Methoden moderner Röntgenphysik II

Streuung und Abbildung

Stephan V. Roth
DESY
12.05.2015

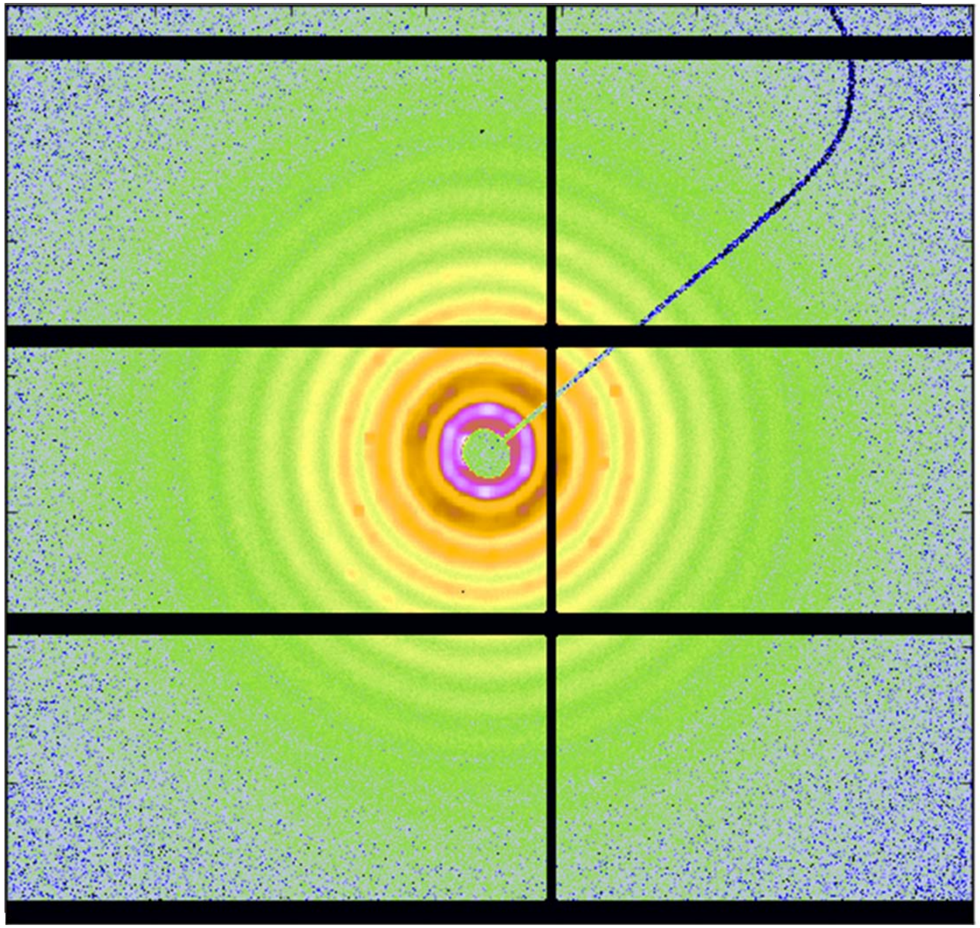
Outline

- 12.05.: Small-Angle X-ray Scattering (SAXS)
- 19.05.: SAXS
- 21.05.: Applications of SAXS
- 02.06.: Grazing incidence SAXS (GISAXS)
- 04.06.: The polymer-metal interface – application of GISAXS
  On the route to organic electronics

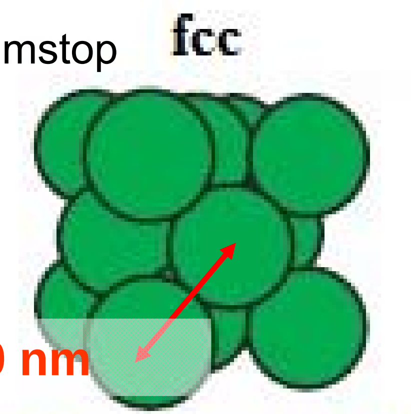
SAXS continued

Illustration

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



Beamstop



http://ab-initio.mit.edu/book

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

Courtesy: V. Boyko (BASF)

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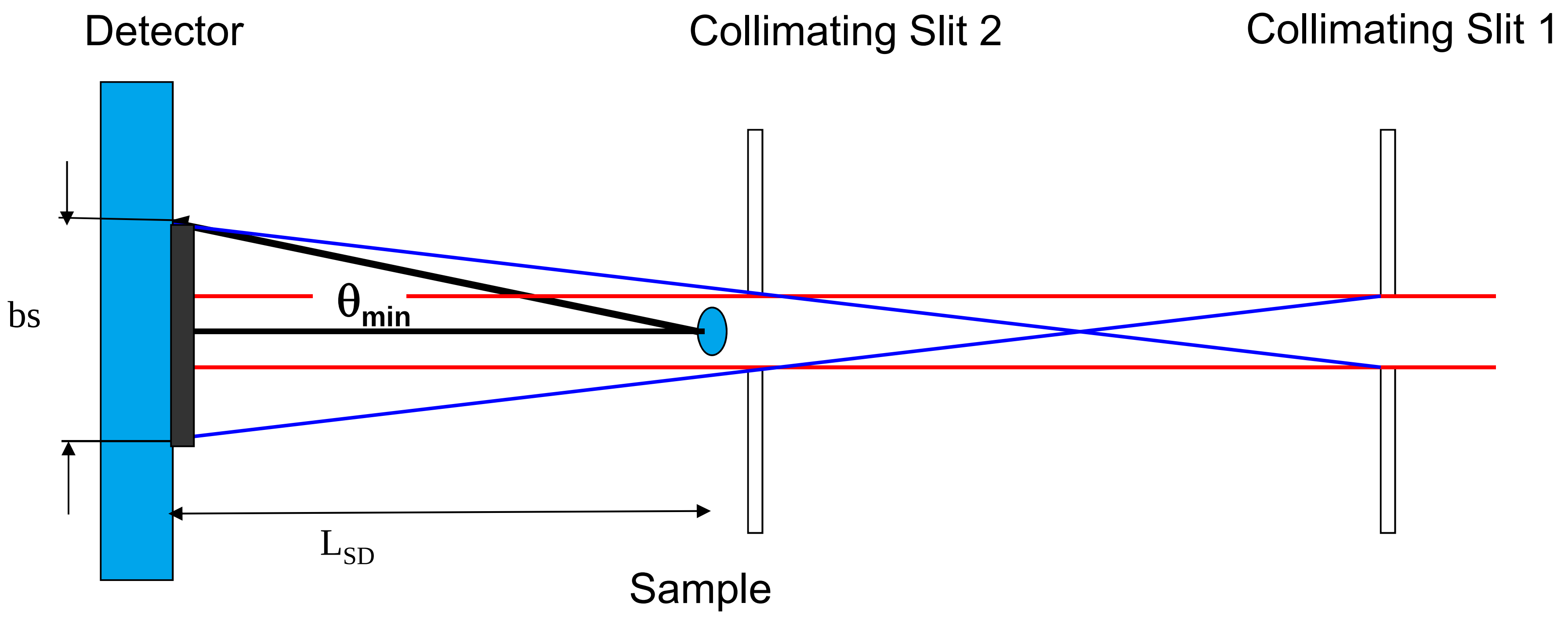
- > SAXS – Introduction
- Instrumentation
  - P03/MiNaXS @ PETRA III
- > Bulk materials ➔ Transmission U/SAXS:
  - Porous materials
  - Ni-base superalloys
  - Droplet drying
  - Chocolate

SAXS collimation and scattering geometry



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

Use Bragg's law:

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

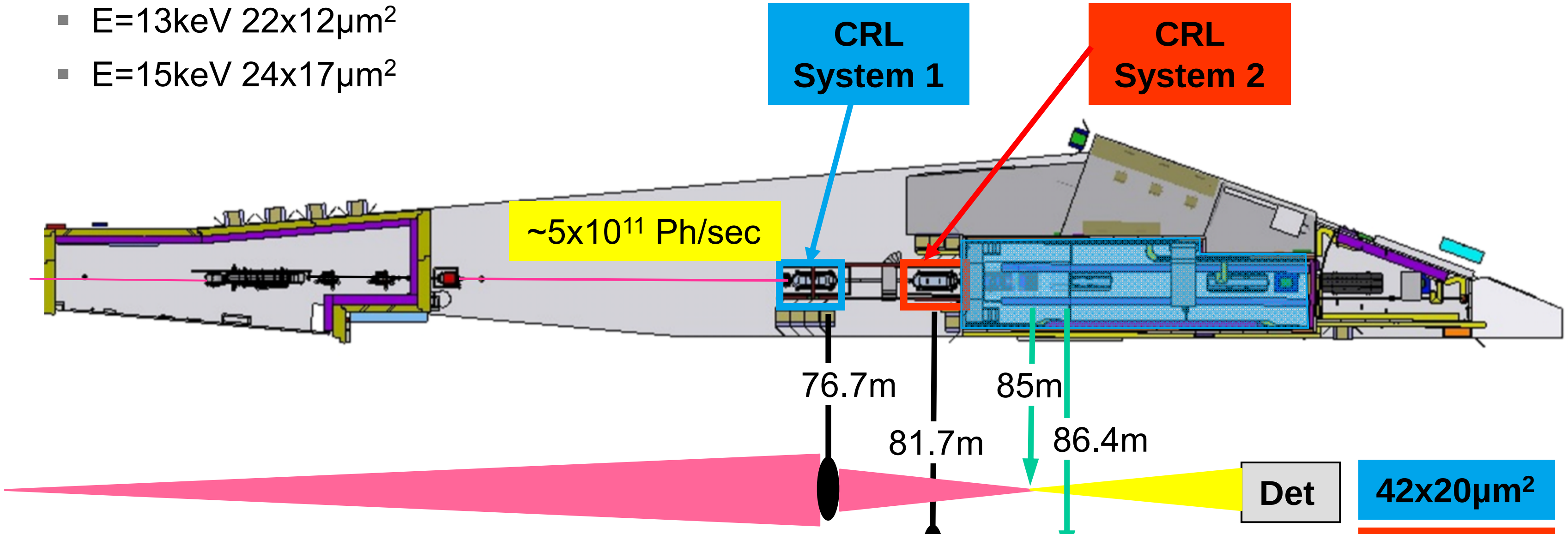
Layout – Different µfocussing schemes

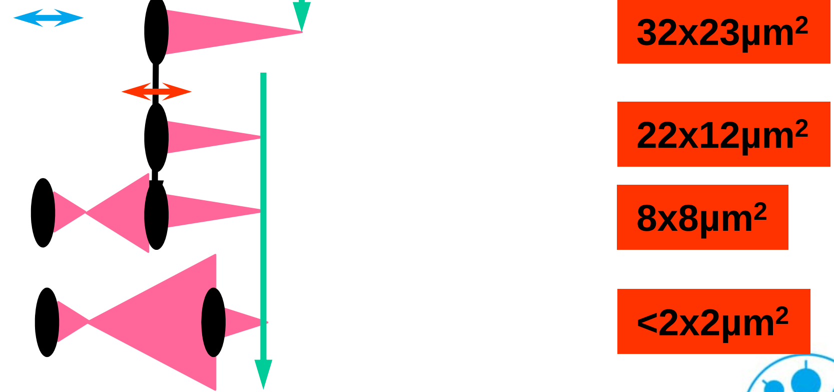
> Flexible choice of beam size and divergence

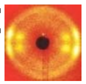
> Fixed focal spot position and size

- E=13keV 22x12µm²
- E=15keV 24x17µm²

> Full user operation within design values!





> Nanofocus end station: 

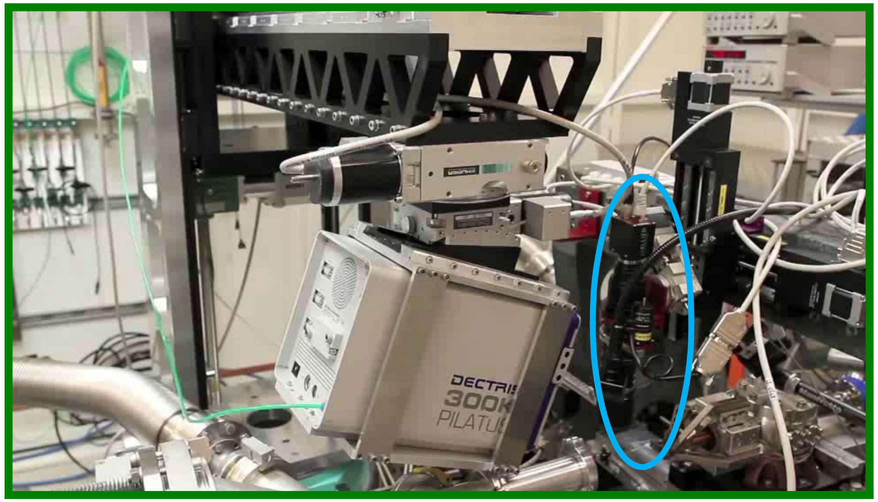
- <1.5x1.5µm²
- 500x500nm²

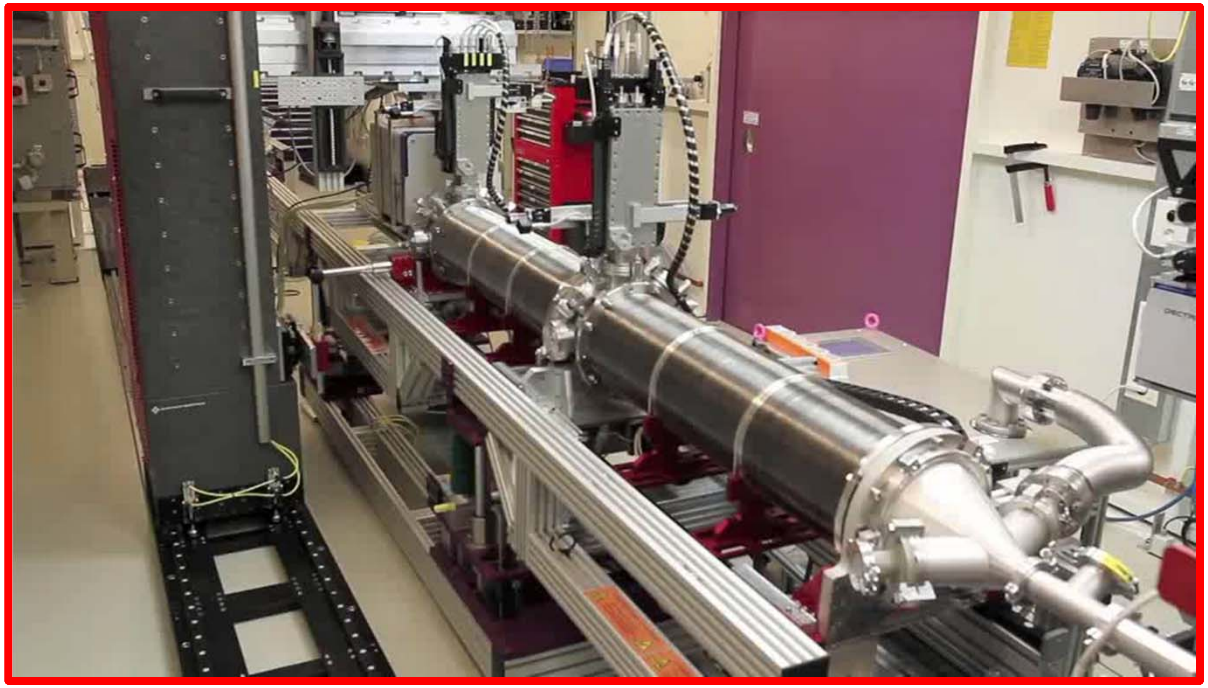
Krywka, SVR et al., J. of Appl. Cryst. **45**, 85 (2012)

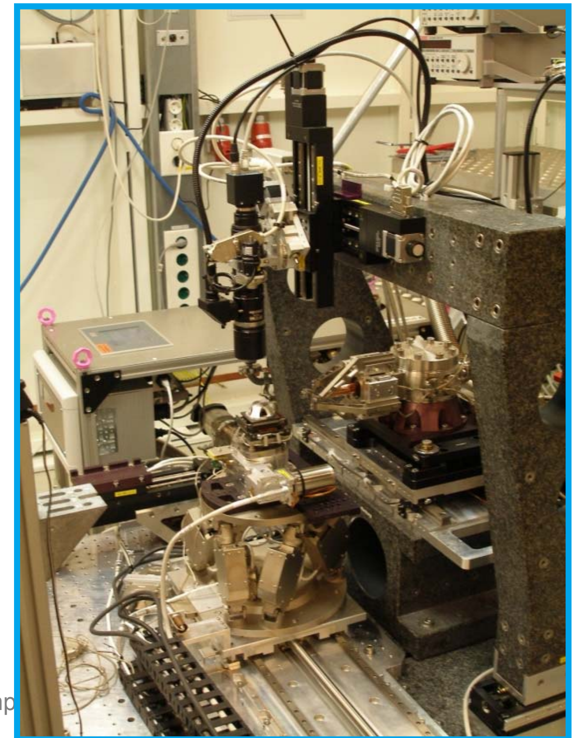
Roth et al., J. Phys.: Cond. Matter **23**, 254208 (2011)
Buffet, SVR et al., J. Synchr. Rad., **19**, 647 (2012)

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

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

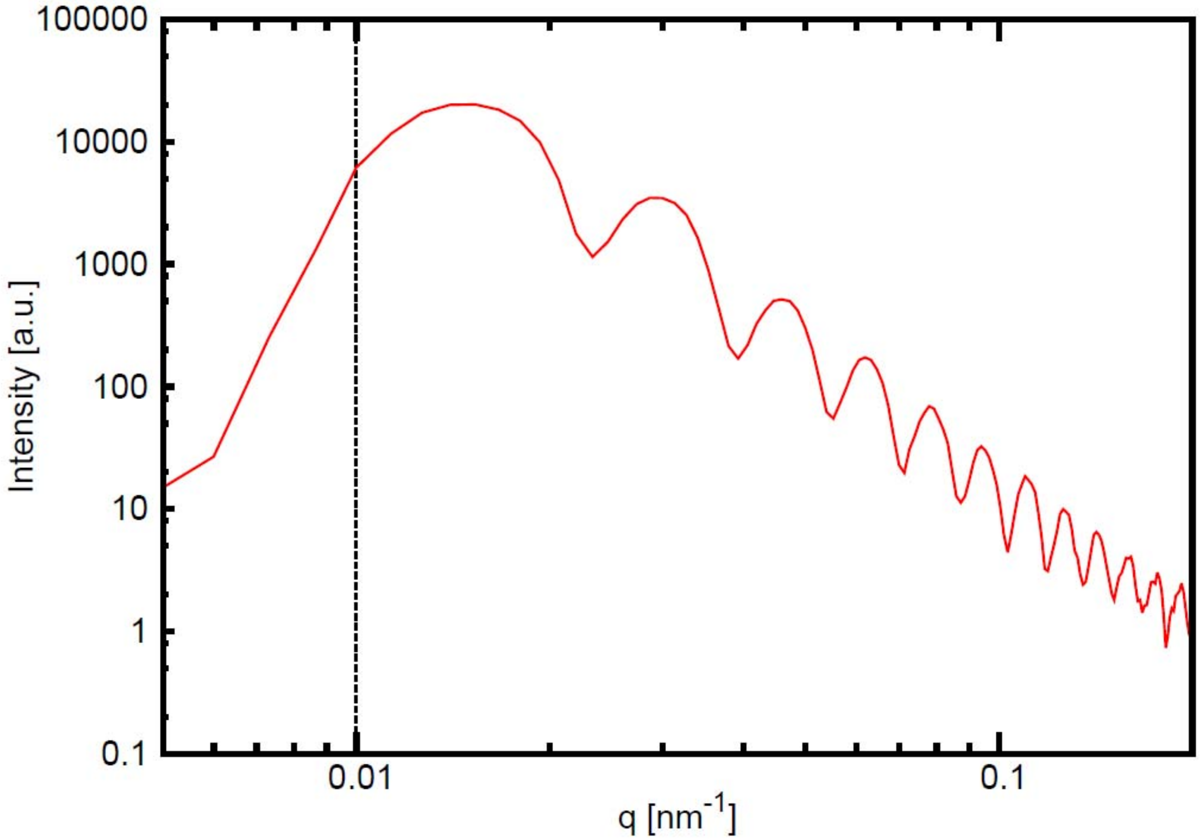






µUSAXS focus

- 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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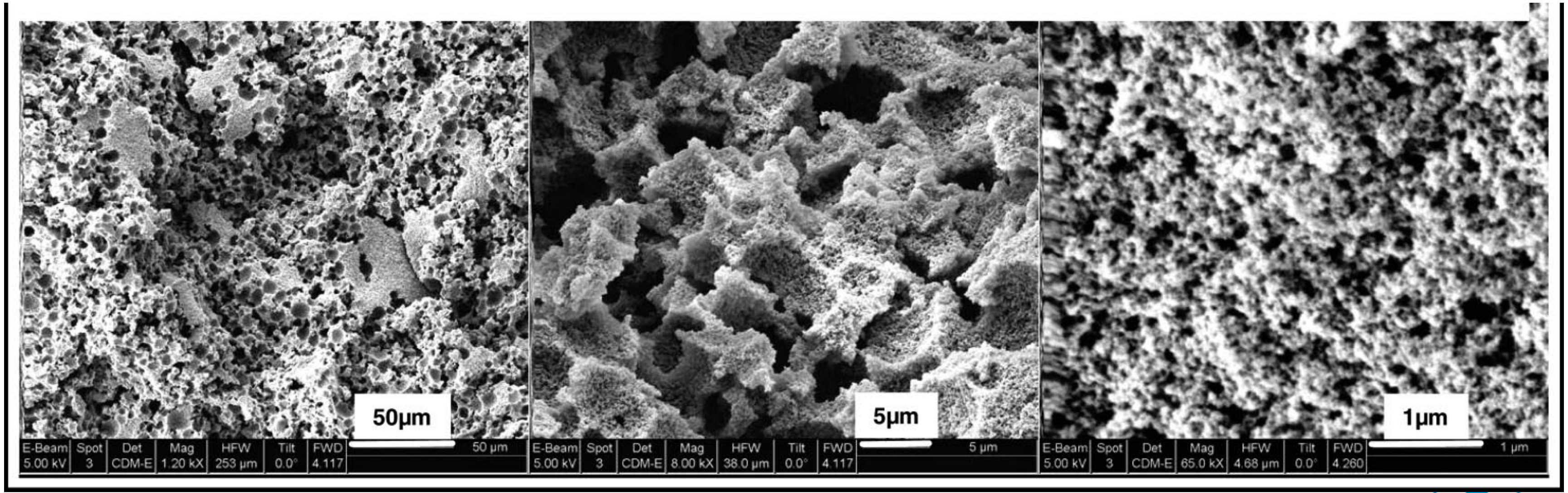
Aerogels

> Highly porous materials:
  - OLED: matching of refractive indices
  - molecular sieves
  - sensors

> Challenges
  - **Generation of** pores with dimensions greater than 100 nm, yet submicron
  - **Characterization of size**



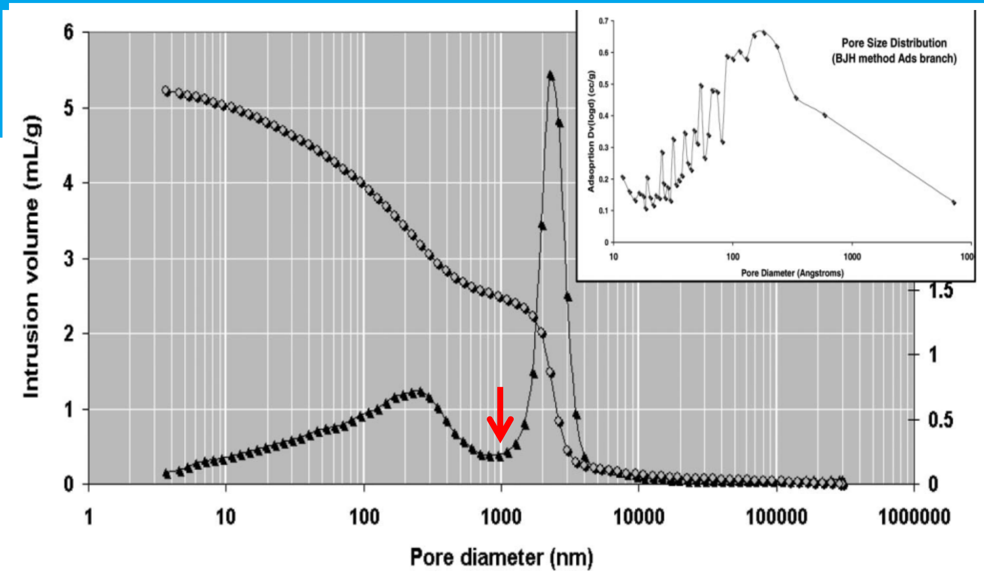
Quantitative analysis

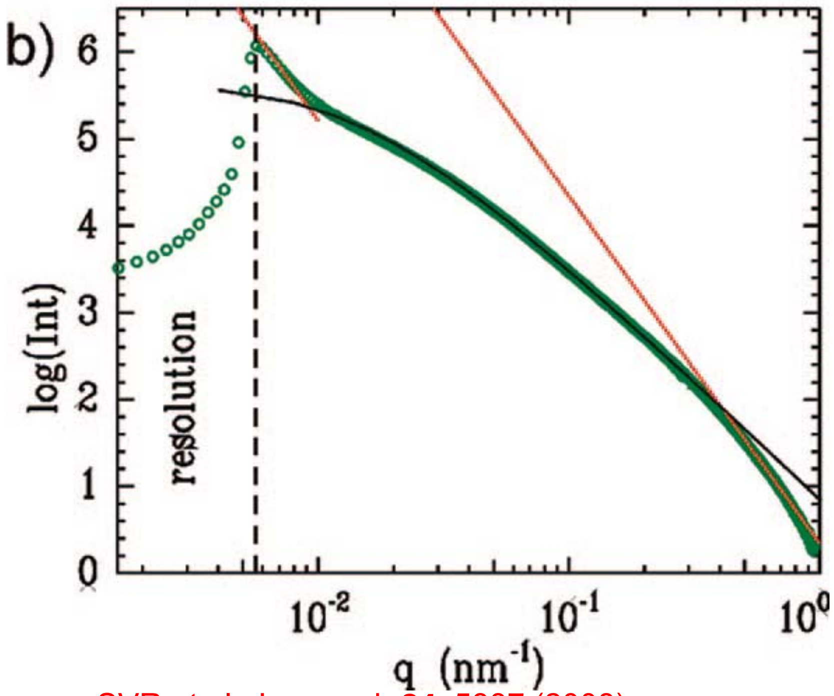
> Bimodal distribution particles

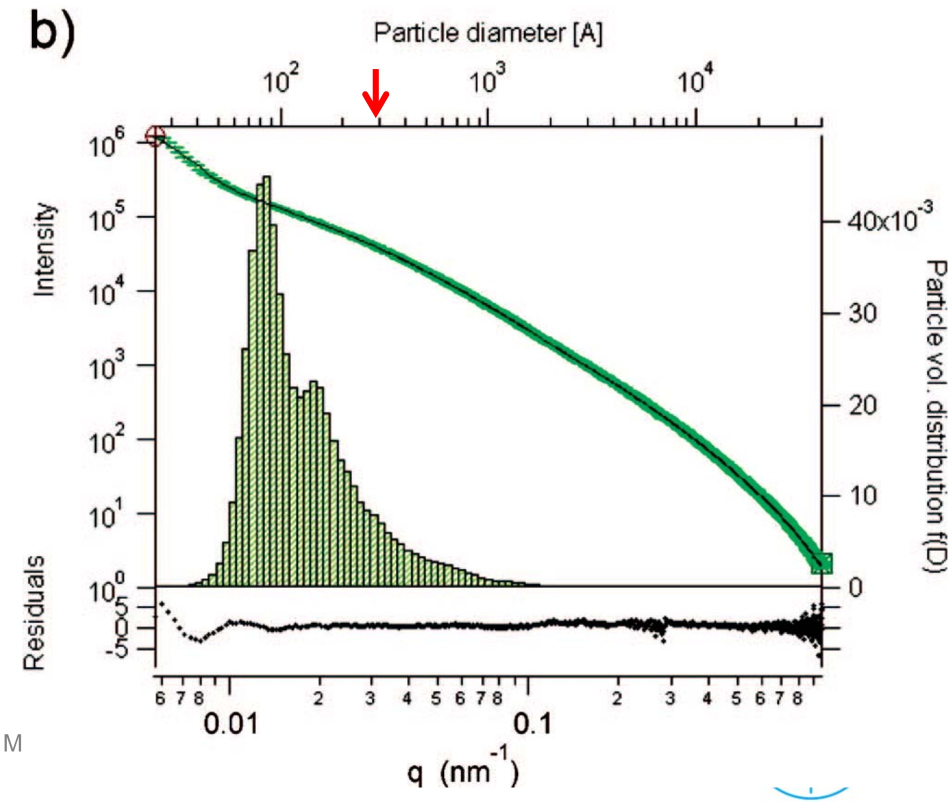
> $I(Q) = \Delta\varrho^2 N \int_0^\infty V_P^2(R) P(R) * D(R) dR$

> Porod law:

- Particle size ~ 30nm
- Pore size estimate >1300nm







Eggers, SVR et al., Langmuir **24**, 5887 (2008)

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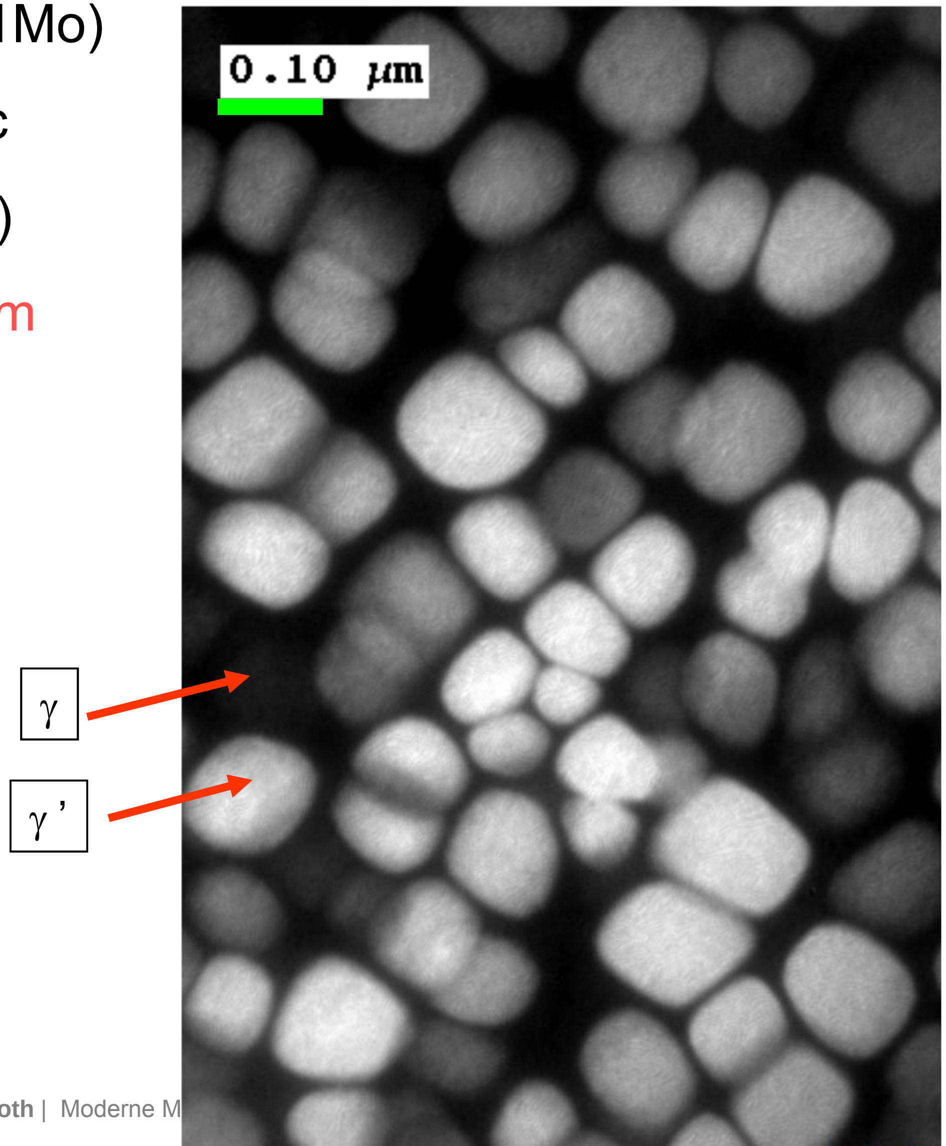
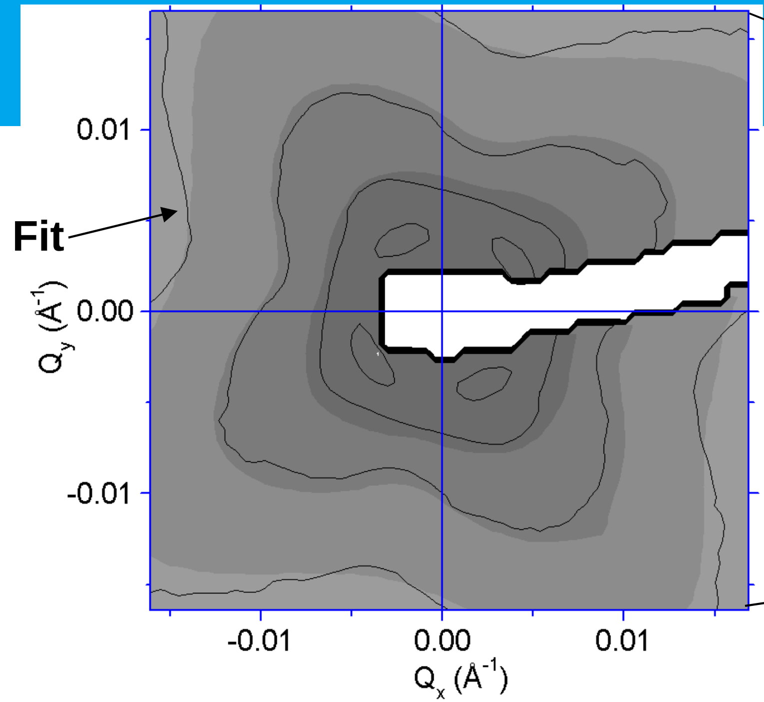
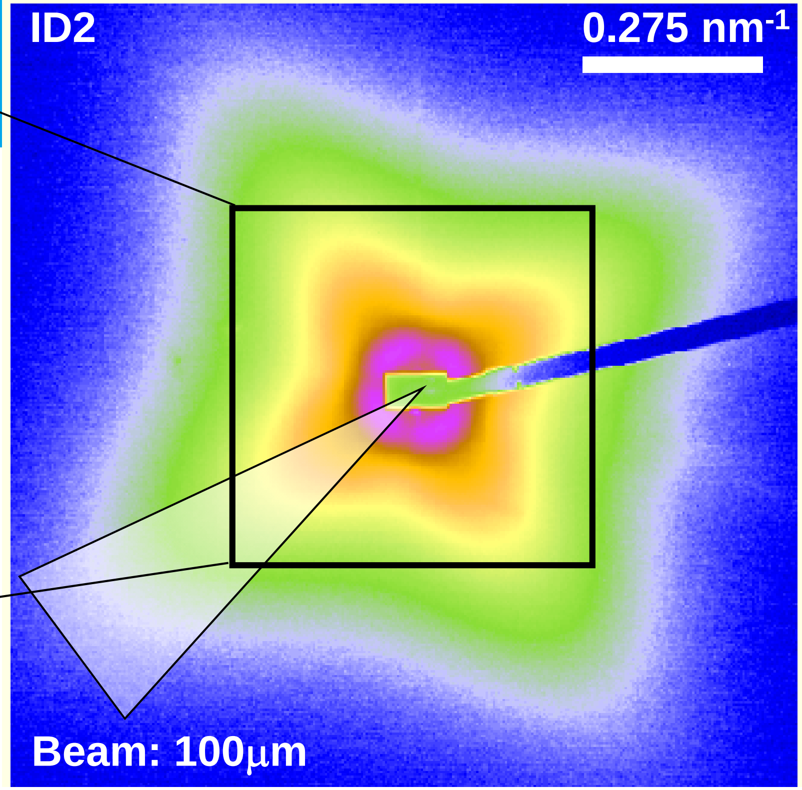
Ni-base superalloys

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

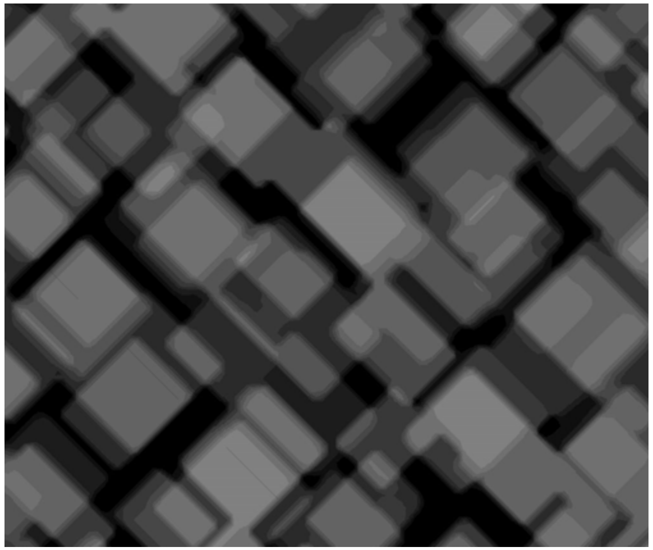


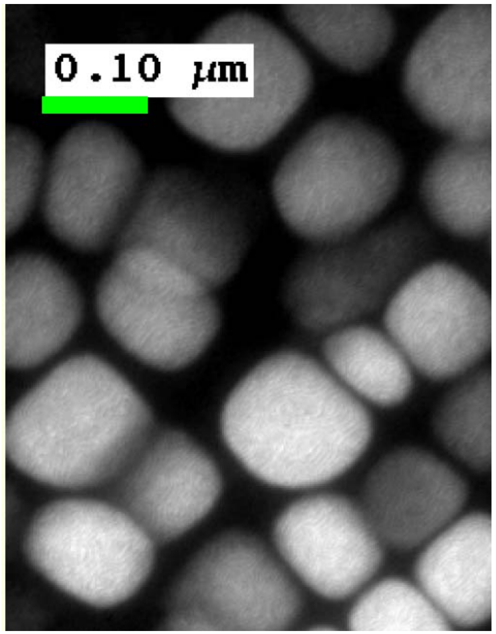




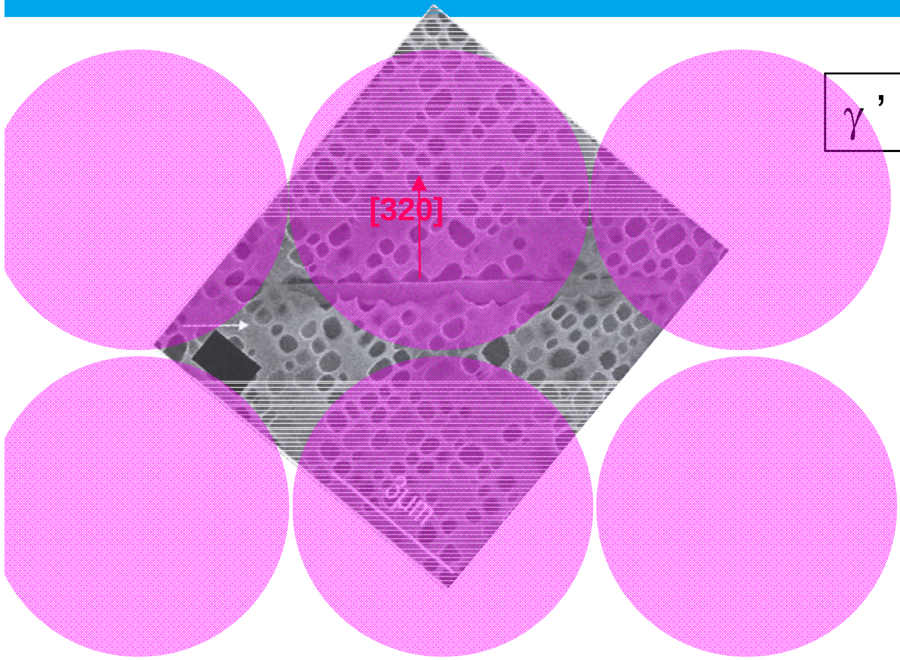
noc_4: P. Strunz et al., J. Appl. Cryst. **36**, 854 (2003)

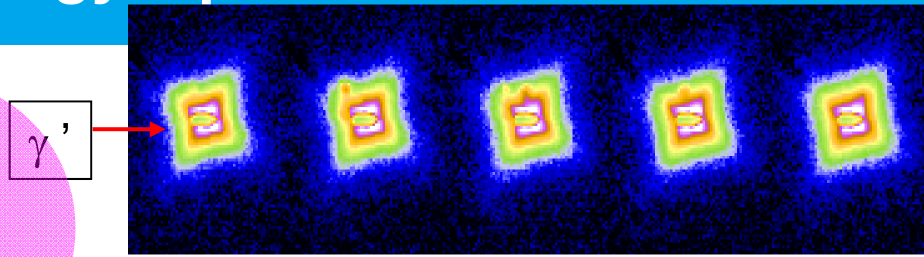
Courtesy:
Gilles
Strunz





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)

[320]
[100]

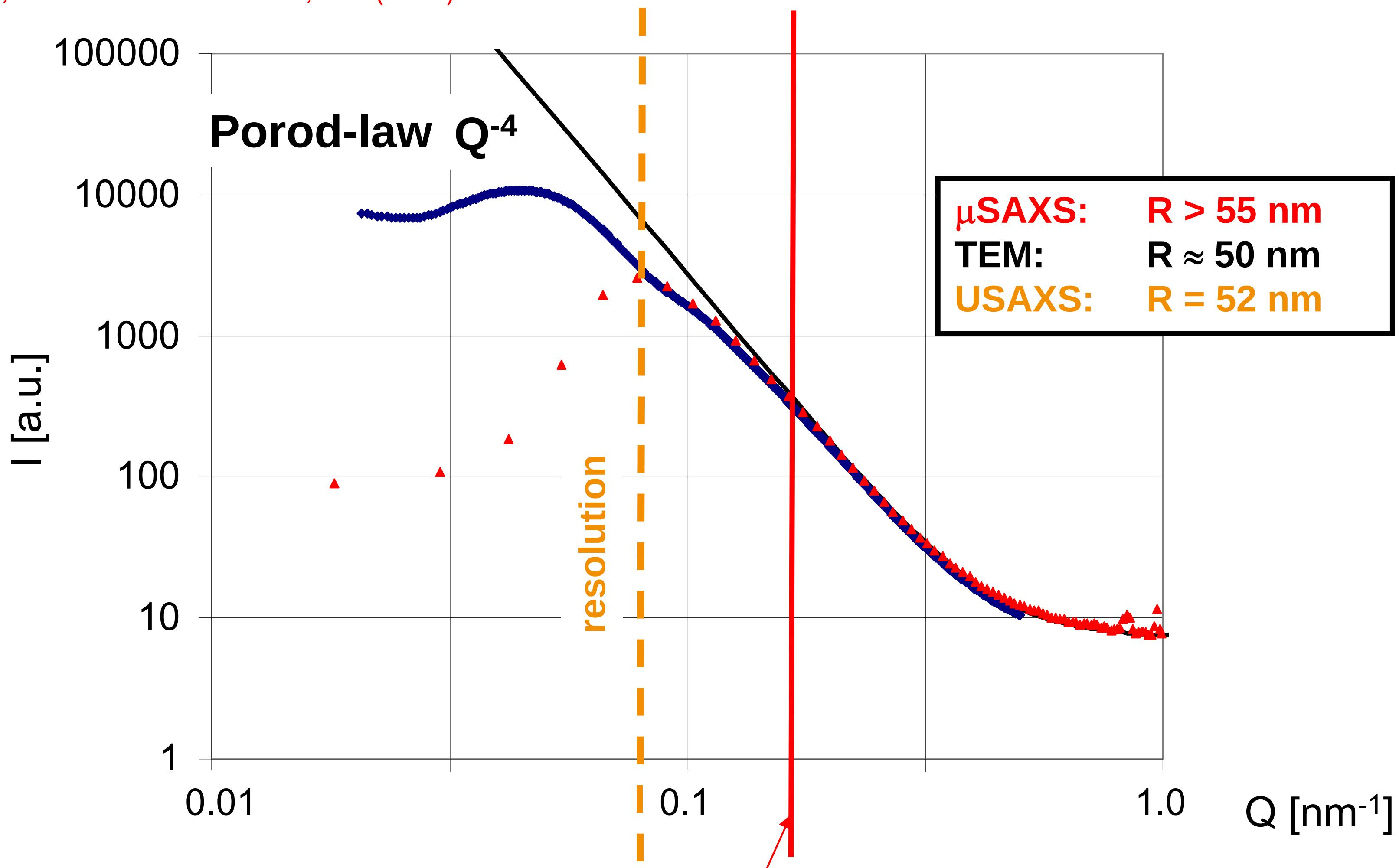
$\Delta z = 5\ \mu m$

$Q = 1.5\ nm^{-1}$

$\Delta y = 5\ \mu m$ $\vec{k}_0 \perp [00\bar{1}]$

Microfocus: local γ'- particle size distribution

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



Lower minimum of particle size distribution

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The drying droplet

> Self-organisation: attractive capillary forces

> correlated nano-structures

> industrial processes

  - spray drying (see also GISAXS part)
  - food processing, pharmaceuticals
  - Paintings/coatings

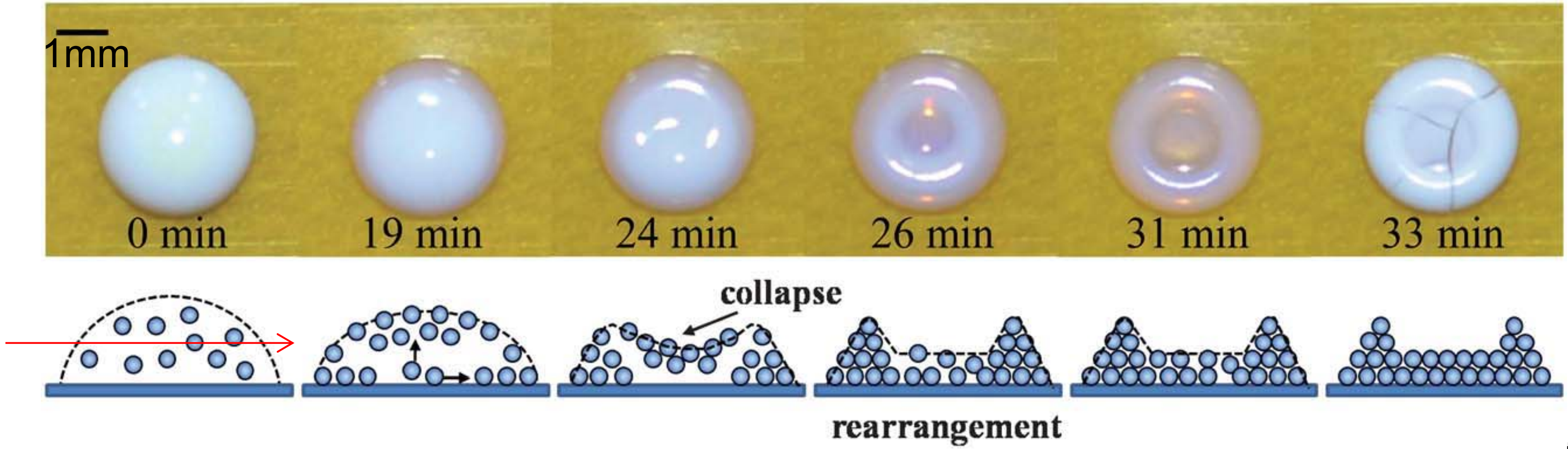
http://www.spray.com/markets_and_applications/food.aspx

Wir machen ein Experiment

- Der trocknende Tropfen
- Wandfarbe!
- Haftung!
- pPS Glassubtrate

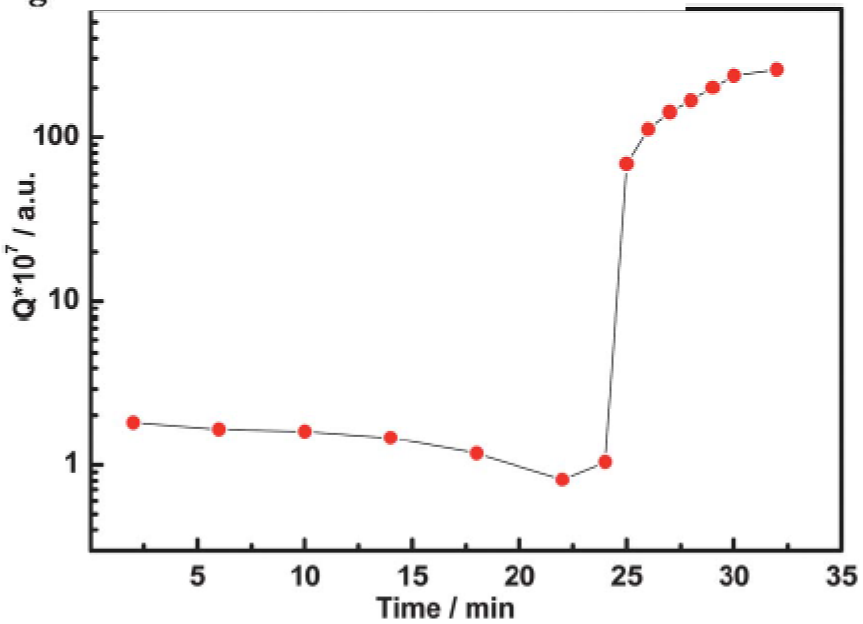
Porod Invariant - practical application

> Colloidal solution: drying thick droplet



> Evaporation of water:

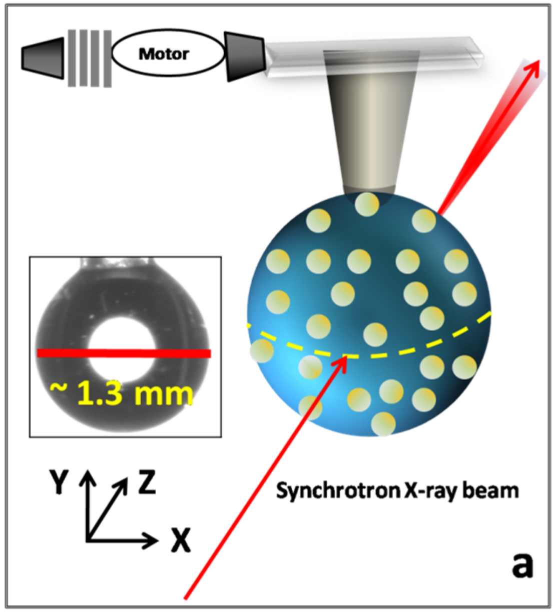
- Irradiated volume becomes smaller: shrinking
- Distance of colloidal partices decreases, $\Phi \rightarrow 1$
- $\Delta\rho$ increases (air!), as water removed from interstitial sites

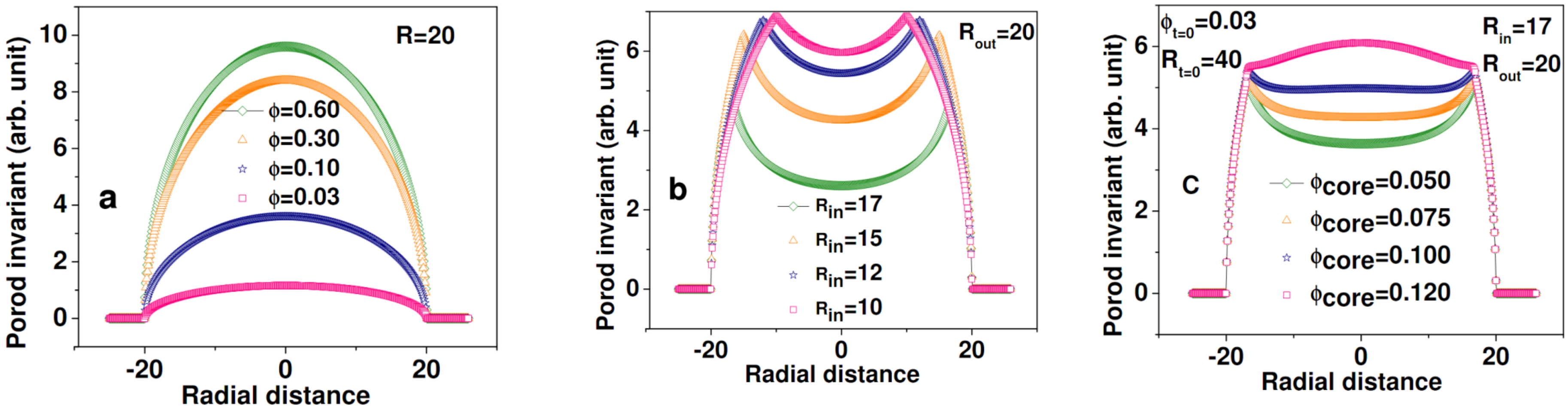


Chen et al., Soft Matter 8, 12093 (2012)

The drying droplet

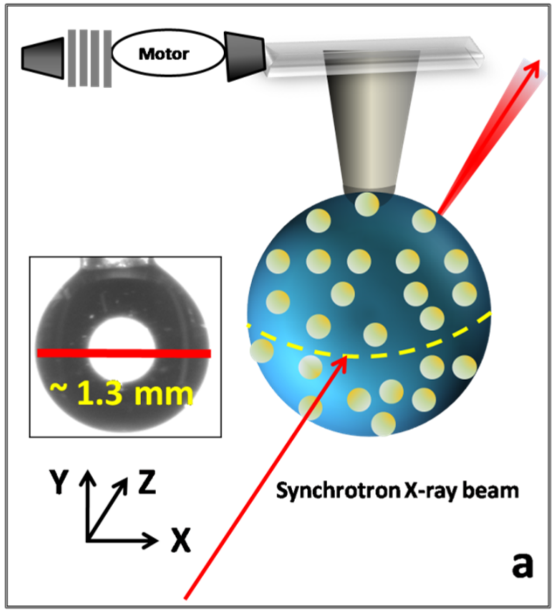
- > Microbeam: local concentration
- > Q~ $\phi(1-\phi)(R^2 - x^2)^{0.5}$
- > Dried droplet: different gradient in ϕ
- > Homogenous distribution
- > Agglomeration in shell
- > Continuous gradient



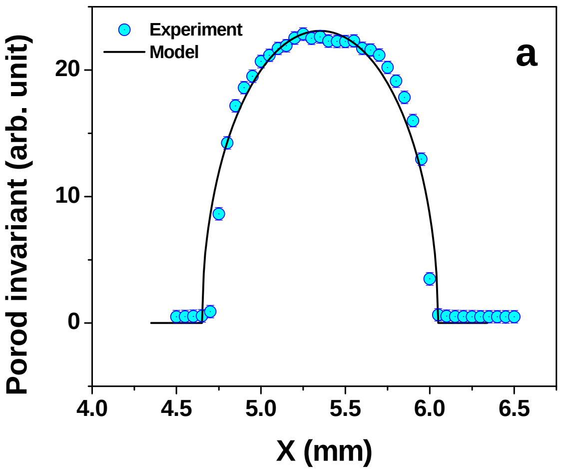


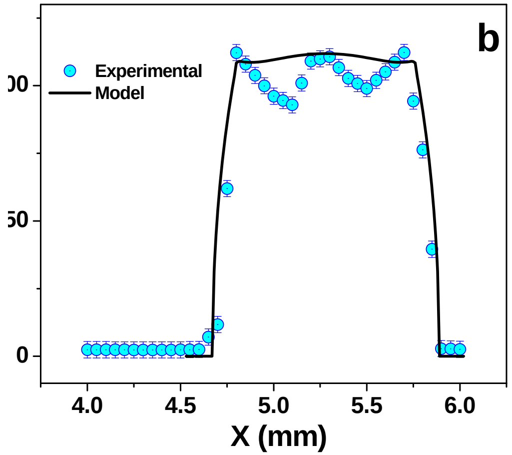
Sen, SVR et al., Soft Matter **10**, 1621 (2014)

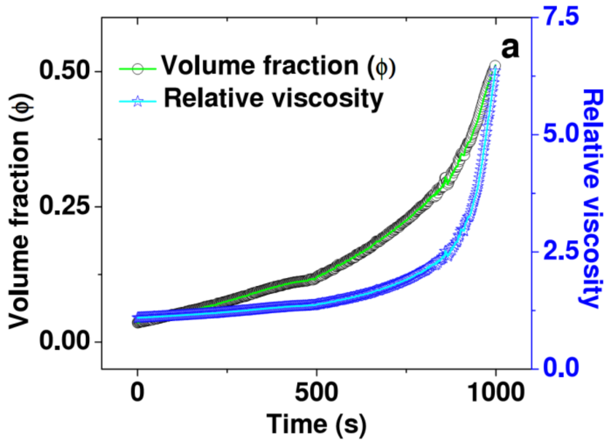
The drying droplet – part 2



- Slow / fast drying
- Concentration of colloids:
  - Arresting of colloids
  - Homogenous
  - Core shell effect (‚coffee ring‘)
- Follow concentration profile in-situ







Q~ $\phi(1-\phi)(R^2 - x^2)^{0.5}$

Sen, SVR et al., Soft Matter **10**, 1621 (2014)

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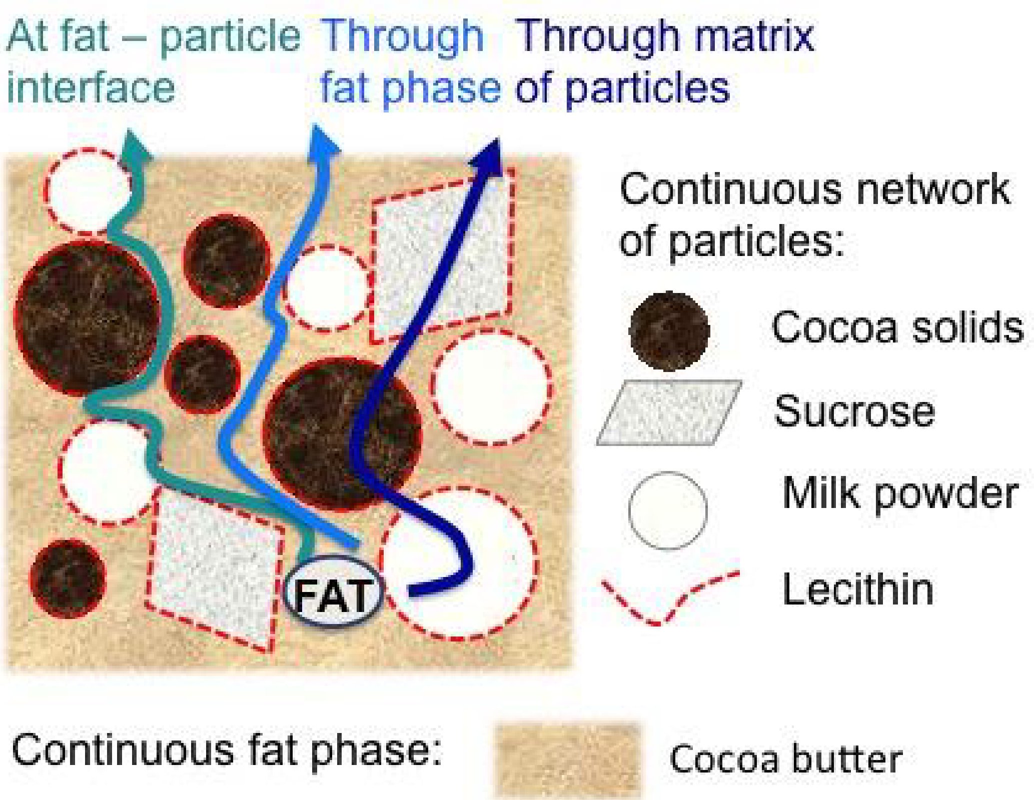
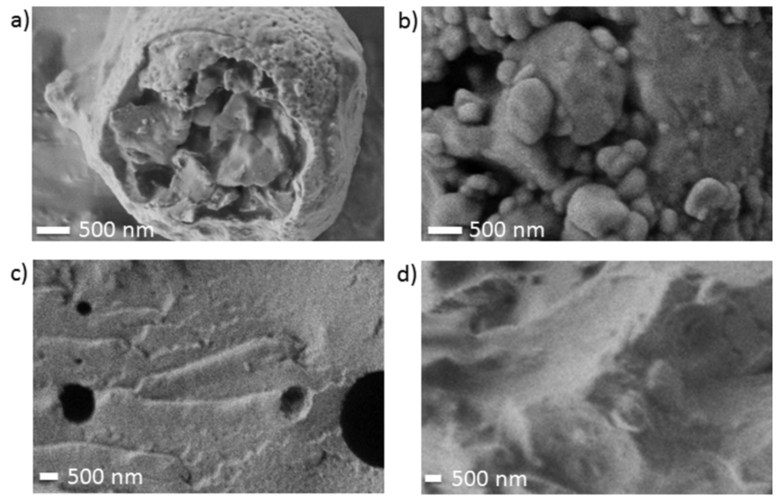
Chocolate

> A real multicomponent system

> Nestlé, TU HH, DESY

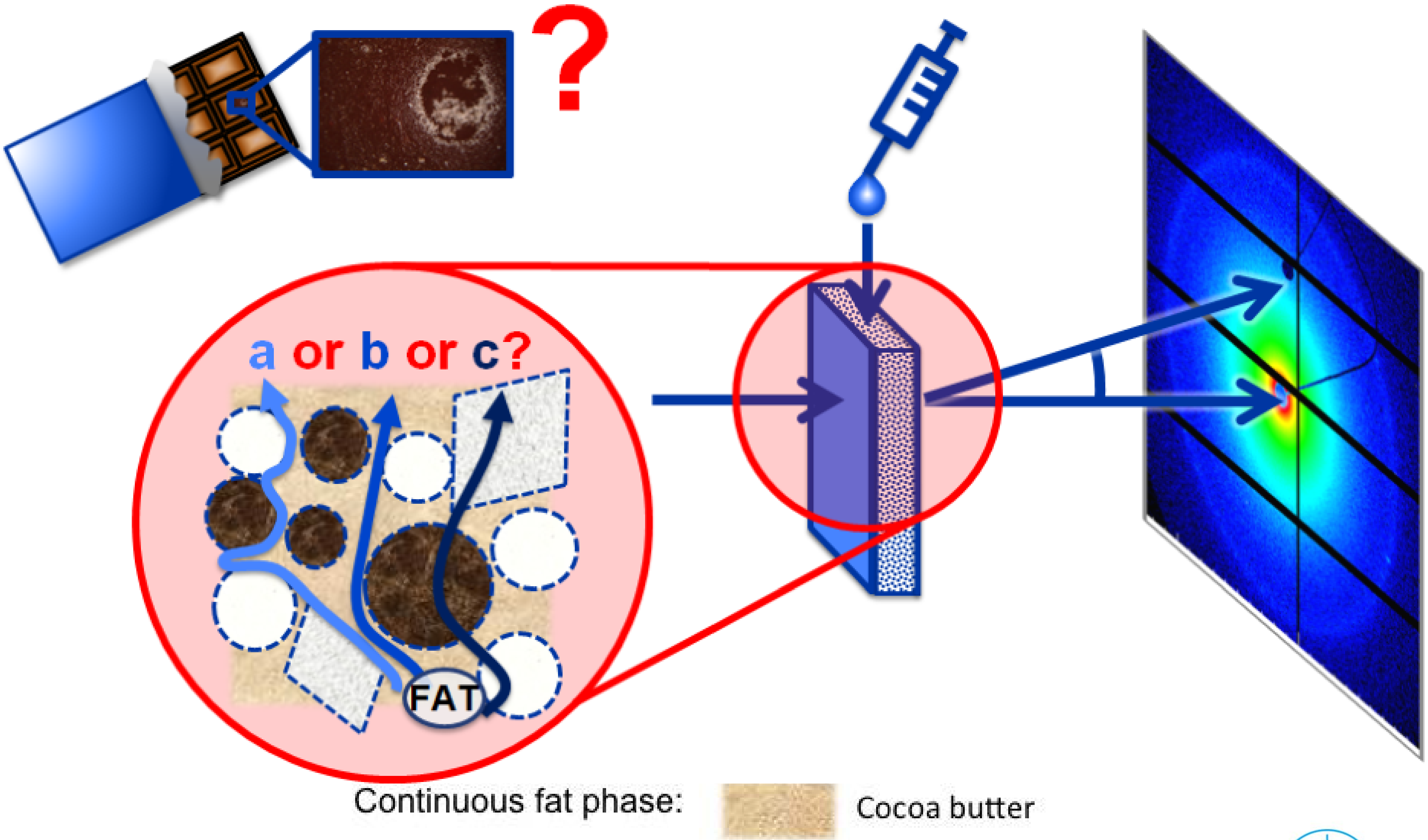
> Fat Blooming - pathways





Reinke, SVR et al., ACS Appl. Mater. Interfaces, DOI: 10.1021/acsami.5b02092 (2015)

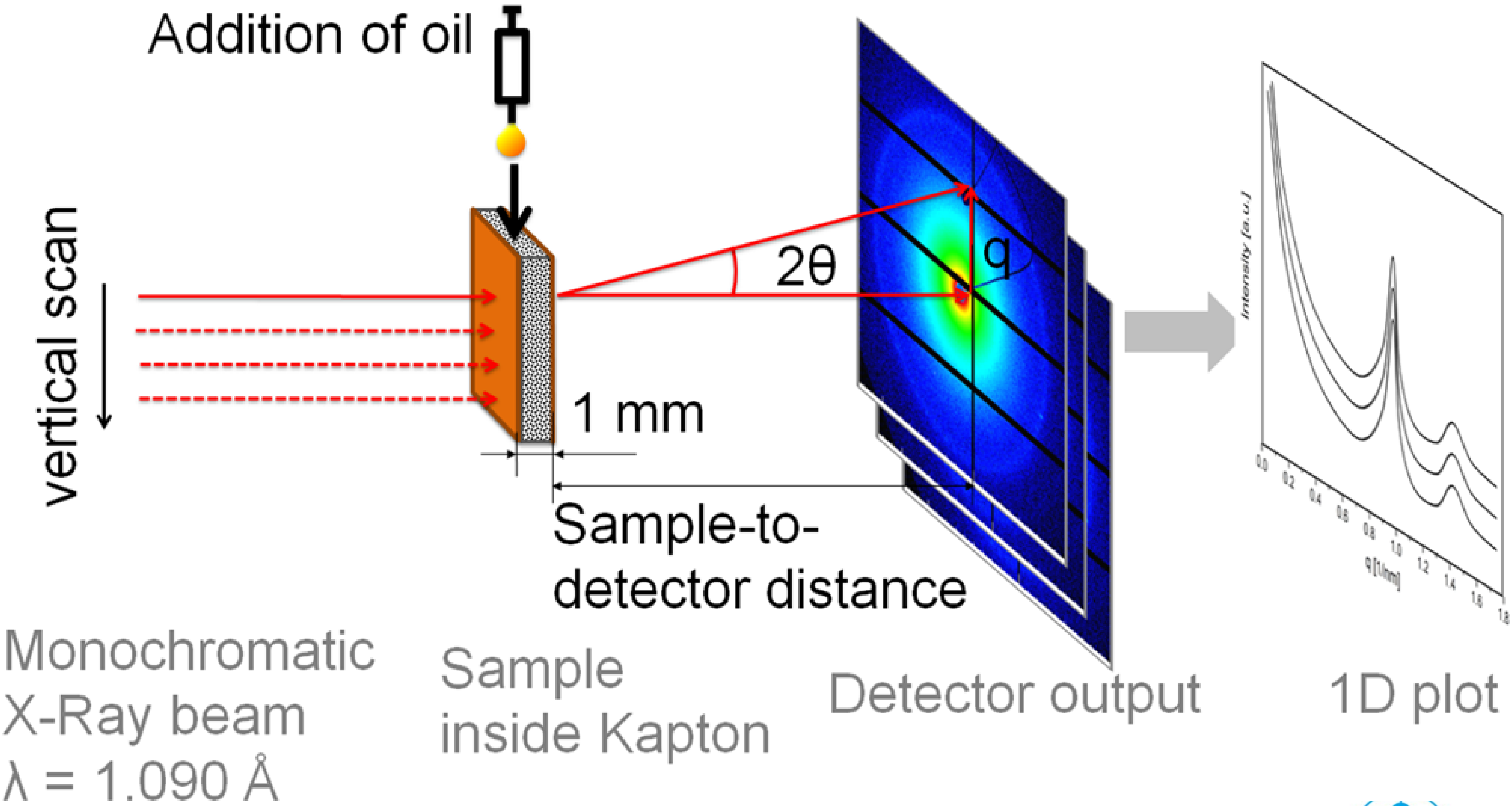
Chocolate



Reinke, SVR et al., ACS Appl. Mater. Interfaces, DOI: 10.1021/acsami.5b02092 (2015)

Chocolate

> A real multicomponent systems

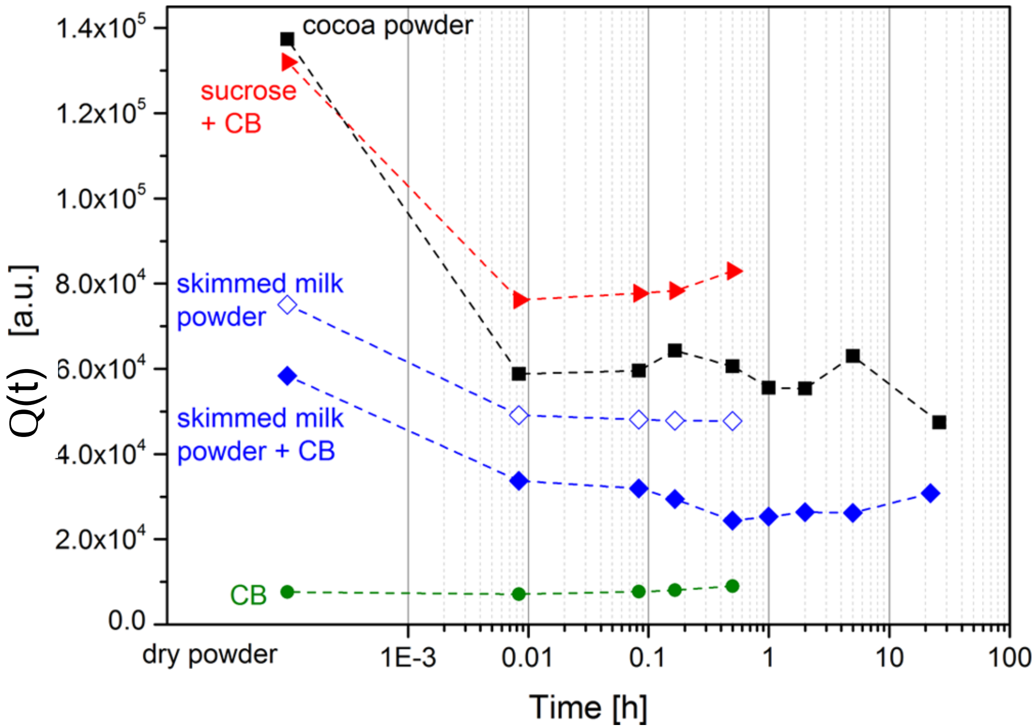


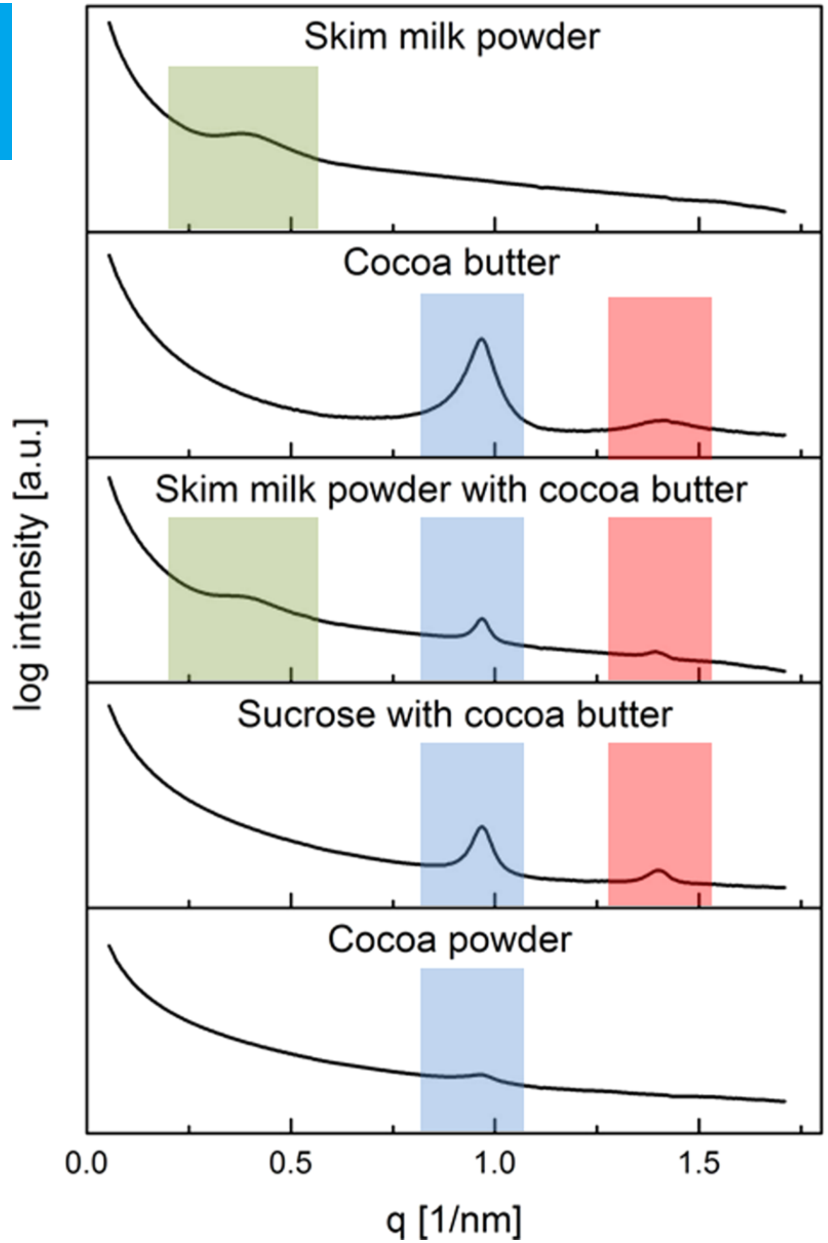
Reinke, SVR et al., ACS Appl. Mater. Interfaces, DOI: 10.1021/acsami.5b02092 (2015)

Chocolate

> A real multicomponent system

> Superposition of SAXS contributions



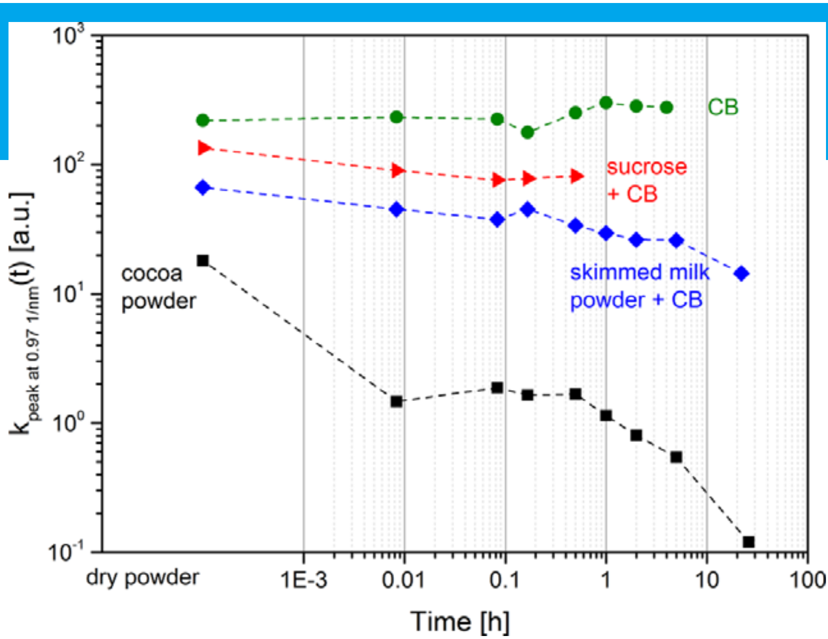


> Different density difference

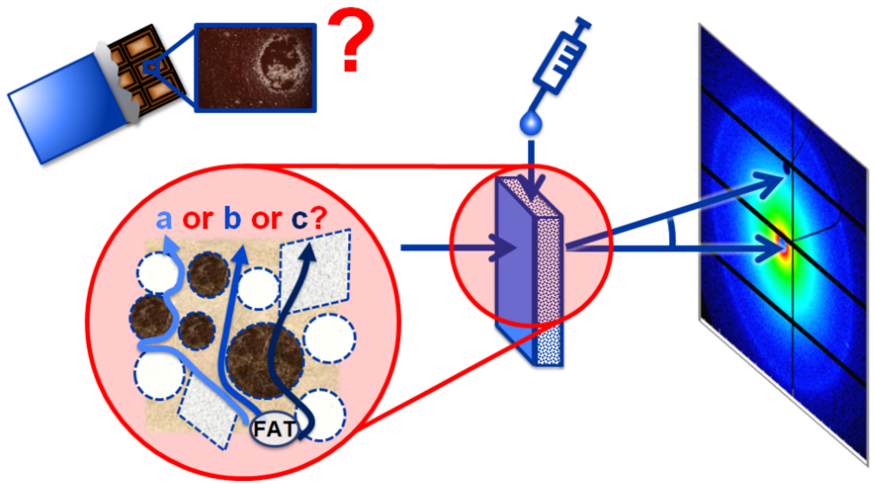
> Migration: filling of voids by oil: Q decreases

Reinke, SVR et al., ACS Appl. Mater. Interfaces, DOI: 10.1021/acsami.5b02092 (2015)

Chocolate



- > Peak intensities
- > Pores, cracks: capillary effect
- > Then: “chemical migration through the fat phase by softening and partial dissolution of the crystalline cocoa butter.“
- > reduction of porosity and a minimization of defects
- > a reduced content of noncrystallized liquid cocoa butter
- > b or c



Reinke, SVR et al., ACS Appl. Mater. Interfaces, DOI: 10.1021/acsami.5b02092 (2015)