Methoden moderner Röntgenphysik II

Streuung und Abbildung

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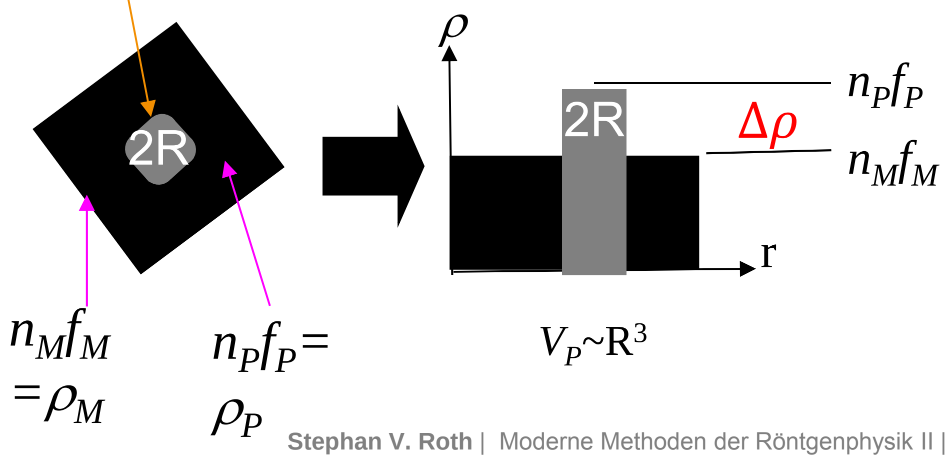
DESY
05.06.2014

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:

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



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- Incoherent sum of intensities:

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

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

Colloid: homogeneous sphere of radius R

A simple, but important calculation:

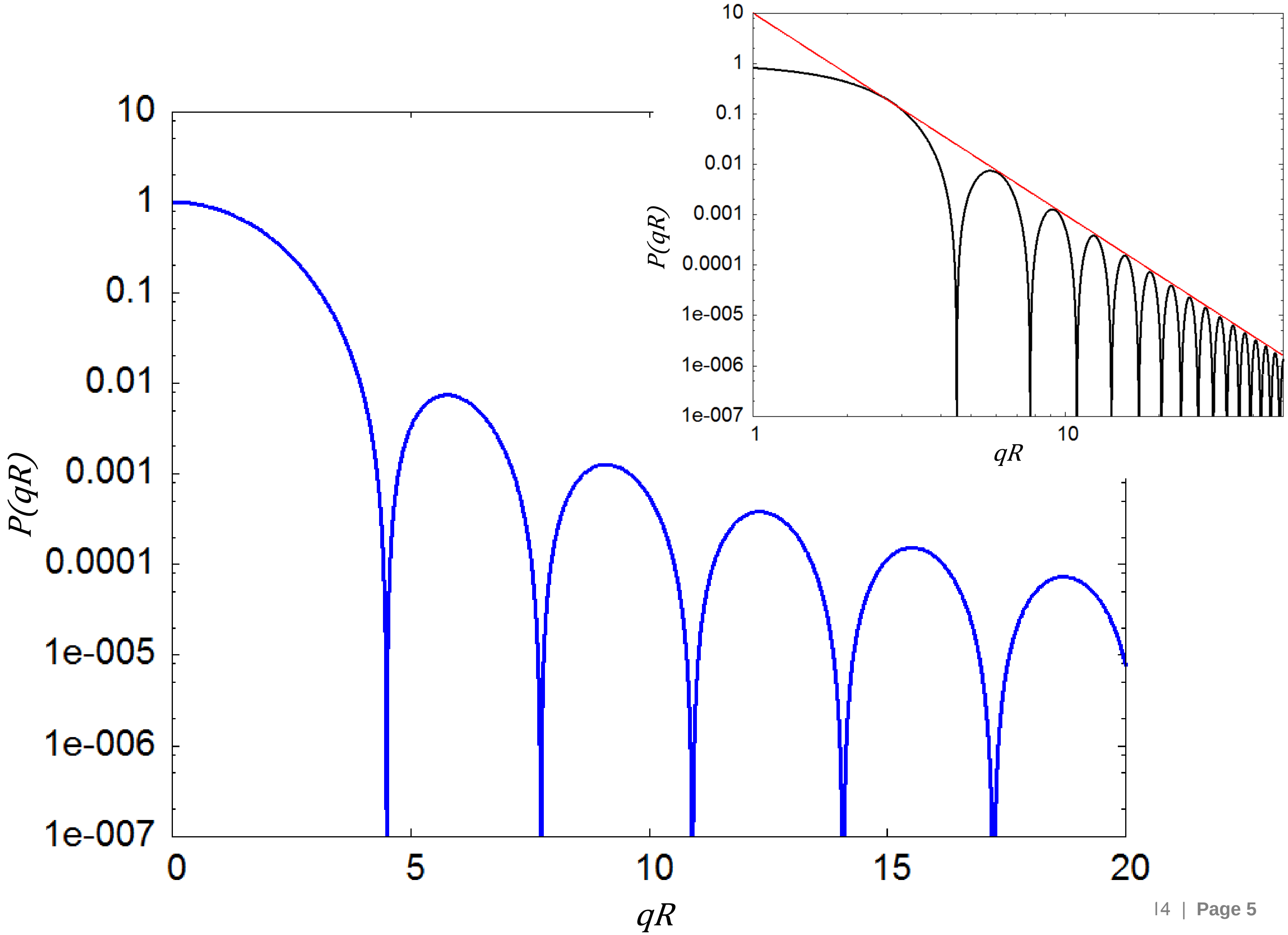
$$F(\vec{q}) = \int\limits_{V=particleVolume} \rho(\vec{r}) \cdot e^{-i\vec{q}\vec{r}} \cdot d^3 r = \int_0^R \int_0^{2\pi} \int_0^{\pi} \rho_0 \cdot e^{-i\vec{q}\vec{r}} r^2 \sin(\theta) d\theta d\varphi dr$$

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

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

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

Colloid: homogeneous sphere of radius R



Guinier radius

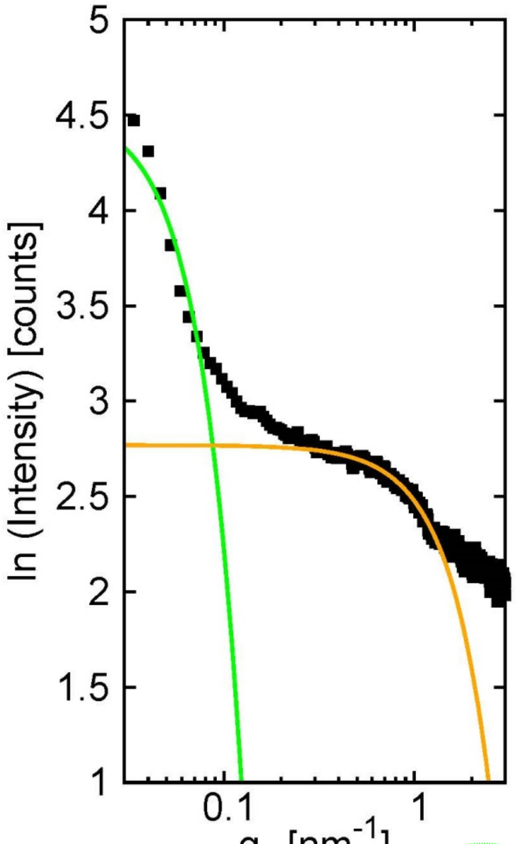
- $Q \rightarrow 0$
- Homogenous sphere of radius R

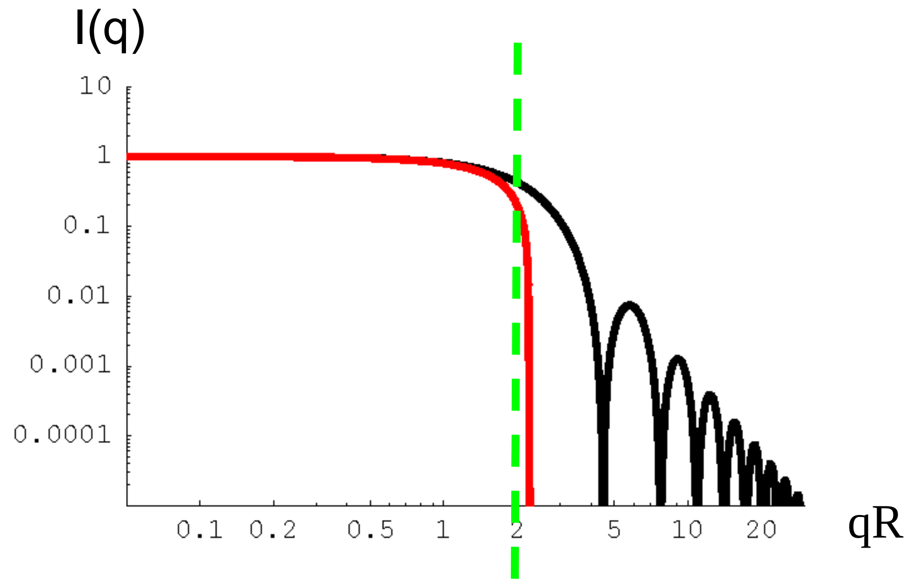
$$P(q) = \left| 3 \frac{\sin(qR) - qR\cos(qR)}{(qR)^3} \right|^2 \sim 1 - \frac{1}{5} q^2 R^2 \sim \exp(-\frac{1}{5} q^2 R^2)$$

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





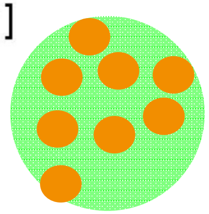
$$\lim_{q\to 0} I(q) = \Delta\rho^2 \cdot V^2 \cdot \exp(-q^2 \cdot \frac{R_g^2}{3})$$

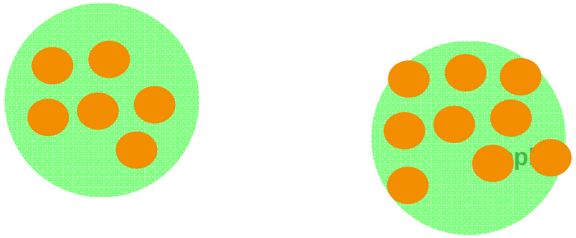
Radius of Gyration R_g

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

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

2nm Colloids
domains

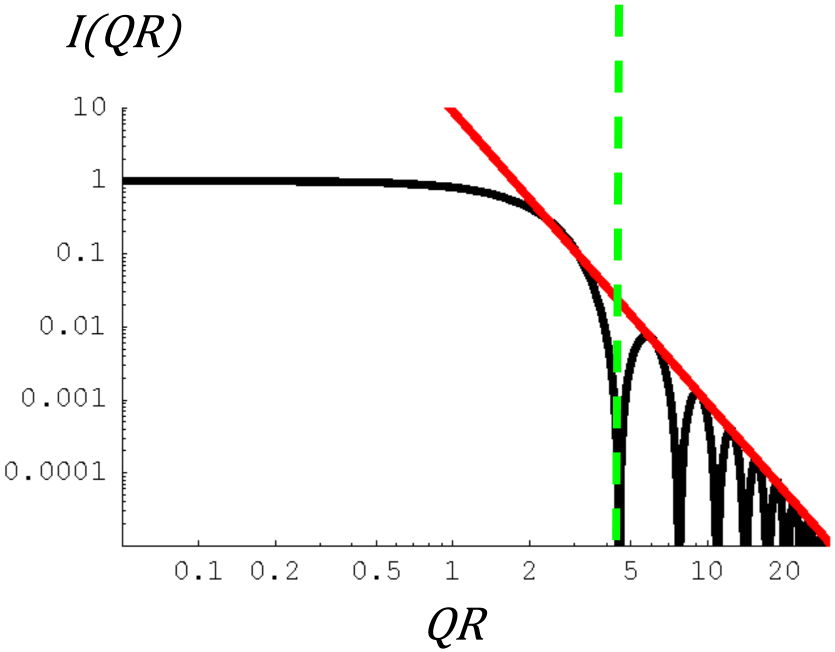




Porod‘s law: large q

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



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

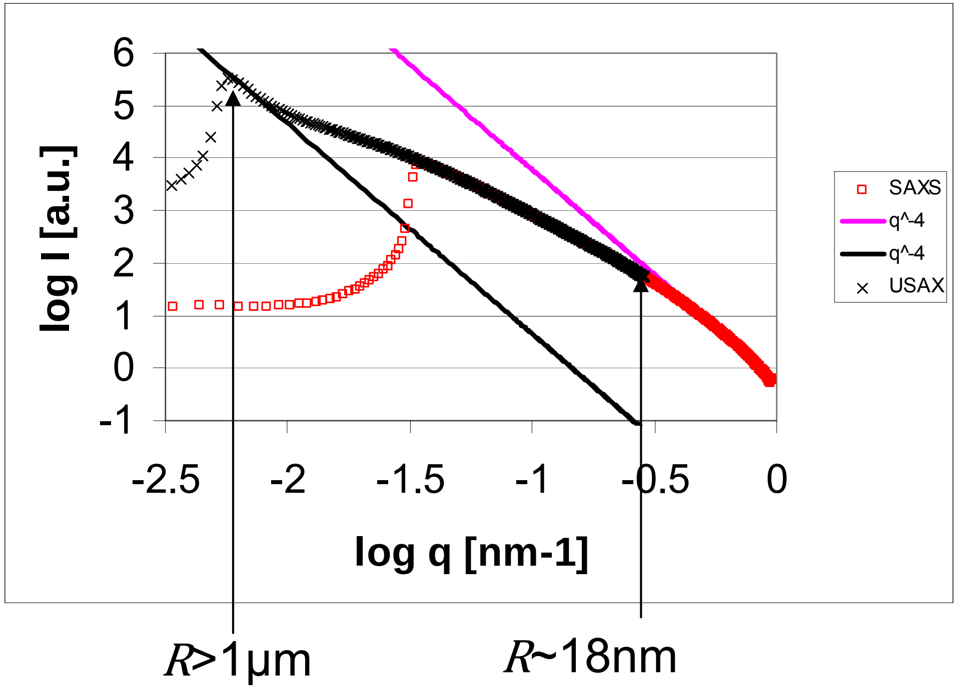
$$\leq \left(4\pi\rho_0 \frac{|\sin(qR)| + qR|\cos(qR)|}{(qR)^3} \right)^2$$

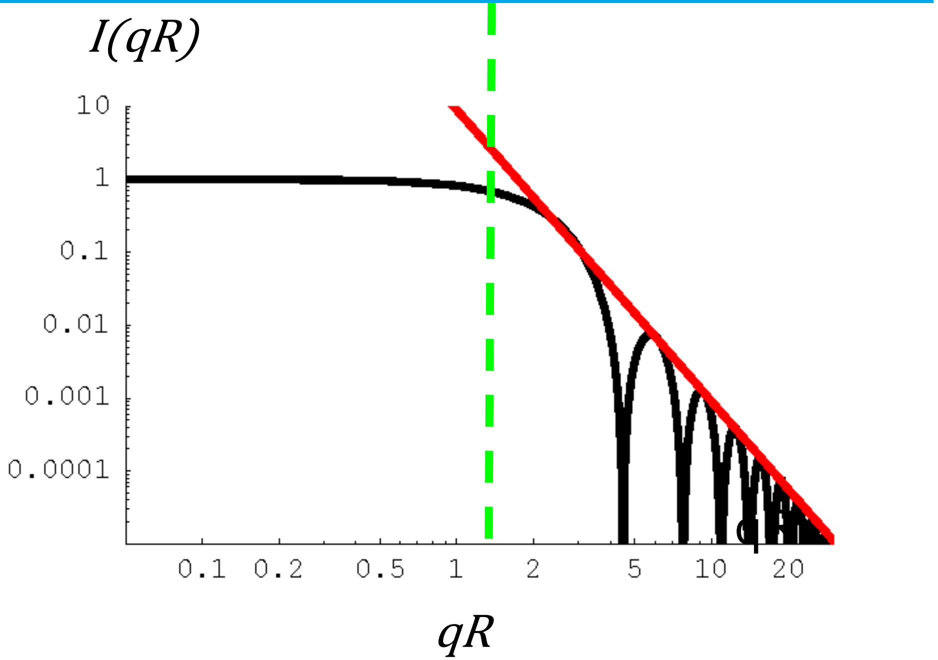
$$\sim \left(4\pi\rho_0 \frac{1+qR}{(qR)^3} \right)^2 \sim \left(4\pi\rho_0 \frac{qR}{(qR)^3} \right)^2$$

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

Surface of sphere

Porod‘s Law





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

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

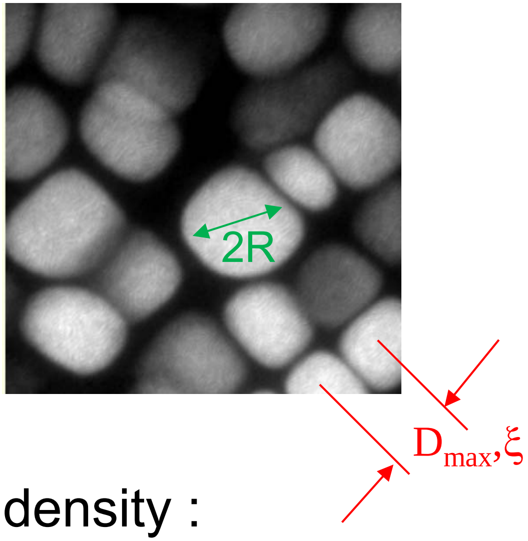
The structure factor – many particles, close distance

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

Form factor

Structure factor

Interference due to assembly of particles



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

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

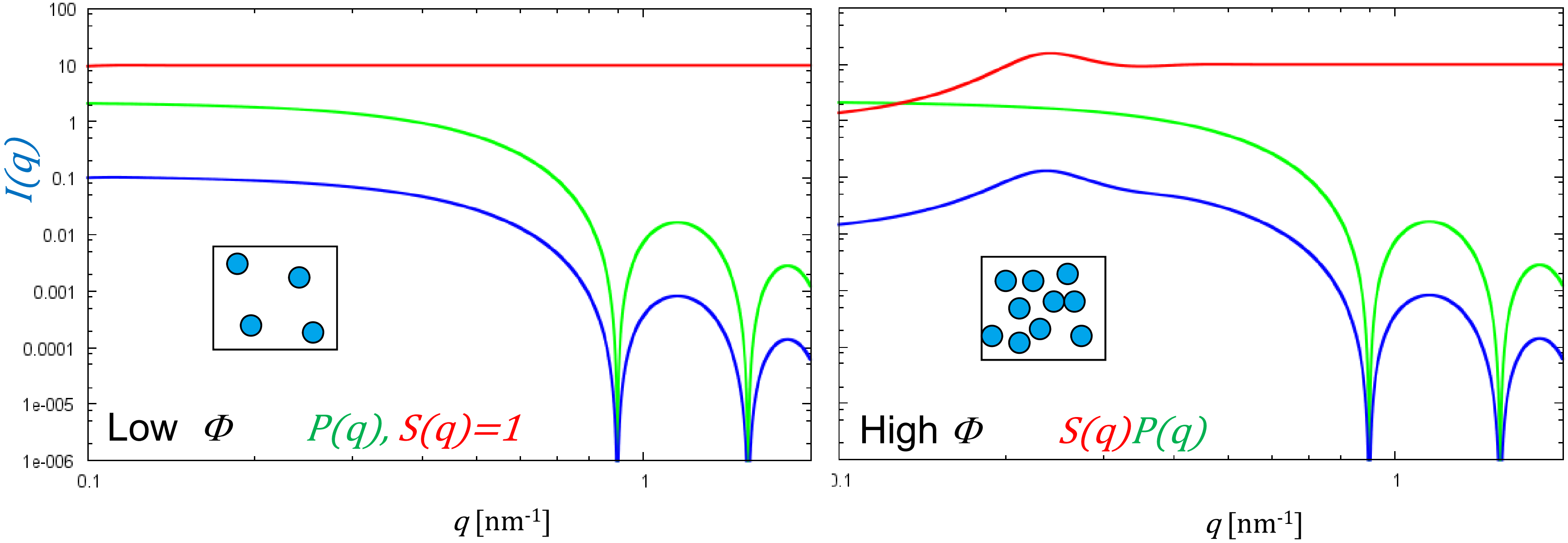
Smearing

Distance of particles

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

The structure factor – many particles, close distance

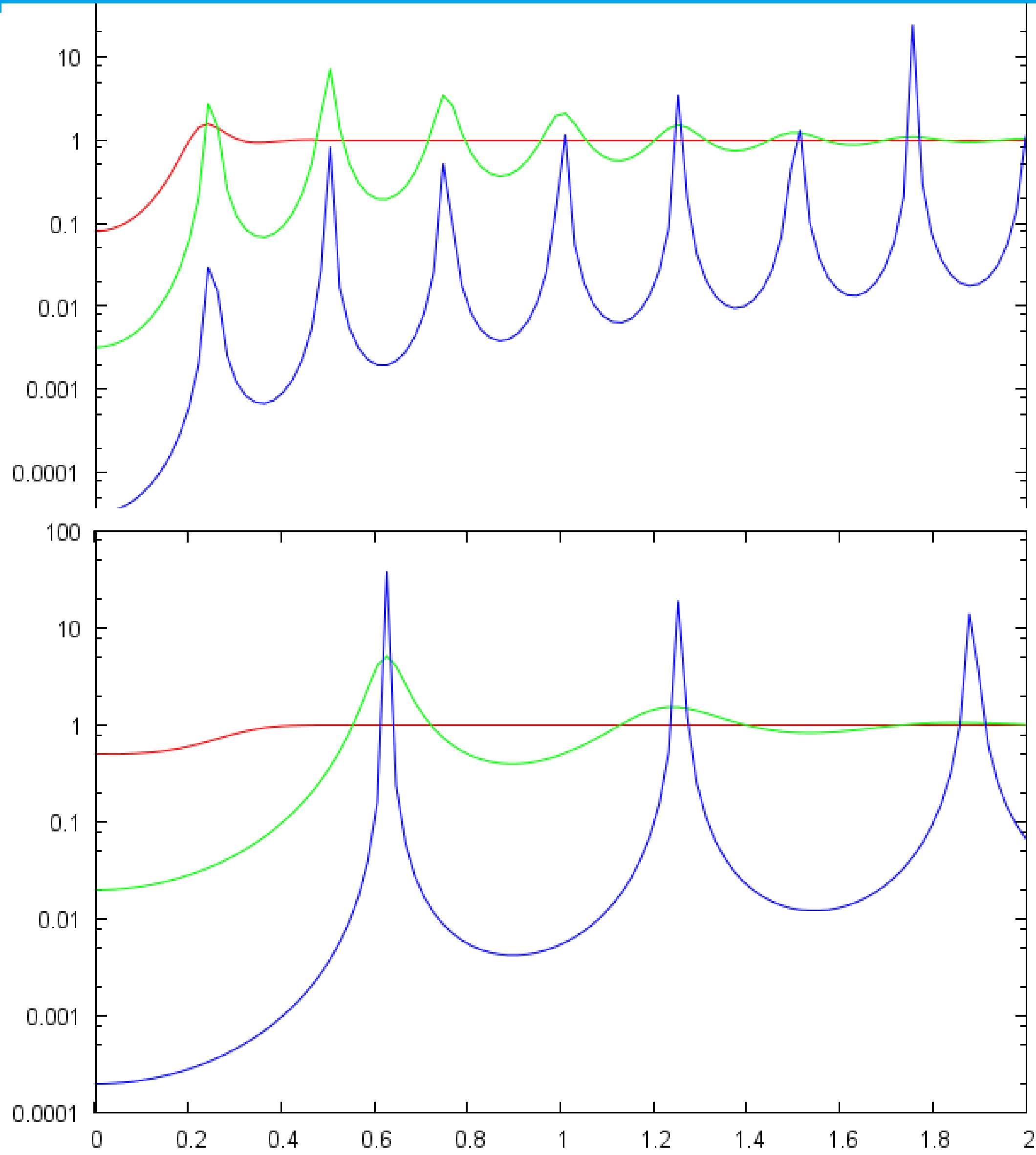
- Real systems: not dilute, many particles…
- Generalisation of Bragg‘s Law in crystallography:
  $I(q) = c\, P(q)\, S(q)$
- Examples: R=5nm, D_{max}=100nm, 25nm, $\sigma D/D_{max}$=25%



Structure factor and form factor

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

  well separated particles

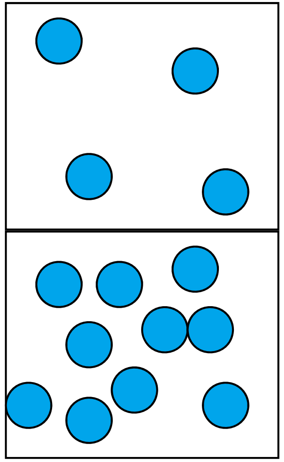


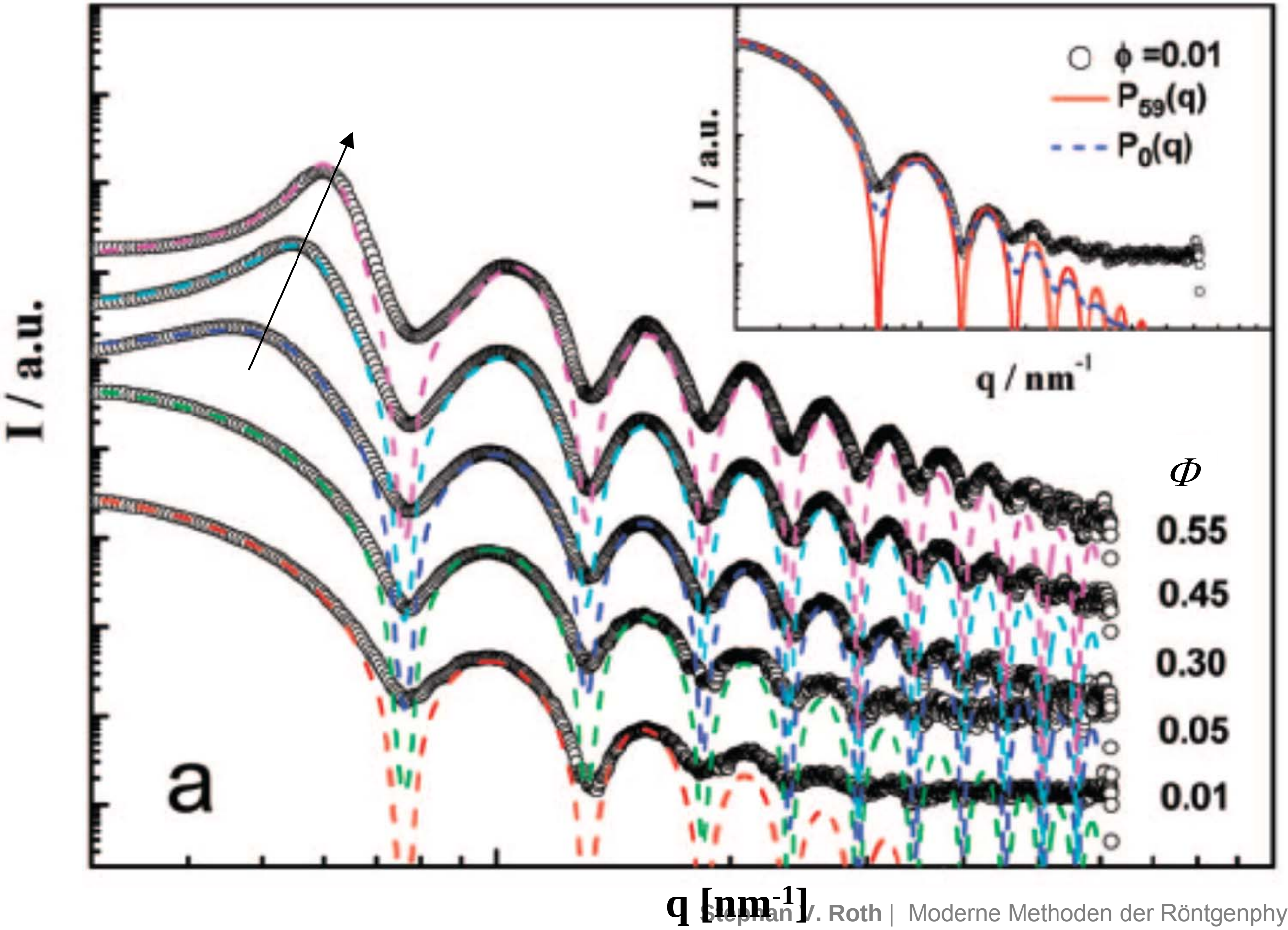
Colloidal systems

- Latex spheres in water

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

Low Φ	$P(q), S(q)=1$
High Φ	$S(q)P(q)$



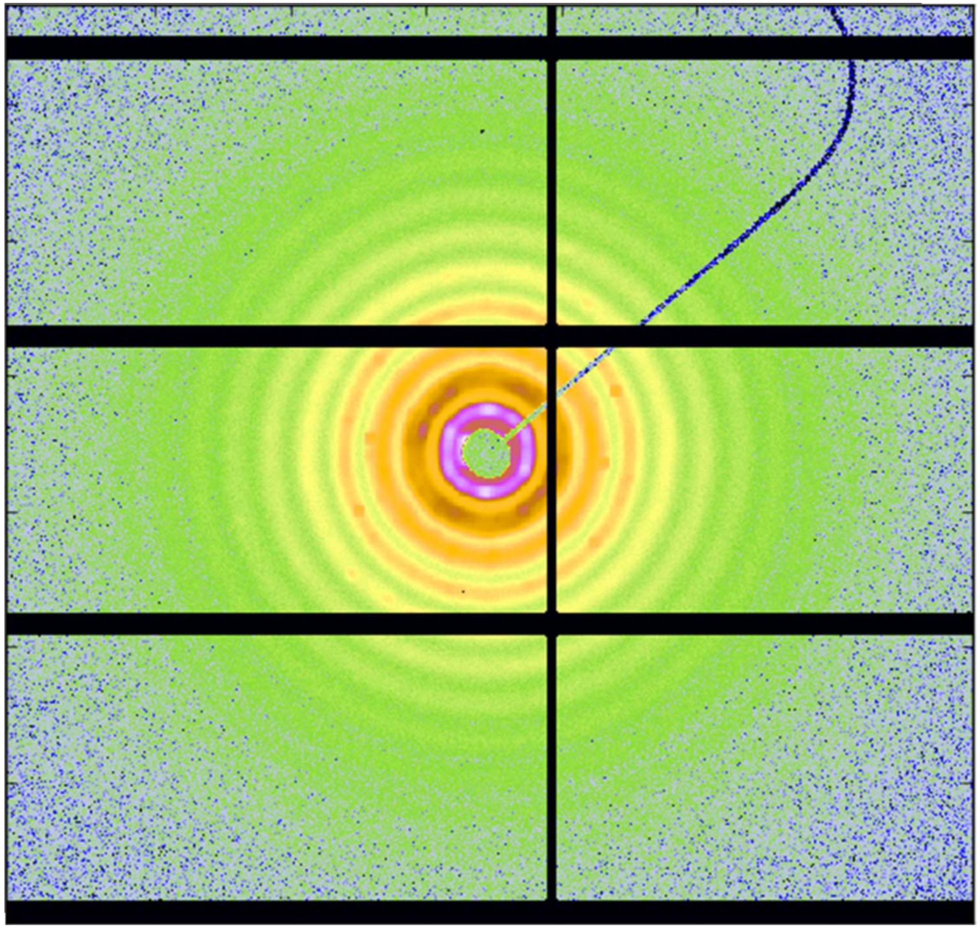


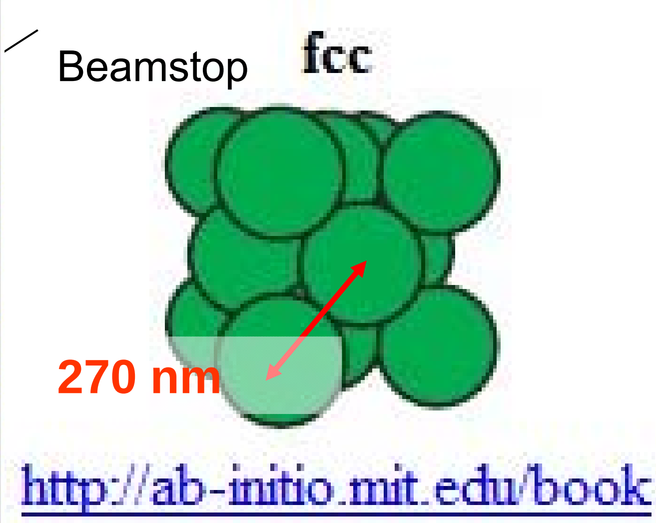
- Gaussian distribution of particle sizes
- Shift in maximum: Decreasing distance

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

Illustration

- USAXS at photonic crystals
- USAXS in highly concentrated colloidal suspensions





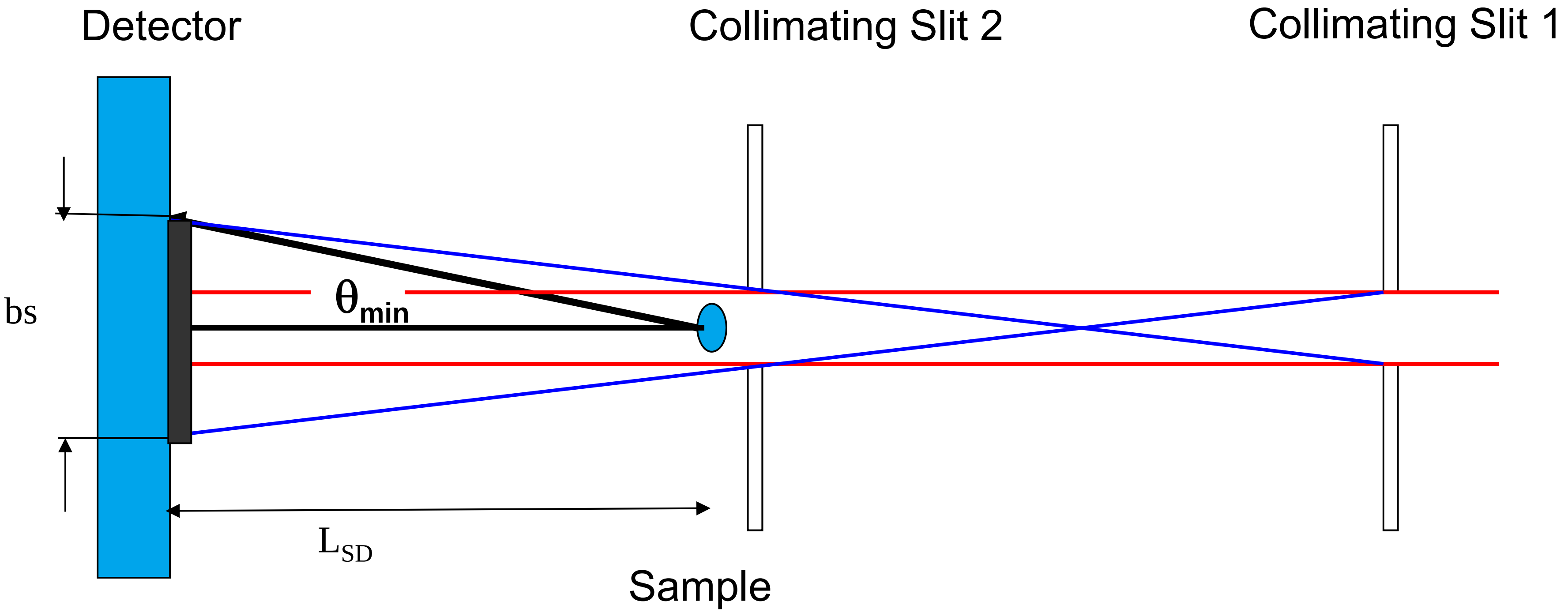
http://lamp.tu-graz.ac.at/~hadley/ss1/emfield/photonic_crystals/photonic_table.html

Courtesy: V. Boyko (BASF)

Outline

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

SAXS collimation and scattering geometry



L_{SD} determines resolution θ_{min}=bs / (2 L_{SD})

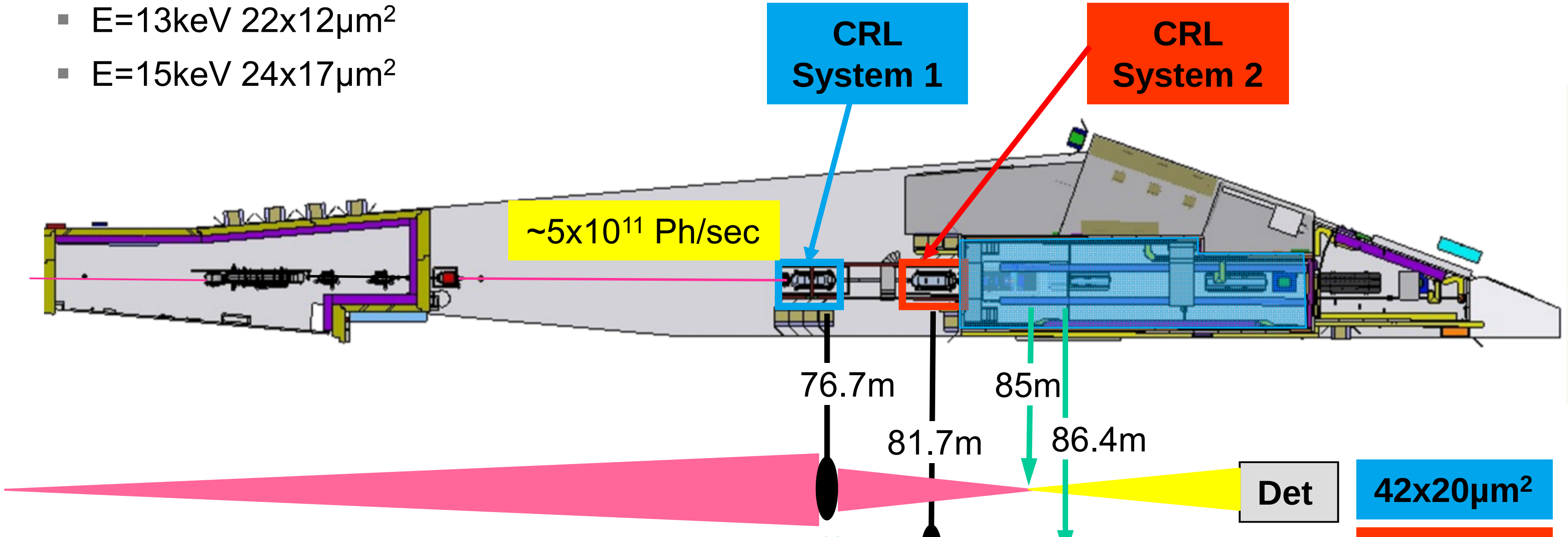
Use Bragg‘s law:

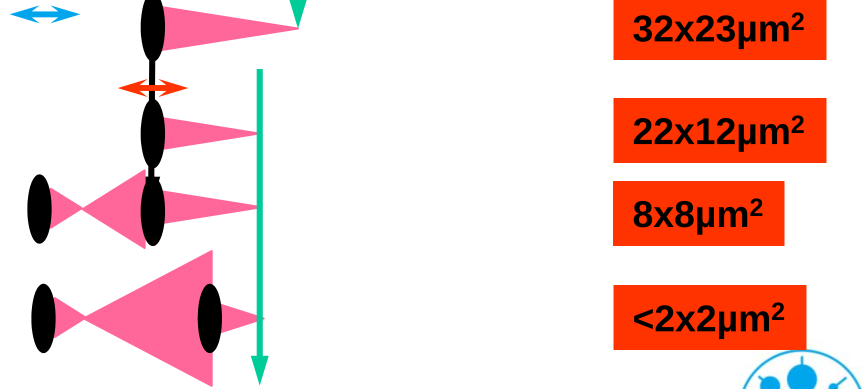
$$\boxed{d_{max} = \frac{\lambda}{\theta_{min}}}$$

Layout – Different µfocussing schemes

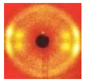
- Flexible choice of beam size and divergence
- Fixed focal spot position and size
  - E=13keV 22x12µm^2
  - E=15keV 24x17µm^2

- Full user operation within design values!





- Nanofocus end station:



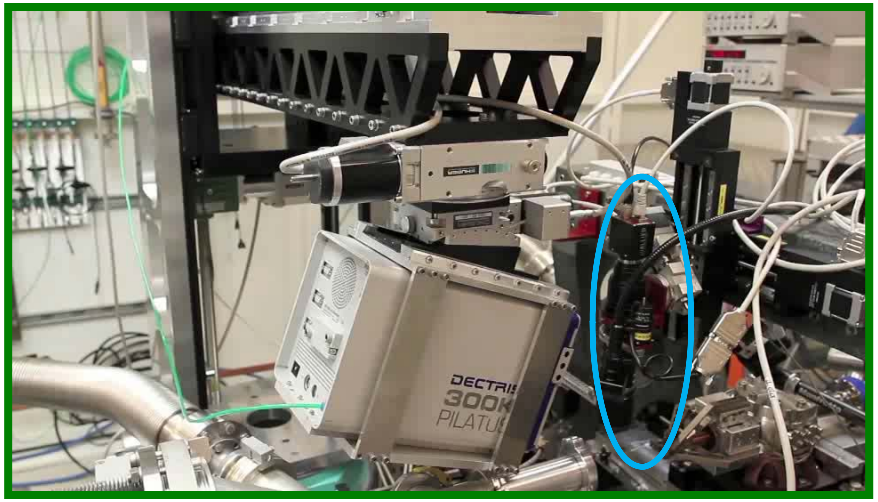
  - <1.5x1.5µm^2
  - 500x500nm^2

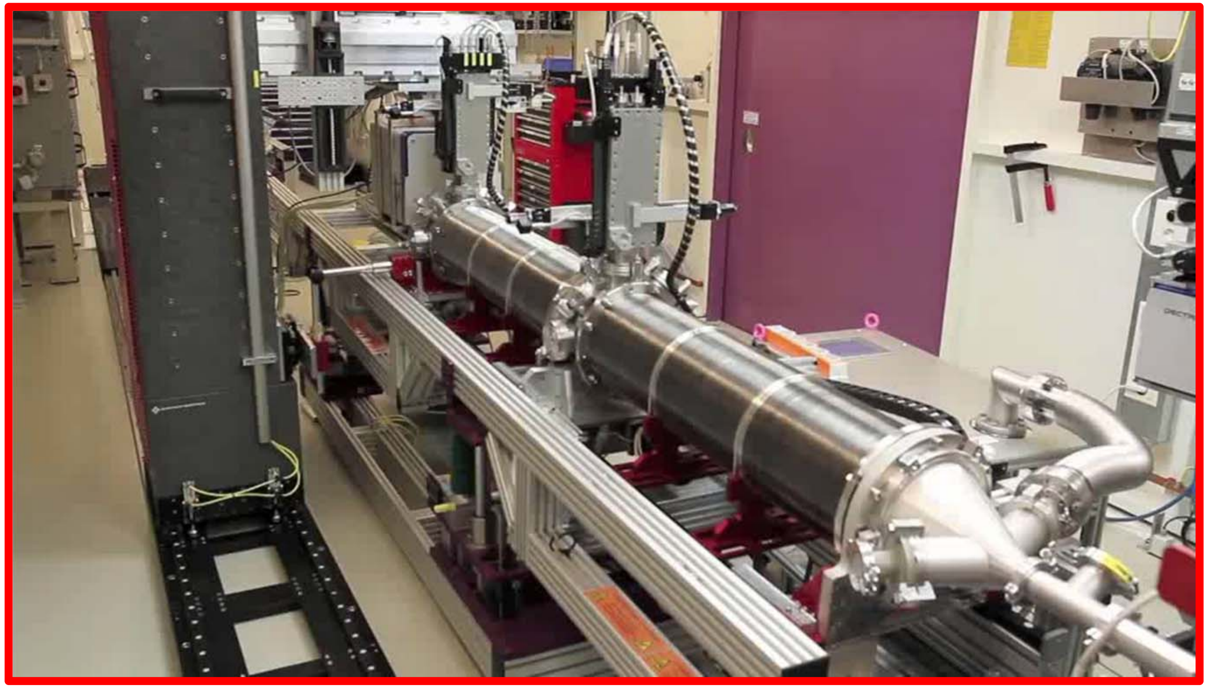
Krywka, SVR et al., J. of Appl. Cryst. **45**, 85 (2012)

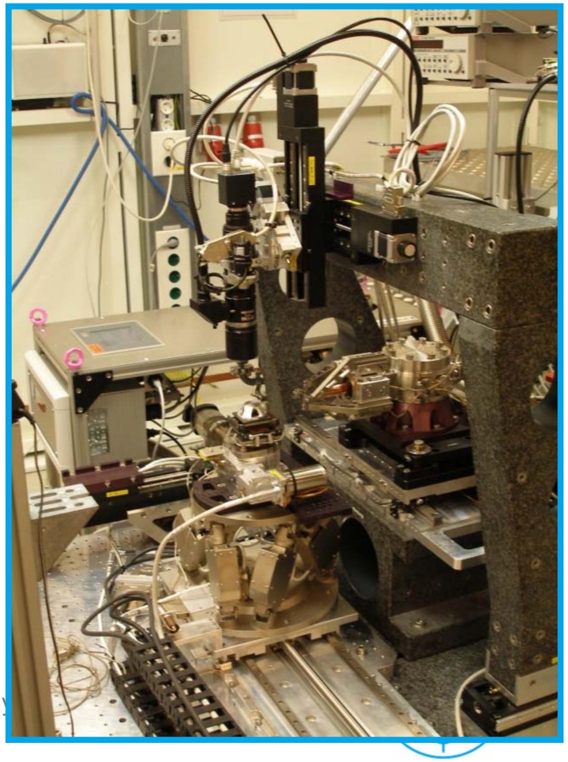
Roth et al., J. Phys.: Cond. Matter **23**, 254208 (2011)
Buffet, SVR et al., J. Synchr. Rad., **19**, 647 (2012)

Rapid Change (GI)SAXS / (GI)WAXS – 2012

- Adjust scattering angles
  ↔ dΩ
  ↔q-ranges
- 5cm<D_{SD}<8.6m
- Highly flexible
- Separate WAXS device

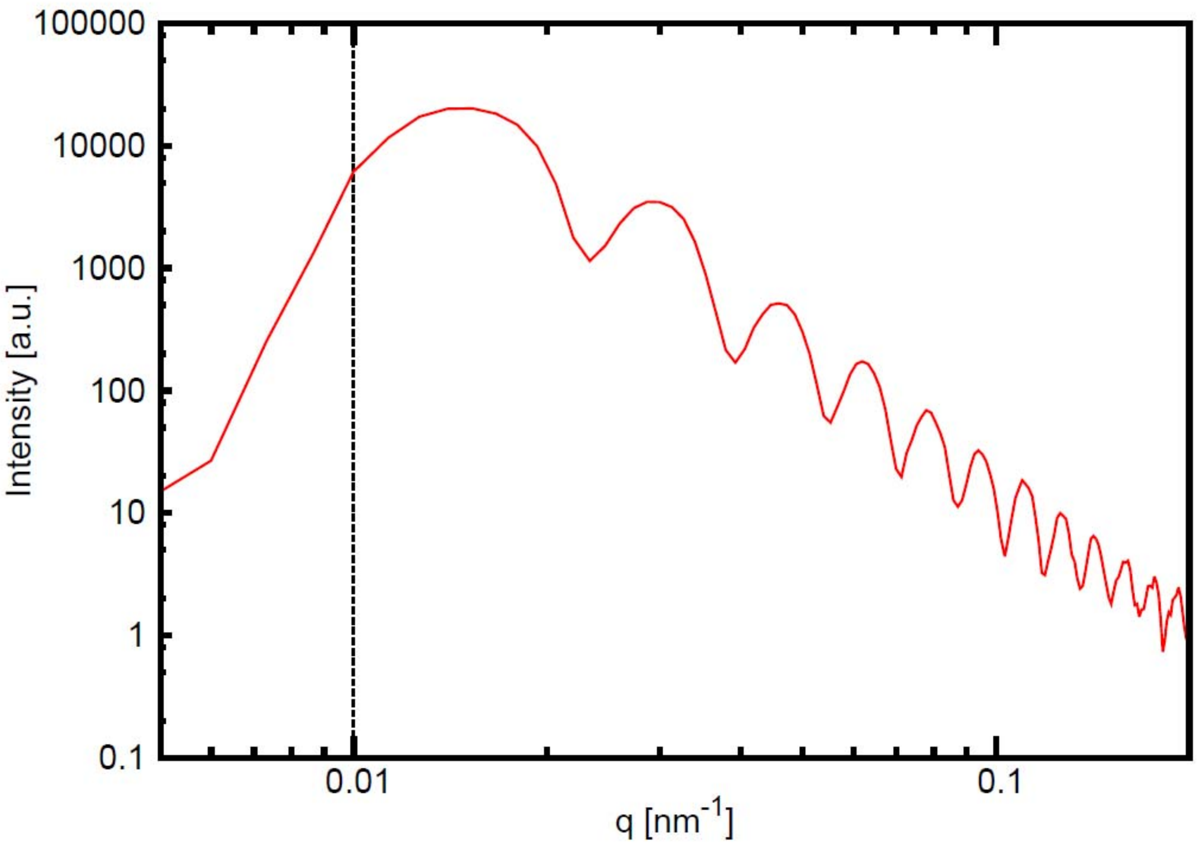






µUSAXS focus

- Beam size: 32x23µm^2
- SDD=8470mm
- N$_2$=12
- PS particles:
  - 400nm
  - Dried on glass slide
  - t$_{acq}$=1s
  - background corrected



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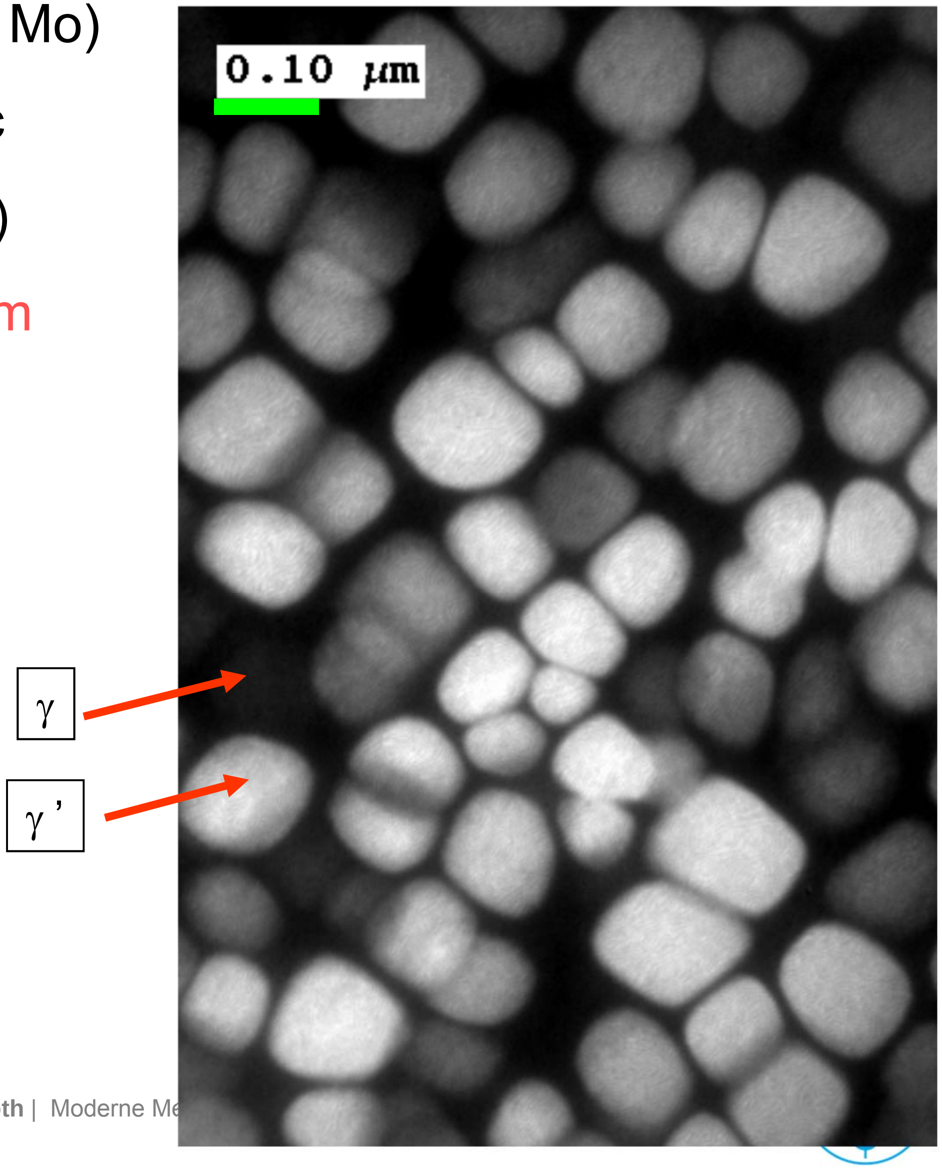
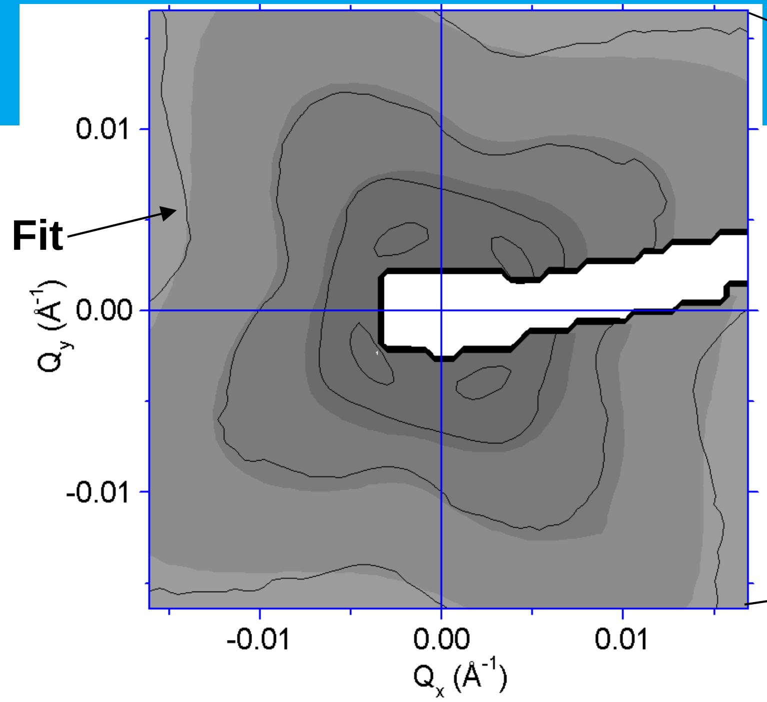
Ni-base superalloys

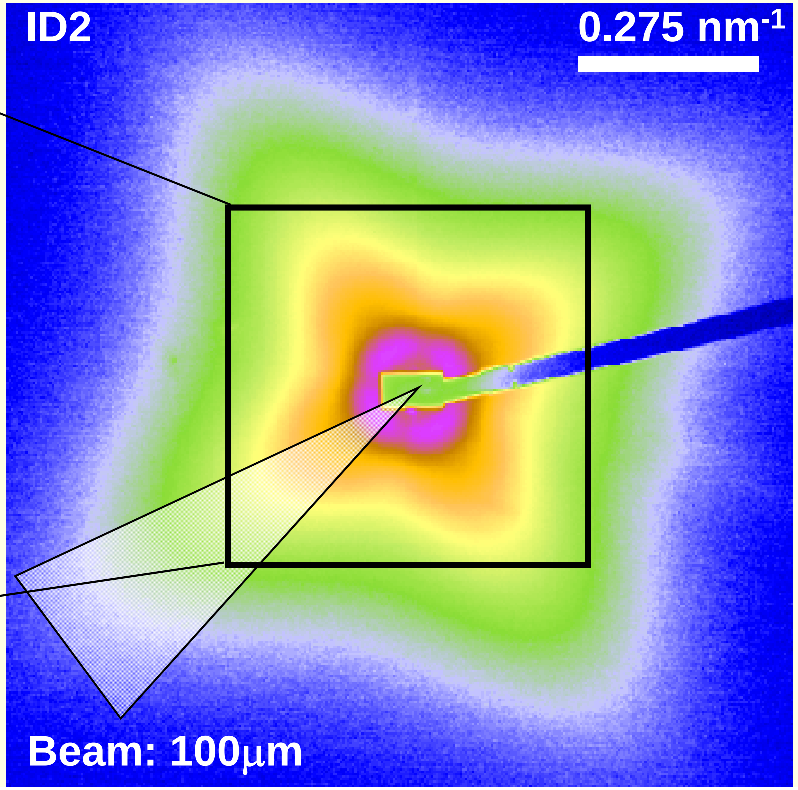
Ni-base superalloys

- Ni-base W-rich experimental single crystal superalloy (Ni-4.6Al-6.4Ta-5.7Cr-10.8W-2.1Mo)
- Ni-Al solid solution *Matrix* (γ), fcc
- *Precipitates* (γ'→Al,…), $Ni_3(Al,Ti)$
- TEM: γ'-precipitates R > 50 nm
- D > 100 nm

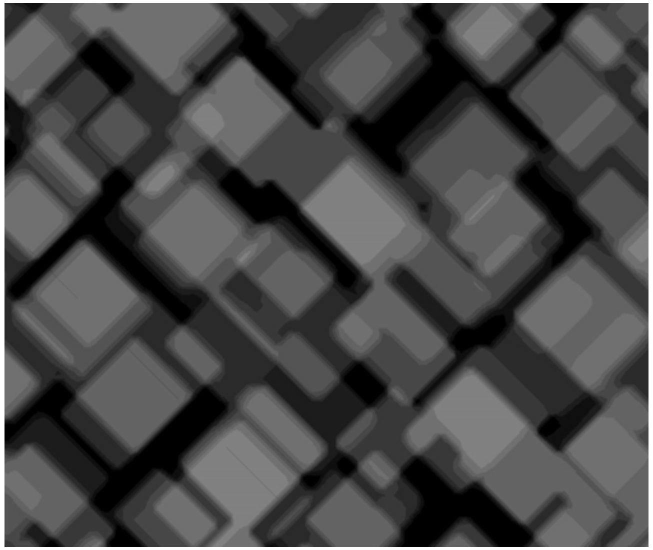


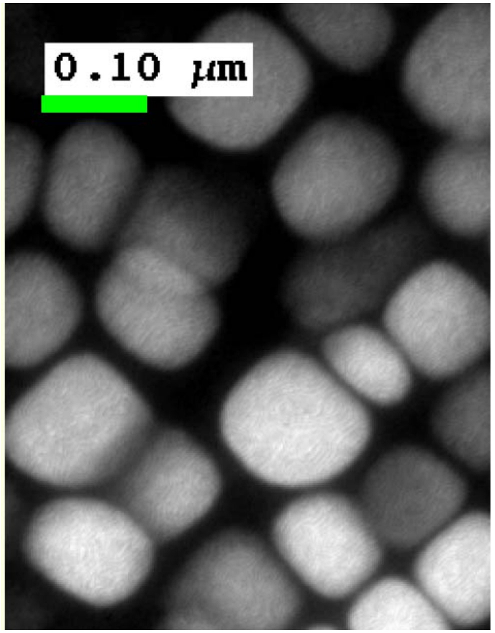


noc_4: P. Strunz et al., J. Appl. Cryst. **36**, 854 (2003)

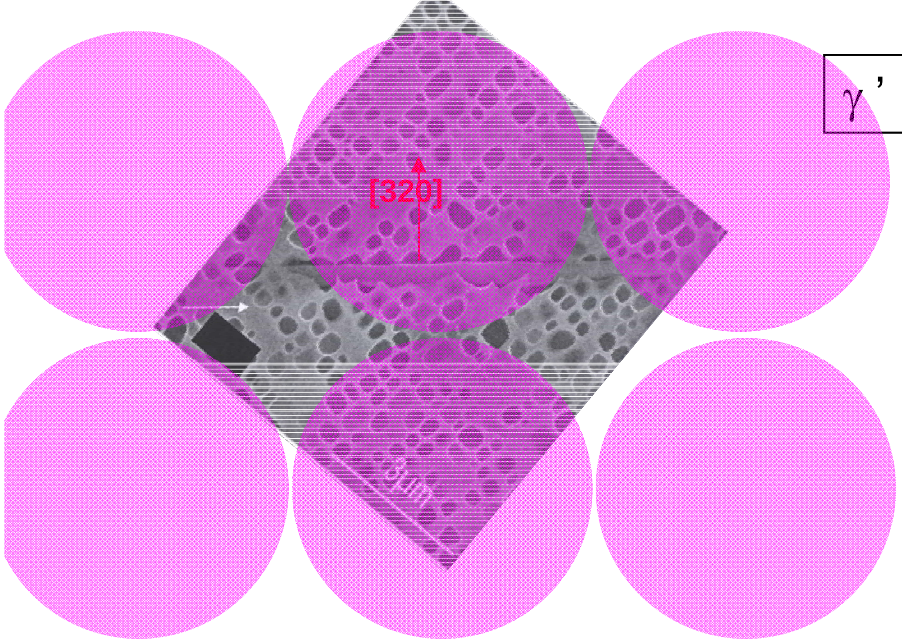


Courtesy:
Gilles
Strunz





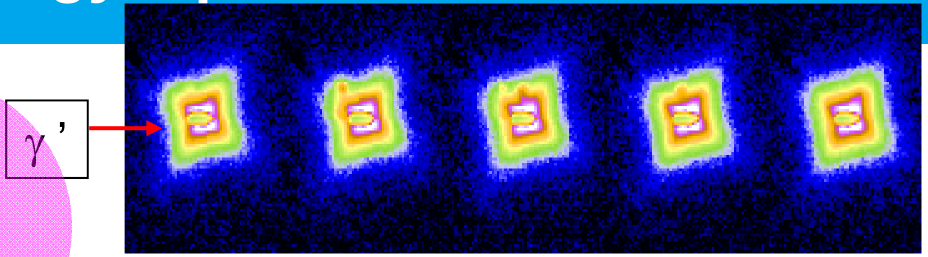
Local precipate morphology – µSAXS

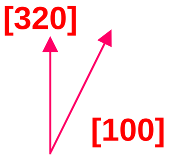


R. Gilles et al.
Scripta Mat. **39**, 715 (1998)

- σ phase precipitate:
  embrittlement of alloy
  crack formation and propagation

- streaking: correct orientation
- σ phase: stack - distance 5 - 15 µm
  diameter 2R < 10 µm
  thickness t > O(100 nm)





Δz = 5 µm

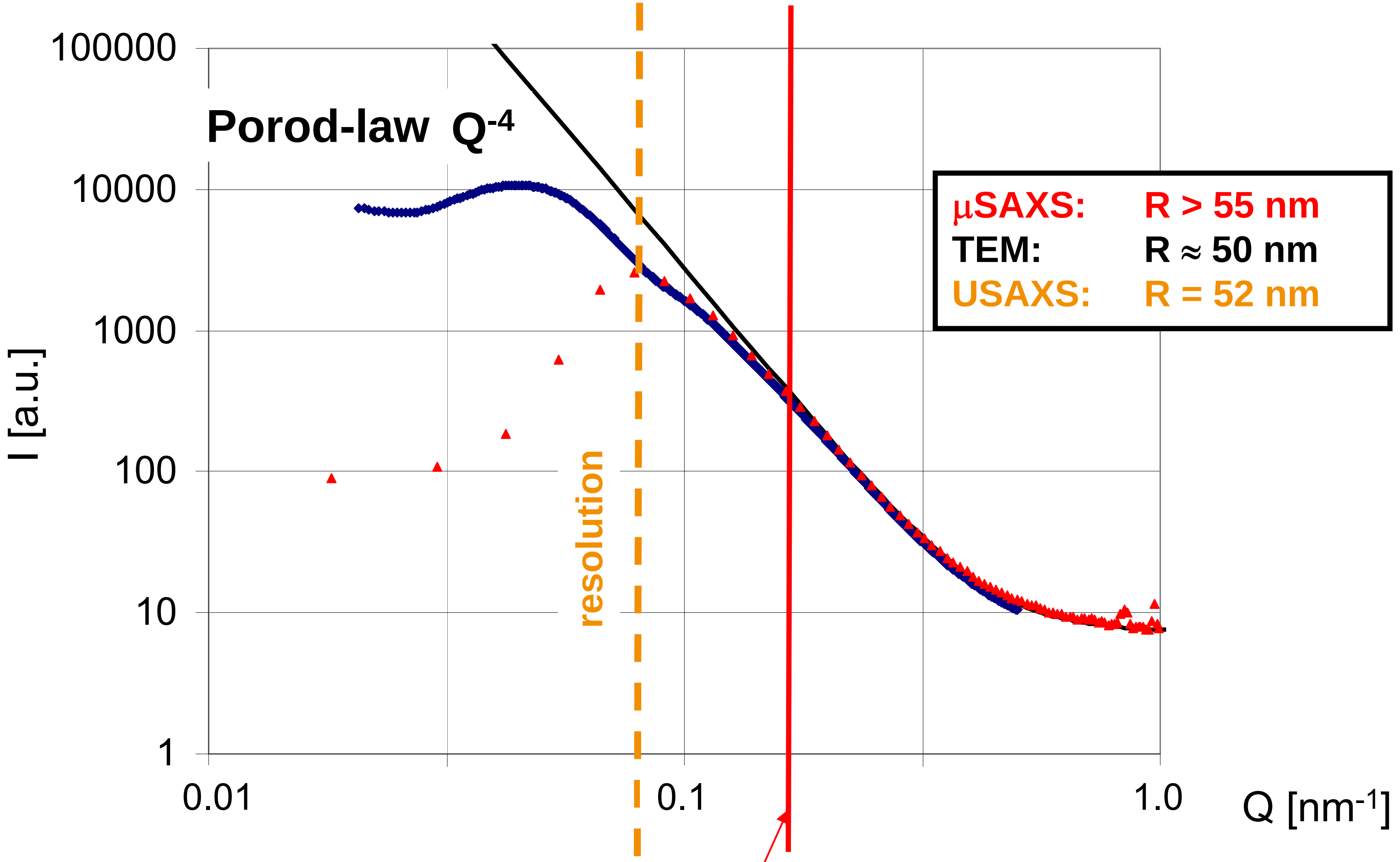
Q=1.5 nm^{-1}

Δy = 5 µm

$\vec{k}_0 \perp [00\bar{1}]$

Microfocus: local γ ’- particle size distribution

Roth et al., Nucl. Instr. Meth. B 200, 255 (2003)



µSAXS:	R > 55 nm
TEM:	R ≈ 50 nm
USAXS:	R = 52 nm

Lower minimum of particle size distribution