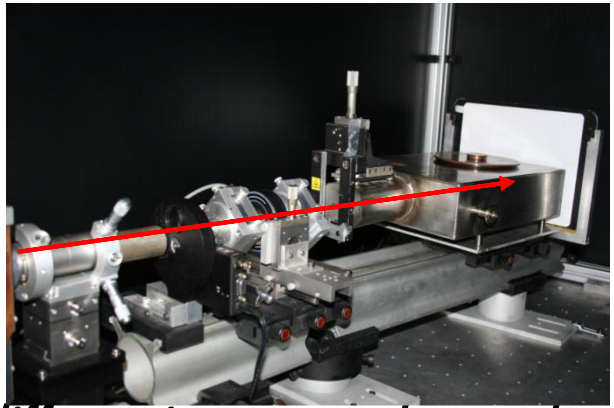
Initial data treatment and absolute intensity

Olivier Spalla
CEA Saclay IRAMIS/LIONS



-Data obtained on different instruments have to be comparable
-Define a quantity independent of the set-up
-Define a quantity linked intensively to the structure of the sample
-Treat the raw data to obtain it

1-Scattering cross section

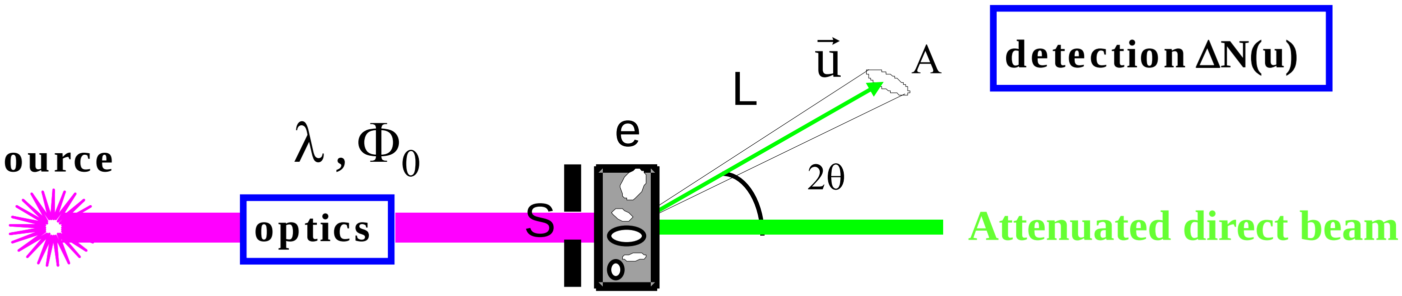
2-Sample requirements

3-Protocol of measure

4-Initial data treatment

5-Normalization

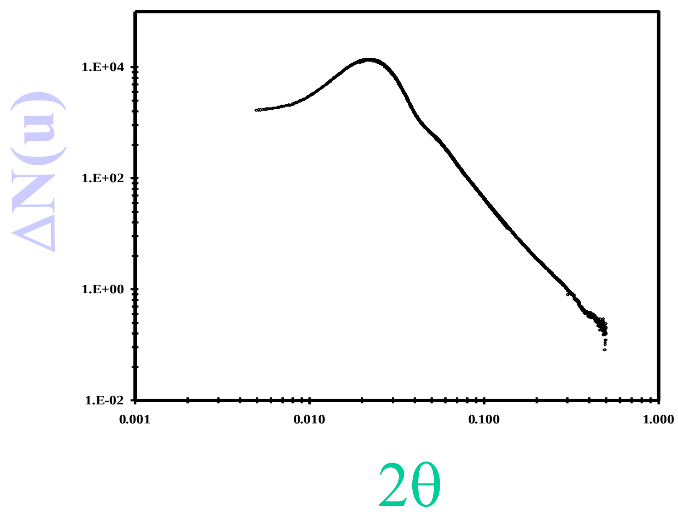
Scheme of a Scattering experiment



Most of incident radiation: *transmitted*

Some part: *absorbed*

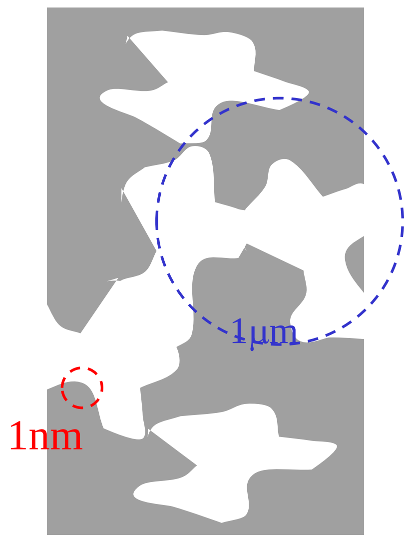
A certain fraction interacts: *scattered ($2\theta > 0$)*
In general: energy transfer ($\Delta E \neq 0$)



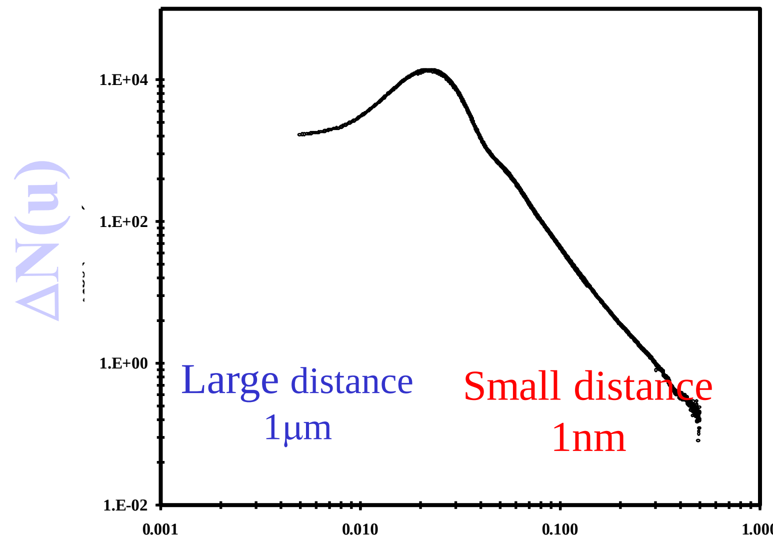
Intensity variation as a function of 2θ & E

(Here we consider elastic scattering $\Delta E=0$)

Why is it interesting?



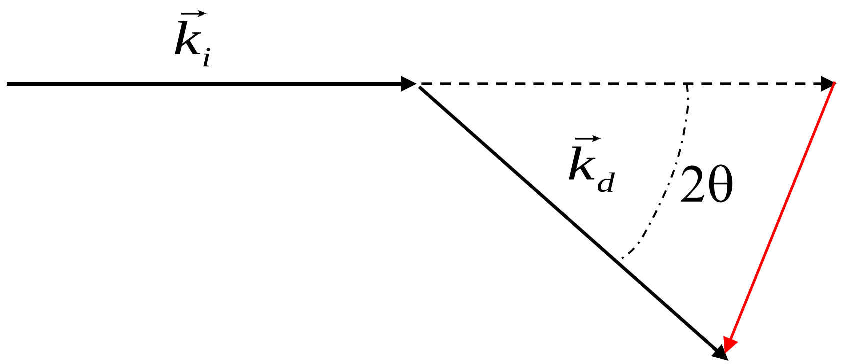
Real space



2θ Scattering diagram

Need for a two units independent of set-ups and only linked to an intensive characteristic of the sample

First axis: Scattering vector



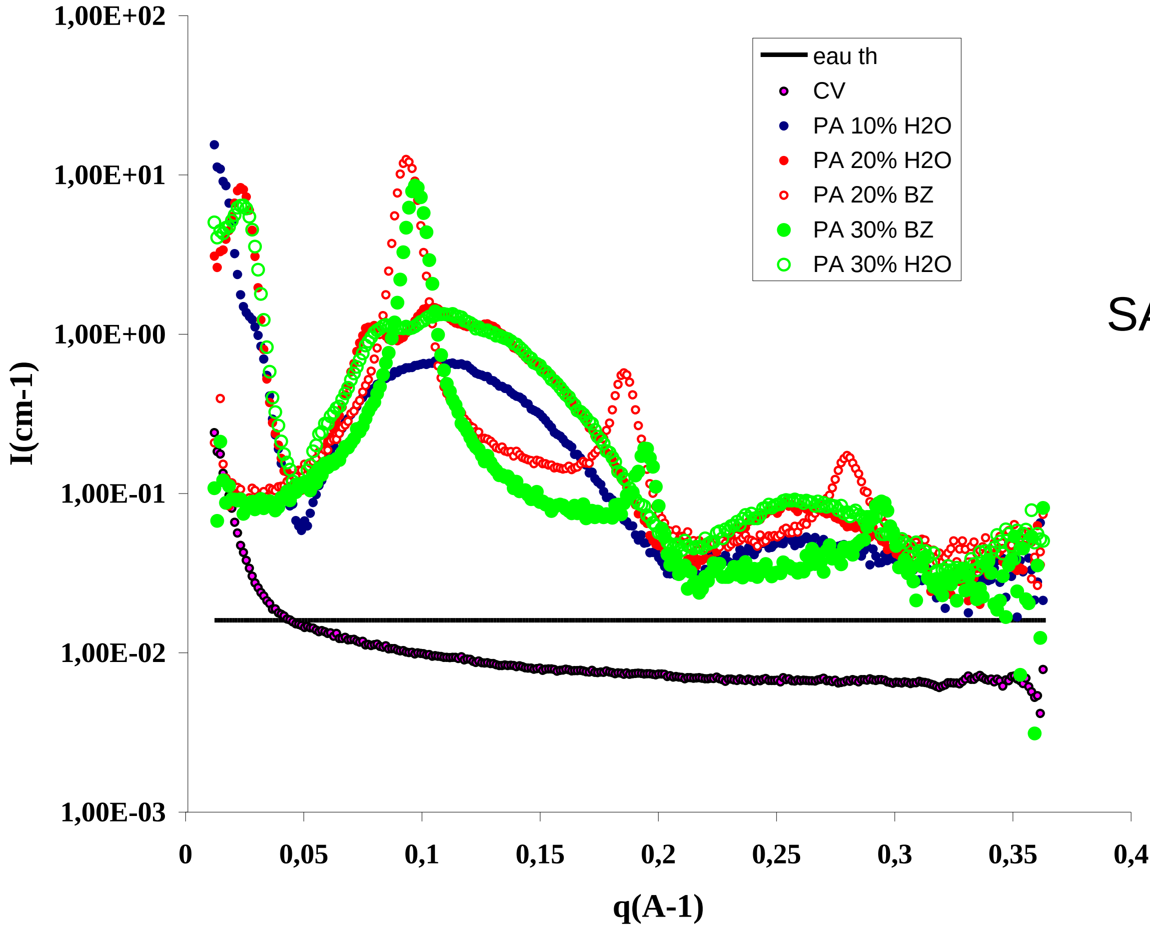
$$\vec{q} = \vec{k}_d - \vec{k}_i$$

$$\boxed{q = \frac{4\pi \sin(\theta)}{\lambda}}$$

q is classically expressed in $Å^{-1}$ or (nm^{-1})

SAXS and SANS: Why do we talk of « small angle »?

Typical diagrams of vesicles and lamellar phases



SAXS diagram

For these samples, relevant q are from 0.01 to 0.6 $Å^{-1}$

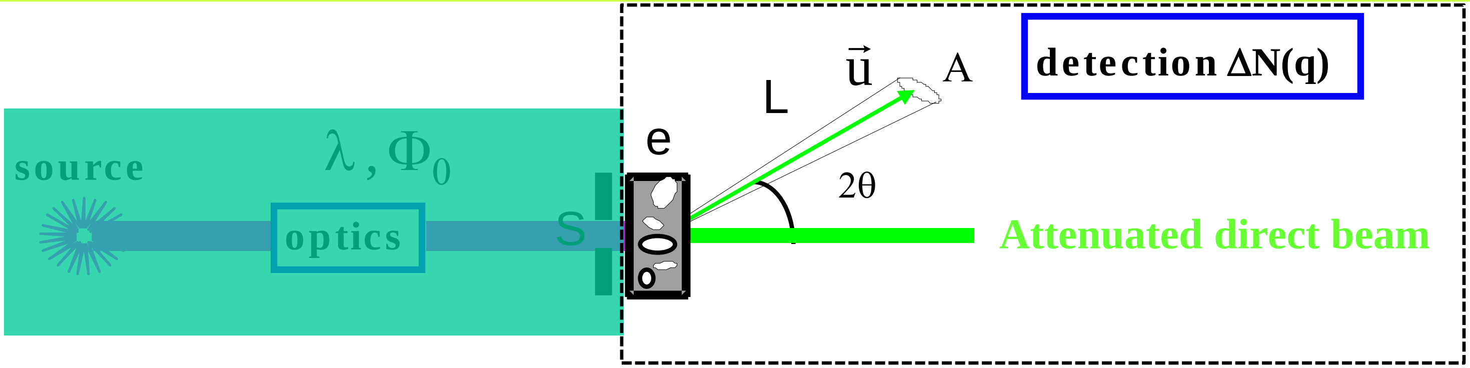
$$\vec{q}.\vec{k}_i \approx 0$$

λ=1.54 Å

This corresponds to angles 2θ going from 0.15° to 8°

SMALL ANGLES

Second axis: Scattering cross section



$$N_0 = S\,\Phi_0$$

Total counts/s in the direct beam

$$N_T = T\,N_0$$ *Total counts/s in the transmitted beam*

Transmission of the sample

$$N_T = S\,\phi_T$$ ***Φ_T: Counts per sec/m²***

On a detector of extension A at a distance L : counts per sec $$\Delta N = \Phi_L A$$ ***Φ_L Counts per sec/m²***

Looking for an intrinsic property of the sample $$\frac{\Phi_L}{\Phi_T}$$ ***depends on L*** $$\Phi_L = \frac{\Phi}{L^2}$$

Φ Counts per sec independent of L and A

$$\frac{\Phi}{\Phi_T}$$

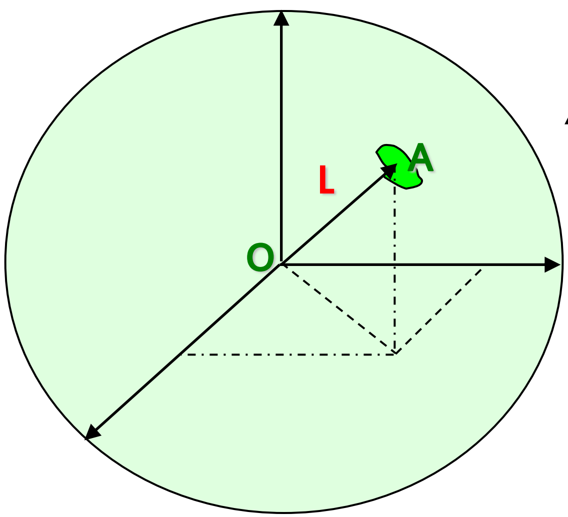
Independent of A, L

Homogeneous to a surface => Scattering cross section

Scattering cross section of the whole sample per unit solid angle

$$\frac{d\sigma}{d\Omega} = \frac{\Phi}{\Phi_T}$$

$$\frac{d\sigma}{d\Omega} = \frac{\Delta N}{\Phi_T}\frac{L^2}{A} = \frac{\Delta N}{\Phi_T}\frac{1}{\Delta\Omega}$$



$$\Delta\Omega = \frac{A}{L^2}$$

Solid angle under which the object A is seen from the centre O

expressed in steradian

For the whole sphere : S= 4π L^2

$$\boxed{\Omega = \frac{A}{L^2} = 4\Pi}$$

Scattering cross section
per unit volume
per unit solid angle

$$\frac{1}{V}\frac{d\sigma}{d\Omega}=\frac{1}{e}\frac{\Delta N}{S\,\phi_T\,\Delta\Omega}$$

"Scattered intensity"

cm^{-1}

$$\frac{d\Sigma}{d\Omega}=\frac{1}{eT\,N_0}\frac{\Delta N}{\Delta\Omega}$$

All these quantities can be measured

Probability to be scattered by the whole sample

$$p(\vec{u})=e\,\frac{d\Sigma}{d\Omega}$$

1-Scattering cross section

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Counts on the detector

Counts/s
in the direction
u in the solid angle $\Delta\Omega$

Incident Flux *Transmission* *Solid angle of the detector*

$$\Delta N = \underbrace{\Phi_0 \; S}_{N_0} \; T \; p(\vec{u}) \; \Delta\Omega$$

Surface of the sample

Probability of being Scattered in the direction u

Probability increases with thickness

$$p(\vec{u}) = e \, \frac{d\Sigma}{d\Omega}$$

Intensive property of the material

$$\Delta N = N_0 \; T \, e \, \frac{d\Sigma}{d\Omega} \, \Delta\Omega$$

Need to be maximized, depends of the sample

Exercice

Using $$\Delta N = T\ N_0\ p(\vec{u})\,\Delta\Omega$$

Calculate the numbers of eyes that would be lost every year if one opens champagne bottles at random !

$$N_0 = 200\,10^6\,bottles\,/\,year$$

$$\Delta\Omega = N_p(0.02/2)^2 = N_p 10^{-4}$$

$$T = 1$$

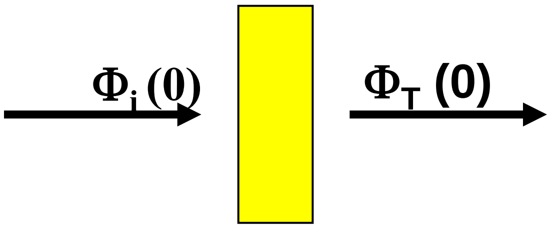
$$N_p = 5$$

$$N = 8000$$

$$\int \Delta N = N_0 = \int N_0\, p(\vec{u})\Delta\Omega$$

$$p(\vec{u}) = 1/4\pi$$

Origin of the direct beam attenuation



$$T = \frac{\phi_T(0)}{\phi} = e^{-\mu e}$$

linear attenuation coefficient

Light: μ = turbidity ~ λ^2
attenuation due to coherent scattering in 4π
$1/\mu$ = 1 m -> 1000 m

X-rays: μ = absorption coefficient μ_{abs}
absorption is essential part of attenuation
$1/\mu$= 0.01 mm -> 1 mm

Neutrons: $\mu = \mu_{coh} + \mu_{abs} + \mu_{inc}$
absorption + coherent + incoherent scattering
$\mu = \Sigma$ "total scattering cross section"
$1/\mu$ = 0.5 mm -> 10 mm

ΔN ~ e T is maximum for e = $1/\mu$ and therefore T=1/e=0.37

but multiple scattering is minimum for e << $1/\mu$

=> look for a compromise

Calculation of the absorption coefficient

Specific to each atom

$$(\mu/\rho)_{mix} = \sum (m_i / m_{tot})\ (\mu/\rho)_i$$

$$\mu_l = \rho_{mix}\ (\mu/\rho)_{mix}$$

Some examples in X-ray

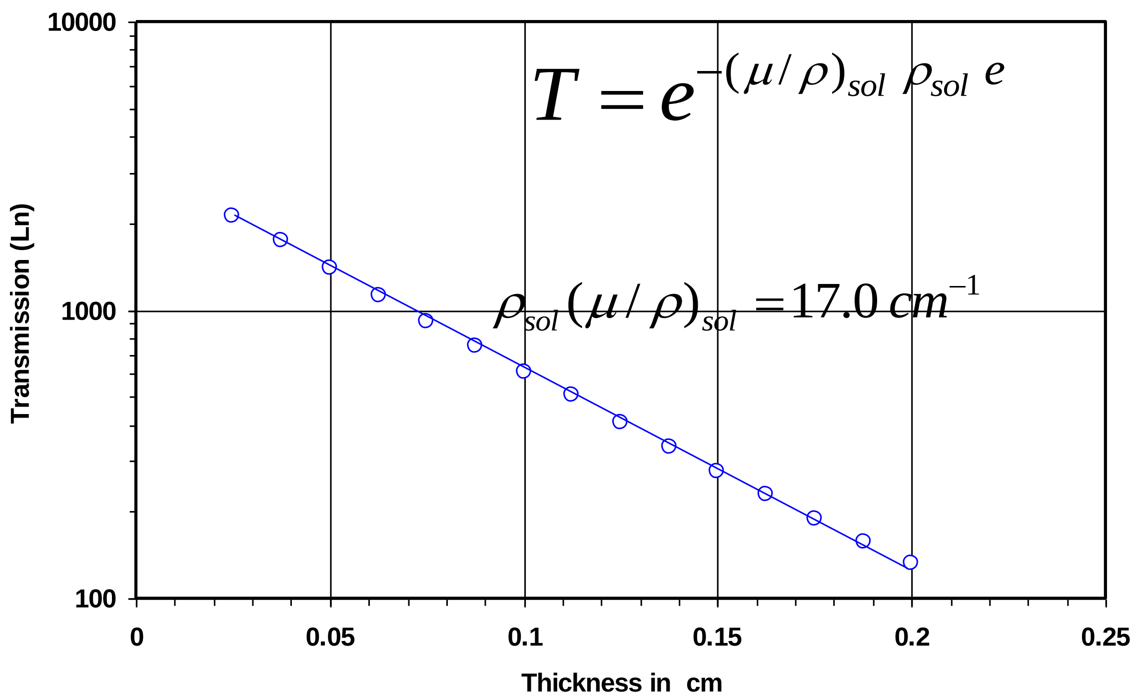
	Cu $K_{\alpha 1}$ 8.047 keV	ID02 ESRF 11.9 keV	Mo $K_{\alpha 1}$ 17.48 keV
H_2O $\mu/\rho\,(cm^2/g)$ d=1 $e = 1/\mu_l\,(mm)$	9.78 1.02	3.38 2.96	0.936 10.7
CeO_2 d=7.15	280.32 0.005	112.32 0.012	38.99 0.036
SiO_2 d=2.3	35 0.124	12.53 0.347	3.72 1.17
Polystyrene d=1	3.862 2.59	1.289 7.76	0.353 28.3
Polybromostyrene d=1.41	39.95 0.178	8.72 0.813	21.28 0.333
Gold d=19.3	197.6 0.003	12.26 0.042	95.26 0.005

Depends on elements

Decrease with energy but close to absorption threshold Au: (L3) 11.919keV Br: (K1s) 13.474

Measure of absorption coefficient

Experimental determination



$$(\mu/\rho)_{sol} = x_{CeO_2}(\mu/\rho)_{CeO_2} + (1 - x_{CeO_2})(\mu/\rho)_{H_2O}$$

$(\mu/\rho)_{CeO_2} = 282\ cm^2/g$

$(\mu/\rho)_{H_2O} = 9.83\ cm^2/g$

$\rho_{sol} = 1.16\ g/cm^3$

$$\rho_{sol}(\mu/\rho)_{sol} = \rho_{sol}(\mu/\rho)_{H_2O} + C_{CeO_2}\left[(\mu/\rho)_{CeO_2} - (\mu/\rho)_{H_2O}\right]$$

Leads to

$$C_{CeO_2} = 20\ g/l$$

Choice of a meaningful volume of sample

V must be the total volume of the sample interacting with the beam

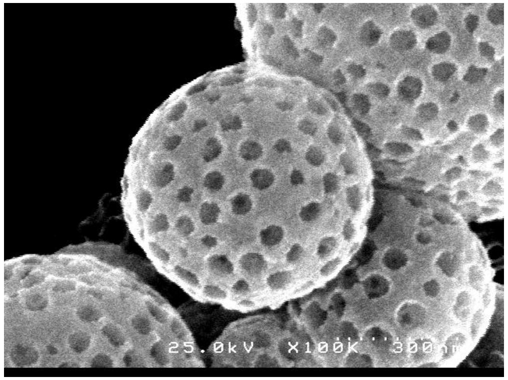
Total volume of the sample V

for homogeneous solution or solids

$$I = \frac{1}{V}\frac{d\sigma}{d\Omega} = \frac{1}{eT\,N_0}\frac{\Delta N}{\Delta\Omega}$$

For powders, material volume of the sample V_s

$$I_1 = \frac{1}{V_s}\frac{d\sigma}{d\Omega} = \frac{1}{e_b T\,N_0}\frac{\Delta N}{\Delta\Omega}$$



V_s solid volume of the powder interacting with the beam

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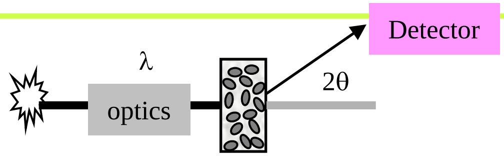
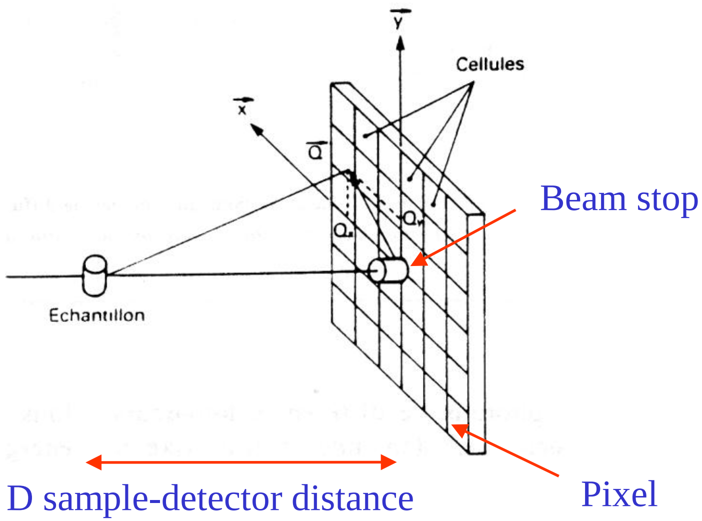
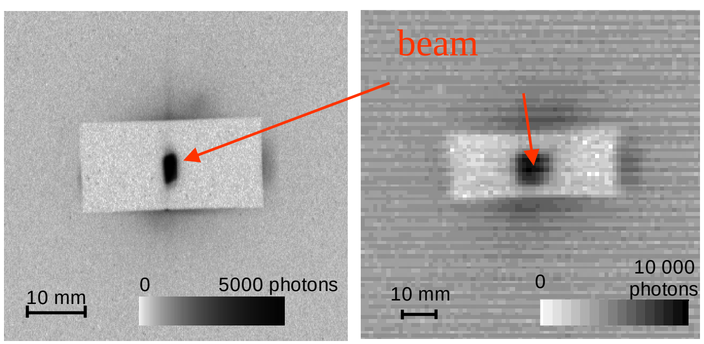
2D position sensitive detector







Detectors are sensitive to the intensity not to the field

(or the probability wave function in case of neutrons)

X-ray : ionizing rays

Gas detector

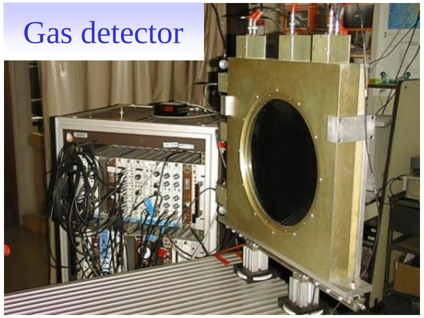
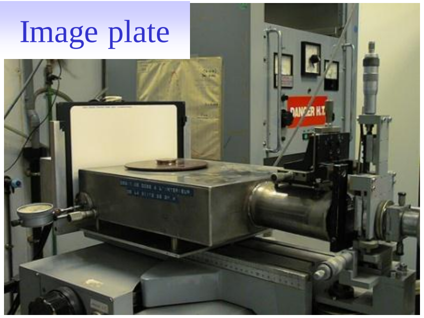


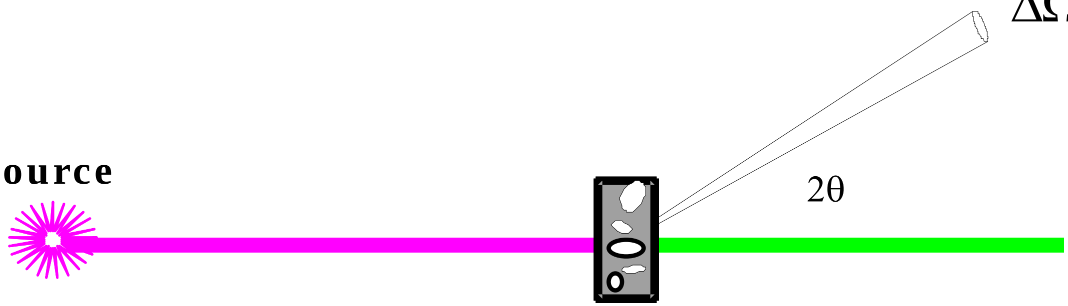
Image plate



CCD Camera

Measure of the scattered signal-1

$$\Delta\Omega = A / L^2$$



$$\Delta\Omega_{Direct} = \frac{A_{FV}}{L^2} = 10^{-6}$$

Attenuated direct beam

in the direct beam

$$\Delta N(2\theta \approx 0) = TN_0 \frac{\Delta\Omega}{\Delta\Omega_{Direct}}$$

in the scattered beam

$$\Delta N(2\theta) = TN_0 \; e \frac{d\Sigma}{d\Omega} \Delta\Omega$$

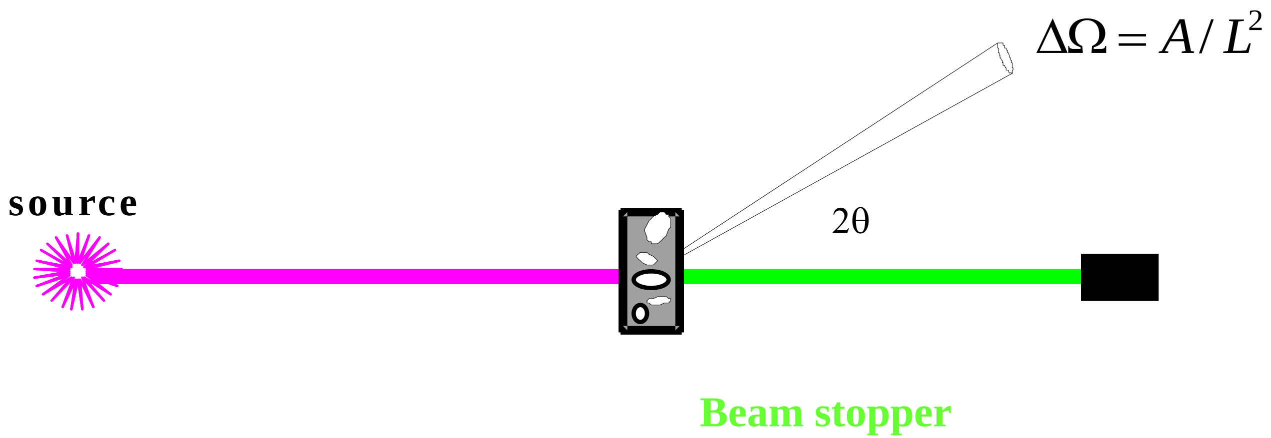
Ratio of counts on the detector

$$r = e \frac{d\Sigma}{d\Omega} \Delta\Omega_{Direct}$$

$$r = 0.1 * 0.016 * 10^{-6} = 1.6\,10^{-9}$$

The two signals cannot be measured in one shot

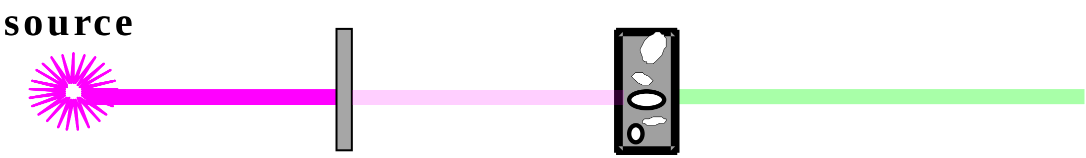
Measure of the scattered signal-2



Measure of the transmission-One way

Protocol of measure

Beam stopper withdrawn
Attenuator in

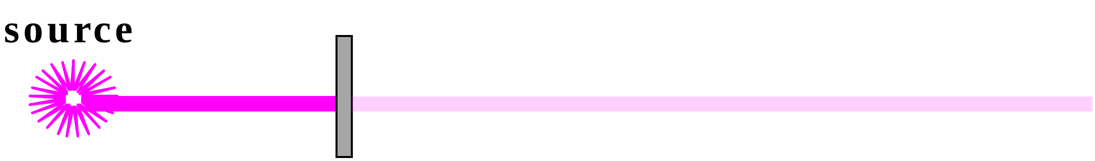


$$\Delta\Omega_{Direct} \longrightarrow N_{tot}$$

Attenuator in

Beam center

2-D detectors: $\sum$I (central window)
-> 1st moment of int. distribution
-> x_0, y_0 for circ. averaging

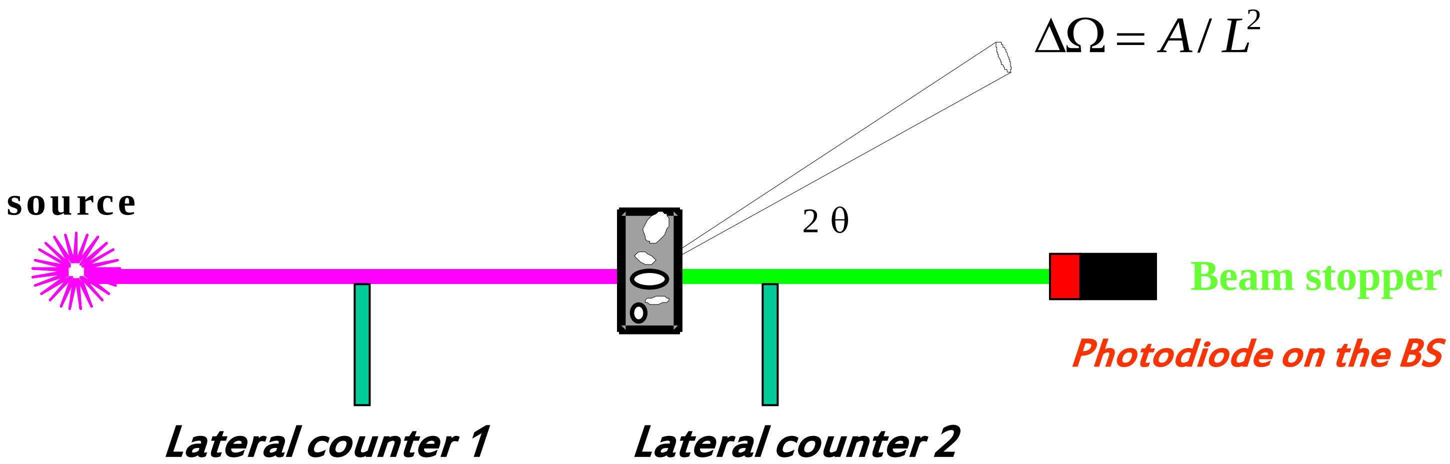


$$\Delta\Omega_{Direct} \longrightarrow N_{tot,FD}$$

Attenuator in and sample withdrawn

$$T = \frac{N_{tot}}{N_{tot,FD}}$$

Measure of the transmission-other way



$$T = \frac{L_2}{L_1}$$

$$T = \frac{PD(with\ sample)}{PD(without\ sample)}$$

1-Scattering cross section

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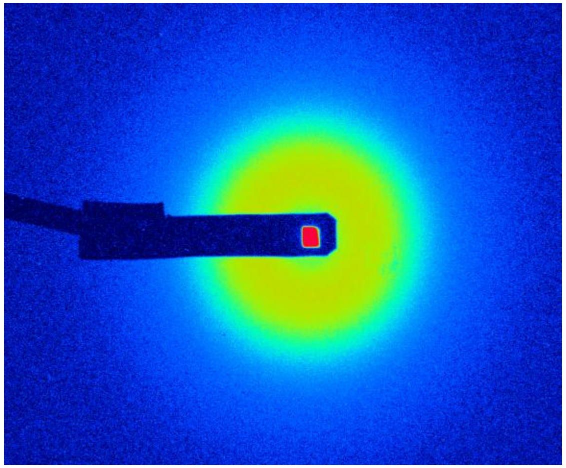
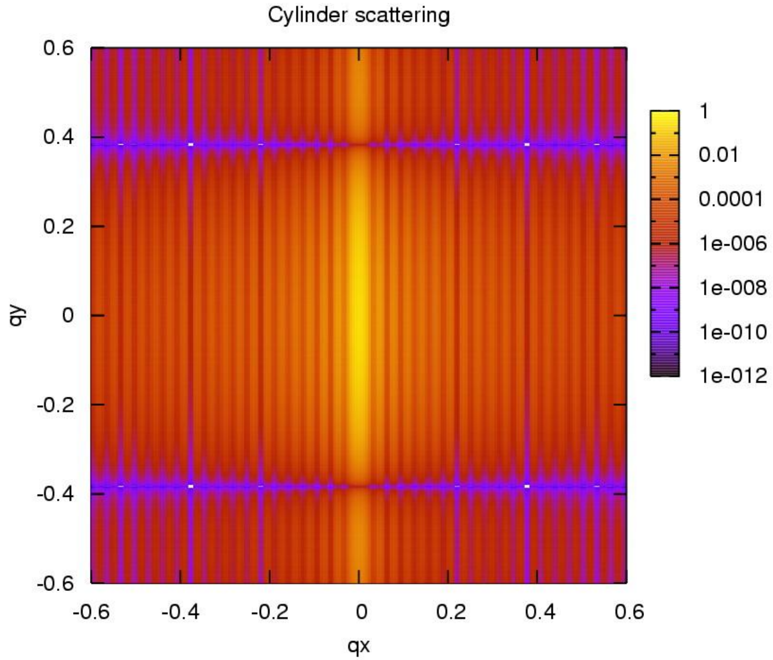
1- Isotrope scattering



2- Anistrope scattering

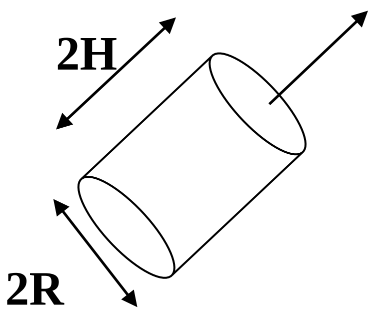


Examples of scattering

1- Homogeneous sphere of radius R

$$P(q) = 9\frac{(\sin(qR) - qR\cos(qR))^2}{(qR)^6}$$

2- Orientated cylinders



$$P(\vec{q},\vec{u}) = 4\frac{\sin(q_{\perp}H)^2}{(q_{\perp}H)^2}{}_{\vec{u}}\frac{J_1(q_{\parallel}R)^2}{(q_{\parallel}R)^2}$$

$$\vec{q}_{\perp} = \vec{q}.\vec{u}$$

$$\vec{q}_{\parallel} = \vec{q} - \vec{q}_{\perp}$$

3- Disorientated cylinders

$$P(q) = 4\int_0^{\pi/2}\frac{\sin^2(qH\cos(\alpha))}{[qH\cos(\alpha)]^2}\frac{J_1^{\,2}(qR\sin(\alpha))}{[qR\sin(\alpha)]^2}\sin(\alpha)d\alpha$$

Subtraction of backgrounds

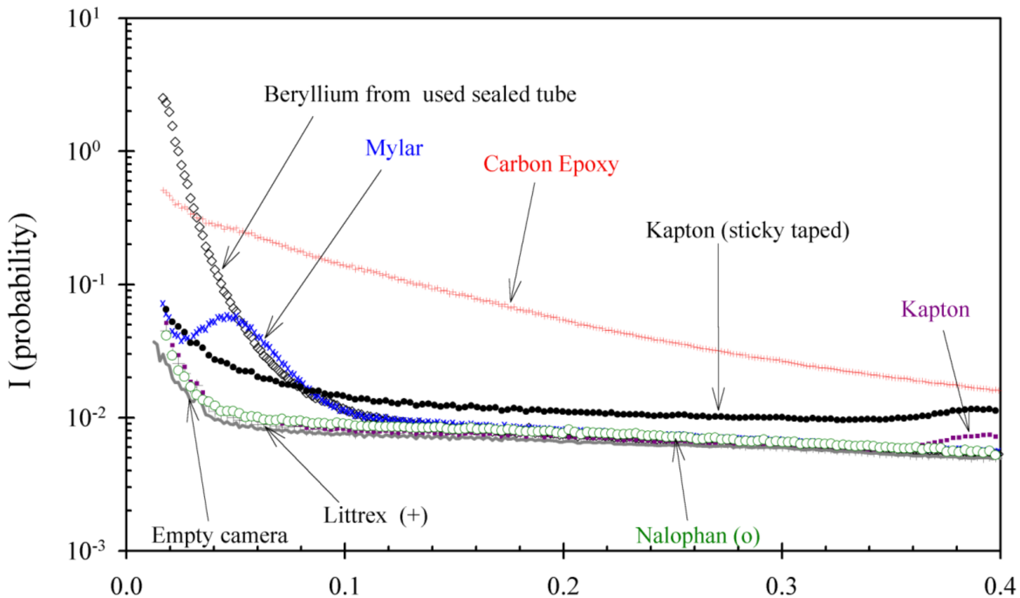
External ⇨

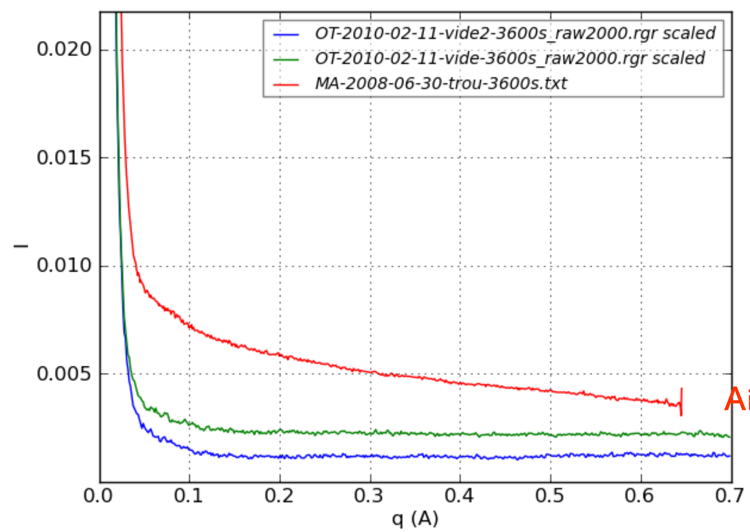
- ✓Room background
- ✓Electronic noise
- ✓Tails of direct beam, close to beamstop
- ✓Sample container, “windows”

Internal ⇨

Sample itself
e.g. incoherent background for neutrons
Fluctuation in the solvent

External : windows…



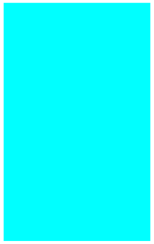


Air gap > 50mm

No air gap

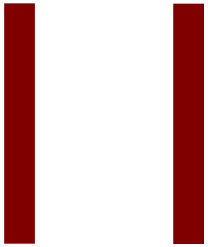
Subtraction of external background

Sample
$T_S\ e_S$



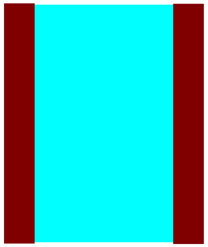
$$\frac{\Delta N_S}{\Delta\Omega} = EB + N_0\, T_S\, e_S\, I_S$$

Windows
T_{EC}



$$\frac{\Delta N_{EC}}{\Delta\Omega} = EB + N_0\, T_{EC}\, e_{EC}\ I_{EC}$$

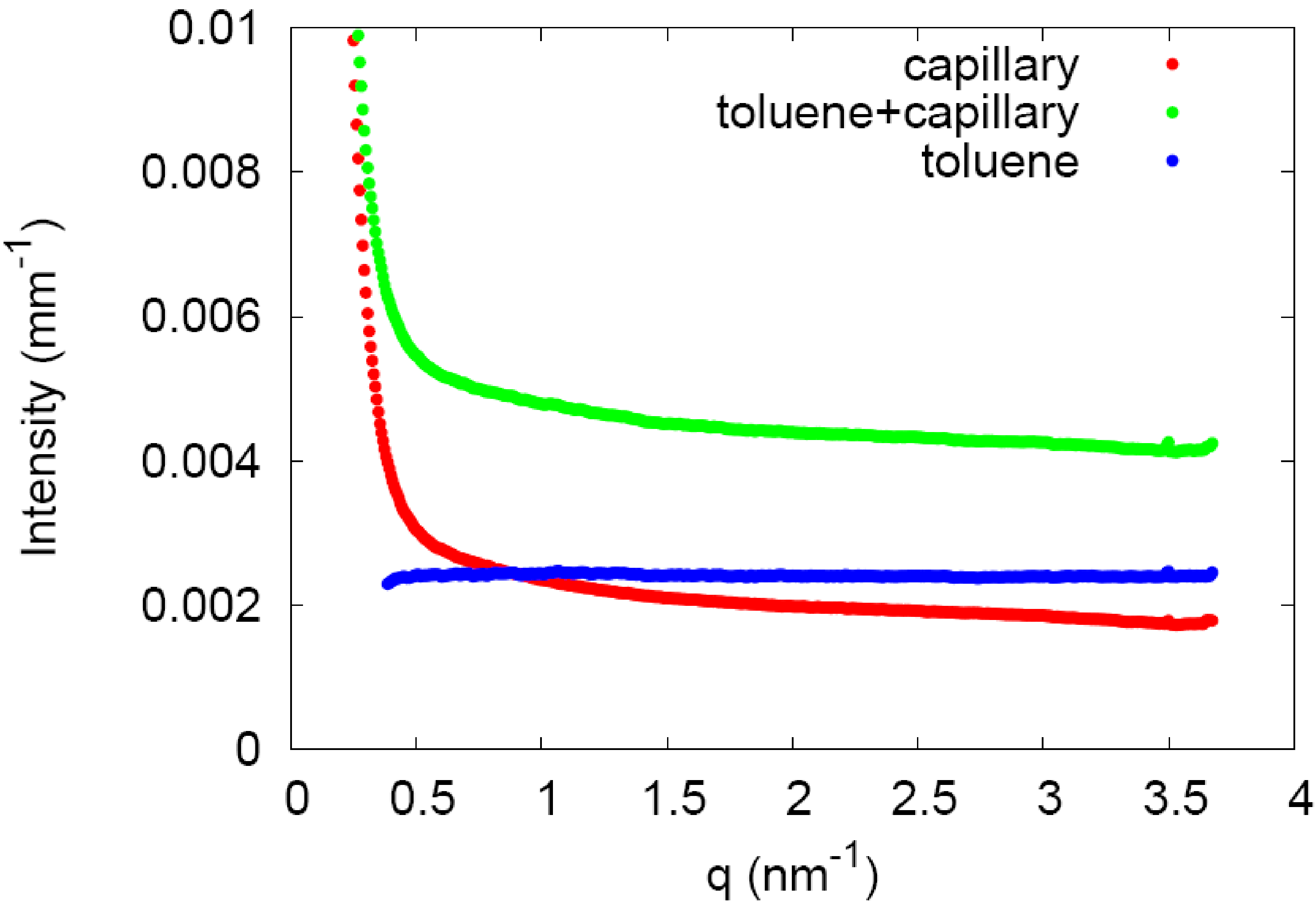
Total
$T = T_{EC}\ T_S$



$$\frac{\Delta N_{Tot}}{\Delta\Omega} = EB + T_{EC}\left(\frac{\Delta N_S}{\Delta\Omega} - EB\right) + T_S\left(\frac{\Delta N_{EC}}{\Delta\Omega} - EB\right)$$

$$I_S = \frac{1}{N_0 e_S}\left[\frac{1}{T}\left(\frac{\Delta N_{Tot}}{\Delta\Omega} - EB\right) - \frac{1}{T_{EC}}\left(\frac{\Delta N_{EC}}{\Delta\Omega} - EB\right)\right]$$

Example



Intensity (mm-1)
0.01
0.008
0.006
0.004
0.002
0
q (nm-1)
0
0.5
1
1.5
2
2.5
3
3.5
4
capillary
toluene+capillary
toluene

Internal background : coherent scattering

$$I = \rho\, b^2\, S(0)$$

$$S(0) = \rho k T \chi_T$$

Number of molecules per unit volume

Scattering length of a molecule

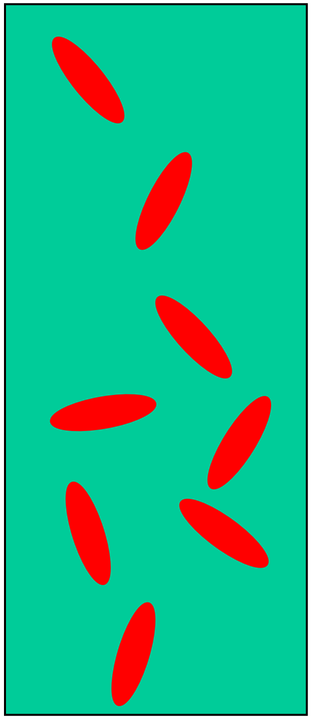
$$I = \rho^2\, b^2\, kT \chi_T$$

Solvent	ρ $(molecules / cm^3)$	$b(cm)$	$\chi_T\ (Pa^{-1})$	$I(cm^{-1})$
water	3.3 10^{22}	2.82 10^{-12}	4.57 10^{-10}	**0.0162 (25°C)**

Hexane ***I = 0.0287 cm^{-1}***

Toluene ***I = 0.0236 cm^{-1}***

Subtraction of internal background



$$I_{solv} = \rho^2\, b^2\, kT\, \chi_T$$

$$I_{total} = I_{Part} + (1-\phi_{Part})\, I_{Solv}$$

Valid when the dispersed phase is incompressible

Case of neutrons incoherent scattering-1

neutrons: $d\Sigma/d\Omega$ contains *sample inherent background*
origin: incoherent scattering cross section (^1H samples !)

Internal background : incoherent scattering (case of neutrons)

it can be shown:

$$\frac{d\sigma}{d\Omega} = <b>^2 \sum_{i,j} < e^{i\vec{q}(\vec{r}_i - \vec{r}_j)} > + N(<b^2> - <b>^2)$$

$$= (d\sigma/d\Omega)_{coherent} + (d\sigma/d\Omega)_{incoherent}$$

q-dependent
(interference of scattered waves
at different nuclei i and j with sc. length <b>)

not q-dependent

structure + flat background

Like before $I = I_{Part} + (1-\phi_{Part})I_{Solv}$

Case of neutrons incoherent scattering-2

Total scattering cross section

$$\sigma_{coh} = 4\pi < b >^2 \qquad \sigma_{incoh} = 4\pi (< b^2 > - < b >^2)$$

Isotope (nuclear spin)	$\sigma_{coh} \quad in\ 10^{-28} m^2$	$\sigma_{incoh} \quad in\ 10^{-28} m^2$
^{1}H (1/2)	1.8	79.7
^{2}H (1)	5.6	2
^{12}C (0)	5.6	-
^{14}N (1)	11.6	0.3
^{16}O (0)	4.2	-

For light water, incoherent scattering dominates

Other corrections

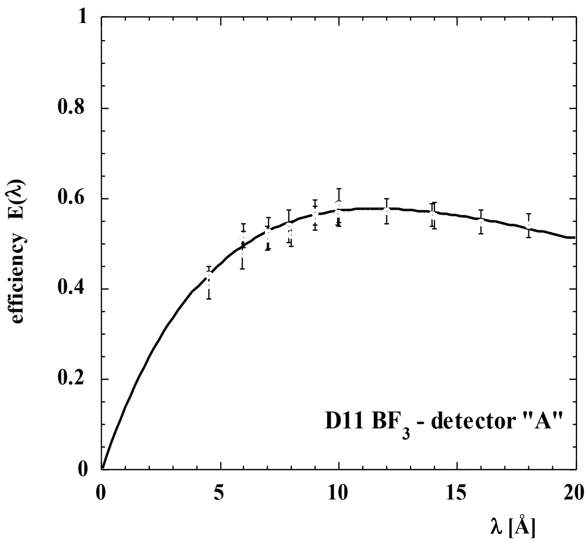
Camera distortion: measure with grids, set-up dependent

Camera efficiency: measure a flat fields with a flat scatterer

Convolution: due to finite divergence (SAXS) and non monochromaticity (neutrons)

see lecture J S Pedersen

detector efficiency
depends on λ



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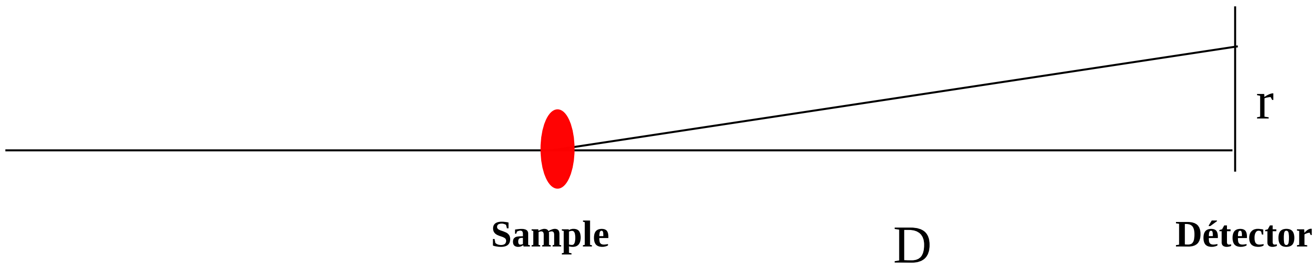
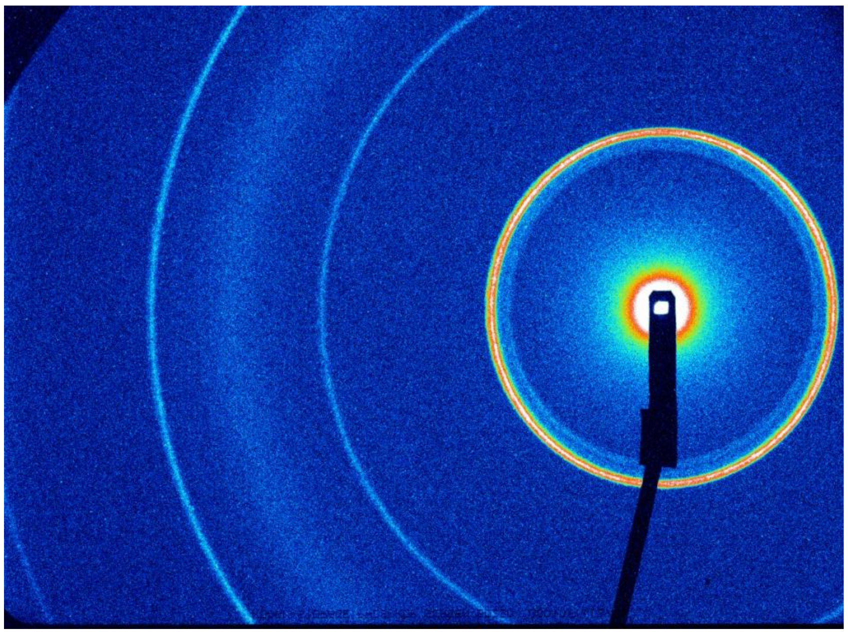
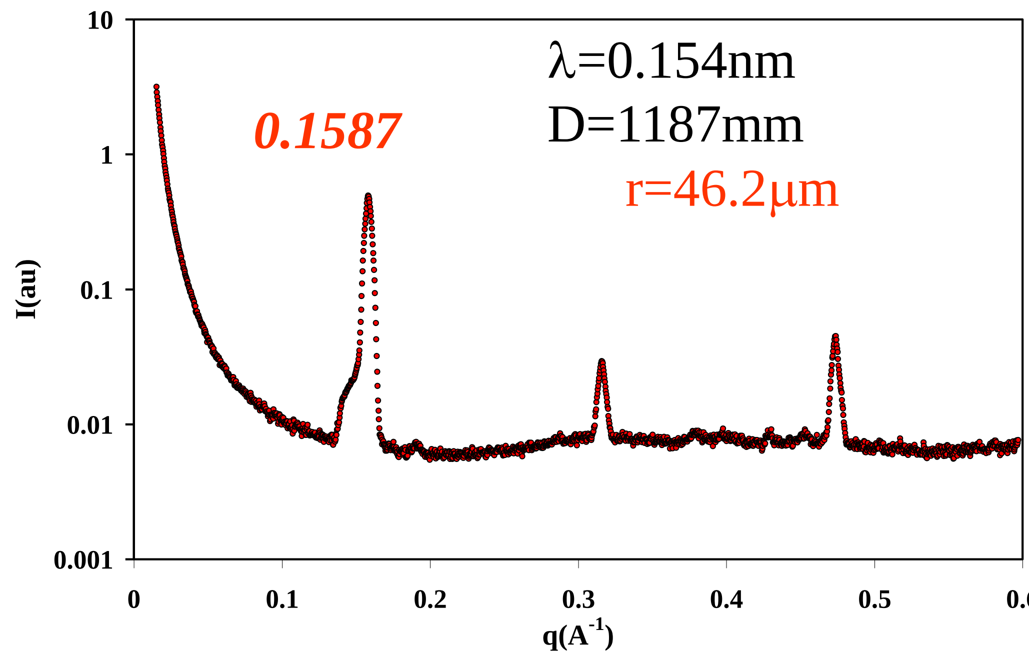
Calibration of q



$$q = \frac{2\pi}{\lambda}\frac{r}{D}$$





Scattering by reference
like tetradecanol
Silver behenate

"Absolute scaling"

$$\frac{d\Sigma}{d\Omega} = \frac{1}{eT\ N_0}\frac{\Delta N}{\Delta\Omega}$$

$$N_0 = k_0 N_0^{mes}$$

$$\Delta N = k_1 \Delta N^{mes}$$

Efficiency of the detector

$$\frac{d\Sigma}{d\Omega} = \frac{1}{eT\ k_0 N_0^{mes}}\frac{k_1 \Delta N^{mes}}{\Delta\Omega}$$

All the terms
are measurable experimentally.
k_0 and k_1 have to be determined in dedicated experiments

Nevertheless, we simply need their ratio

Direct calibration of the intensity-a

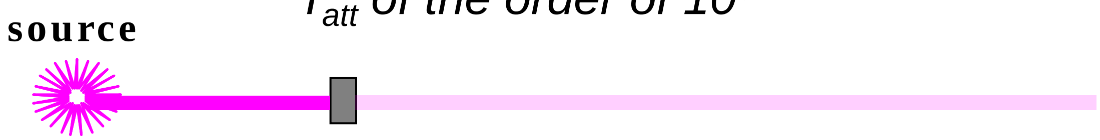
Direct calibration: Measure of the direct and scattered flux with the same detector

$$k_0 = k_1$$

The direct beam has to be attenuated by a calibrated amount

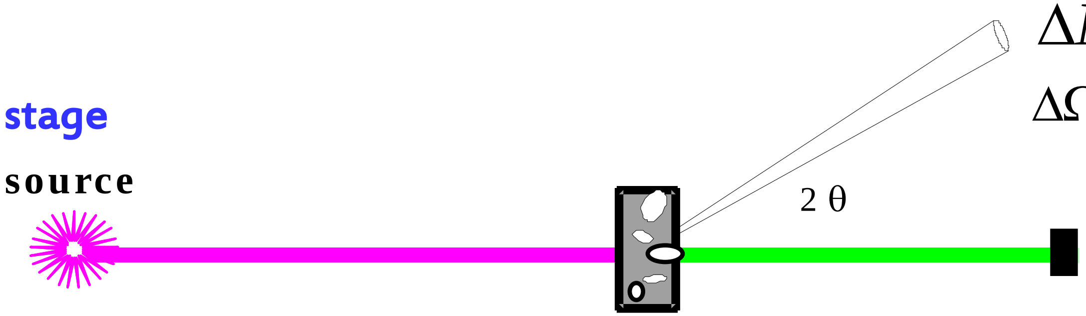
Initial stage

T_{att} of the order of 10^6



Measure of N_0

Sample stage



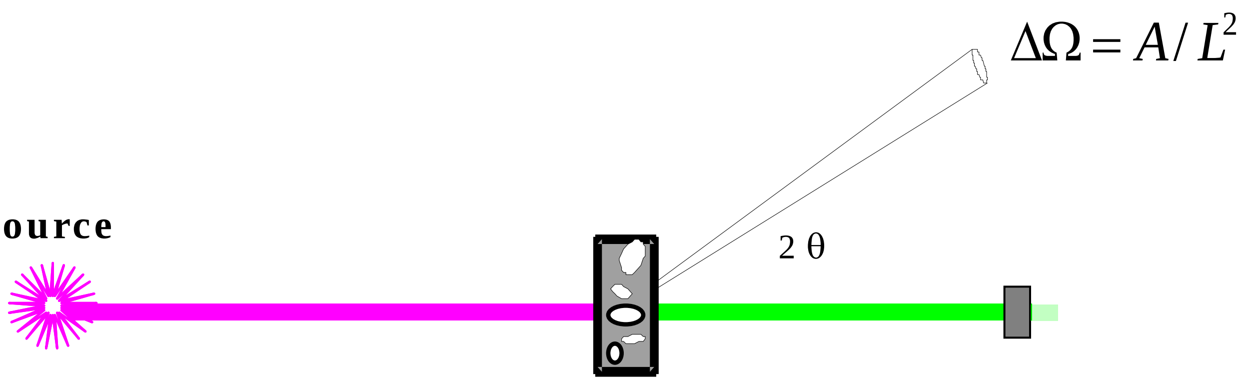
ΔN

$\Delta\Omega = A / L^2$ ***can be obtained geometrically***

$$\frac{d\Sigma}{d\Omega} = \frac{1}{eT} \frac{1}{T_{att} N_0} \frac{\Delta N}{\Delta\Omega}$$

-The method requires a good spectral purity because of the strong attenuation of the direct beam
-It requires the measure of the transmission

Direct calibration of the intensity-b



$$k_0 = k_1 \qquad \frac{d\Sigma}{d\Omega} = \frac{1}{e\, k_1 T_{att} N_T^{mes}} \frac{k_1 \Delta N^{mes}}{\Delta\Omega}$$

✓ Semi transparent Beam stopper of attenuation 10^6

-No need to measure the transmission

$$k_0 \neq k_1 \qquad \frac{d\Sigma}{d\Omega} = \frac{1}{e\, k_0 N_T^{mes}} \frac{k_1 \Delta N^{mes}}{\Delta\Omega}$$

✓Photo diode

-requires to measure k_1/k_0

Calibration of the intensity using standard

Standard of calibration for X-rays

- **-Lupolen™**
- **-Water**
- **-other solvents**

Initial stage : measuring the standard

$$\frac{d\Sigma}{d\Omega}(ref) = \frac{1}{eT}\,\frac{1}{k_0 N_0^{ref}}\,\frac{k_1 \Delta N^{ref}}{\Delta\Omega} = \frac{1}{eT}\,K\,\frac{\Delta N^{ref}}{N_0^{ref}}$$

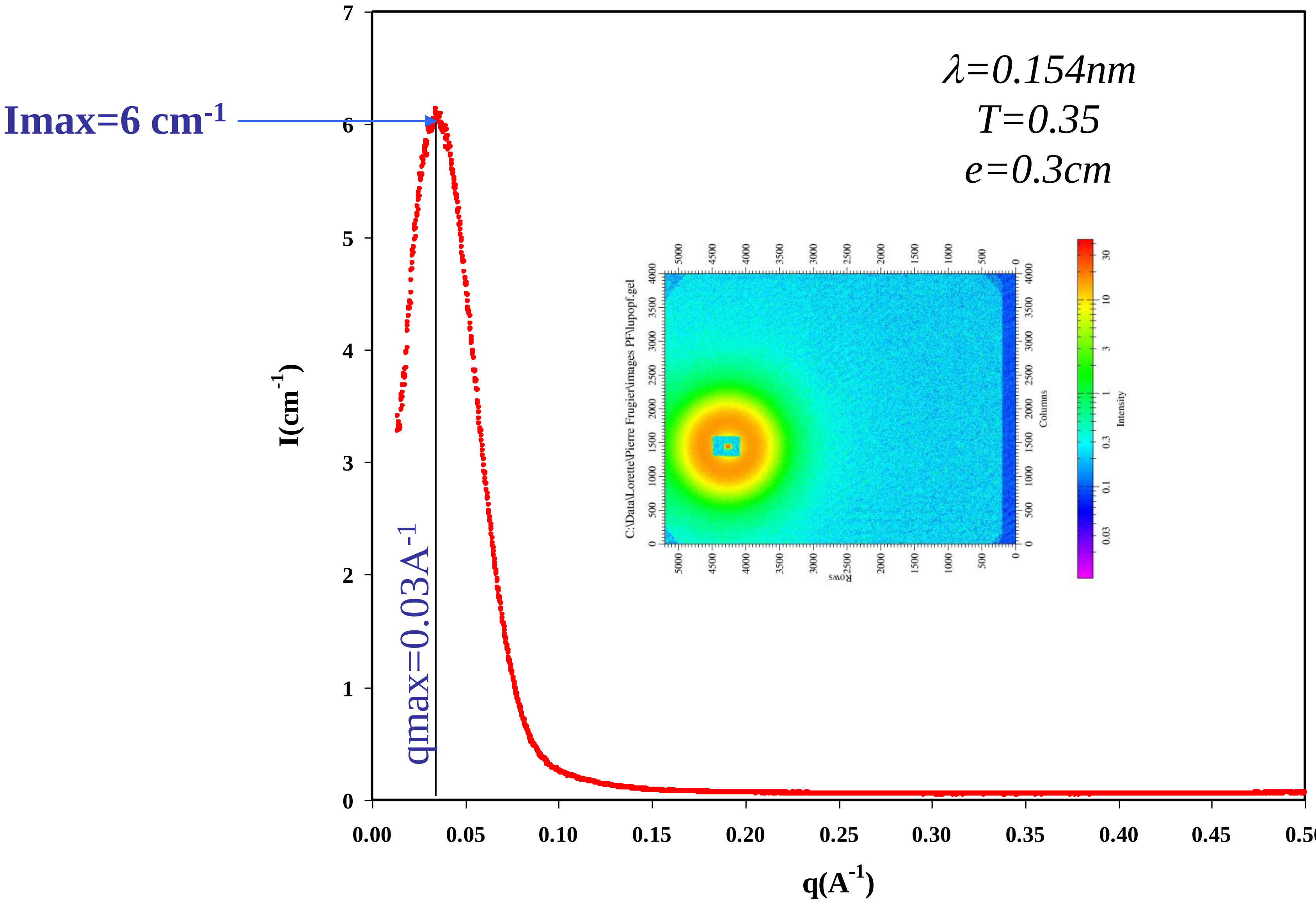
Measure of the constant K

Sample stage : measure direct beam monitor and the transmission

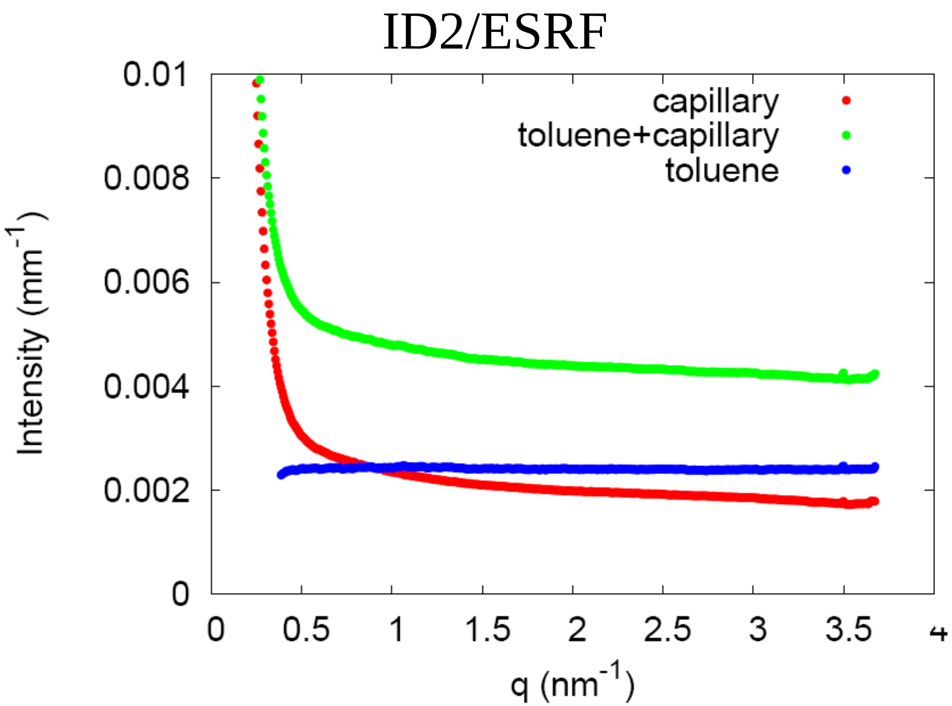
$$\frac{d\Sigma}{d\Omega}(sample) = \frac{1}{e_s T_s}\,K\,\frac{\Delta N^{sample}}{N_0^{sample}}$$

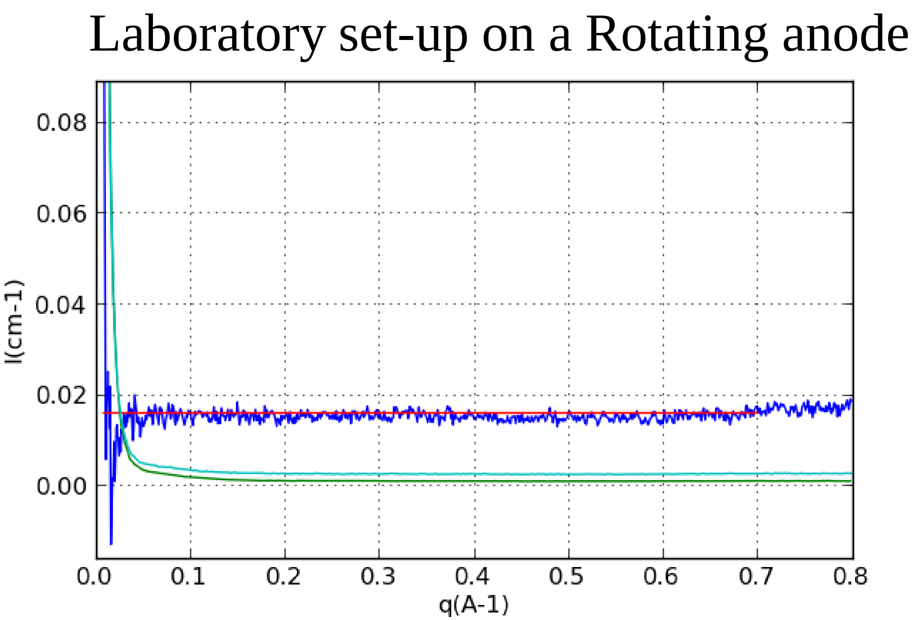
Requires -the measure of the transmission
-to monitor the direct beam
No need to measure the solid angle
Initial standard measurement
No need to introduce attenuator

Most common standard Lupolen



Using solvents





Toluene ***I = 0.0236 cm^{-1}***

Water ***I = 0.0162 cm^{-1}***

Hexane I = 0.0287 cm^{-1}

-The method does not work for neutrons since the coherent scattering is too weak.
Incoherent scattering of water can serve a secondary standard

Exercice (more serious)

A circle of 0.05m on the detector at 2m sample/detector separation for a wavelength of 1A defines :
q=0.157A^{-1}

Using

$$\Delta N = Te\, N_0\, I\, \Delta\Omega$$

On ID2 (synchrotron line),
calculate the numbers of counts (per second) scattered by 1mm of water in this circle using a 200microns step resolution

$$N_0 = 2\,10^{13}\, photons/\sec \quad at \quad \lambda = 1nm$$

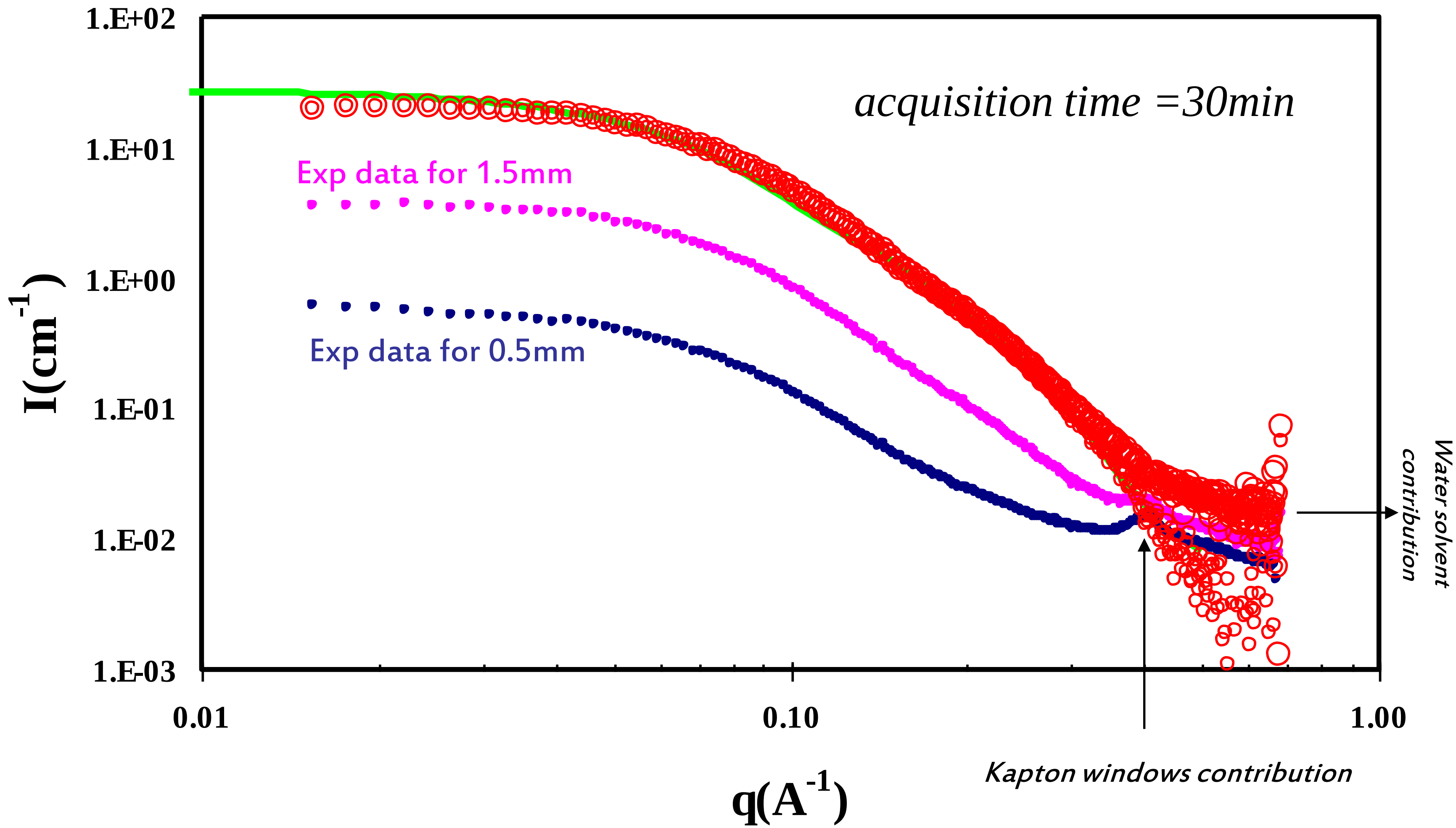
$$\Delta\Omega = (2\pi * 0.05 * 200\,10^{-6})/(2)^2 = 1.57\,10^{-5}$$

$$e = 1mm \quad T = 0.71$$

$$I_{H_2O} = 1.6\,10^{-2}\, cm^{-1}$$

$$\Delta N_{pixel} = 3.57\,10^{5}\, cps$$

Example of measurement on a rotating anode



$$C_{CeO_2} = 20\ g/l$$

d=7.13 g/cm^3

ρ_{CeO2}=5.27 10^{-11} cm^{-2}

$$I = (\rho_{CeO_2} - \rho_{H_2O})^2 \phi\, v_{part}\ P(q)$$