INSTITUT DE CHIMIE
SEPARATIVE DE MARCOULE

Introduction to the study of surface by Small Angle X-ray Scattering

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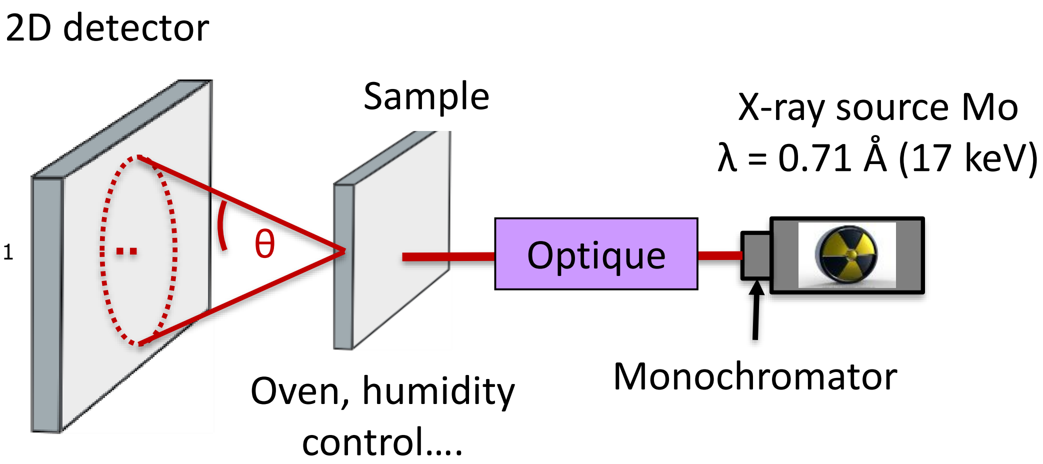
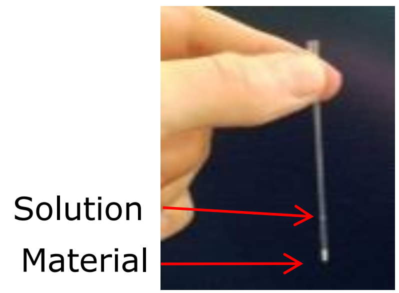
SAXS



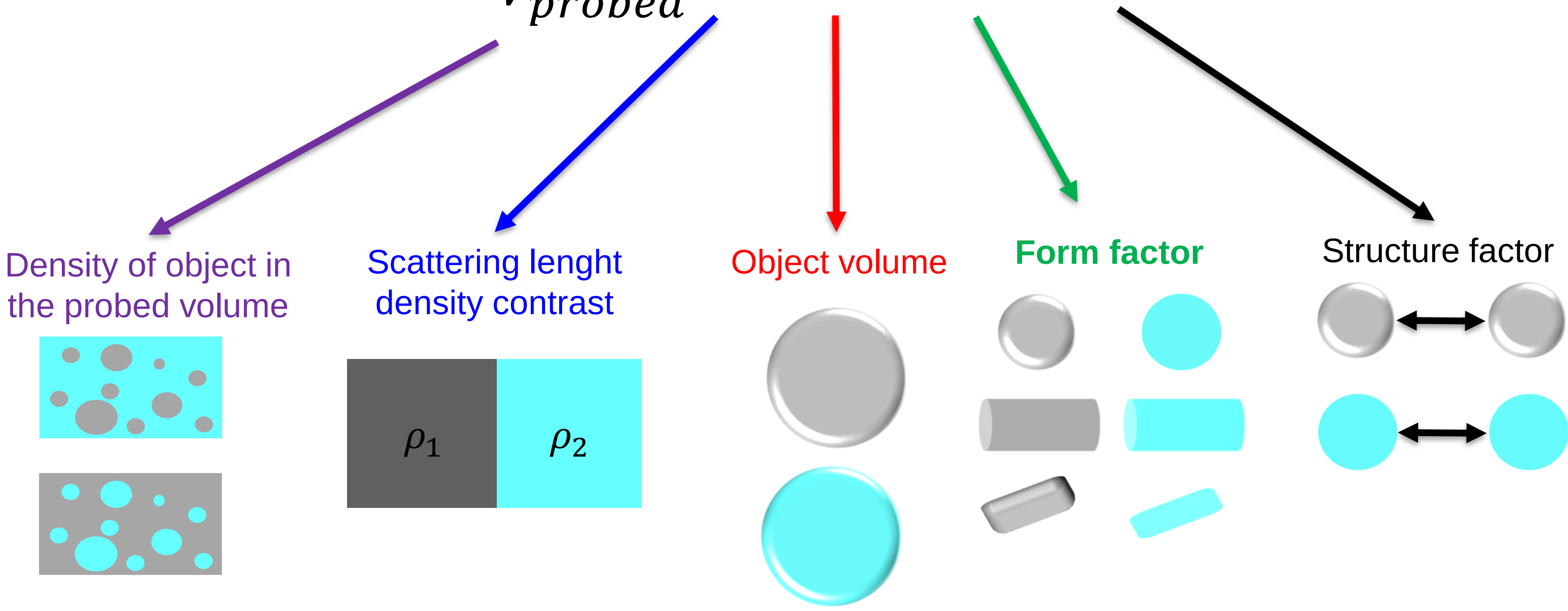
accessible q range : 0.2 – 30 nm^{-1}

scattering vector $q = 4\pi \sin(\theta) / \lambda$

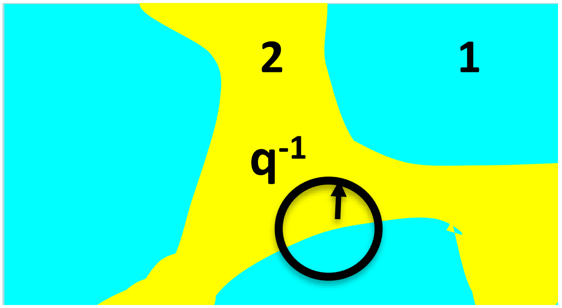


Absolute intensity

$$I_{abs}(q) = \frac{N}{V_{probed}} . \Delta\rho^2 . V_{obj}^2 . P(q) . S(q)$$



Porod's law



$q^{-1} << R$

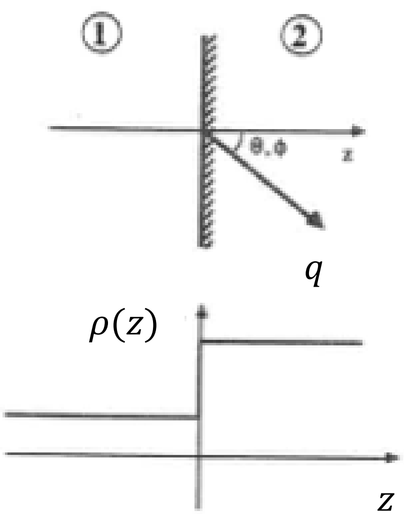
If q >> curvature → flat at q^{-1} scale → **Porod's Regime**

$$d = 2\pi/q$$

Porod's law

$$I(q) = 2\pi(\rho_1 - \rho_2)^2 \Sigma \frac{1}{q^4}$$

Total interfacial area per unit volume (S/V)



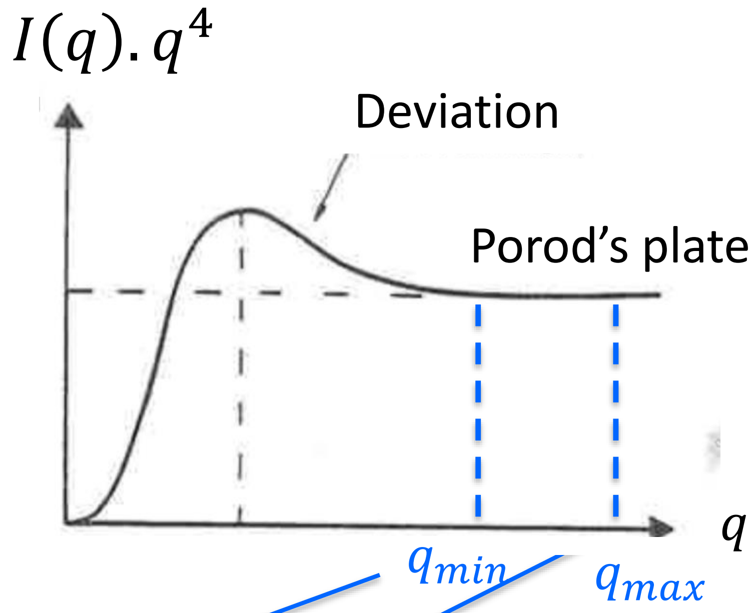
Thus Porod's law traduces the reflection of the incident beam on the portions of interface in the samples which have the right orientation to yield a reflected beam at a given scattering angle. In this sense, Porod's law is nothing else than Fresnel's law of reflectivity calculated in the Born approximation, a point of view particularly developed in ref. [7].

L. Auvray and P. Aurroy, Bombannes summer school lecture : Scatering by interfaces (1991)

Porod’s law deviation

Porod’s law

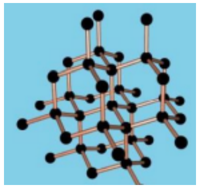
$$I(q) = 2\pi(\rho_1 - \rho_2)^2 \Sigma \frac{1}{q^4}$$



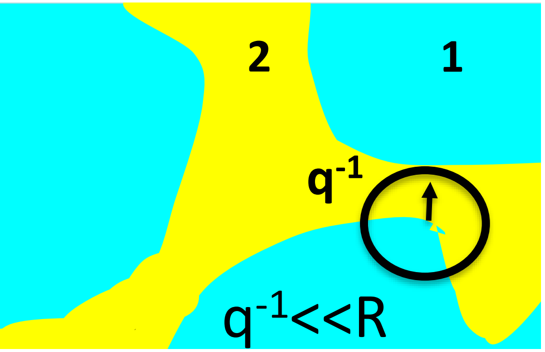
Courvature
Roughness
Fractality

$$d_{max} = \frac{\pi}{q_{min}}$$

$$d_{min} = \frac{\pi}{q_{max}}$$



Atomic scattering
(crystallography)

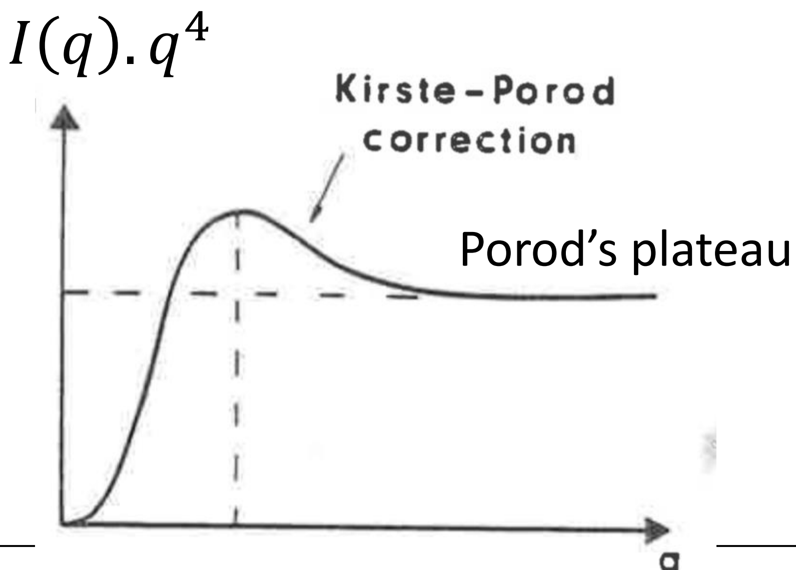


$q^{-1} \equiv$ Interface curvature

Kirste-Porod Formula => addition of q^{-6} term

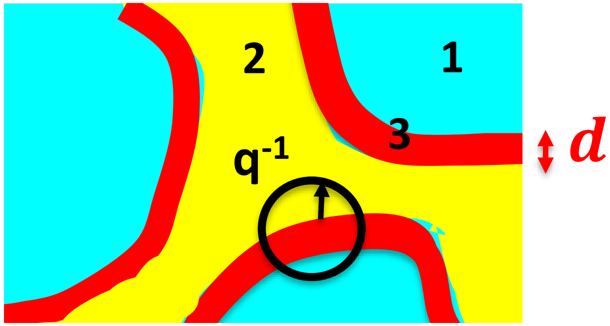
$$I(q) = 2\pi(\rho_1 - \rho_2)^2 \Sigma \frac{1}{q^4}\left(1 + \frac{1}{q^2}\left[\frac{1}{4} < (C_1 + C_2)^2 > + \frac{1}{8} < (C_1 - C_2)^2 >\right]\right)$$

Local principal surface curvature



L. Auvray and P. Aurroy, Bombannes summer school lecture : Scaterring by interfaces (1991)
R. Kirste, G. Porod, Koll, Z., Z. für Polym, 184, 1 (1962)

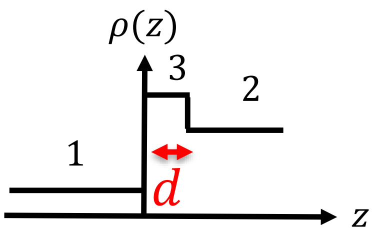
When the interface is grafted or covered

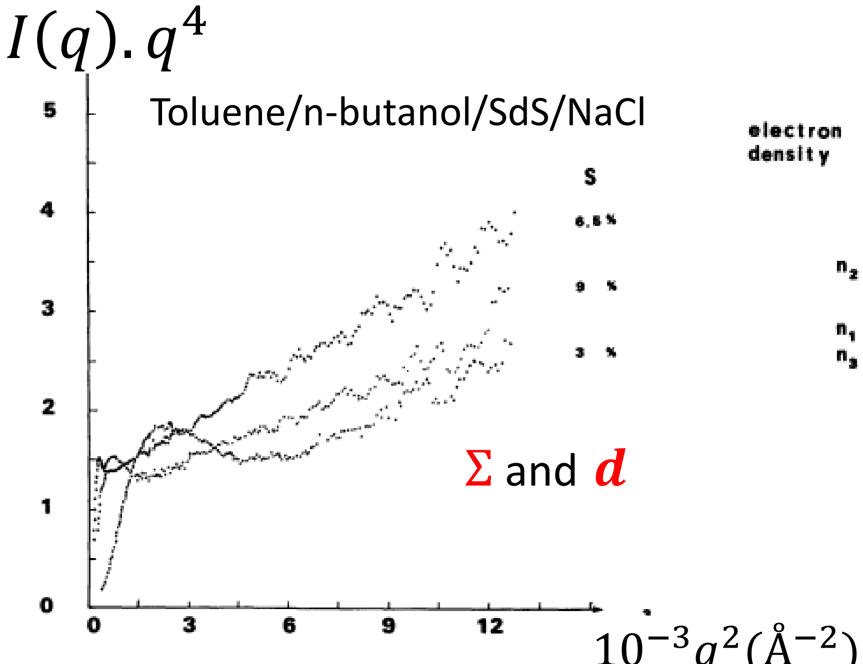


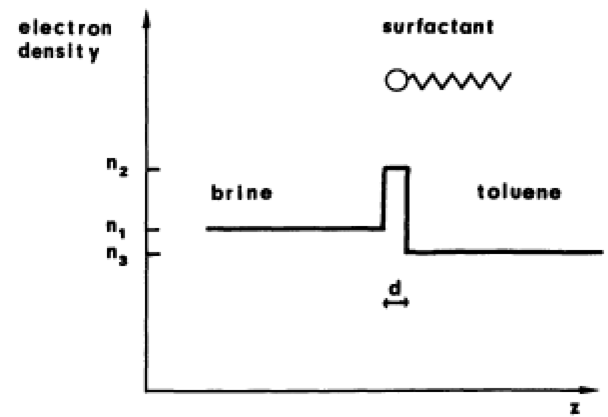
$q^{-1} << R$

$$\lim_{qd<1} I(q)\,q^4 = 2\pi\Sigma(\rho_2-\rho_1)^2.\left(1+\frac{(\rho_3-\rho_1)(\rho_3-\rho_2)}{(\rho_2-\rho_1)^2}(qd)^2+\varepsilon(qd)^4\right)$$

Scattering of disk







=> amount of surfactant grafted per nm² of surface

L. Auvray et al , Microemulsions: a small angle X-ray scattering study. Journal de Physique, 1984, 45 (5), pp.913-928.

L. Auvray, J.P. Cotton, R. Ober, C. Taupin, Structure of concentrated Windsor microemulsion by SANS, Physica 136B (1986) 281-283.

Diffuse interface

negative deviations from the Porod law due to the diffuse interface

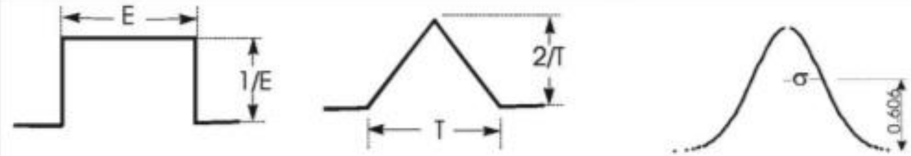
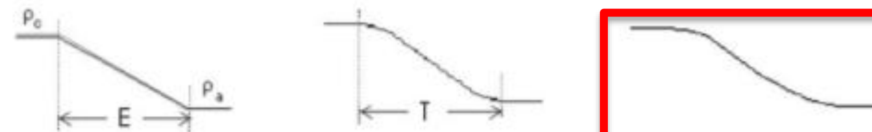
$$\lim_{q\to\infty}[I(q)] = I_p(q)H^2(q) + I_{FI}(q)$$

Density fluctuation within the diffuse layer

$$I_{FIcor} = I_p(q)H^2(q)$$

$$K_p = 2\pi\Sigma(\Delta\rho)^2$$

K_p = Porod constant

Smoothing (Ghost) Function, h(r)			
Expected Electron Density Profile, $\tilde{n}(r) = g(r) * h(r)$			
Modified Porod's Law			
- exact	$I_{FlCor}q^4 = K_p \frac{\sin^2(E\cdot q/2)}{(E\cdot q/2)^2}$	$I_{FlCor}q^4 = K_p\left[\frac{4\sin(T\cdot q/4)}{(T\cdot q)}\right]^4$	$I_{FlCor}q^4 = K_p \cdot \exp(-\sigma^2 \cdot q^2)$
- expanded	$I_{FlCor}q^4 = K_p(1-\frac{E^2\cdot q^2}{12})$ (for $E\cdot q/2 << 1.0$)	$I_{FlCor}q^4 = K_p(1-\frac{T^2\cdot q^2}{24})$ (for $T\cdot q/4 << 1.0$)	$I_{FlCor}q^4 = K_p\cdot(1-\sigma^2\cdot q^2)$ (for $\sigma\cdot q << 1.0$)
Required Plot			
- exact	-	-	$\ln(I_{FlCor}q^4)$ vs. q^2
- expanded	$I_{FlCor}q^4$ vs. q^2	$I_{FlCor}q^4$ vs. q^2	$I_{FlCor}q^4$ vs. q^2
Determination of	transition layer thickness, E and T		standard deviation, σ
- exact	-		$\sigma = \sqrt{-m}$
- expanded[a]	$E = \sqrt{\frac{-12\cdot m}{K_p}}$	$T = 2\sqrt{\frac{-6\cdot m}{K_p}}$	$\sigma = \sqrt{-m/K_p}$
Relationship	$T(=2\sqrt{6}\sigma) > E(=\sqrt{12}\sigma) > \sigma$		
References	Vonk (1973)	this work	Ruland (1971)

(a) K_p and m are Porod's constant (see the text for definition) and slope in each plot.

Kim, J. of Appl. Cryst, 2003, 643-651

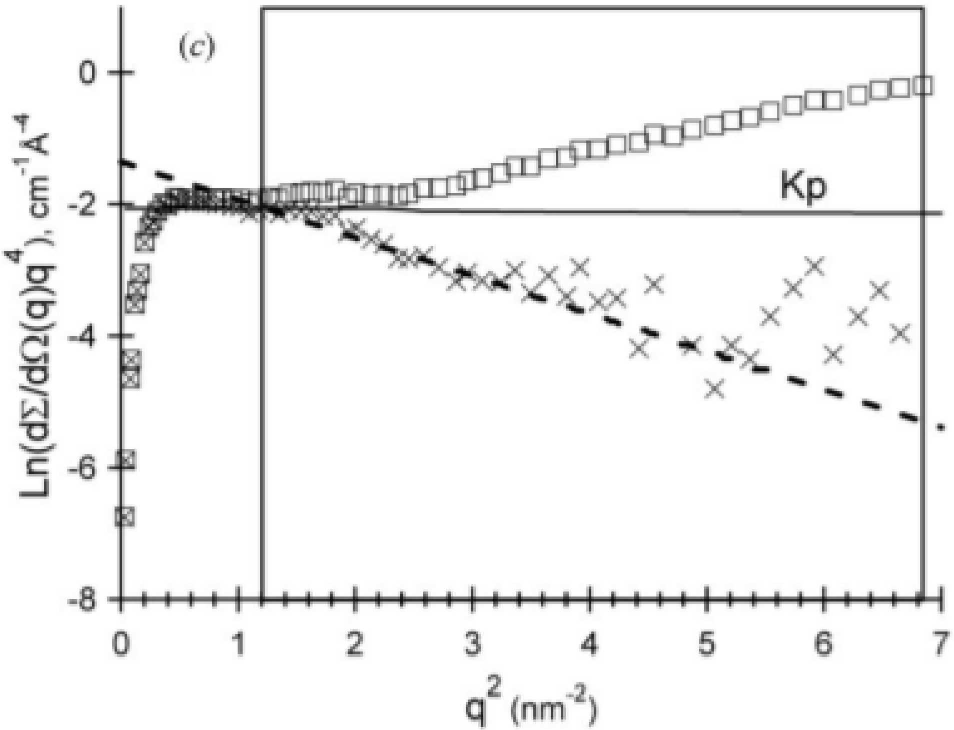
Diffuse interface

Modified Porod's law plot for sigmoidal (σ model) gradient

$$I_{FICor}q^4 = K_p \cdot \exp(-\sigma^2 \cdot q^2)$$

$$I_{FICor}q^4 = K_p \cdot (1 - \sigma^2 \cdot q^2)$$

(for $\sigma \cdot q << 1.0$)



□ $I_{obs}(q)$

– – $I_{FI}(q)$

× $I_{FIcor} = I_{obs}(q) - I_{FI}(q)$

— K_p=0.1271

$$K_p = 2\pi\Sigma(\Delta\rho)^2$$

Crystallized ethylene/1-octene (EO) random copolymers with hexyl branch content

Heterogenous media at all lengthscale

Fully random dispersion of 2 phases at any scale

=> Debye Model

$$I(q) \sim \frac{1}{(1 + q^2 l_p^2)^2}$$

$$l_p \boldsymbol{\Sigma} = 4\Phi(1\text{-}\Phi)$$

Porod’s lenght

Volume fraction of one phase

☹ $I(q)q^4$ => monotonously increasing + no asymptotic behavior

☹ Not satisfying for smooth surfaces

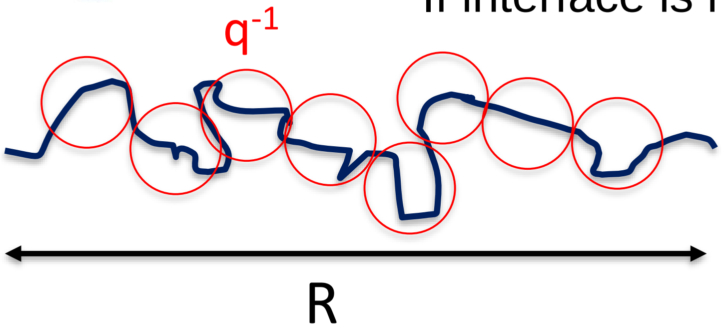
☹ Not realistic since it assumes a too broad of pore sizes

P. Debye, H.R. Henderson, H. Brumberger, J. Appl. Phys. 28, 679 (1957)

E.W. Käler, S. Prager, J. Coll. Interf. Sci. 86, 359 (1982).

Rough interface

If interface is rough => its area depends on the scale of observation



$$I(q) \sim N_s(q^{-1}).\, g_s^{2}(q^{-1})$$

Number of blob ← $N_s(q^{-1})$

Number of scattering element in one blob ← $g_s^2(q^{-1})$

Because the scattering element occupied a fraction of the blob volume $\sim q^{-d}$

$$g_s \sim \left(\frac{q^{-1}}{a}\right)^{d}$$

a → size of the scattering element

$N_s \Rightarrow$ depends on the roughness

$$\sum(q^{-1}) \sim N_s(q^{-1})(q^{-1})^{d-1}$$

Apparent area seen at the resolution q^{-1}

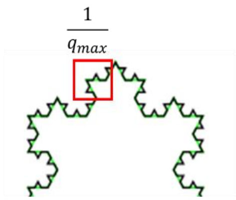
$$I(q) \sim N_s g_s^2 \sim \frac{\sum(q^{-1})}{a^{2d} q^{d+1}}$$

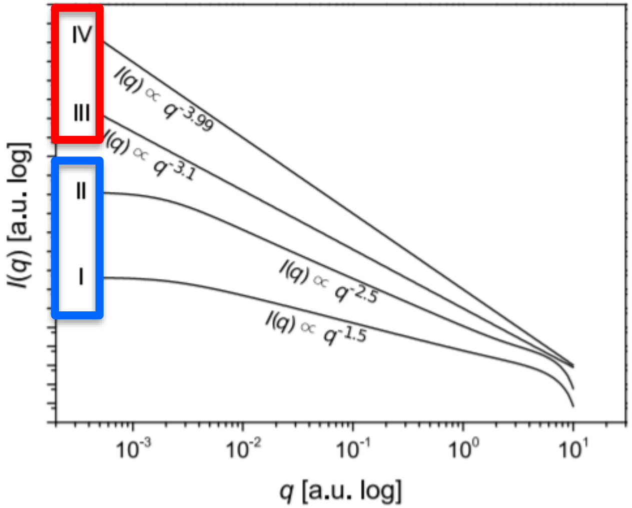
Ex: For d=3
Porod's law

$$I(q) \sim \frac{\sum(q^{-1})}{a^{6} q^{4}}$$

Fractal structures

$I(q) \propto q^{-D}$





Surface fractal

Diffusion from surfaces $\quad I(q) \propto q^{D_s-6} \quad 3 < 6 - D_s < 4$

$$I(q) = A\frac{\Gamma(5-D_s)sin[\pi(3-D_s)/2]}{(3-D_s)}q^{D_s-6}$$

$$\Sigma(R) = \Sigma_x R^{2-D_s}$$

Length scale
R = 4 Å for N_2

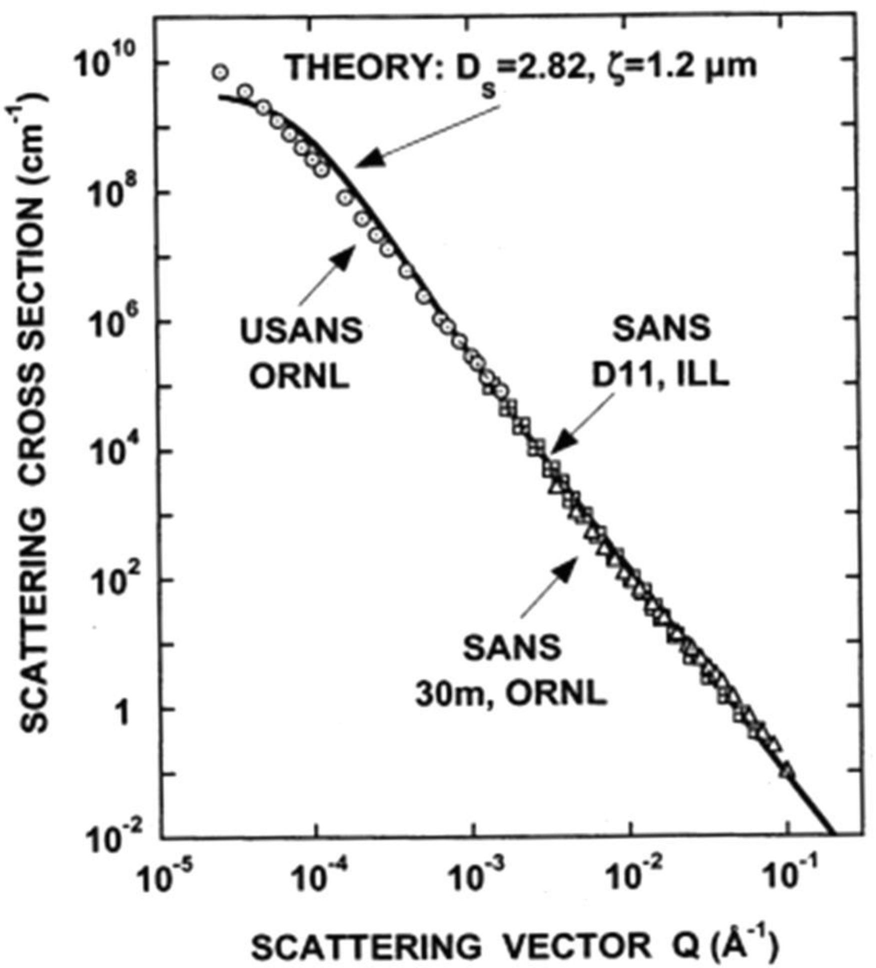
$D < 3$ Diffusion from volume

More complicated

Wong et al, 1988

Mass and surface fractal structures

Several instruments to cover a large q range



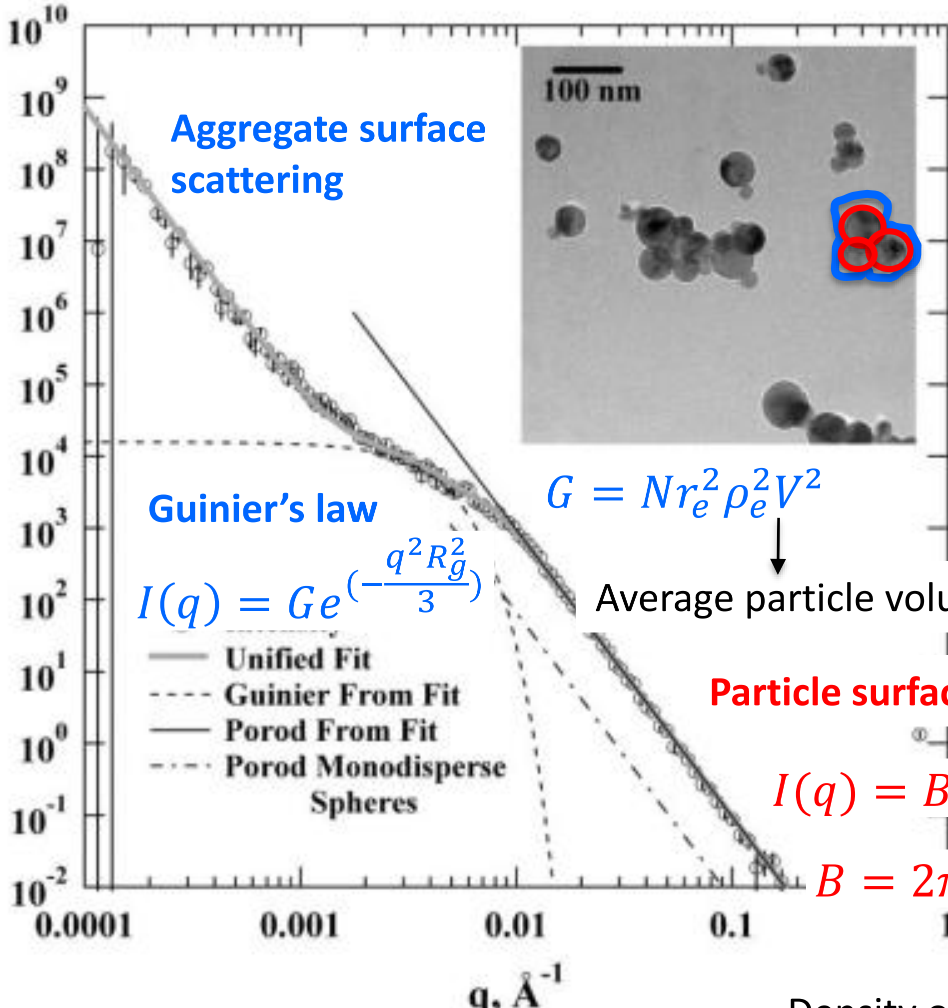
sedimentary rock

A. P. Radlinski, E. Z. Radlinsk , M. Agamalian , G. D. Wignall , P. Lindner and O. G. Randl, The fractal microstructure of ancient sedimentary rocks, J. Appl. Cryst. (2000) 33, 860-862.

Generalization to packing of polydisperse particles

Spherical primary particles

USAXS



Aggregate surface scattering

Guinier's law

$$I(q) = Ge^{\left(-\frac{q^2 R_g^2}{3}\right)}$$

$$G = N r_e^2 \rho_e^2 V^2$$

→ Average particle volume

Particle surface scattering

$$I(q) = Bq^{-4}$$

$$B = 2\pi r_e^2 N \rho_e^2 S$$

→ Average surface area for a primary particle

→ Density of primary particles

Global unified scattering function

$$I(q) = Ge^{\left(-\frac{q^2 R_g^2}{3}\right)} + B(q^*)^{-4}$$

$$q^* = \frac{q}{\left[erf\left(qR_g / 6^{\frac{1}{2}}\right)\right]^3}$$

Monodisperse spheres $I(R,q) = \frac{1.62G}{R_g^4} q^{-4}$

Polydisperse spheres $\frac{\pi B}{Q} = \Sigma$

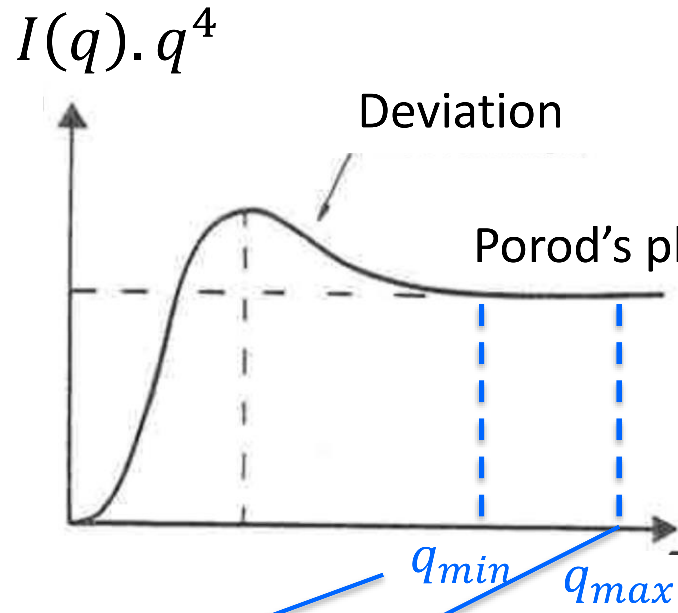
Beaucage 1995, 1996, 2004

Summary

Porod's law

$$I(q) = 2\pi(\rho_1 - \rho_2)^2 \Sigma \frac{1}{q^4}$$

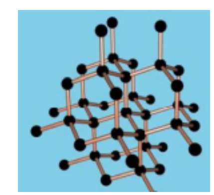
Total interfacial area
per unit volume



Courvature
Roughness
Fractality

$$d_{max} = \frac{\pi}{q_{min}}$$

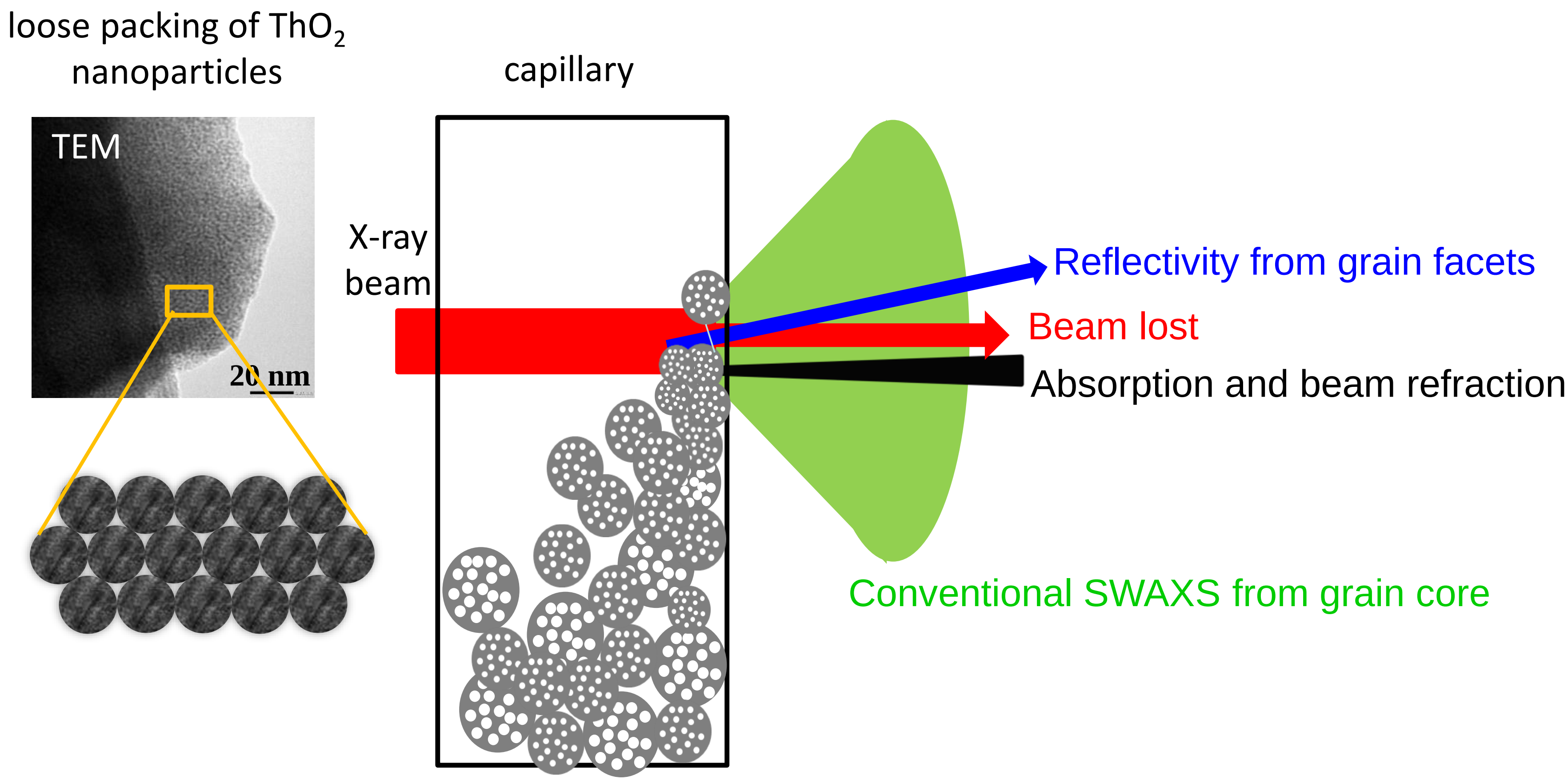
$$d_{min} = \frac{\pi}{q_{max}}$$



Atomic scattering
(crystallography)

Highly absorbing materials

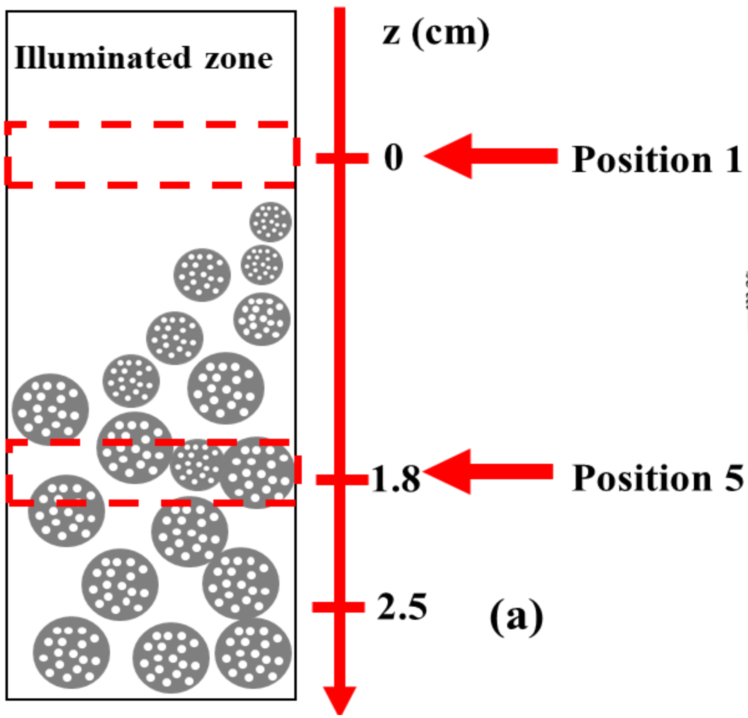
UO_2 or ThO_2 => Absorption length ≈ 10 µm (17.4 keV)

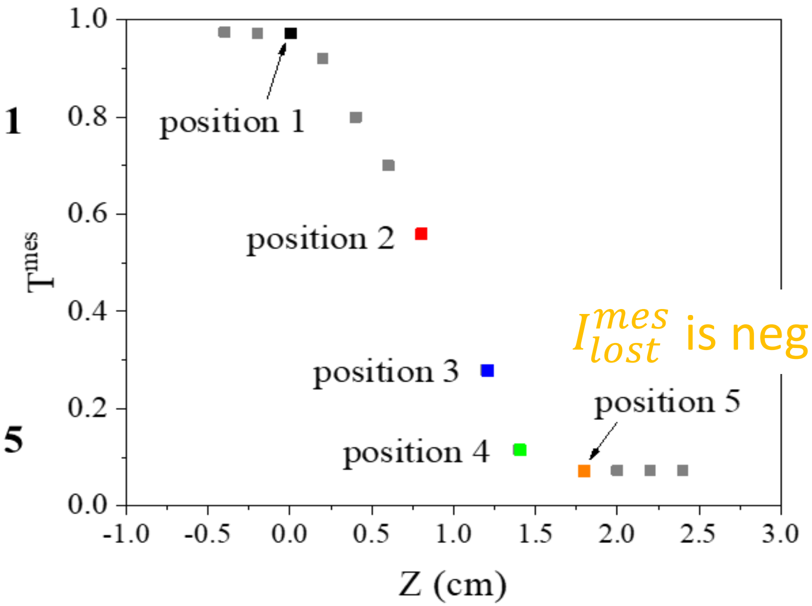


Highly absorbing materials

How to obtain the I abs with the right transmission?

1. Measured transmission T^{mes} as a function of the vertical distance z from the interface powder/air



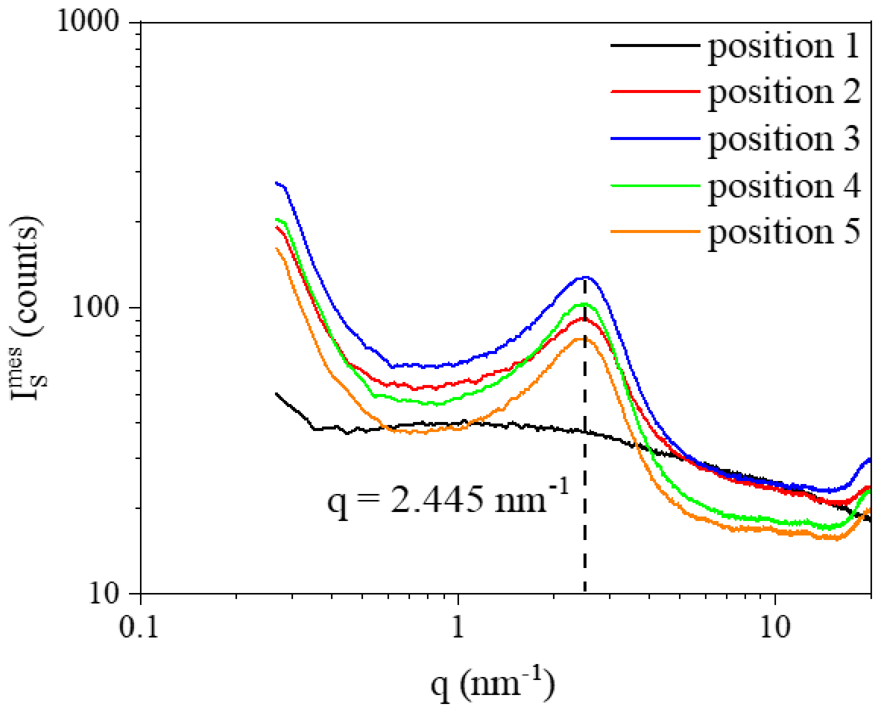


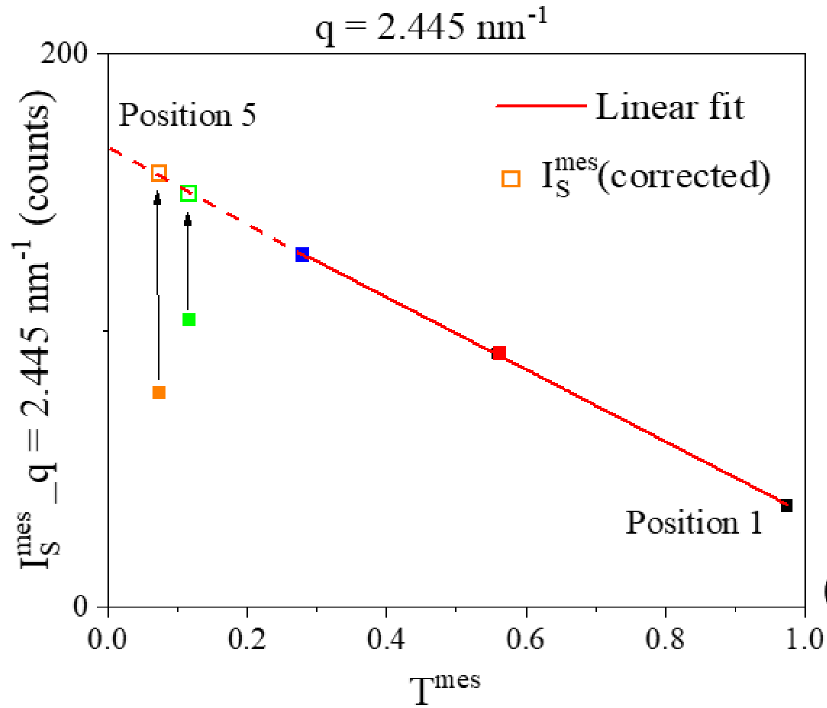
I_{lost}^{mes} is negligible

Highly absorbing materials

How to obtain the I abs with the right transmission

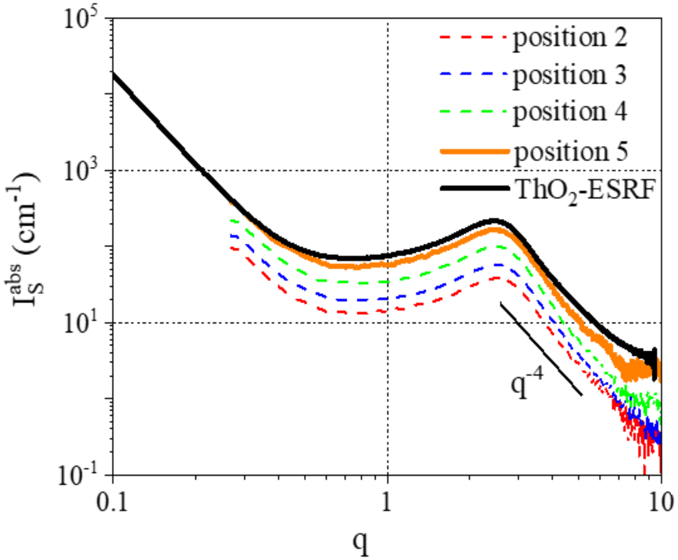
2. I_S^{mes} has to be corrected from the multi-scattering and indirect absorption effects occurring in low transmission case





Highly absorbing materials

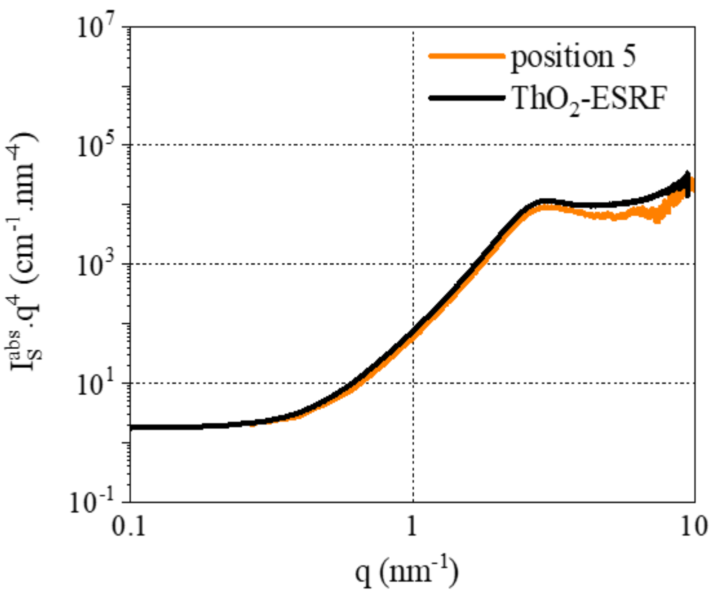
How to obtain the I abs with the right transmission



$$I_S^{abs} = \frac{1}{J_{in} A \epsilon \Delta\Omega e_b} \left(\frac{\alpha I_S^{mes}(sample) - I_B}{t_{sample} T_{sample}^{mes}} - \frac{I_S^{mes}(tube) - I_B}{t_{tube} T_{tube}^{mes}} \right)$$

$$\frac{S}{V} = \frac{\lim_{q \to \infty} I_S^{abs} q^4}{2\pi \Delta SLD^2}$$

ESRF (16 keV) => lower absorption and smaller beam size



position	S (m²/g)	Porosity ϕ
2	60	0.08
3	80	0.11
4	127	0.19
5	**284**	**0.34**
ESRF	310	0.45