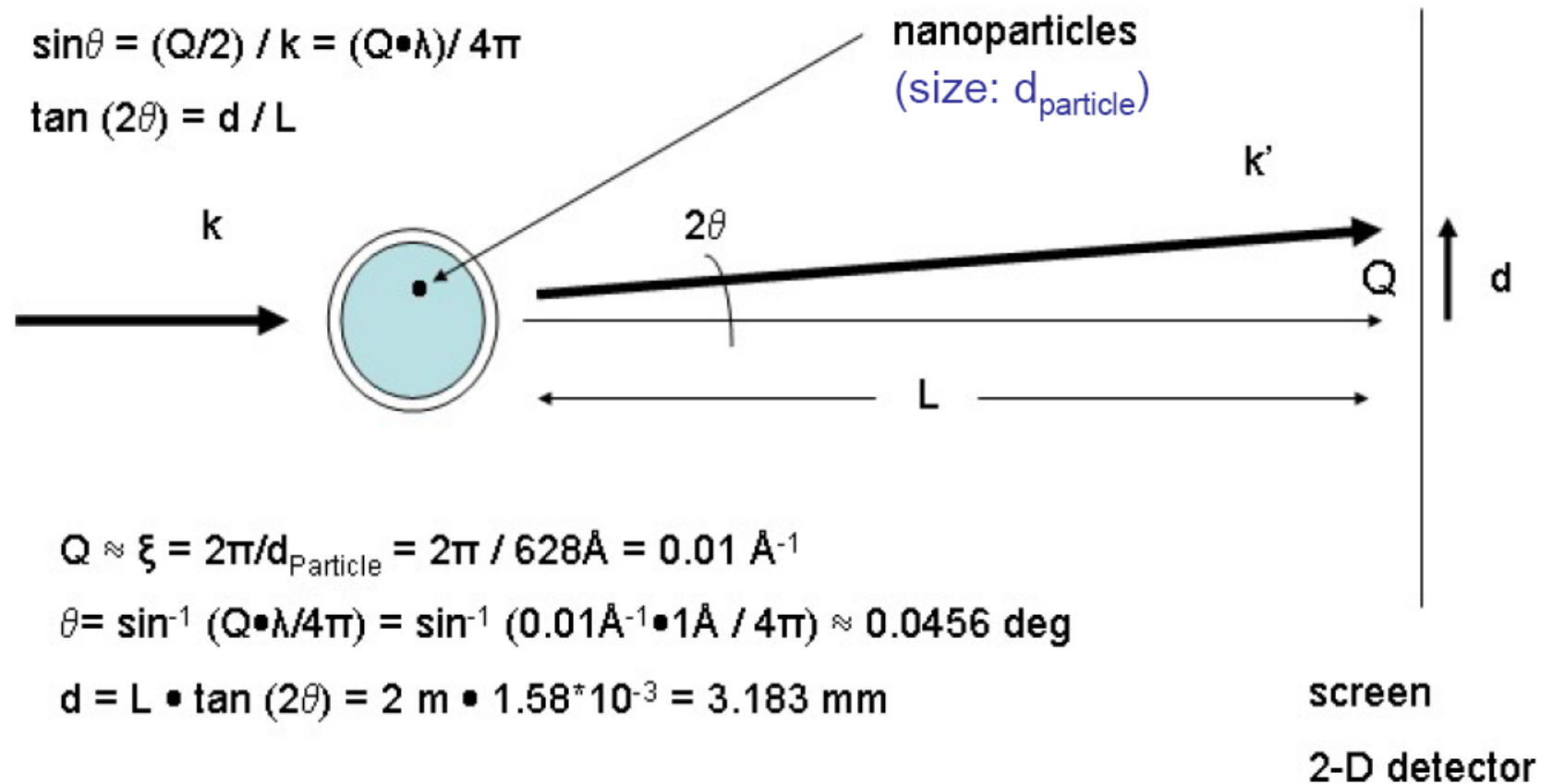
A Note in advance

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



Scattering geometry

$$I_{\text{scattered}} = I_0 N \Delta\Omega (d\sigma/d\Omega)$$

I_0 : incident intensity

N : number objects

$\Delta\Omega$: solid angle

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

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

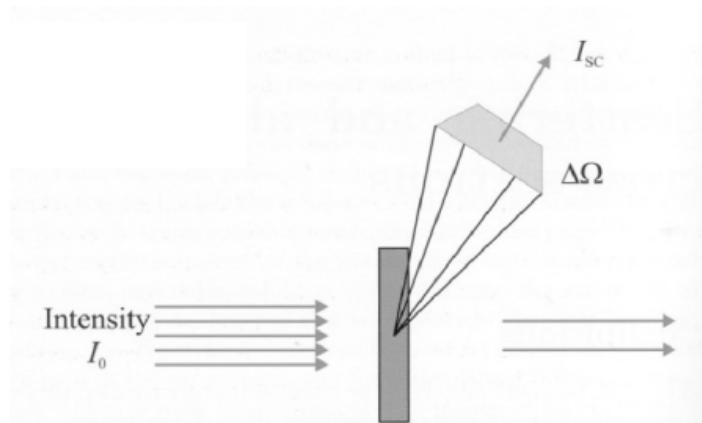
n : volume fraction

ρ : electron density

v : particle volume

$F(Q)$ formfactor

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

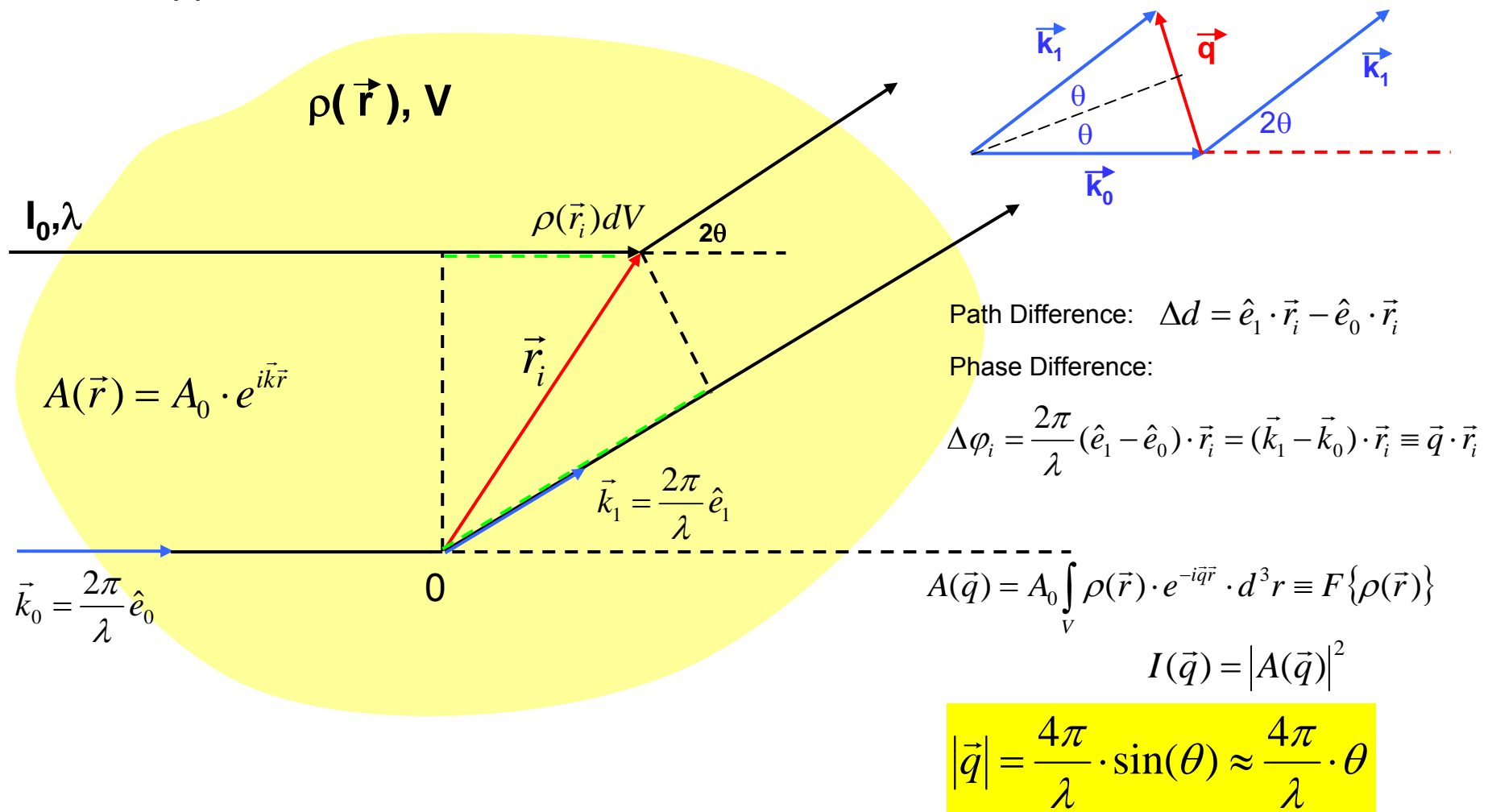


Important approximations for Form factor

We will derive them, as they are frequently used:

- Guinier approximation
- Porod approximation

Single particle scattering, dilute Systems



Form factor and structure factor

Single particle

$$\rho_p(\vec{r})$$

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

Particle distribution function $P(\vec{r}) \rightarrow$ Electron density distribution

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

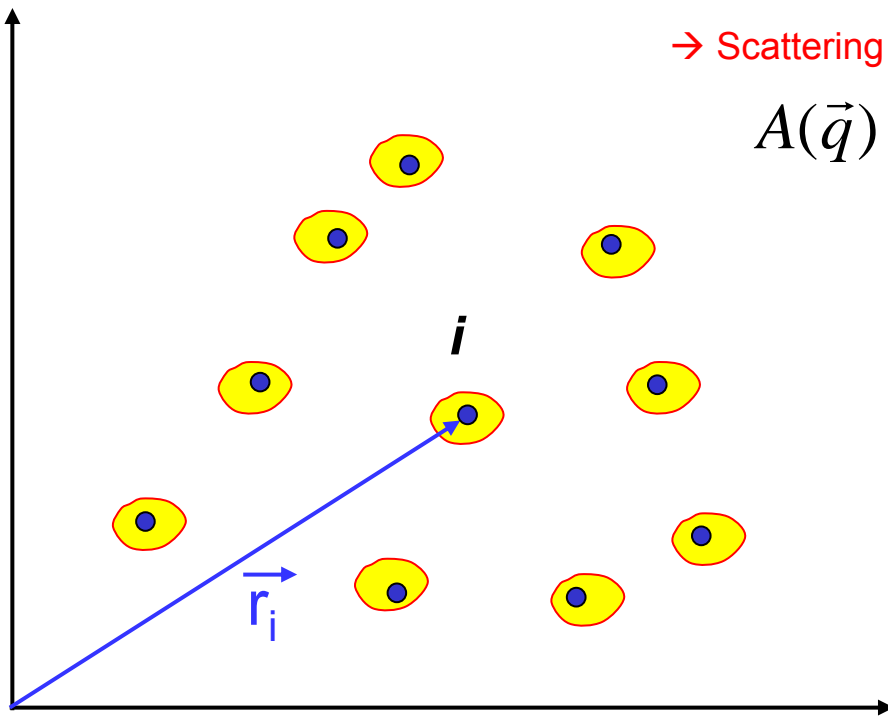
\rightarrow Scattering amplitudes of the whole arrangement

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

\rightarrow Scattered Intensity

$$I(\vec{q}) = |A(\vec{q})|^2 = \underbrace{|F(\vec{q})|^2}_{\text{Formfactor}} \cdot \underbrace{|S(\vec{q})|^2}_{\text{Structurefactor}}$$

Now let's take a closer look into $F(\vec{q})$



Single Particle Scattering in Dilute Systems

$$I_s = N \langle |F(\mathbf{q})|^2 \rangle$$

$$\text{with } F(\vec{q}) = \int_{V=\text{particleVolume}} \rho(\vec{r}) \cdot e^{-i\vec{q}\vec{r}} \cdot d^3r$$

Incoherent superposition of single particle scattering (S=1)

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

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

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

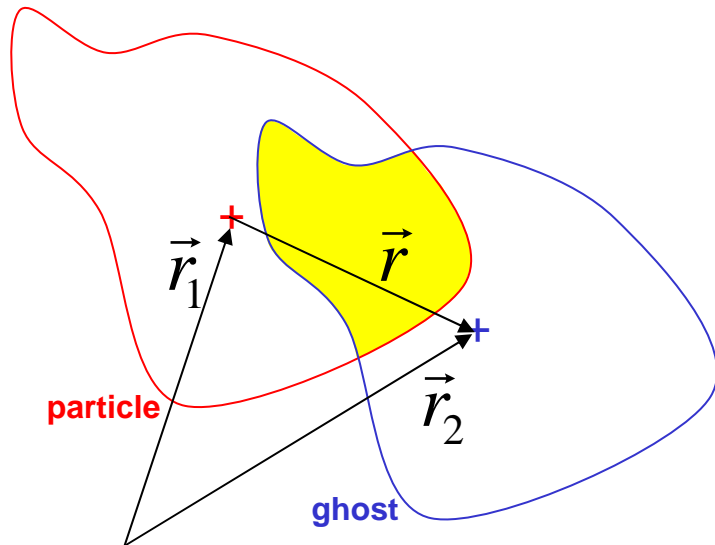
$$\gamma(\vec{r}) \equiv \int_V \rho(\vec{r}_1) \rho(\vec{r}_1 - \vec{r}) d\vec{r}_1$$

convolution square of the density distribution

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

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

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



Colloid: homogeneous sphere of radius R

A simple, but important calculation:

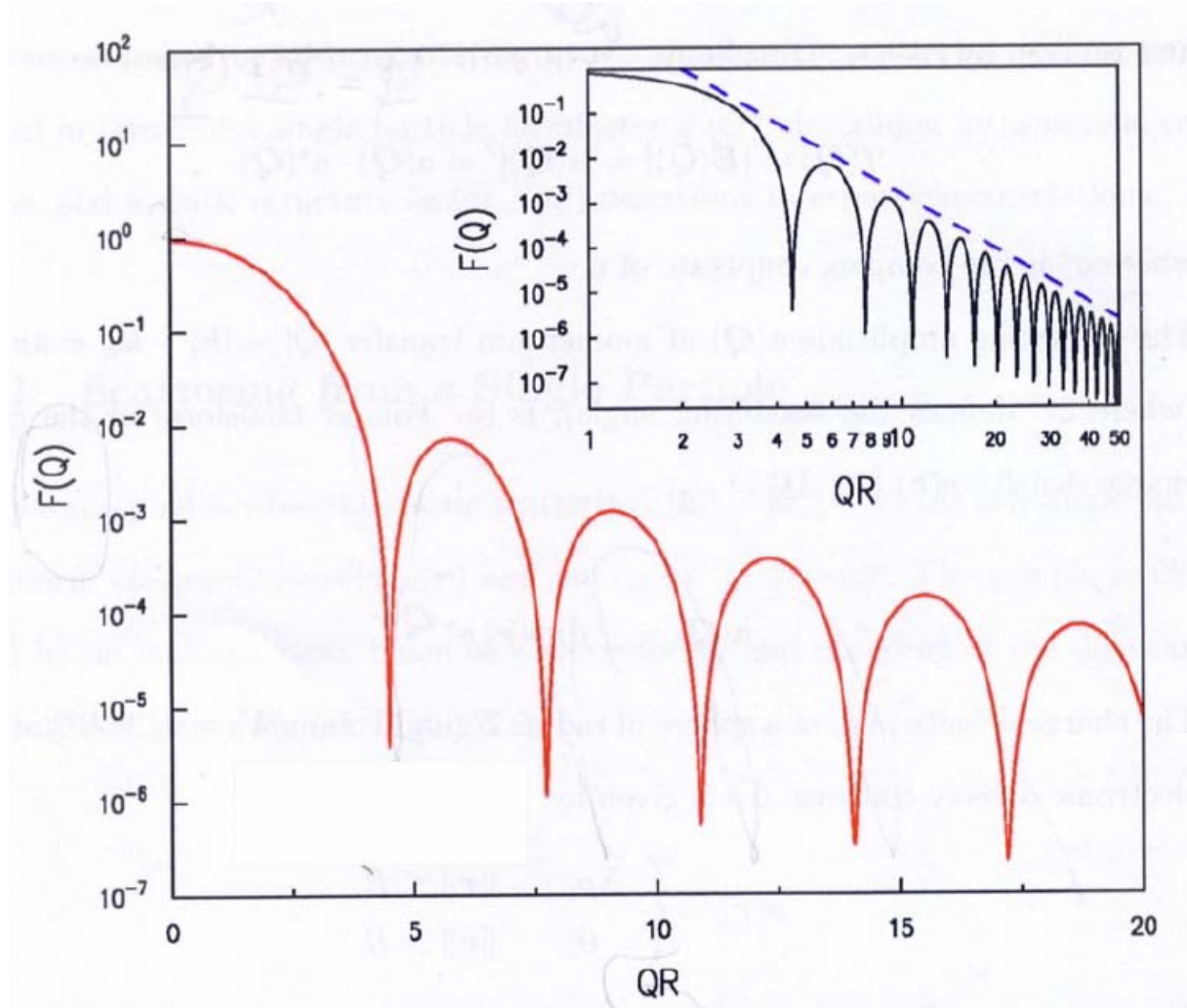
$$F(\vec{q}) = \int_{V=\text{particleVolume}} \rho(\vec{r}) \cdot e^{-i\vec{q}\vec{r}} \cdot d^3r = \int_0^R \int_0^{2\pi} \int_0^\pi \rho_0 \cdot e^{-i\vec{q}\vec{r}} r^2 \sin(\theta) d\theta d\varphi dr$$

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

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

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

Colloid: homogeneous sphere of radius R



See lecture 4 of GG

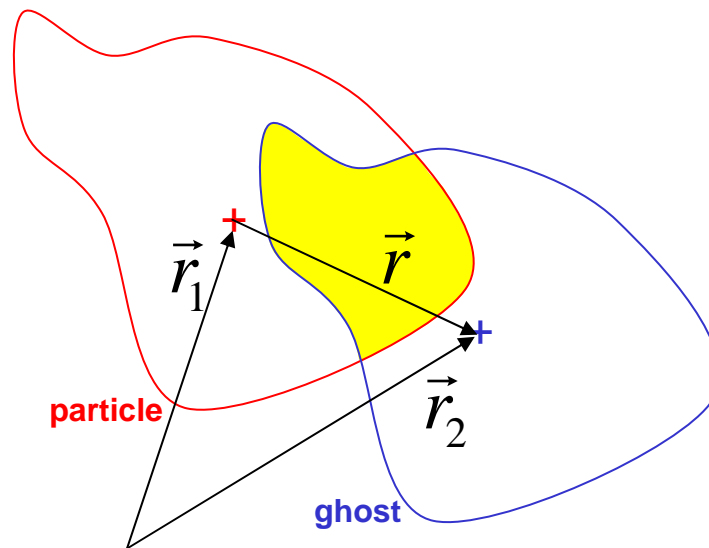
Single Particle Scattering in Dilute Systems

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

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

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

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



Guinier-Approximation

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

$$I(q) = \langle |F(\vec{q})|^2 \rangle = 4\pi \int_0^\infty \gamma(r) \cdot r^2 \cdot \frac{\sin(qr)}{qr} \cdot dr \quad q \rightarrow 0 \quad \text{Forward scattering}$$

We use: $\frac{\sin(qr)}{qr} = \frac{qr - \frac{1}{6}(qr)^3 + \dots}{qr} = 1 - \frac{1}{6}(qr)^2 + O((qr)^4)$ Taylor series expansion for $qr \rightarrow 0$ or $q \ll 1/r$!

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

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

$I(q=0)$

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

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

Radius of Gyration

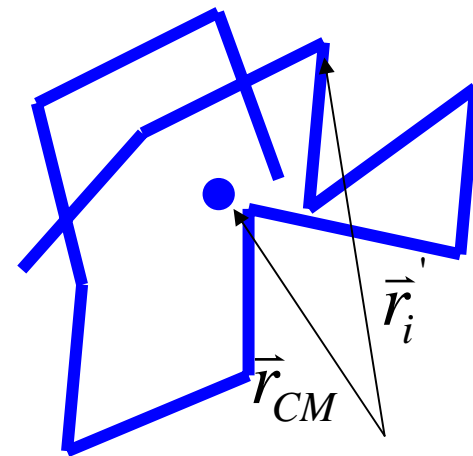
$$R_G = \sqrt{\frac{1}{M} \sum_1^N \langle m_i \vec{r}_i^2 \rangle}$$

Guinier-Approximation – for polymer systems

$$R_G = \sqrt{\frac{1}{M} \sum_1^N \langle m_i \bar{r}_i^2 \rangle} \quad \text{Say } M=N \text{ } M_0 \quad R_G^2 = \frac{1}{N} \sum_1^N \langle \bar{r}_i^2 \rangle = \frac{1}{N} \sum_1^N \langle (\bar{r}'_i - \bar{r}_{CM})^2 \rangle$$

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

$$\Rightarrow R_G^2 = \frac{1}{2N^2} \sum_{j,i=1}^N \underbrace{\langle (\bar{r}'_i - \bar{r}'_j)^2 \rangle}_{|j-i|a^2} \quad a \sim \text{mean length}$$



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

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

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

Guinier-Approximation – for polymer systems

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

\downarrow
 $\langle \dots \rangle \rightarrow 0$

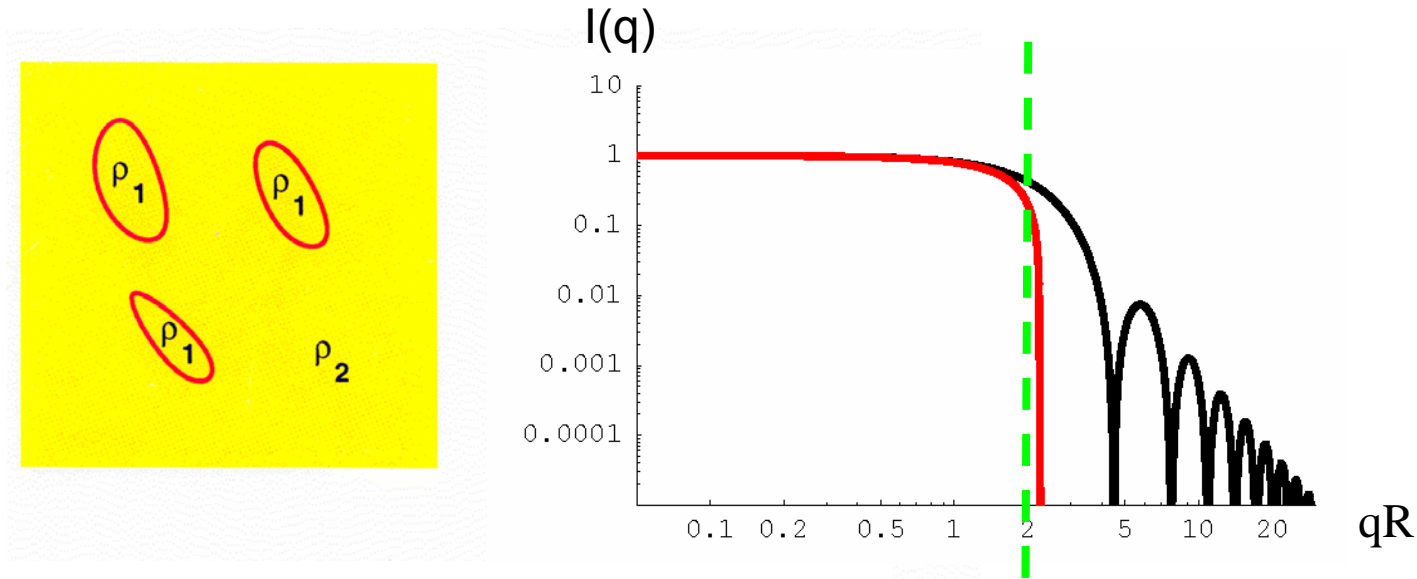
$$\langle |\vec{q}(\vec{r}_j - \vec{r}_k)|^2 \rangle = |q^2| \underbrace{\langle |\vec{r}_j - \vec{r}_k|^2 \cos(\theta)^2 \rangle}_{\text{Only r-dependence, no } \theta\text{-dependence}} = \frac{1}{3} q^2 \langle |\vec{r}_j - \vec{r}_k|^2 \rangle$$

Only r-dependence, no θ -dependence

$$\begin{aligned} \langle |F(\vec{q})|^2 \rangle &= \frac{1}{N} \sum_{j,k=1}^N \left(1 - \frac{1}{6} q^2 \langle |\vec{r}_j - \vec{r}_k|^2 \rangle \right) \\ &= \frac{1}{N} \left(N^2 - \frac{1}{3} q^2 \frac{1}{2} \sum_{j,k=1}^N \langle |\vec{r}_j - \vec{r}_k|^2 \rangle \right) \end{aligned}$$

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

Guinier approximation - spheres



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

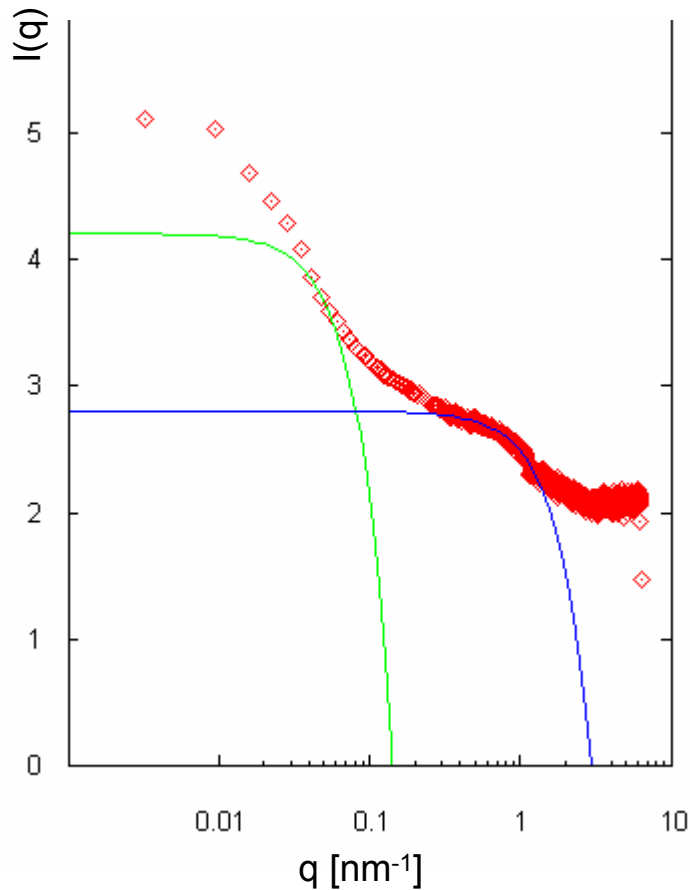
$$\rightarrow \ln(I) = \ln I(0) - \frac{1}{3} R_G^2 \cdot q^2$$

Radius of Gyration R_g

Monodisperse spheres of radius R :

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

Guinier Approximation



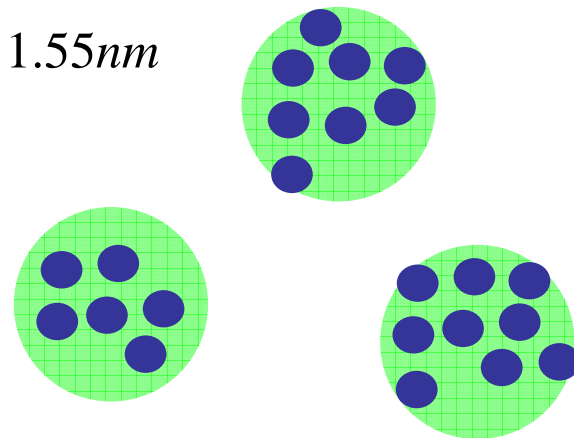
$$\lim_{q \rightarrow 0} I(q) = \Delta\rho^2 \cdot V^2 \cdot \exp\left(-q^2 \cdot \frac{R_g^2}{3}\right)$$

Radius of Gyration R_g

Monodisperse spheres of radius $R=2\text{nm}$:

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

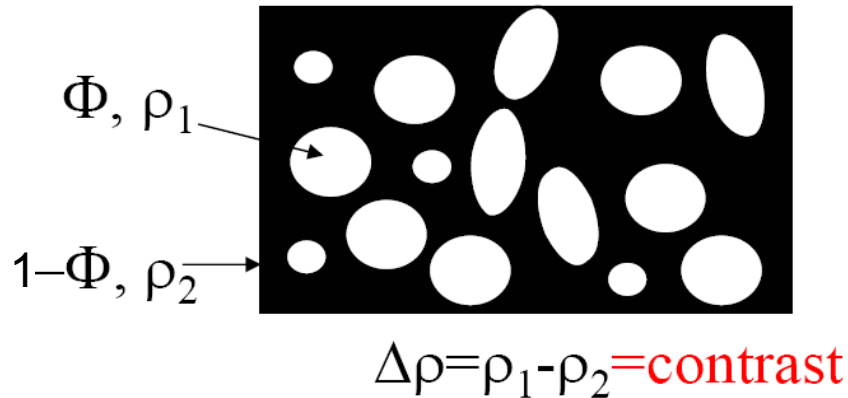
2nm Colloids
domains



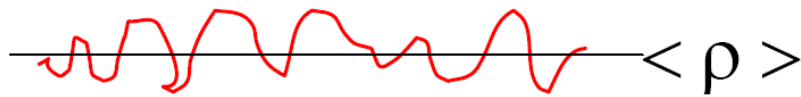
Very useful to get a hand on length scales!
Sometimes only valid in limited q -range

Porod's Theorems - I:

Two-phase system



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



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

Isotropic:

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

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

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

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

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

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

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

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

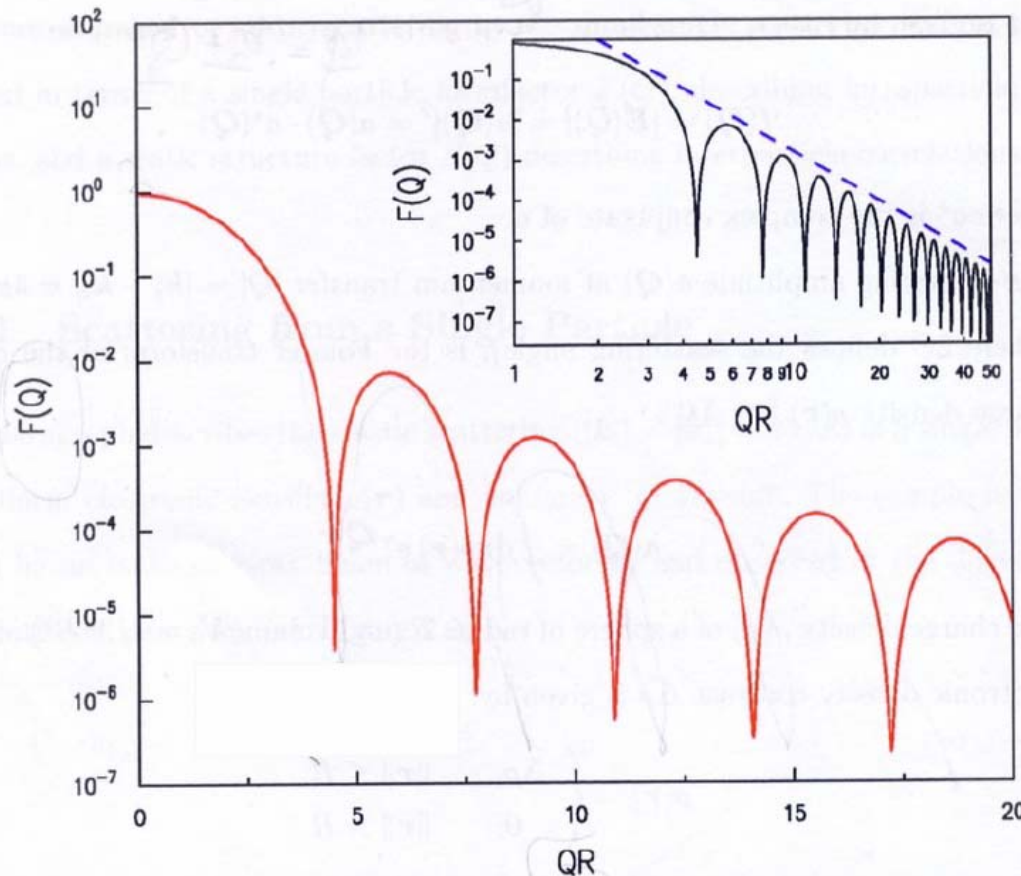
$$\int I_m(\vec{q}) d\vec{q} I_m(\vec{q}) = \langle \rho^2 \rangle - \langle \rho \rangle^2$$

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

Porod's Theorems - II: 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



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

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

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

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

Surface of sphere

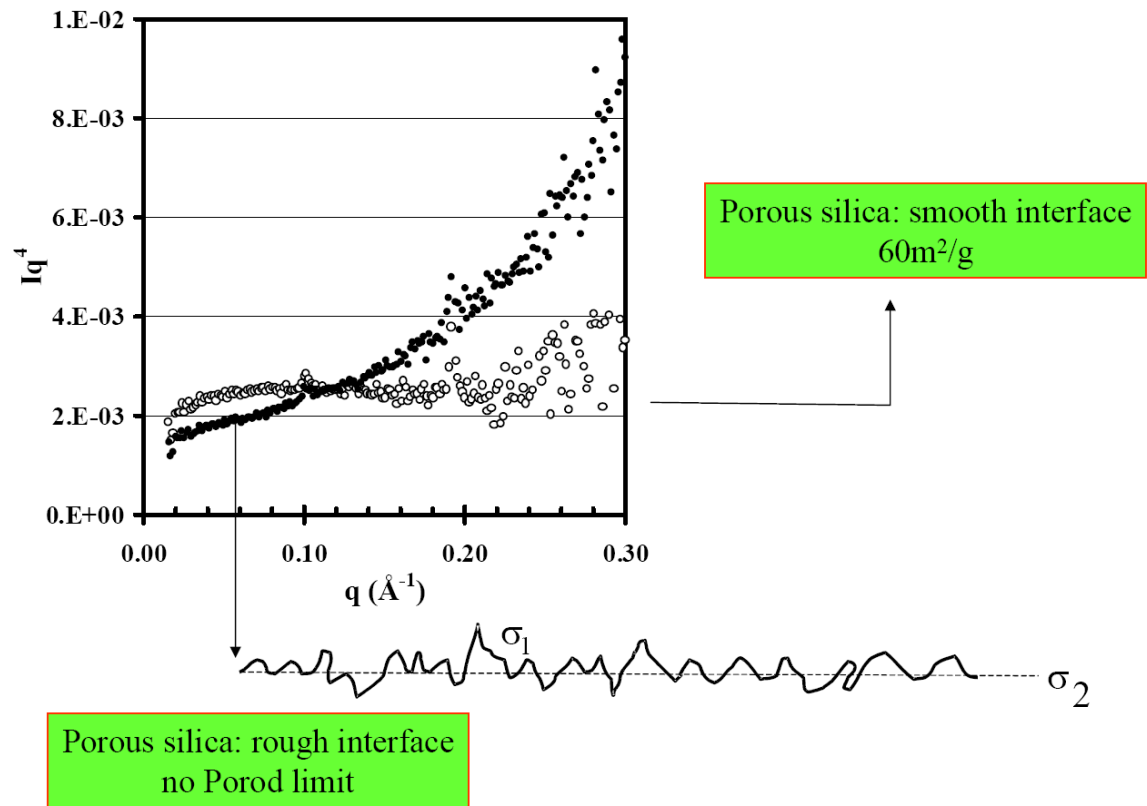
General

Two phases with sharp interface

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

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

Means to determine specific surface σ/V

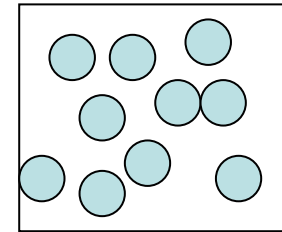
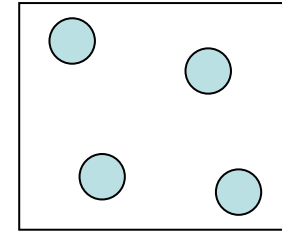


Structure factor

Latex spheres

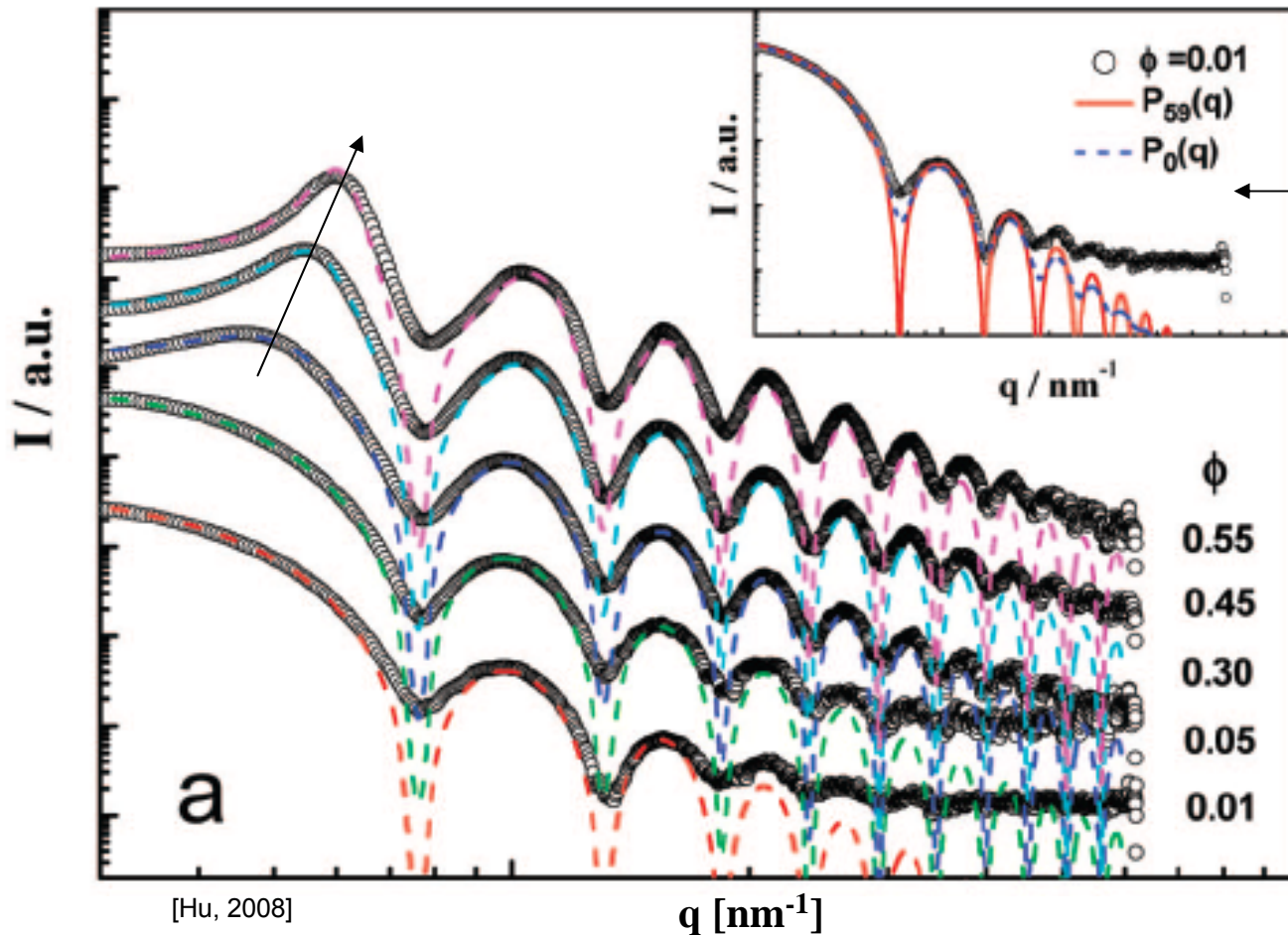
$$I(q) = S(q)P(q)$$

Low ϕ $P(q)$
 High ϕ $S(q)P(q)$



Gaussian distribution of particle sizes

Shift in maximum:
 Decreasing distance



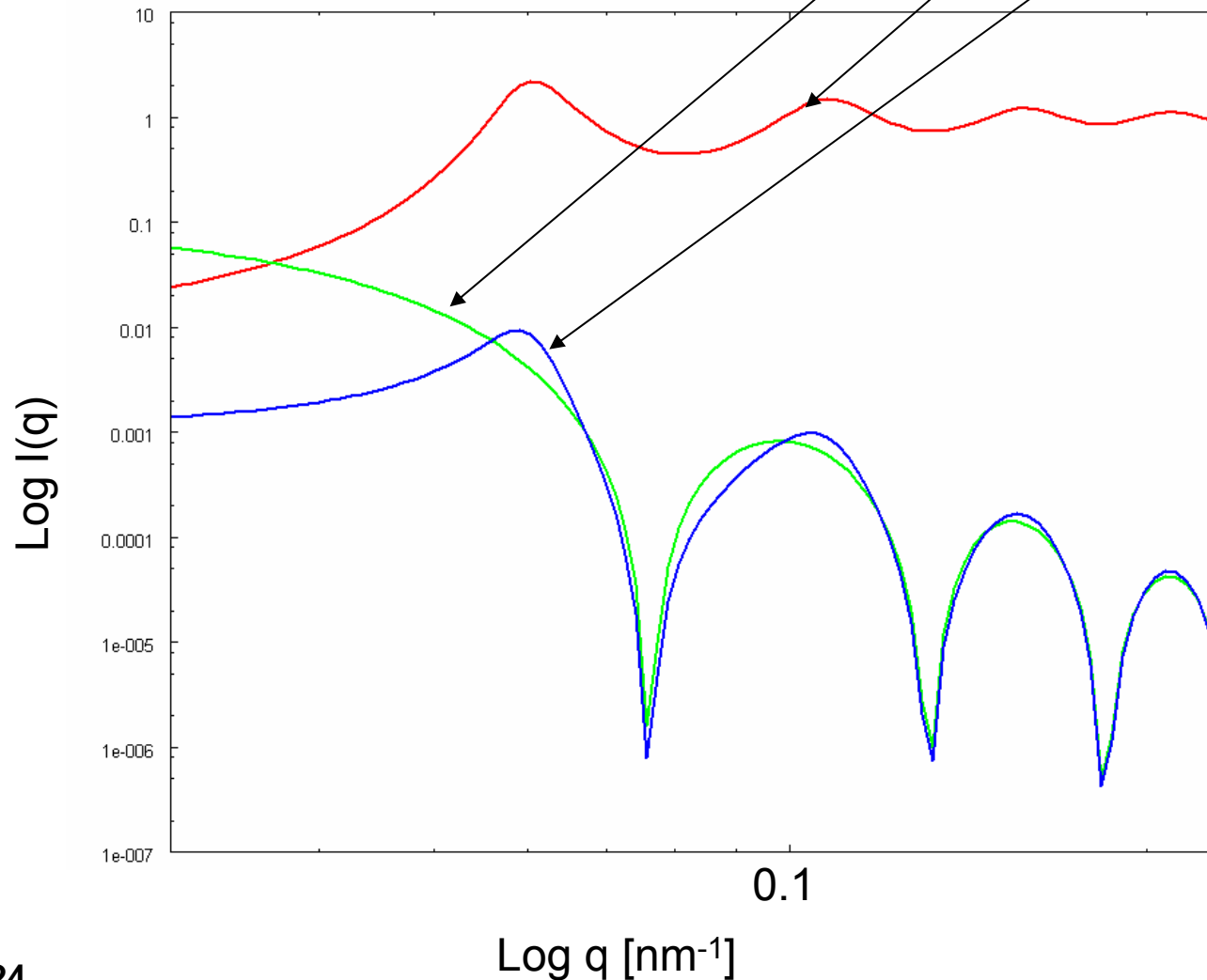
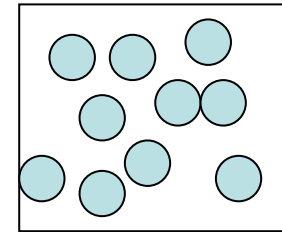
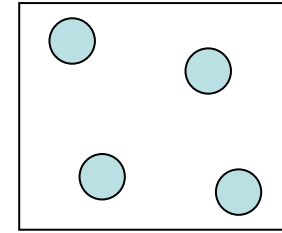
[Hu, 2008]

Structure factor

Latex spheres

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

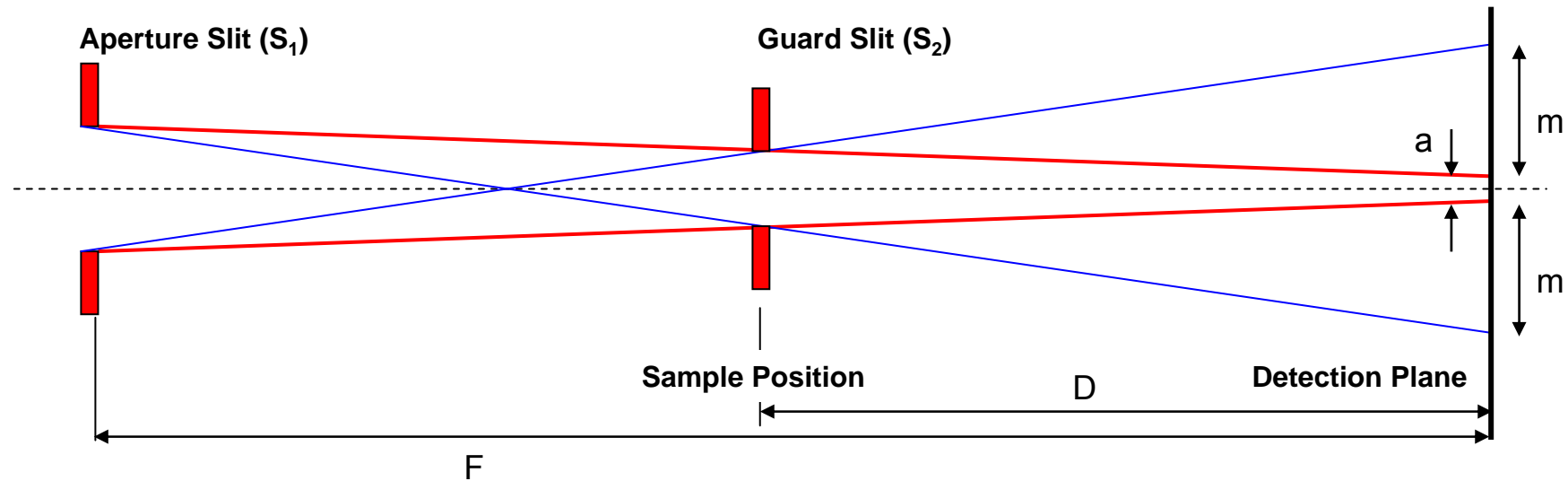
Low ϕ $P(q)$
High ϕ $S(q)P(q)$



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)

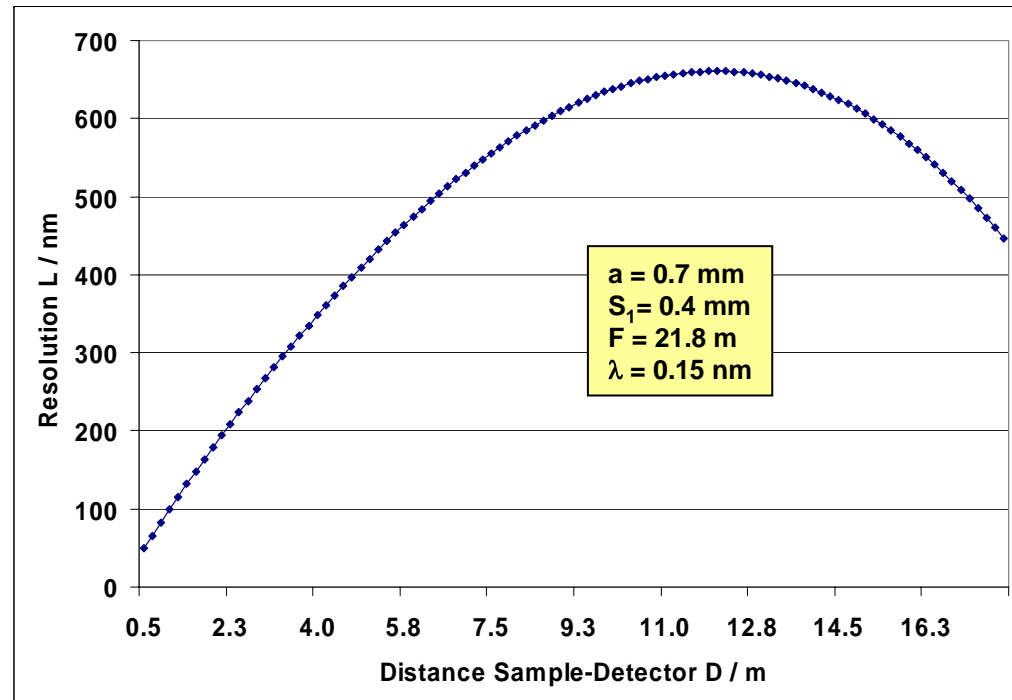
Resolution of a SAXS Instrument



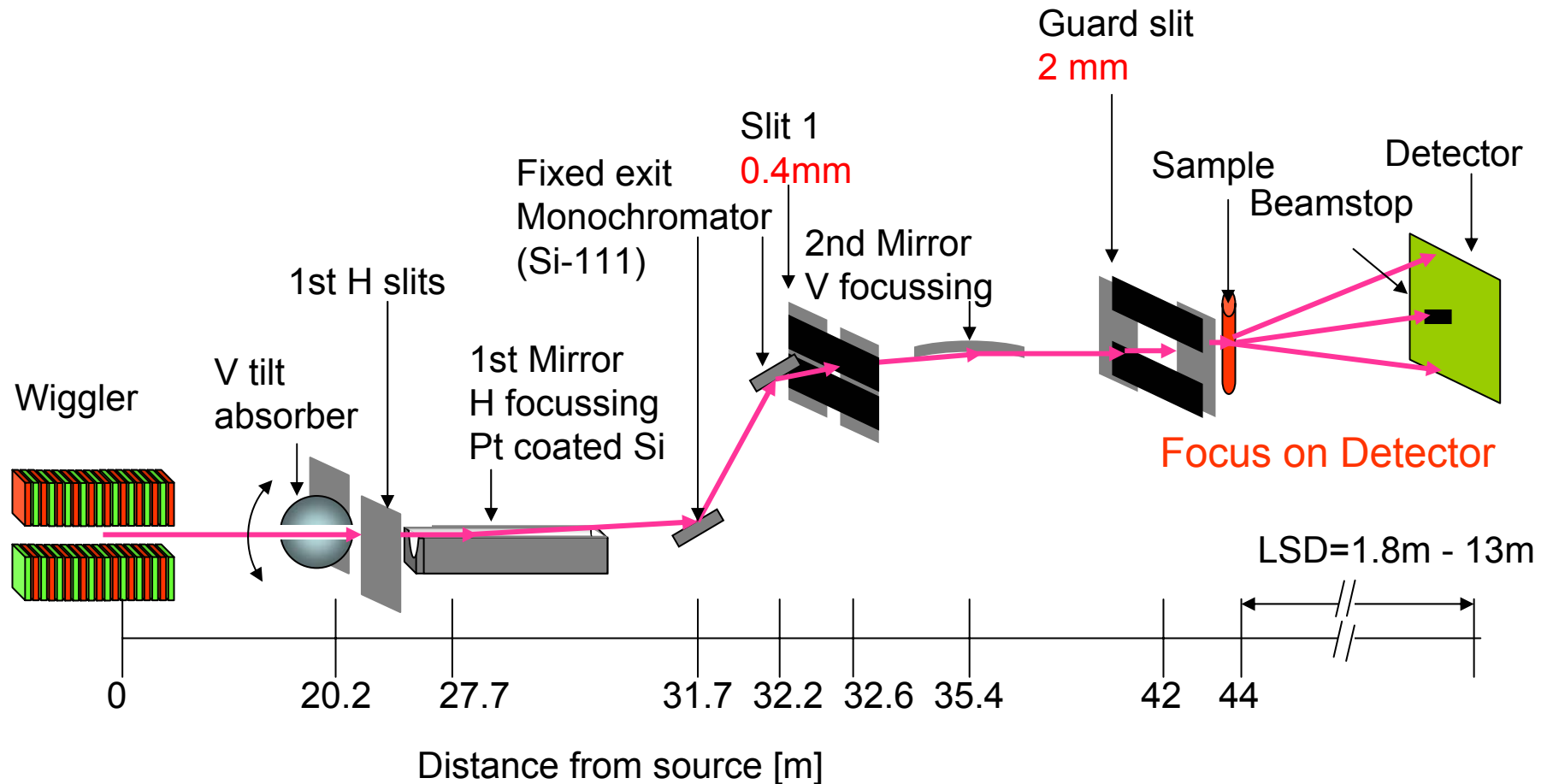
$$S_2 = \frac{S_1 - a}{F} \cdot (D + a)$$

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

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

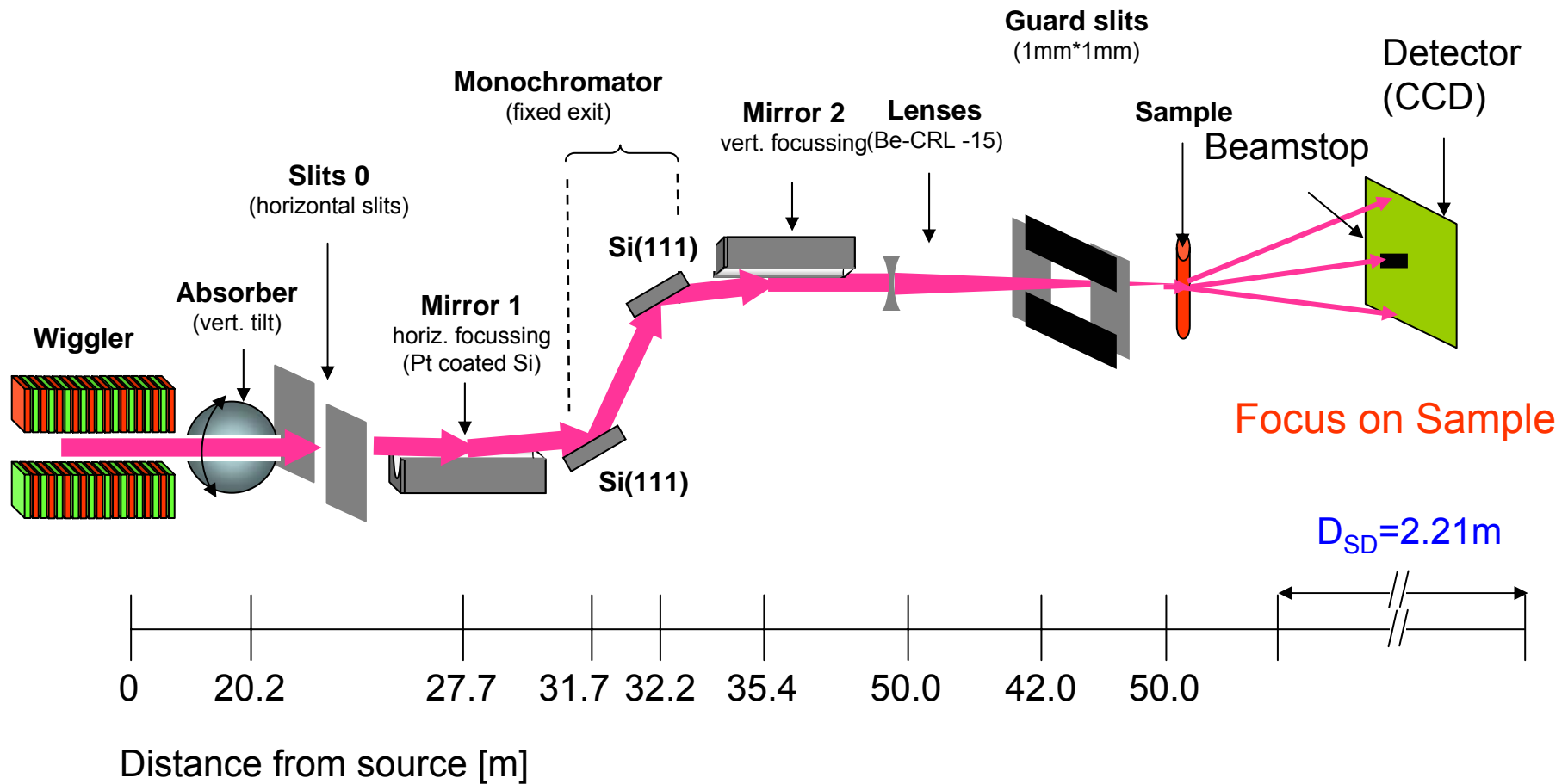


SAXS Instrument - Example BW4 - USAXS

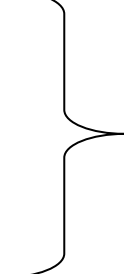


Resolution (maximum observed correlation distances) depends on sample to detector distance: 90 nm to 700 nm, photon flux $5 \cdot 10^9 \text{ sec}^{-1}$ (monochromatic)

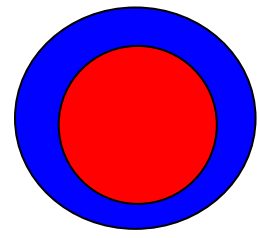
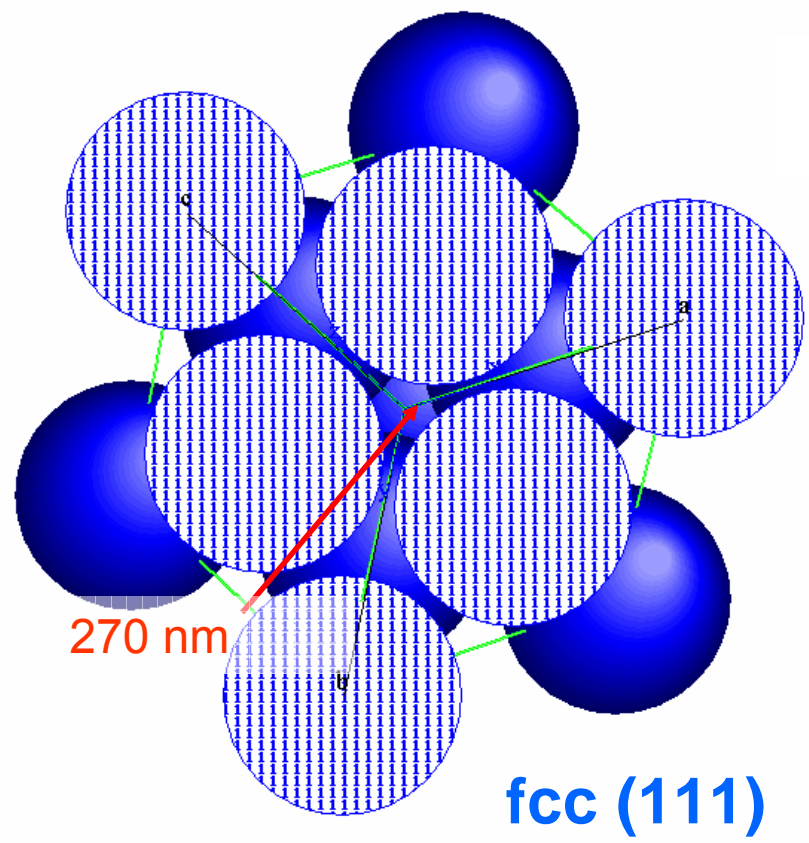
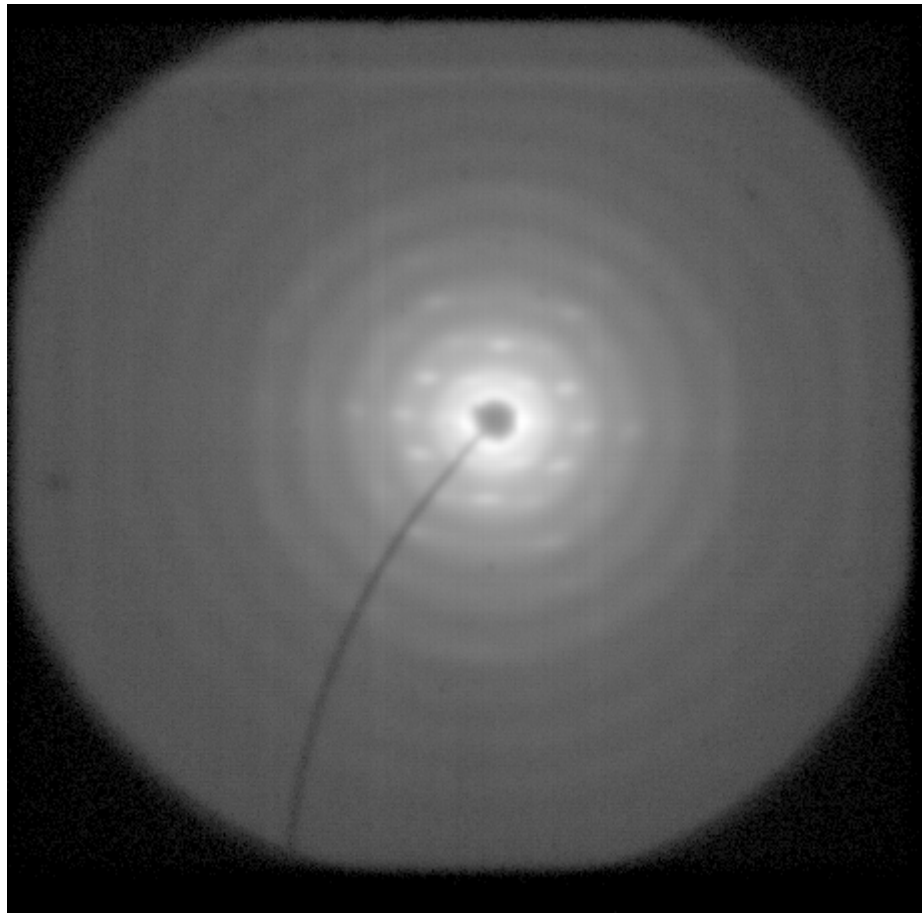
Microfocus @ BW4



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)



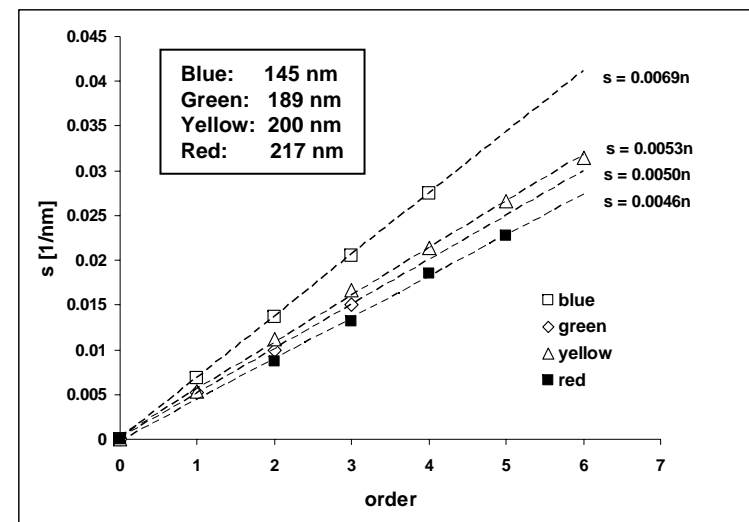
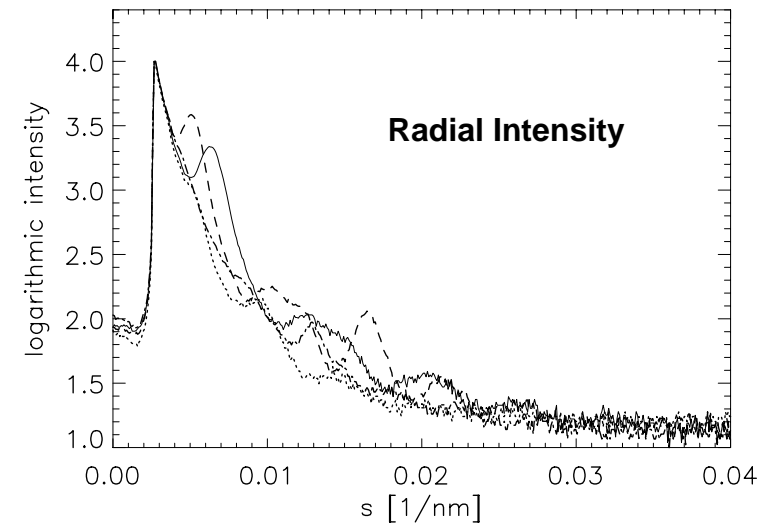
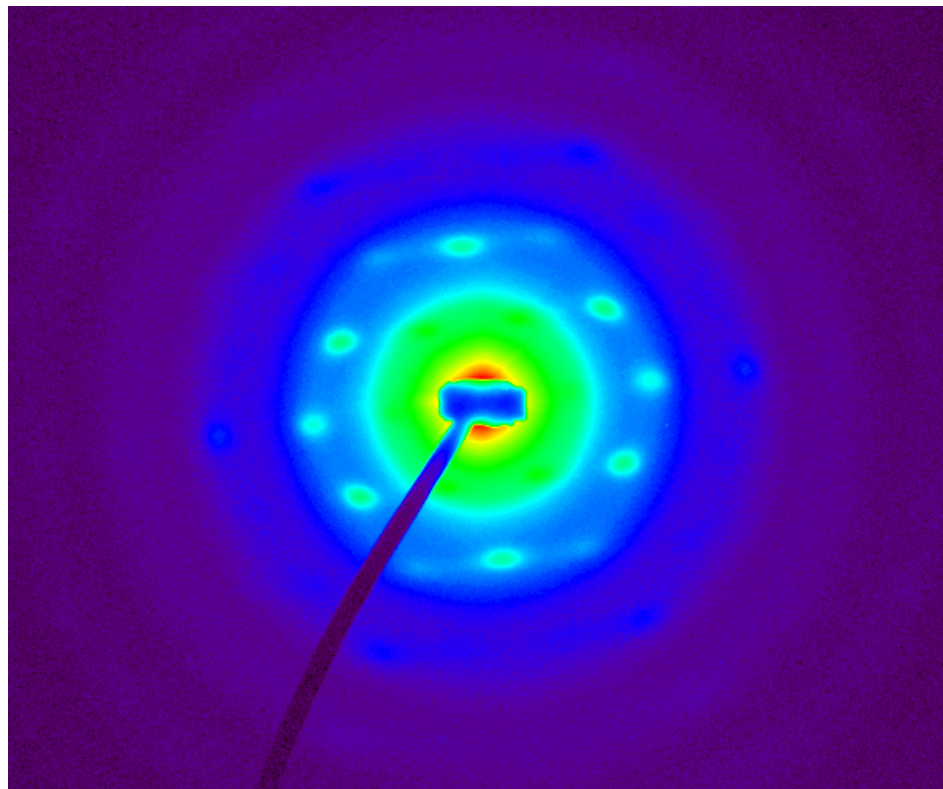
Core: PS (hard)
Shell: PMMA (soft)

Colloidal Crystals in Latex Films

Core: Polystyrene

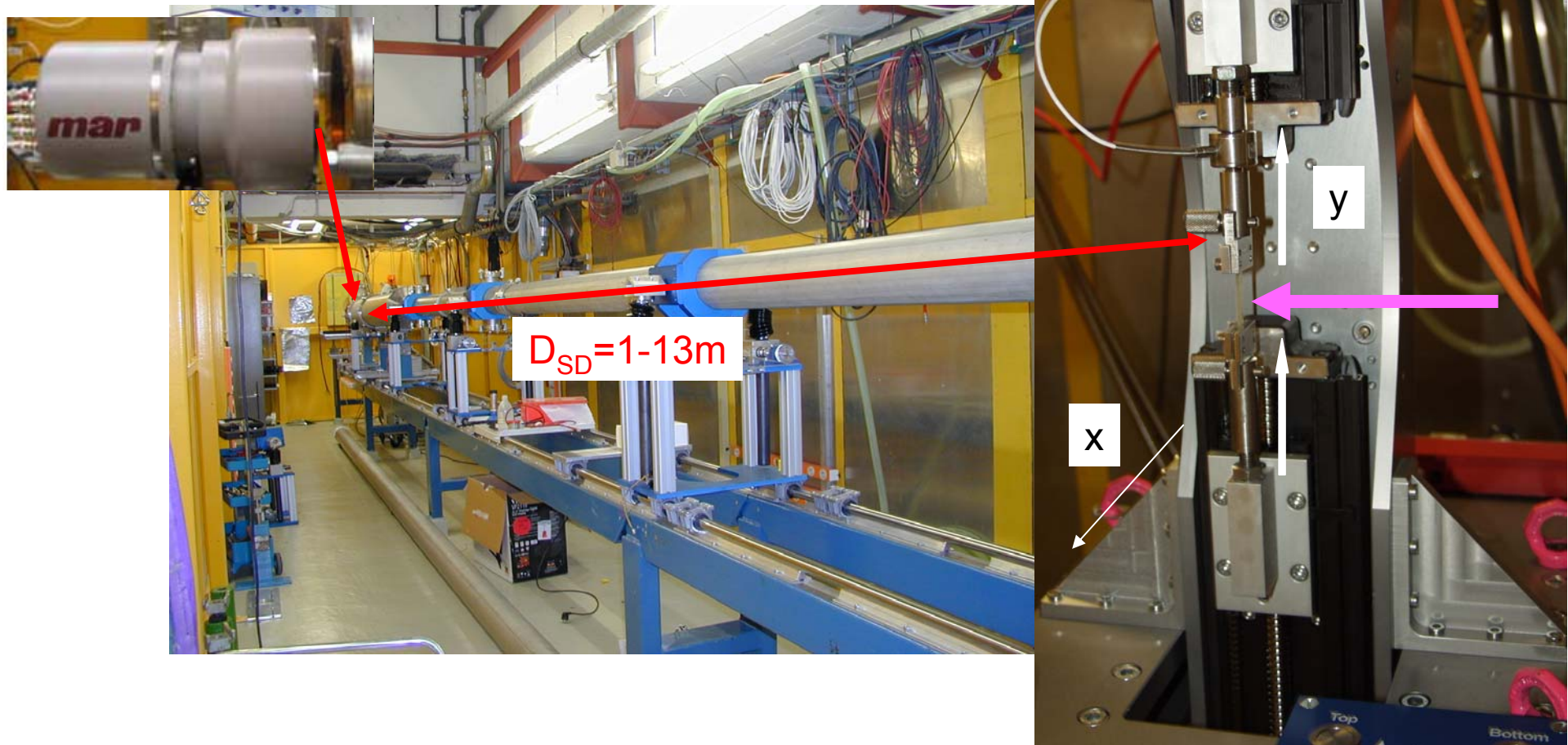
Shell: Polymethylmetacrylate - polyethylacrylate

Fcc lattice

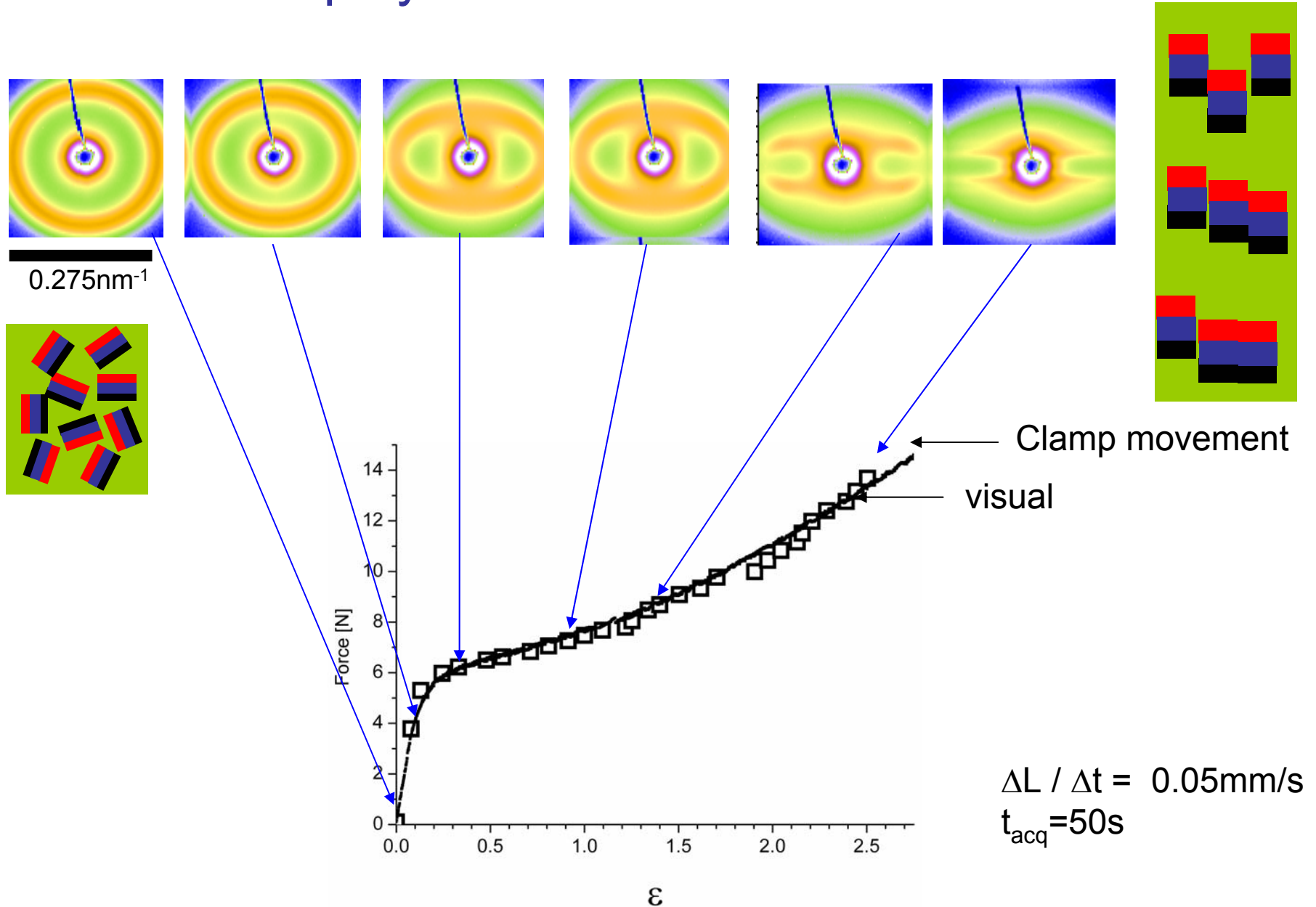


Deformation of polymers - SBS

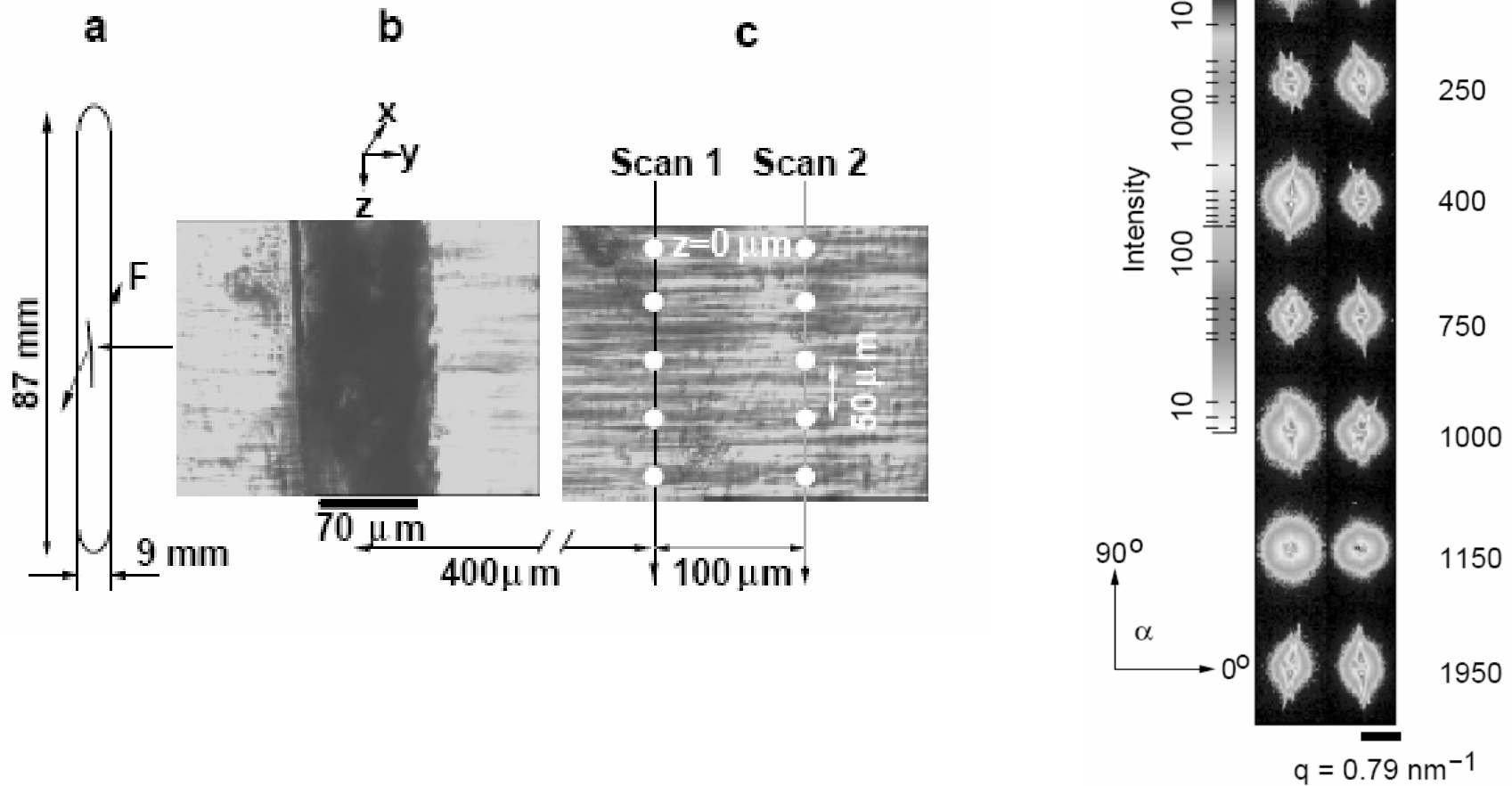
Triblock-copolymer



Deformation of polymers - SBS



Deformation – cracks & crazes

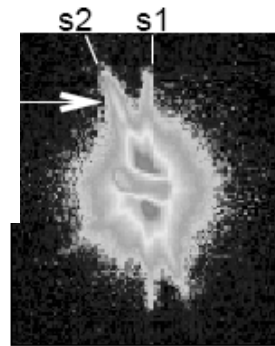
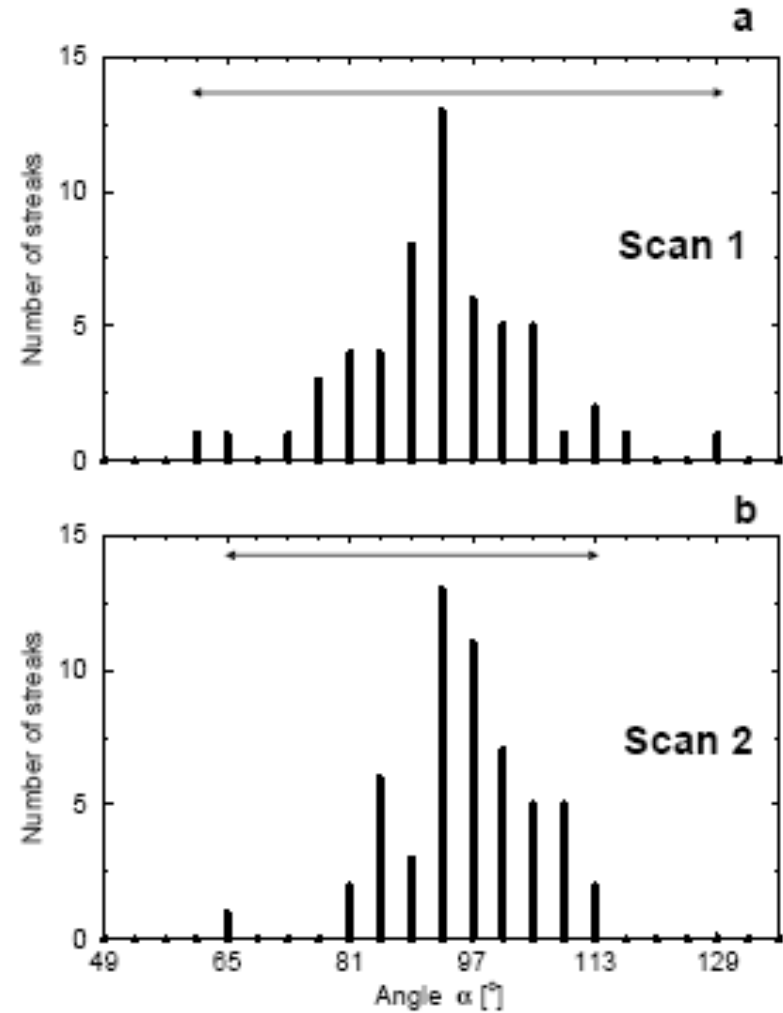
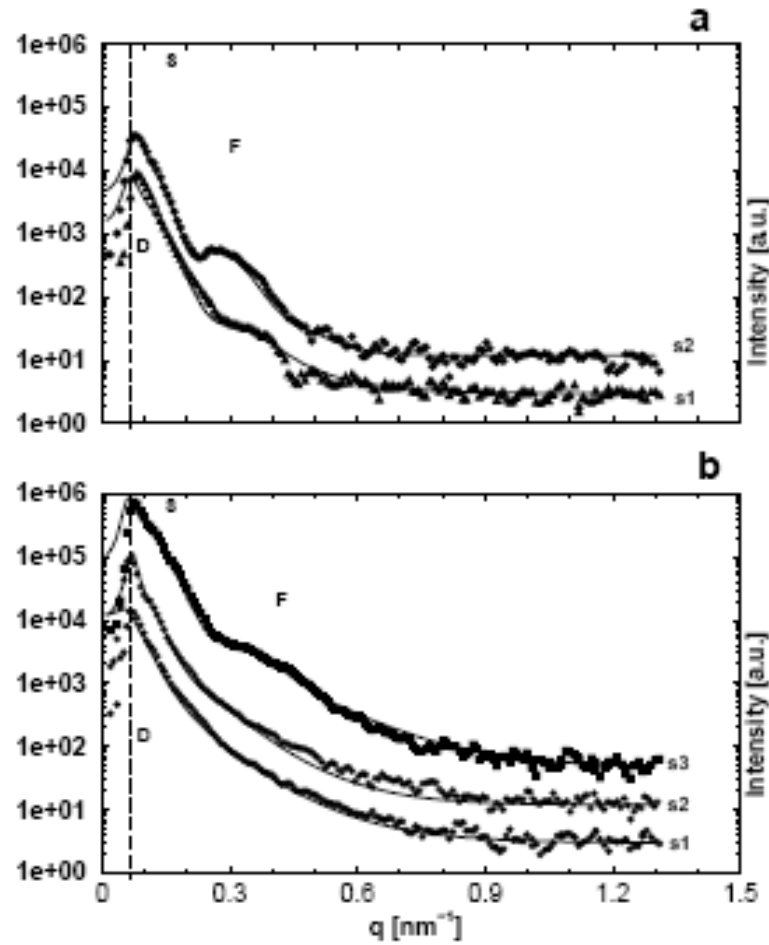


Roth et al., J. Appl. Cryst. 36, 684 (2003)

Strong overlap to materials science

Deformation – cracks & crazes

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

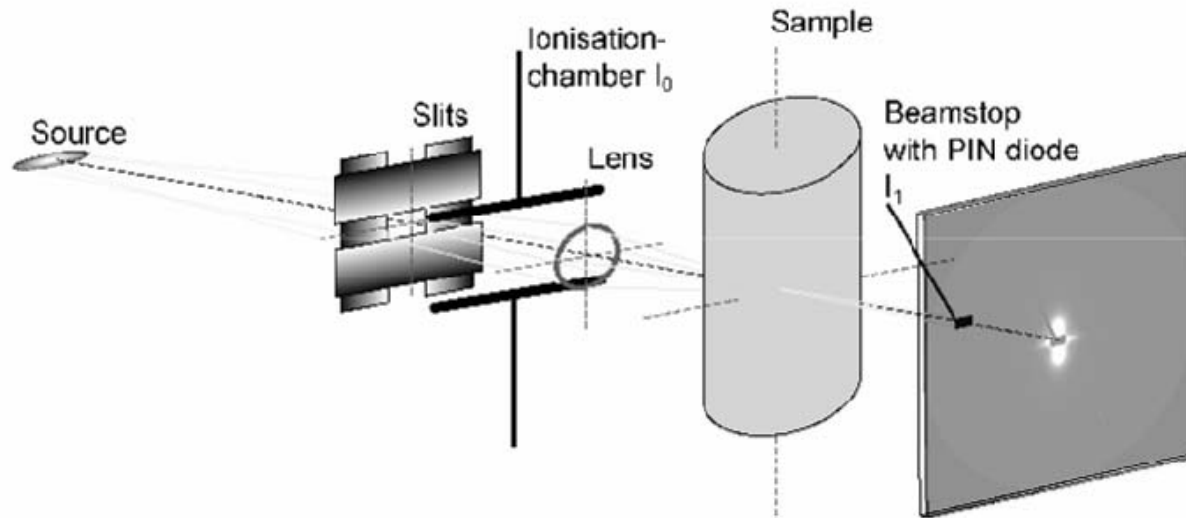


$q = 0.79 \text{ nm}^{-1}$

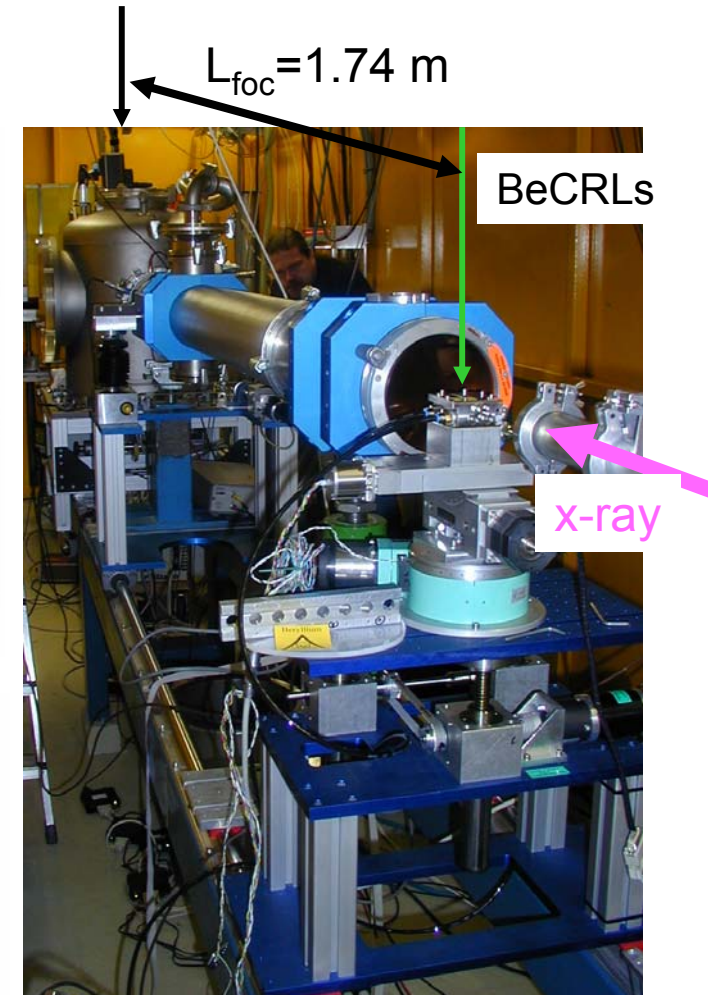
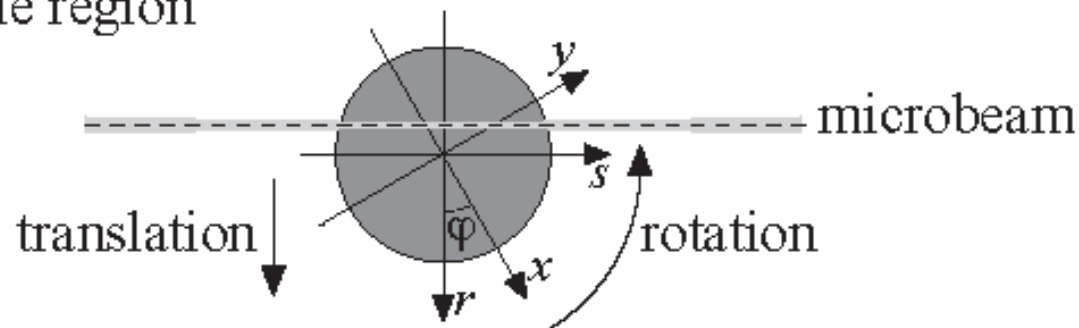
Statistics!
Thick sample

Tomographic Reconstruction of μ SAXS Pattern (BW4)

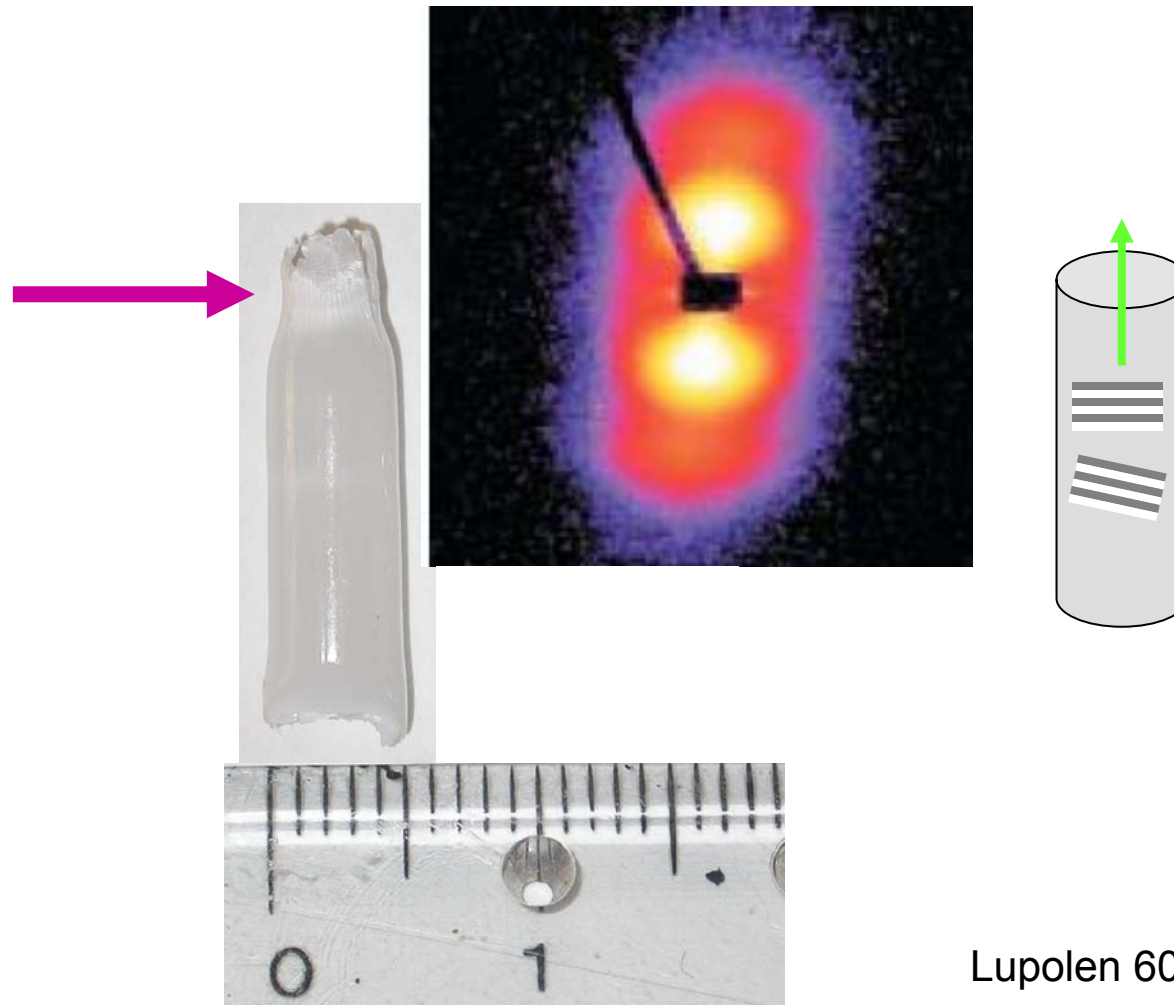
Irradiation direction of a volume element is **varied** step-by-step during the tomographic acquisition



top view of sample region



Tomographic Reconstruction of μ SAXS Pattern (BW4)



Lupolen 6021D by BASF

Beam size $60 \times 30 \mu\text{m}^2$

Results

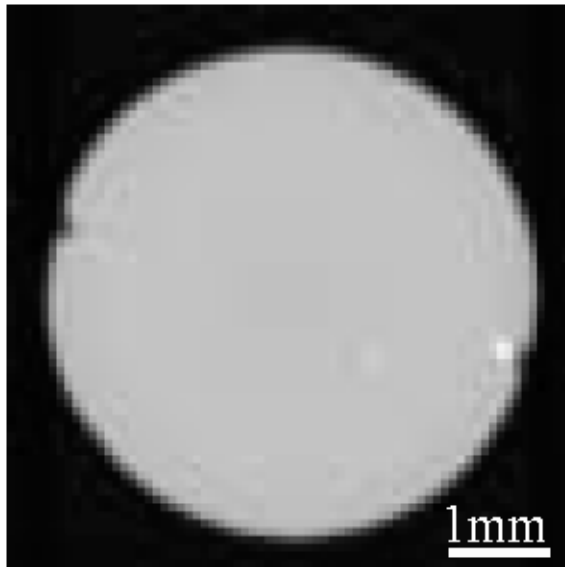
For each translation and rotation $(r, \phi) \Rightarrow$ one value for $I_q(r, \phi)$

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

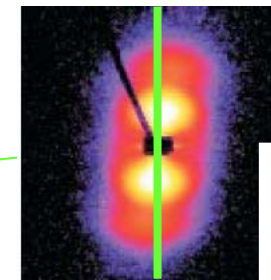
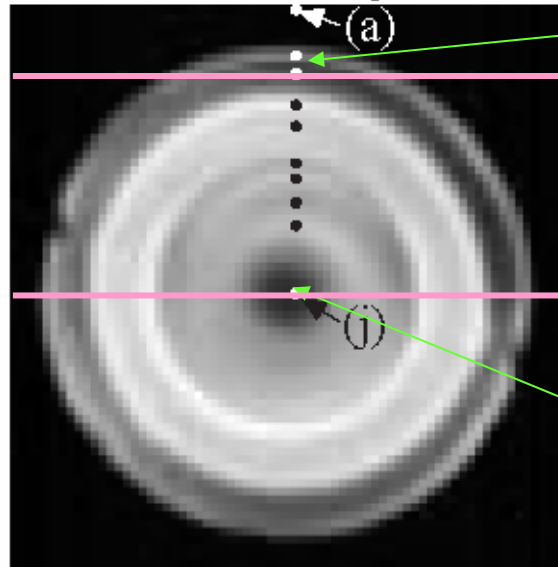
$$I_q(r, \phi) = I_1 \int ds p_{q, \phi} [x(s, r), y(s, r)] \sim \sum_k p_{q, \phi_j} [x(s_k, r_j), y(s_k, r_j)]$$

SAXS cross section

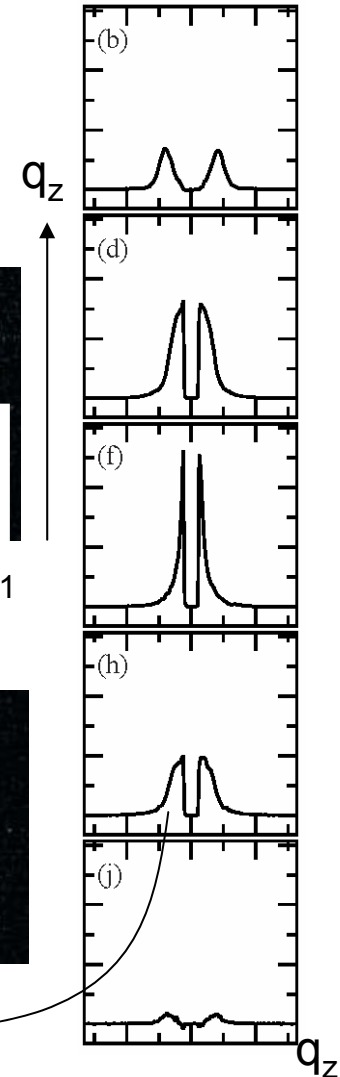
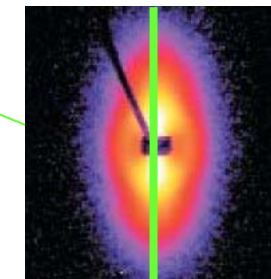
attenuation



scattered intensity



$q = 1 \text{ nm}^{-1}$



Integral of curve = grey scale

Results

