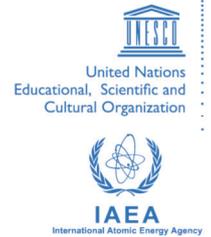




**The Abdus Salam
International Centre for Theoretical Physics**



2332-6

School on Synchrotron and FEL Based Methods and their Multi-Disciplinary Applications

19 - 30 March 2012

Small-Angle X-Ray Scattering - Fundamentals and Applications

Peter Laggner
University of Graz (Austria)

Small-Angle X-Ray Scattering –
Fundamentals and Applications

BRUKER

Peter Laggner, Heinz Amenitsch, Michael Rappolt, Georg Pabst,
Maria Schmuck, Benedetta Marmiroli, and Manfred Kriechbaum

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- I. What is SAXS ?
- II. General Areas of Application
- III. Some Basic Physics
- IV. Key Examples
- V. Advanced Techniques / Synchrotron / Home-Laboratory

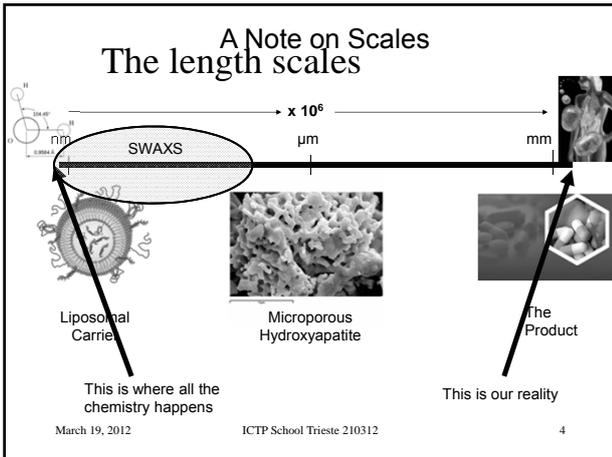
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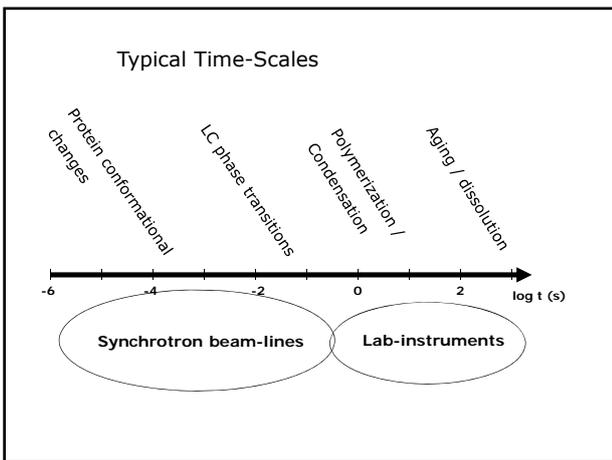
X-rays

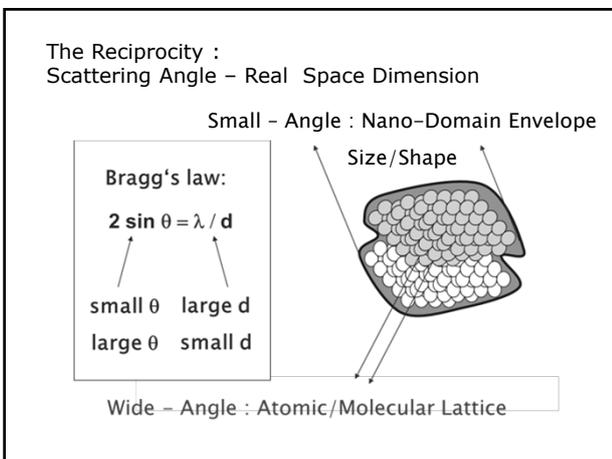
SAXS
Nanoparticle Size and Shape,
10 – 1000 Å

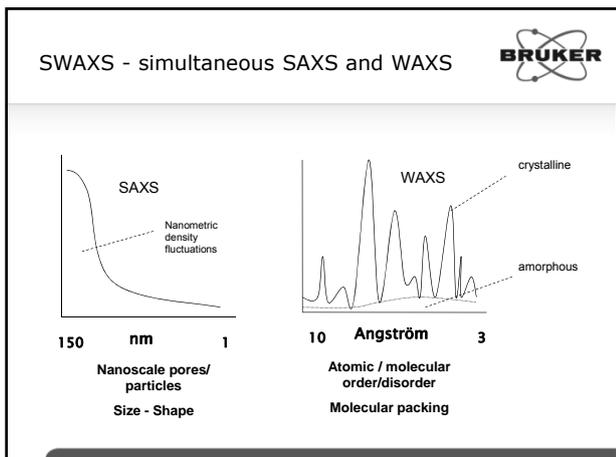
WAXS
Inner Molecular Structure
< 10 Å

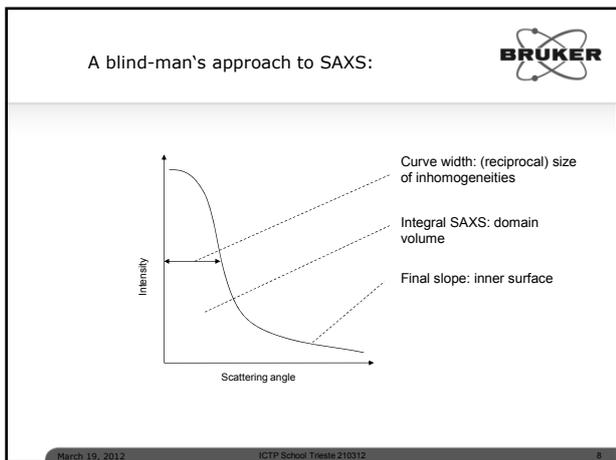
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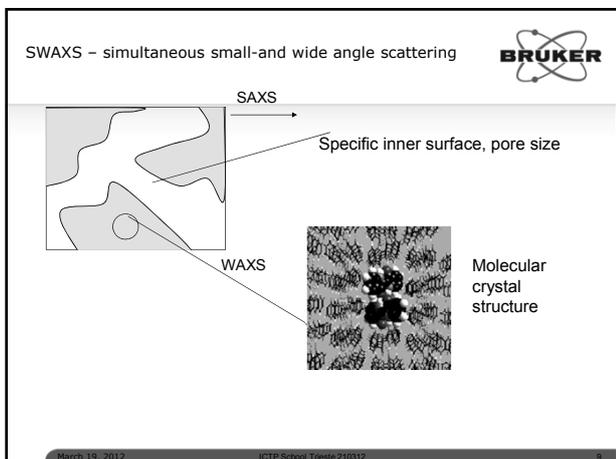


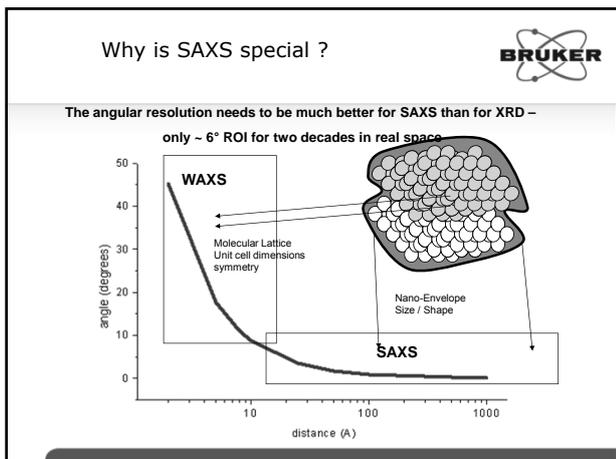


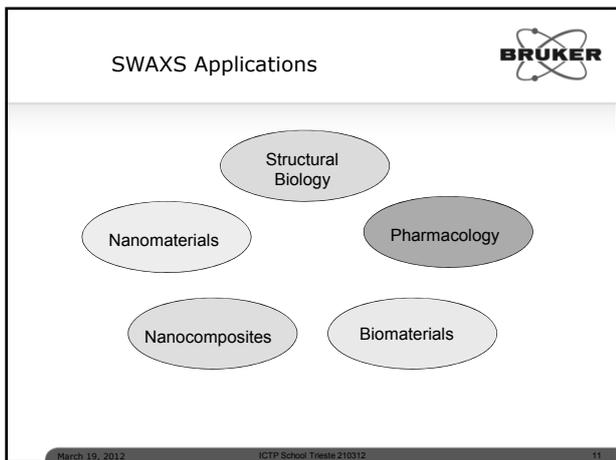


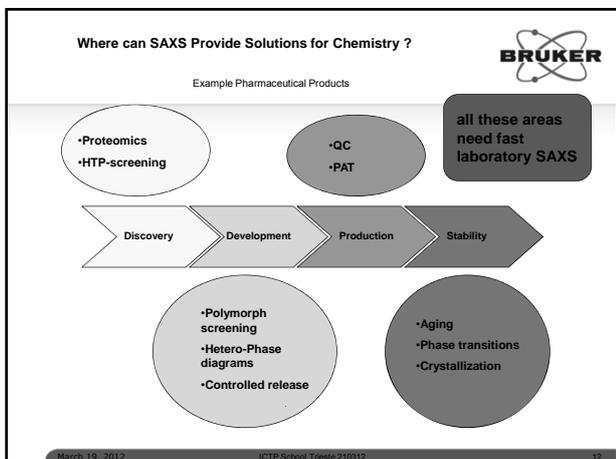




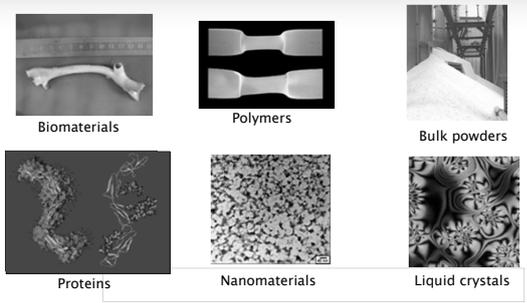








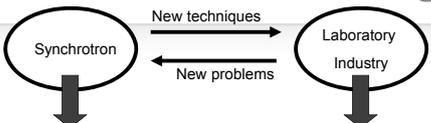
SAXS – wherever nanostructure counts 



Biomaterials Polymers Bulk powders

Proteins Nanomaterials Liquid crystals

The Route of Innovation 



Extreme conditions:

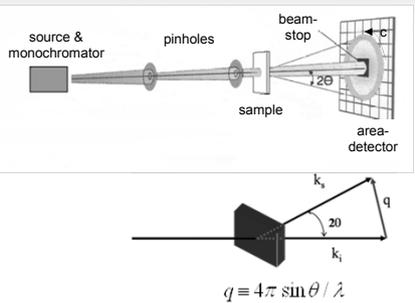
- fast kinetics – molecular movie
- thin film structure – GISAXS
- microfluidics
- micro- and nanobeams
- gas phase
- integration with other techniques

Tools for R&D, QC, PAT:

- constant availability
- speed and economy
- reliable, robust, automation
- on-line process control
- lab-GISAXS
- integration with other techniques

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The SAXS Experiment 



Resolution $\approx 1 - 100 \text{ nm}$

Other definitions:

$$s \equiv 2\pi \sin \theta / \lambda$$

$$h \equiv \sin \theta / \lambda$$

$$q \equiv 4\pi \sin \theta / \lambda$$

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SAXS Theory

$$I(Q) = \left| \sum_n b_n \exp(iQ \mathbf{R}_n) \right|^2 = \sum_{n,m} b_n b_m^* \exp(iQ(\mathbf{R}_n - \mathbf{R}_m))$$

neutrons: b = nuclear scattering length (magnetic formfactor)
X-rays: b = atomic formfactor $f \ll Z$

SAS: length scale \gg atomic distances
 $b \rightarrow \rho(r)$ Continuous scattering-length density
 $\Sigma \rightarrow \int$

$$I(Q) = I_0 \left| \int_V \rho(\mathbf{r}) e^{i\mathbf{Q}\mathbf{r}} d\mathbf{r} \right|^2$$

Fourier-integral

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Two-phase Approximation

Two homogeneous phases (α and β) with sharp interfaces



$$I(Q) = I_0 (\rho_\alpha - \rho_\beta)^2 \left| \int_V e^{i\mathbf{Q}\mathbf{r}} d\mathbf{r} \right|^2$$

$$I(Q) = I_0 \Delta \rho^2 \left| \int_V e^{i\mathbf{Q}\mathbf{r}} d\mathbf{r} \right|^2$$

Isotropic systems: spherical average
 For isotropic systems (fluids, glasses, polycrystals)
 → no direction dependence of the scattered radiation

$$I_S(Q) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi I(Q, \chi, \varphi) \sin \chi \, d\chi \, d\varphi$$

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Two general laws

Integrated Intensity Φ = volume fraction

$$\tilde{I} = \int_0^\infty I_S(Q) Q^2 dQ = I_0 2\pi^2 \Delta \rho^2 \Phi(1 - \Phi)$$

Porods Law

$$I_S(Q) = \frac{I_0 2\pi \Delta \rho^2 S}{Q^4} = \frac{P}{Q^4} \quad QR \gg 1$$
 S = total interface per unit volume

→ Porod radius

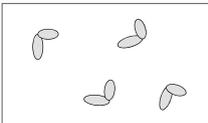
$$R_p = \frac{\tilde{I}}{P} = \pi \frac{\Phi(1 - \Phi)}{S}$$
e.g. $\Phi \ll 1$ and spherical particles
 → $R_p = (\pi/3) R \approx R$

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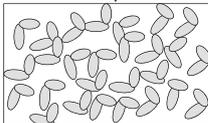
The four limiting cases



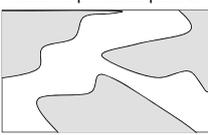
Dilute particles



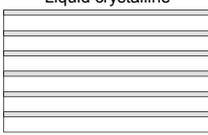
Crowded particles



Random porous/2-phase



Liquid crystalline



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Radius of gyration, particle size, shape

Solution structure factor

Specific inner surface, pore size

Lattice dimensions, unit cell structure

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Dilute, Monodisperse System

Examples:

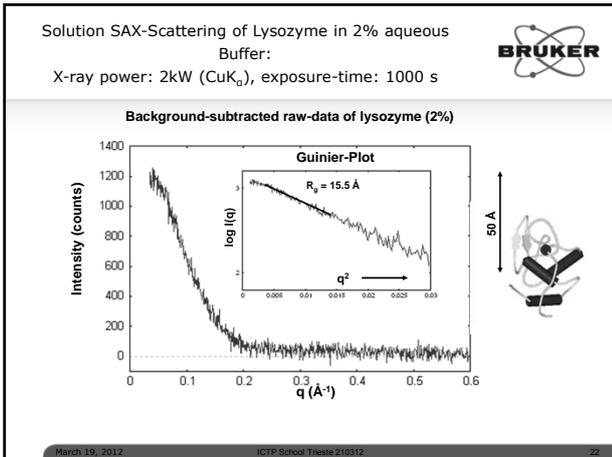
- Protein solutions
- Polymer solutions
- Nanoparticle solutions

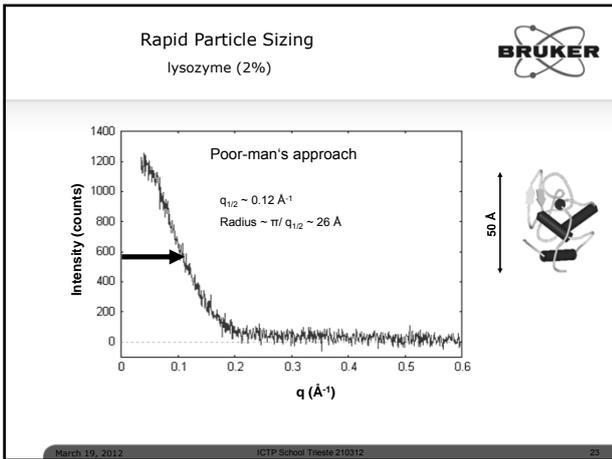
Parameters

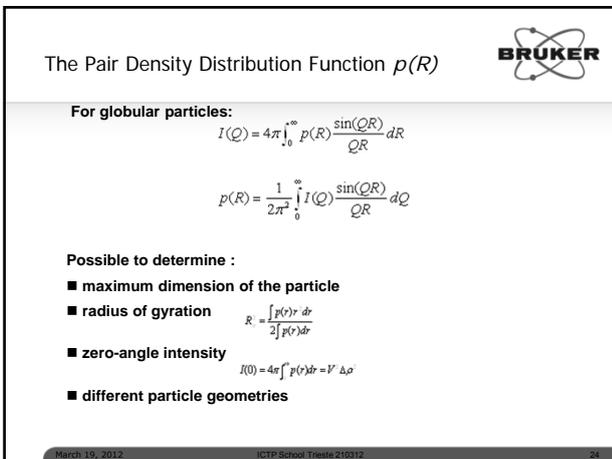
- Radius of Gyration
- Particle weight
- Particle Volume

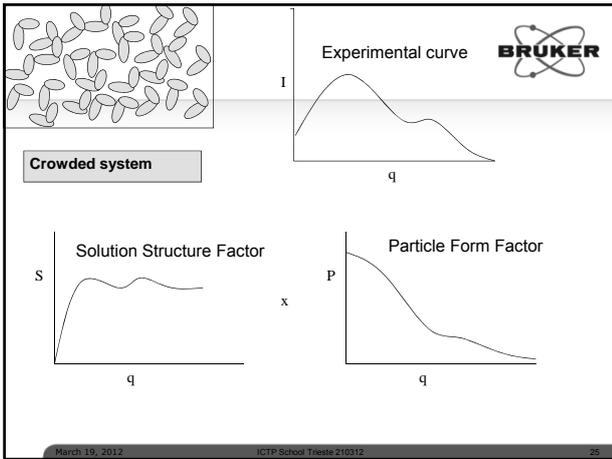
Particle Shape

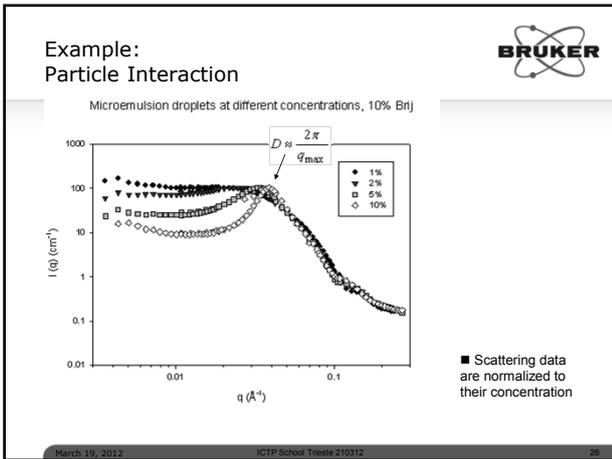
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Principle of Solid-State SAXS

SAXS is the most universal method for nanostructure analysis:

- Sensitive – low concentration (down to 0.1 %)
- Noninvasive – no preparation, staining or drying
- In-situ, real-time capabilities
- Extremely versatile (solids, liquids, gas phase)

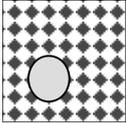
The problem is how to retrieve the structural information from the scattering patterns

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The Solid-State Problem: Inner Surface 

The thermodynamic stability of a heterogeneous system (e.g. crystalline/amorphous) is not primarily determined by the percentage of the phases but by the **interface per unit volume**.

1 % amorphous can be harmless, or disastrous – depending on S_i



Lower inner surface
Higher stability

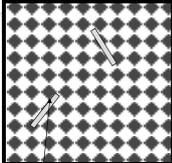
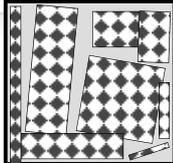
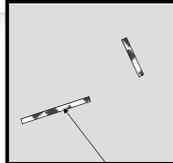
Equal %
amorphous
or
porosity



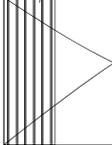
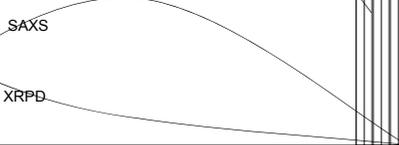
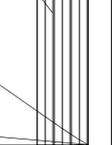
Higher inner surface
Lower stability

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μm

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SAXS : A Measure of Stability 

SAXS provides a measure for the **specific inner surface** (area per volume) between domains of different density

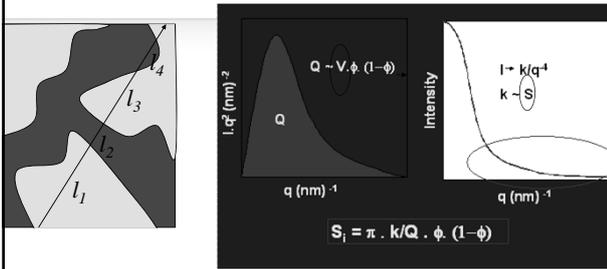
Density differences can arise from

- Crystalline/amorphous domain structure
- nanopores

Both are thermodynamic instabilities: Gibbs' free energy grows with inner surface area – the larger the inner surface, the lower the stability

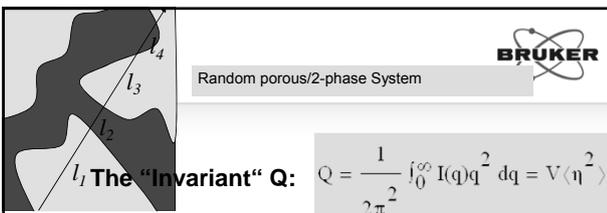
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Recalling an old principle of small-angle scattering: 



Porod, G. , Kolloid-Z. 124, 83 (1951)

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Random porous/2-phase System

The "Invariant" Q:
$$Q = \frac{1}{2\pi^2} \int_0^\infty I(q) q^2 dq = V \langle \eta^2 \rangle$$

The integral scattering, the „Invariant“, is equal to the total irradiated volume times the mean-square electron density fluctuation - independent of domain shape.
(Debye, Bueche)

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GENERAL RELATIONS (2) 

In the case of a two-phase system (e.g. crystalline/ amorphous polymer), the invariant is related to the volume fractions ϕ , and the electron densities ρ_c and ρ_a

$$Q = V (\rho_c - \rho_a)^2 \phi_a \phi_c$$

total irradiated volume

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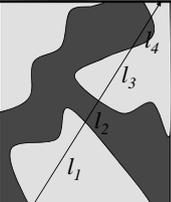
GENERAL RELATIONS (3)

The decay constant k from a two-phase system is given by

$$k = \lim_{q \rightarrow 0} q^4 \cdot I(q) = 2\pi \cdot S \cdot (\rho_c - \rho_a)^2$$

K depends on the total inner surface and the mean-square electron density fluctuations

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The inverse of k/Q is equal to the **mean chord length**:

$$\bar{l} = \frac{Q}{k} = \frac{4V}{S}$$

The mean pore diameters and wall diameters can be calculated from the relations:

$$l_p = \frac{Q}{k \cdot (1 - \phi_p)} \quad \text{and} \quad l_s = \frac{Q}{k \cdot \phi_p}$$

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How to obtain S_i from experimental data:

- use the relation: $\lim_{q \rightarrow \infty} I(q) = k \cdot \frac{K}{q^4}$

determine Porod limits from $\log I / \log q$ -plot.

The slope should be -4 (at least close to that), according to $I \sim q^{-4}$. If far from -4 , system is fractal or has transition layer, and S_i cannot be determined.

- determine K , from extrapolation to $\lg q = 0$
- determine Q from integration (extrapolation to zero and infinity)
- Calculate S_i in units of m^2/g from:

$$S_i = \pi \cdot 10^4 \cdot \frac{K}{Q} \cdot \frac{\phi_p \cdot (1 - \phi_p)}{\rho_s}$$

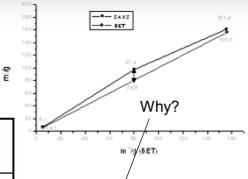
ϕ_p ... volume fraction of pores (e.g. He-pycnometry)
and ρ_s ... matrix density of the solid (e.g. crystal data).

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Comparison SAXS/BET
(BAM – Alumina Standards)



	BET m ² /g	SAXS m ² /g
PM-102	5,41	6,1
PM-104	79,8	97,4
PM-103	156,0	161,4



Why?

SAXS inner surface is higher than BET:

- inaccessible, closed pores
- nanostructured particle surface

Both are equally relevant for stability

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Nanomaterials



Mesoporous Materials - MCM

Inner surface by SAXS

- ... within minutes
- ...without drying

M.Lüchinger, G.Pingrubler, B.Lidlar, R.Prins and P. Laggner, J.Chem.Phys. (2004)

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Monitoring Shape and Size of Pores in M41S Silicas

M.Lüchinger, G.Pingrubler, B.Lidlar, R.Prins and P. Laggner (2004)

