Small-Angle Neutron Scattering

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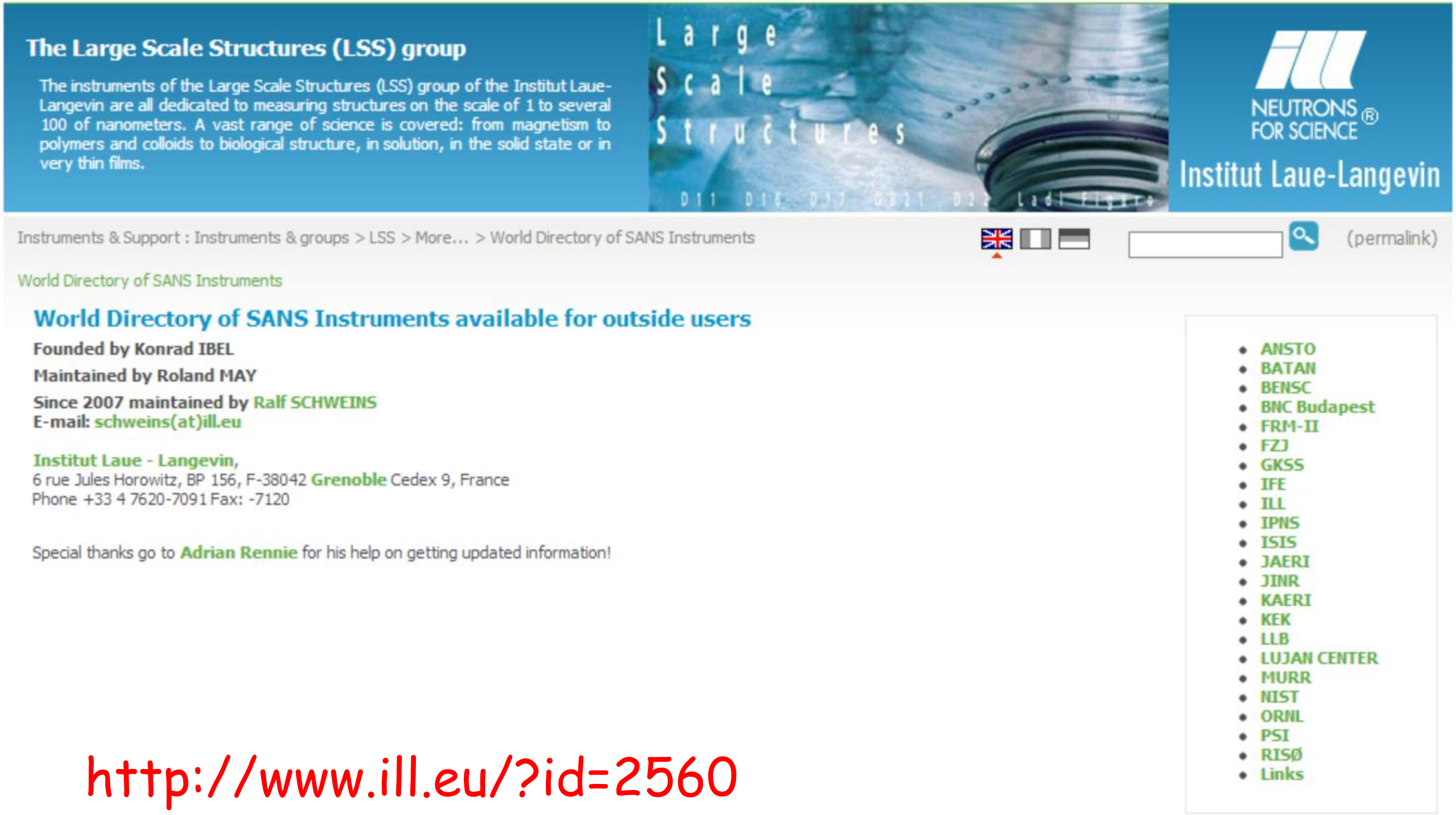
- *Characterisation of matrix inhomogeneities (e.g. precipitates and cavities in hard materials, proteins and polymers in solutions, etc...)*

- *Quantitave information on: particle shape, size distribution, volume fraction, specific surface, ...*

- *Investigable particle size range: 1 nm – 1 μm (approx.)*

- *Complementary technique to Transmission Electron Microscopy (TEM): TEM is limited to a few mm^2 regions of the specimen, SANS can investigate several cm^2 zones; using useful information from TEM (e.g. particle shape and order of magnitude of size)*



The Large Scale Structures (LSS) group

The instruments of the Large Scale Structures (LSS) group of the Institut Laue-Langevin are all dedicated to measuring structures on the scale of 1 to several 100 of nanometers. A vast range of science is covered: from magnetism to polymers and colloids to biological structure, in solution, in the solid state or in very thin films.

Instruments & Support : Instruments & groups > LSS > More... > World Directory of SANS Instruments

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World Directory of SANS Instruments available for outside users

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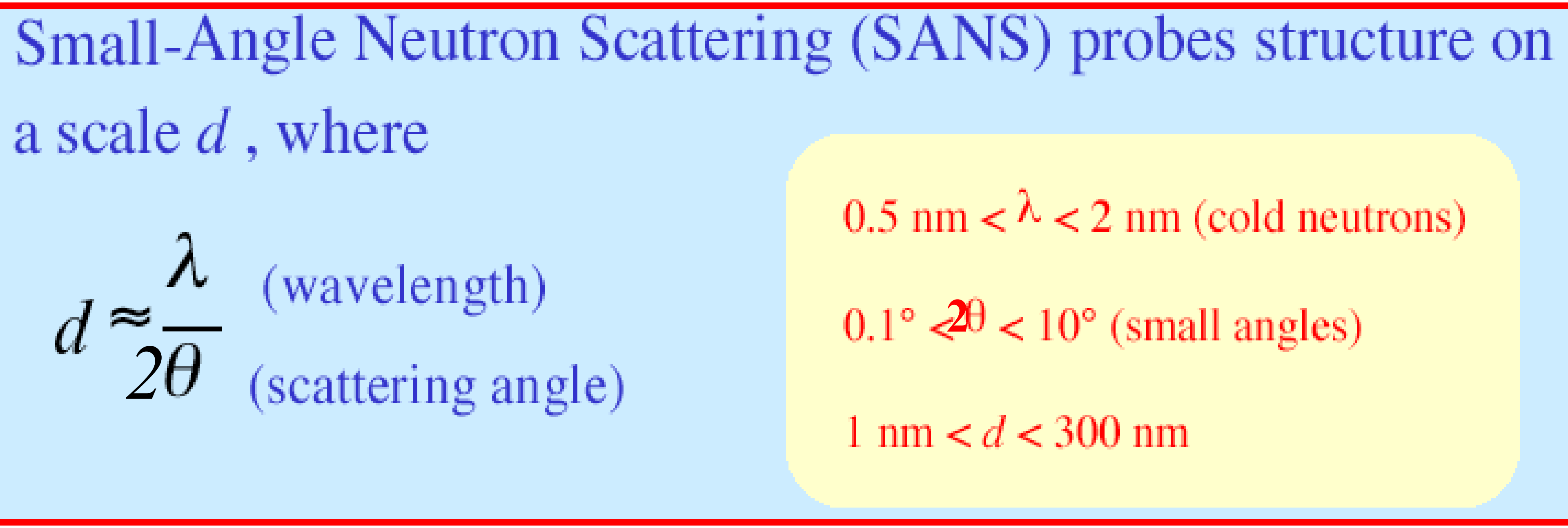


Small-Angle Neutron Scattering (SANS) probes structure on a scale *d* , where

$$d \approx \frac{\lambda}{2\theta}$$

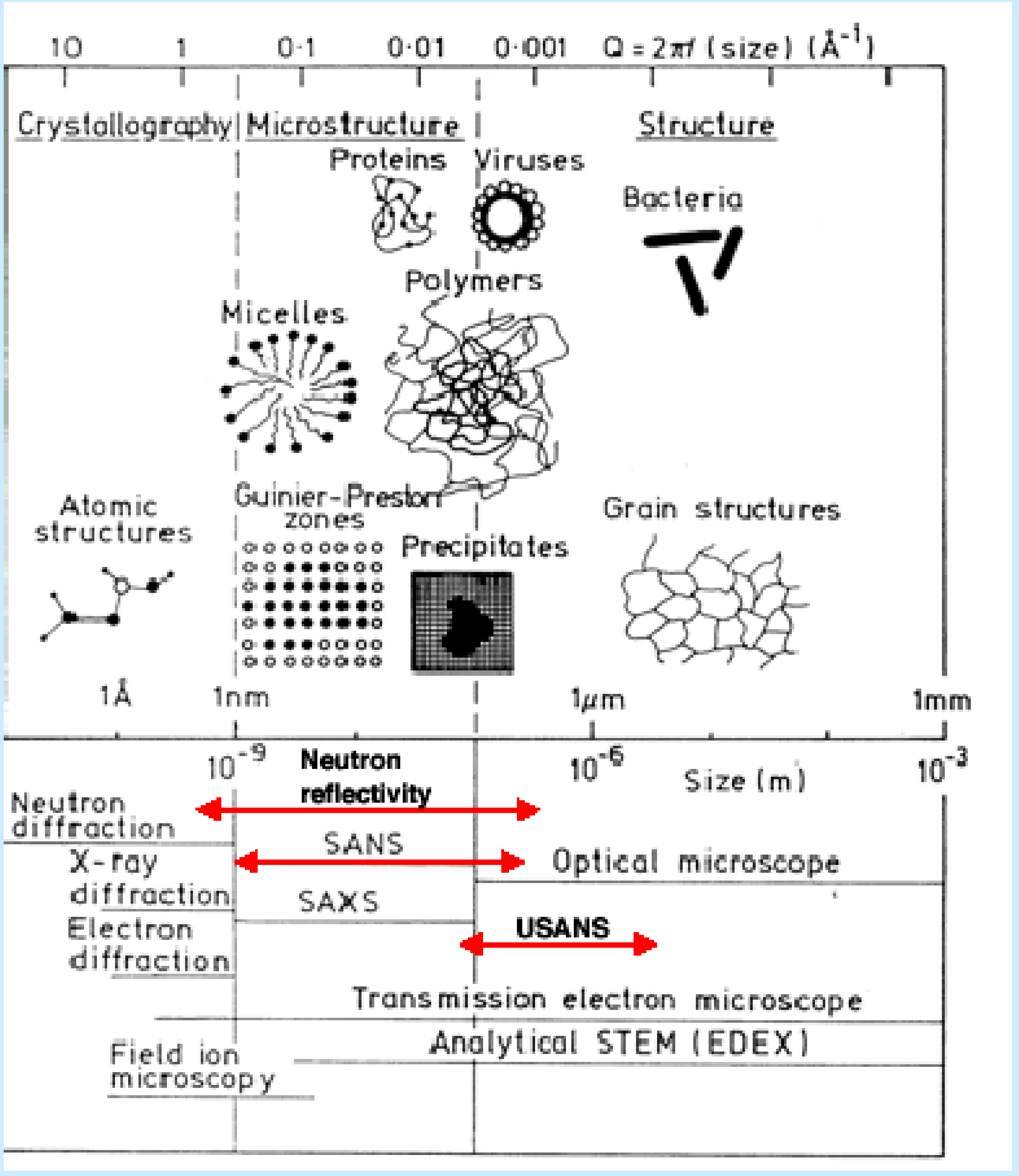
(wavelength)

(scattering angle)

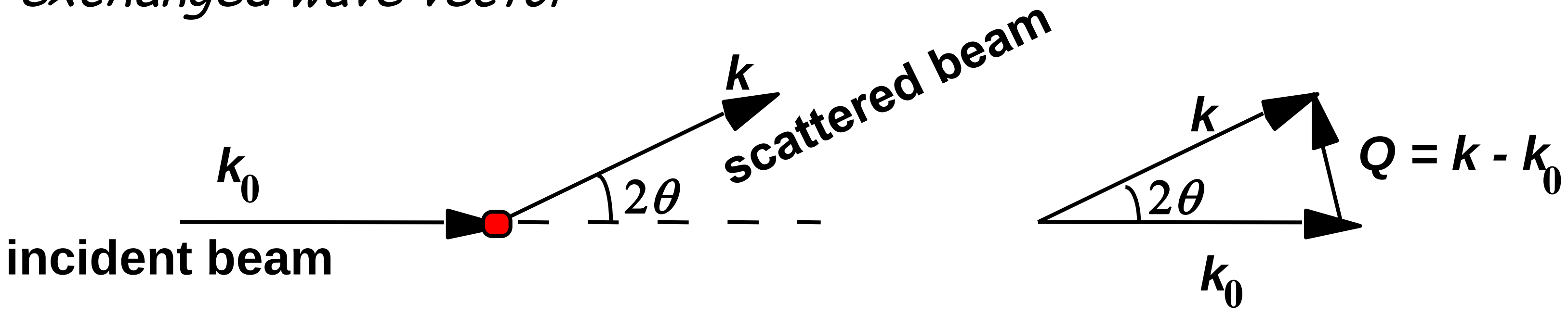
$0.5\ \text{nm} < \lambda < 2\ \text{nm}$ (cold neutrons)

$0.1° < 2\theta < 10°$ (small angles)

$1\ \text{nm} < d < 300\ \text{nm}$


10
1
0·1
0·01
0·001
Q = 2π/(size) (Å^{-1})
Crystallography
Microstructure
Structure
Proteins
Viruses
Bacteria
Polymers
Micelles
Atomic structures
Guinier-Preston zones
Precipitates
Grain structures
1Å
1nm
1μm
1mm
10^{-9}
10^{-6}
10^{-3}
Size (m)
Neutron reflectivity
Neutron diffraction
SANS
X-ray diffraction
SAXS
Optical microscope
Electron diffraction
USANS
Transmission electron microscope
Analytical STEM (EDEX)
Field ion microscopy

$\mathbf{Q}$ = exchanged wave vector



elastic scattering: $|\mathbf{k}_0| = |\mathbf{k}| = 2\pi/\lambda$ →

$$\boxed{Q = \frac{4\pi}{\lambda}\sin\theta}$$

$$\boxed{\frac{d\Sigma}{d\Omega} = \frac{1}{V}\left|\int_V \rho(r)\, e^{iQ\cdot r}\, dv\right|^2}$$

(Rayleigh-Gans equation)

$\rho(r)$ = coherent scattering length density

$$\rho = \frac{\sum_i^n b_i}{\overline{V}}$$

$\overline{V}$ is the volume containing the n atoms

Two-phase model: *identical particles embedded in a homogeneous matrix (monodispersion)*

$$\boxed{\frac{d\Sigma}{d\Omega} = \frac{N_p}{V}(\rho_p - \rho_m)^2\left|\int_{V_p} e^{iQ\cdot r}\, dv\right|^2 S(Q) \quad = n V_p^2 (\Delta\rho)^2 \left|F(Q)\right|^2 S(Q)}$$

$$\boxed{\left|F(Q)\right|^2 = \frac{1}{V_p^2}\left|\int_{V_p} e^{iQ\cdot r}\, dv\right|^2}$$

Form factor

Nuclear contrast

Interparticle structure factor

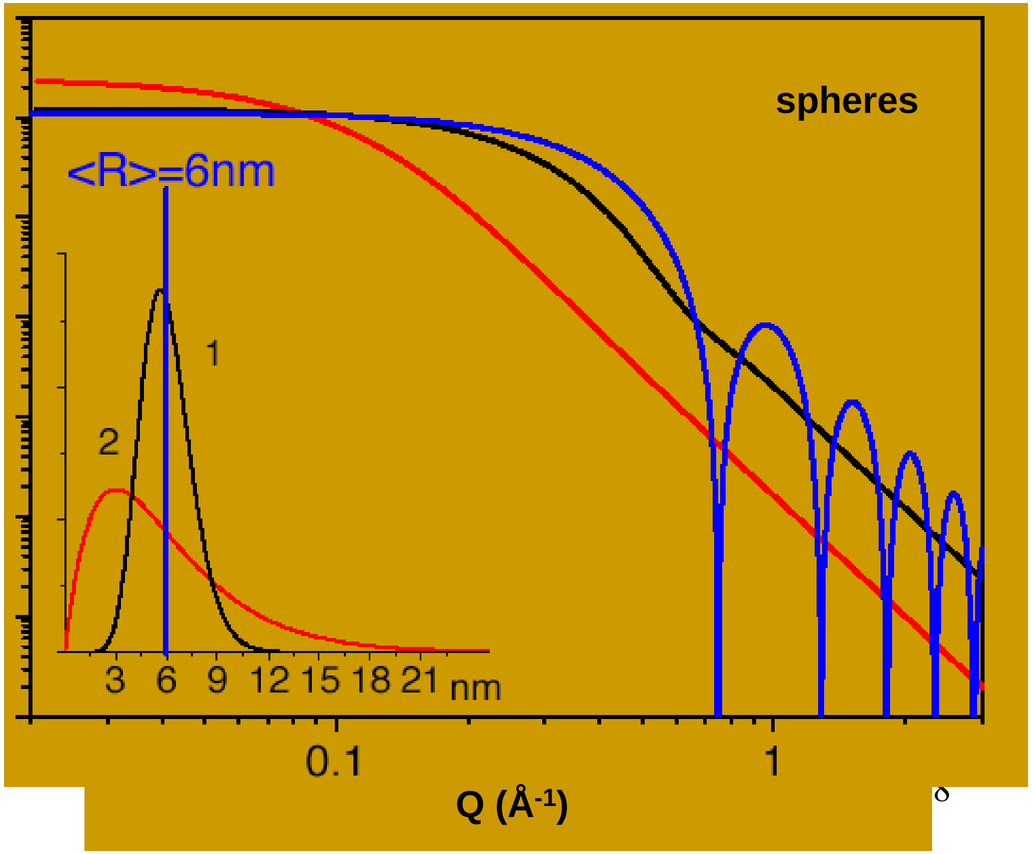
Dilute systems: $S(Q) = 1$

Polydispersion - inhomogeneity particles with a size distribution:

$$\boxed{\frac{d\Sigma}{d\Omega} = (\Delta\rho)^2 \int_0^\infty N(R) V^2(R) \left|F(QR)\right|^2 dR}$$

(S(Q) = 1)

N(R) = size distribution (number of particles per unit volume with size between R and R + dR)



Asymptotic behaviours

$Q \longrightarrow 0$

$$\boxed{\frac{d\Sigma}{d\Omega} \approx nV^2(\Delta\rho)^2 e^{-Q^2R_g^2}}$$

R_g = Guinier radius

$$\boxed{\ln\left(\frac{d\Sigma}{d\Omega}\right) \approx \ln[nV^2(\Delta\rho)^2] - Q^2R_g^2}$$

➡ "Guinier plot"

$Q \longrightarrow \infty$

$$\boxed{\frac{d\Sigma}{d\Omega} \approx \frac{2\pi(\Delta\rho)^2 S_p}{Q^4}}$$

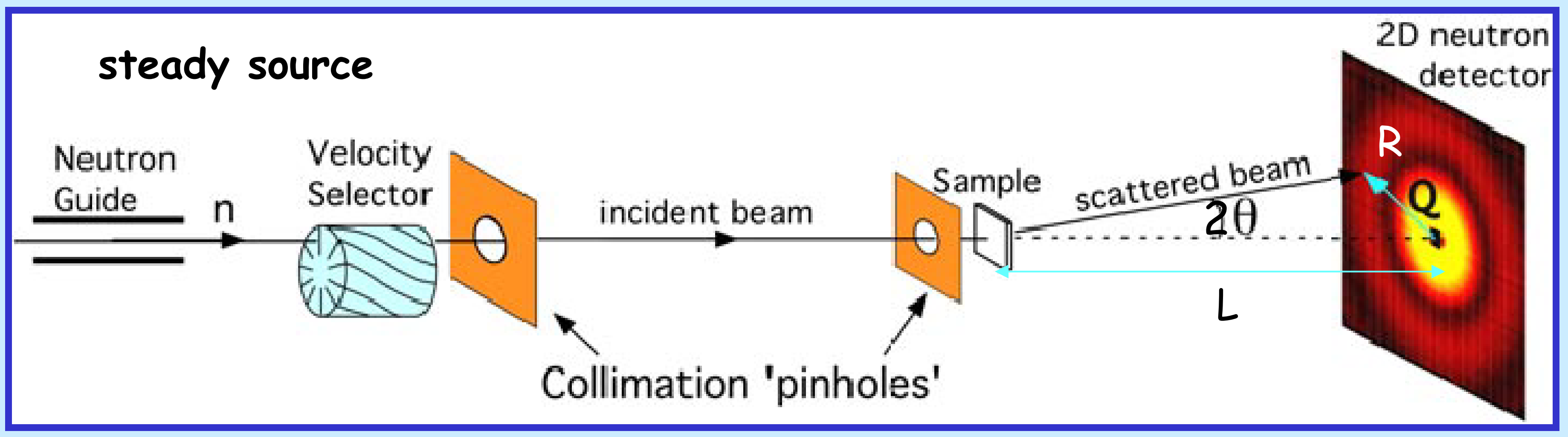
S_p = particle specific surface

Valid for sharp particle-matrix interface

$$\boxed{\frac{d\Sigma}{d\Omega}\cdot Q^4 \approx 2\pi(\Delta\rho)^2 S_p}$$

➡ "Porod plot"

Experimental set-up



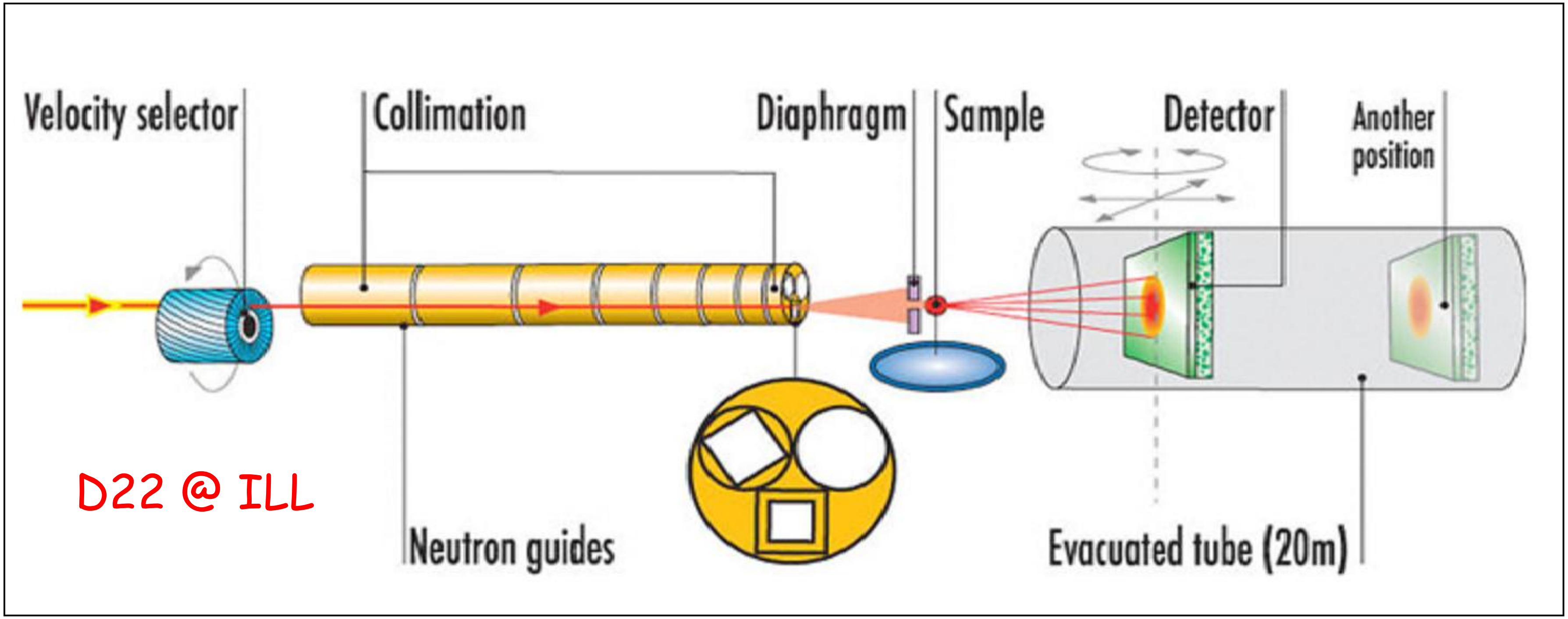
$$Q = \frac{4\pi}{\lambda}\sin\theta \approx \frac{2\pi}{\lambda}\cdot\frac{R}{L}$$

$$I(Q)[n/s] = \phi\cdot A\cdot\varepsilon\cdot\Delta\Omega\cdot s\cdot\frac{d\Sigma}{d\Omega}(Q)$$

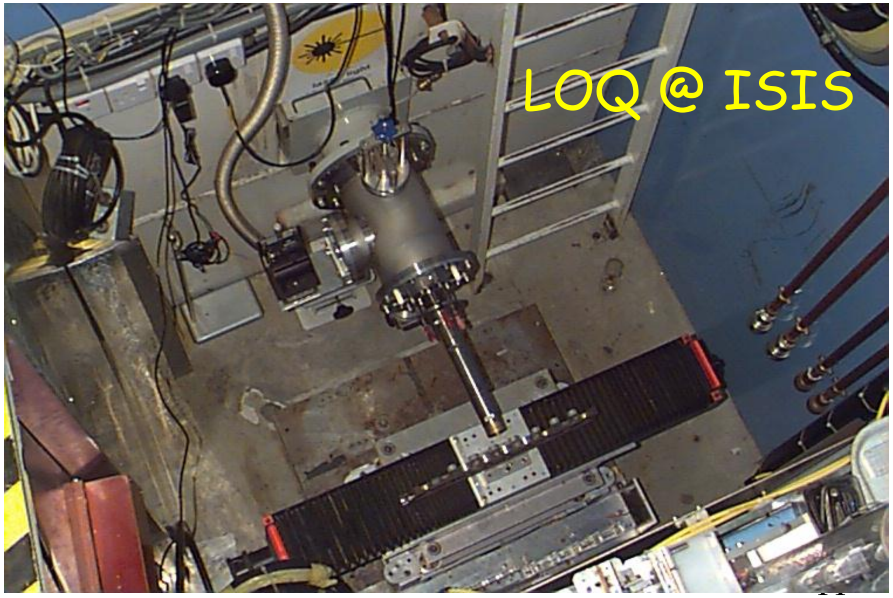
Can be determined by the use of standards (water, vanadium…)

At pulsed sources (TOF technique):

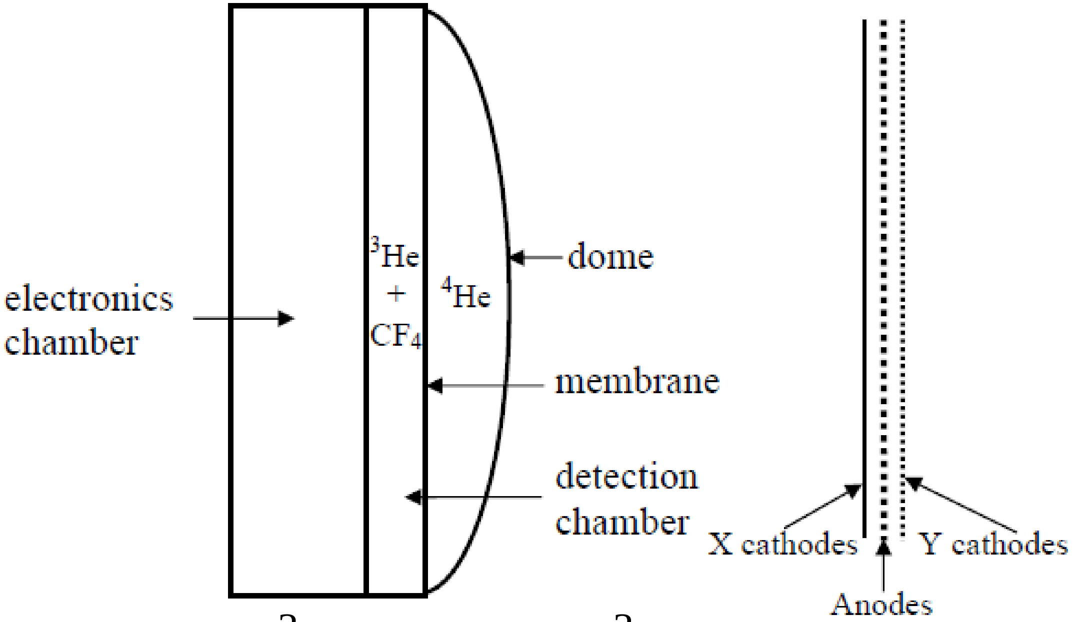
$$Q(t) = \frac{4\pi\, m_N\, L}{h\,t}\sin\theta$$


D22 @ ILL


PAXY @ LLB


LOQ @ ISIS

Area detectors



$$n + {}^3He \rightarrow H + {}^3H + 765\ KeV$$

Active detection area: 64 x 64 cm^2

Spatial resolution: 1x1 or 0.5x0.5 cm^2

Efficiency ≈ 75% for typical λ

Count rates $\approx 5\times10^4\ s^{-1}$

Area detectors

Possible alternatives to ^{3}He

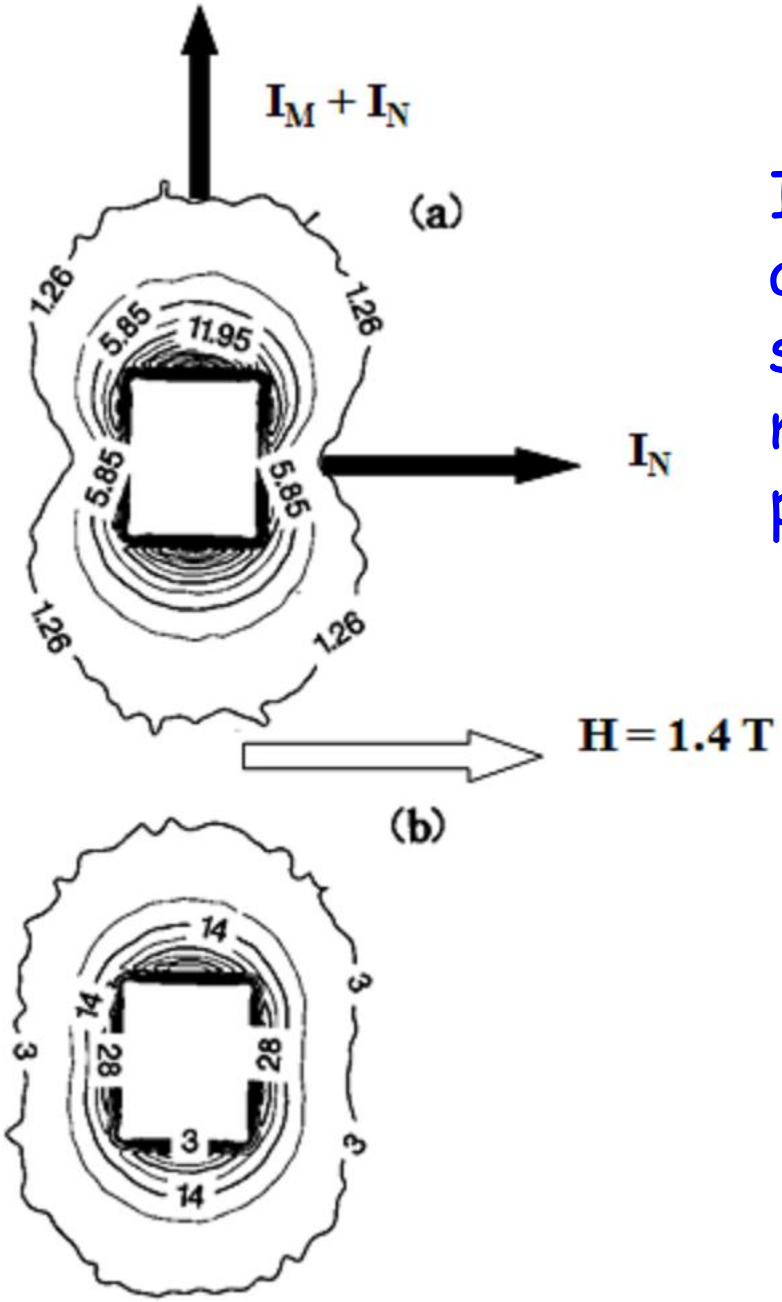
Detector type	Description
Scintillators	Small scintillators (plastic and/or inorganic) elements (mm^2 area) coated with 6Li, Gd, 10B, Cd and stacked to achieve > 60% detection efficiency with SiPM or PMT readout. Charge particle detection (6Li, Gd,10B) or gamma-rays detection (Gd,Cd) for neutron counting. Gamma/neutron discrimination.
GaAs	Schottky barrier detectors coated with 10B,6Li or Gd and stacked to achieve 10-15% detection efficiency (rate capability 1 MHz). MESFET (transistor) detectors mm^2 area coated with 6Li,10B or Gd and stacked to achieve >60% detection efficiency and mm spatial resolution (high rate capability per pixel > 10 MHz) . Good gamma-ray rejection
GEM	Gas Electron Multipliers with borated sapphire sheets array inside to achieve 60-70% detectio efficiency and good gamma-ray rejection

Eventual ancillary equipments

- Movable multi-sample holder for both cuvettes and metallic samples
- Magnetic field (up to about 5 Tesla)
- High-pressure cell (up to about 10 kBar)
- Sample temperature control (e.g. -100 to +200 °C)
- Polarized neutrons (spin flippers)

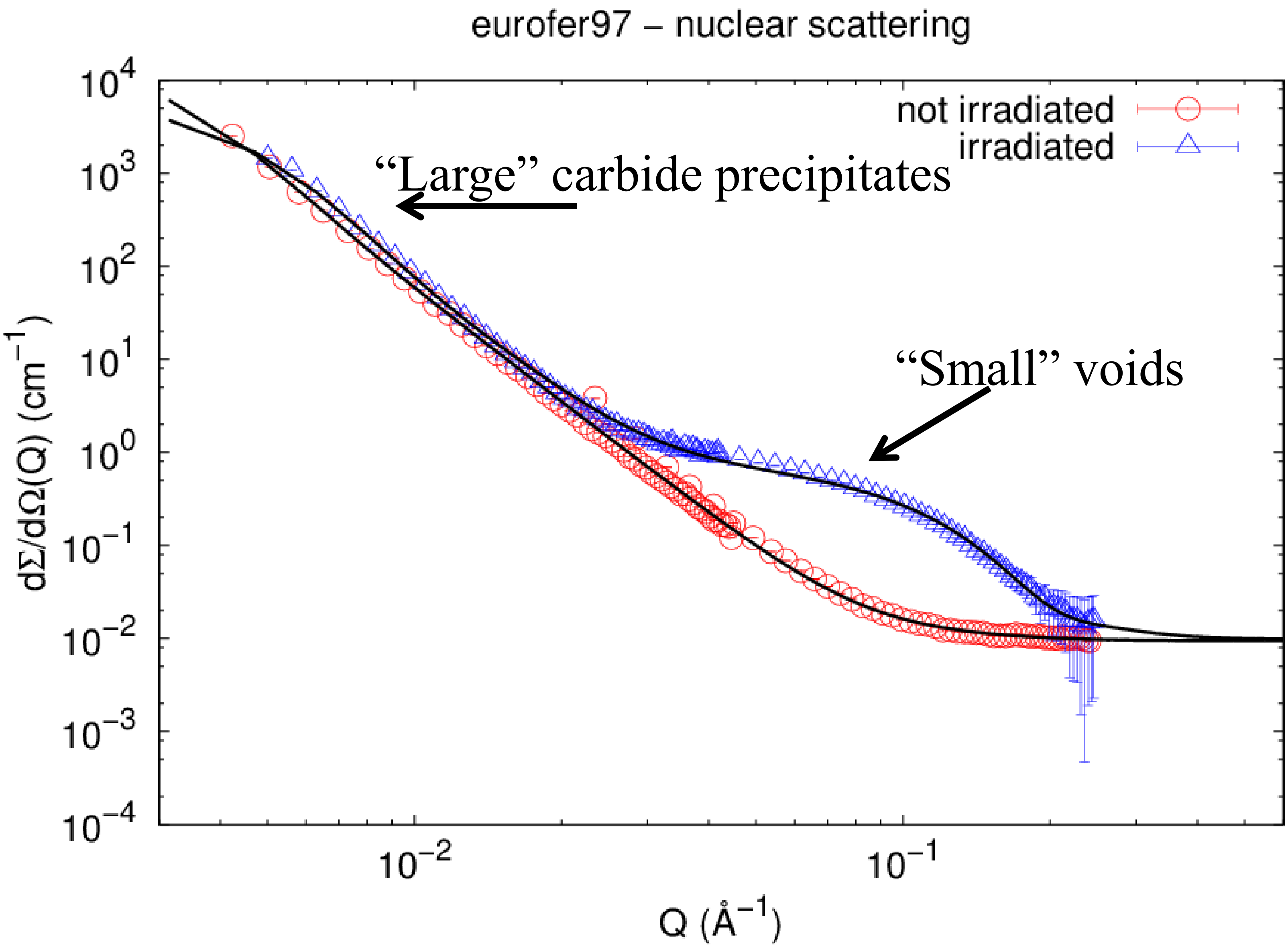
TYPICAL SANS APPLICATIONS INCLUDE

- ♠ Biology
  - Organization of biomolecular complexes in solution
  - Mechanisms and pathways for protein folding
- ♠ Polymers
  - Conformation of polymer molecules in solution
  - Structure of microphase for separated block polymers
- ♠ Chemistry
  - Structure and interactions in colloid suspensions
  - Mechanisms of molecular self-assembly in solutions
- ♠ Materials Science
  - Precipitation mechanisms and kinetics as functions of thermal treatments (e.g. ageing); cavitation induced by thermomechanical processes (e.g. welding)
  - Crystalline structure investigations



In magnetic materials, nuclear and magnetic scattering can be separated by applying a magnetic field at the sample position

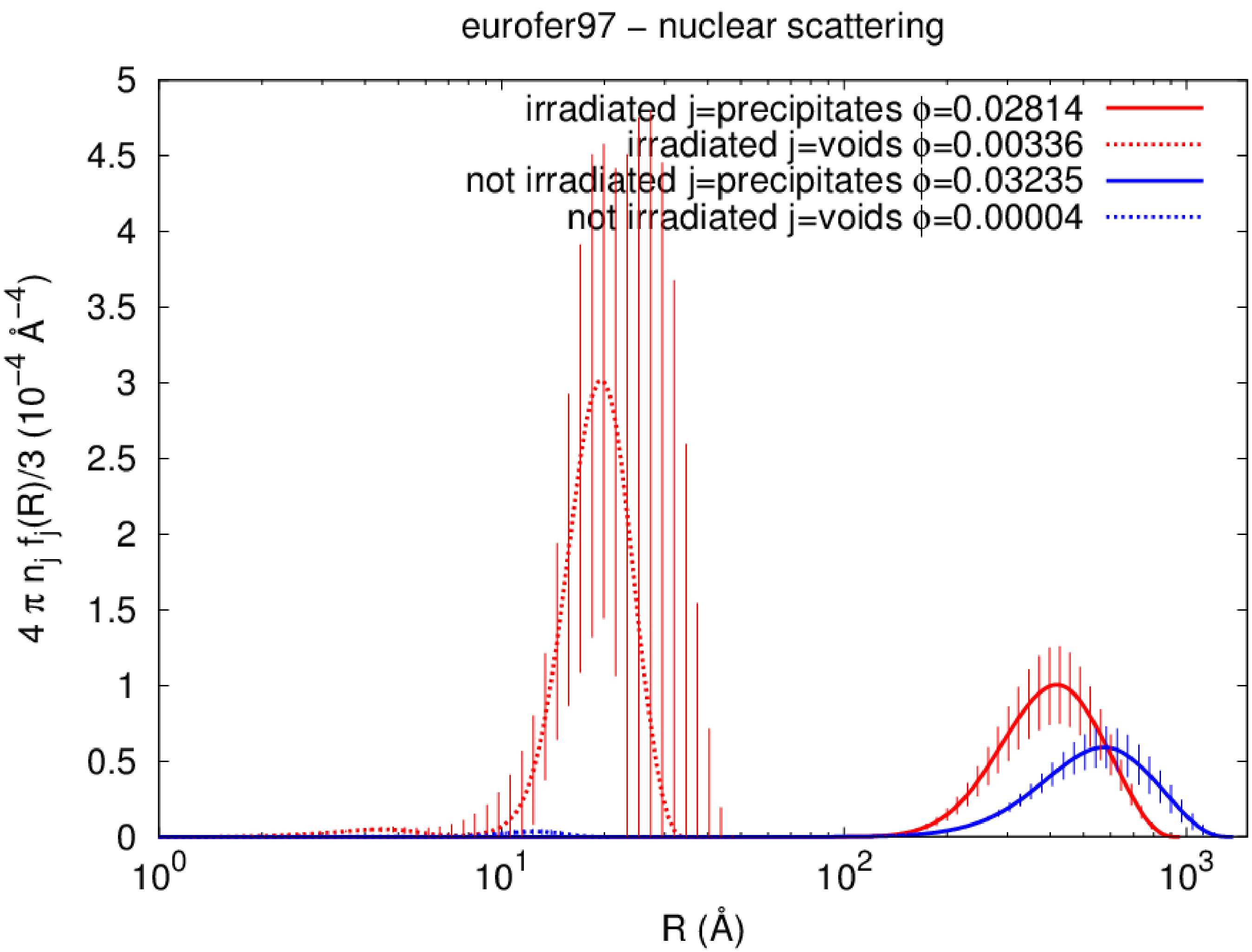
Evaluation of contribution of different kind of particles (carbide precipitates + voids)



"Large" carbide precipitates

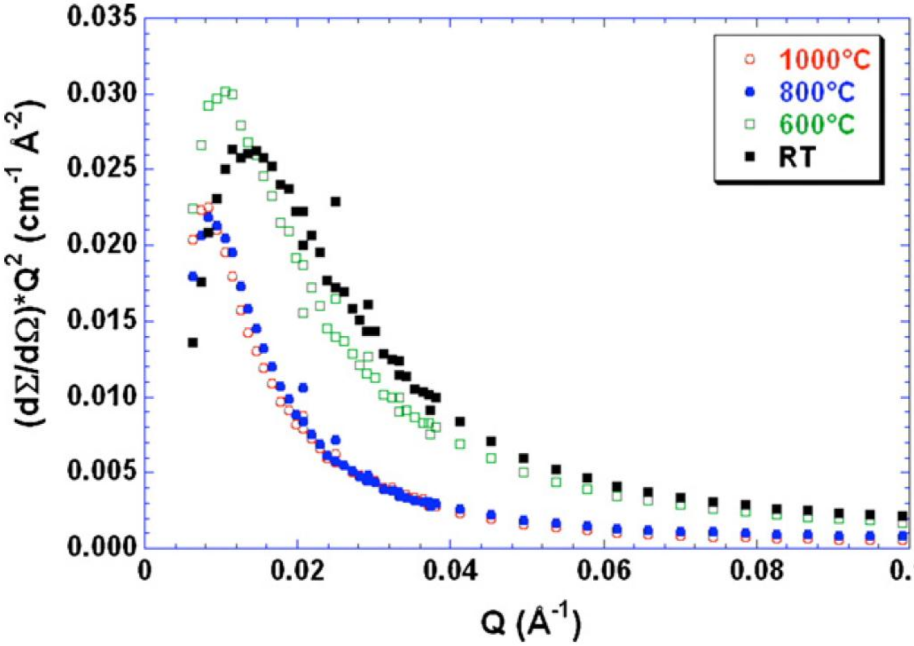
"Small" voids

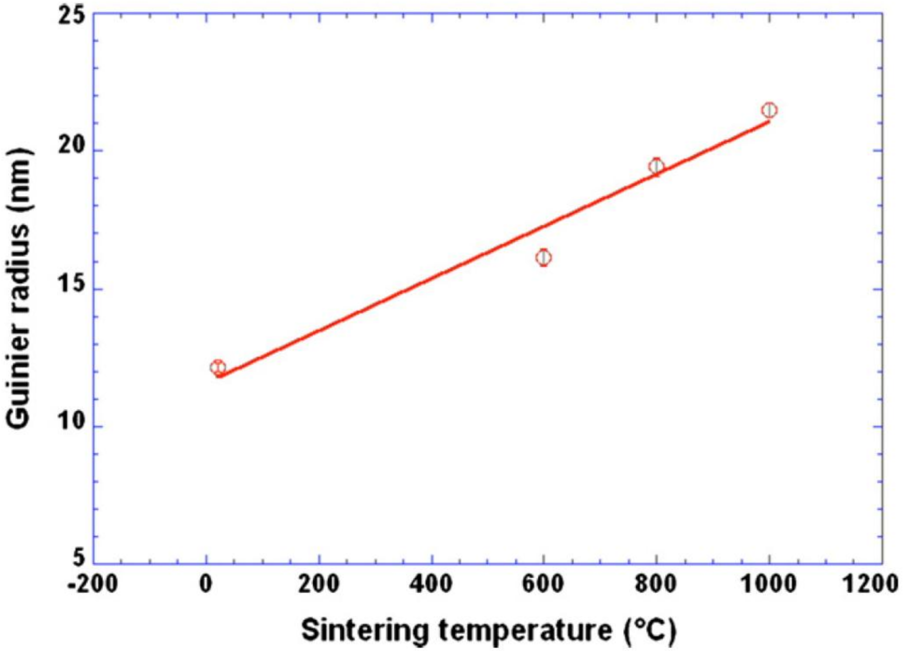
Evaluation of contribution of different kind of particles (carbide precipitates + voids)
- GENFIT -



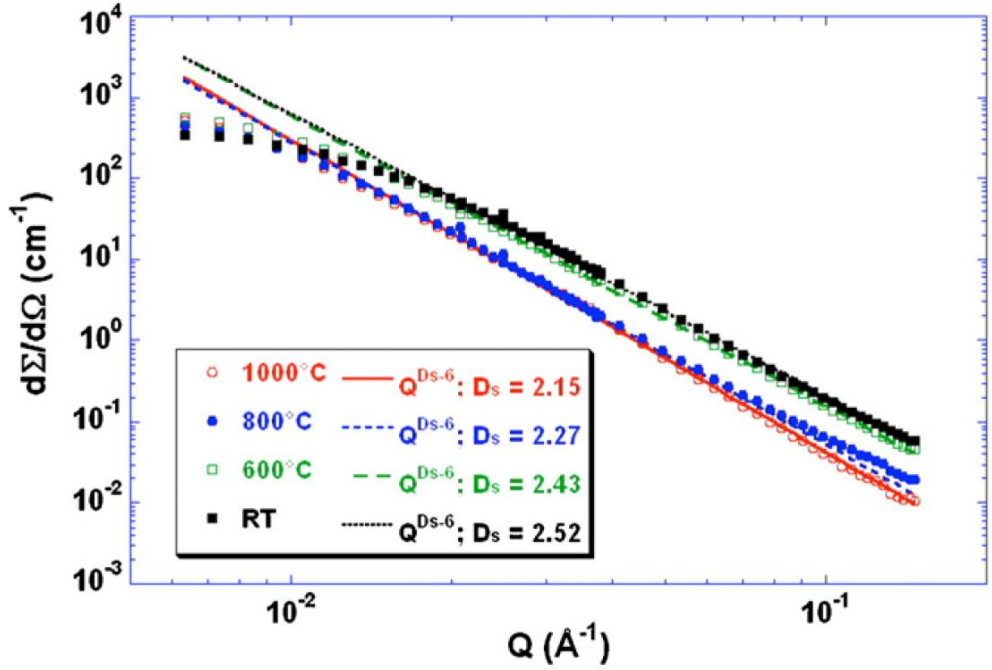
Al2O3/Ni-P nanocomposites

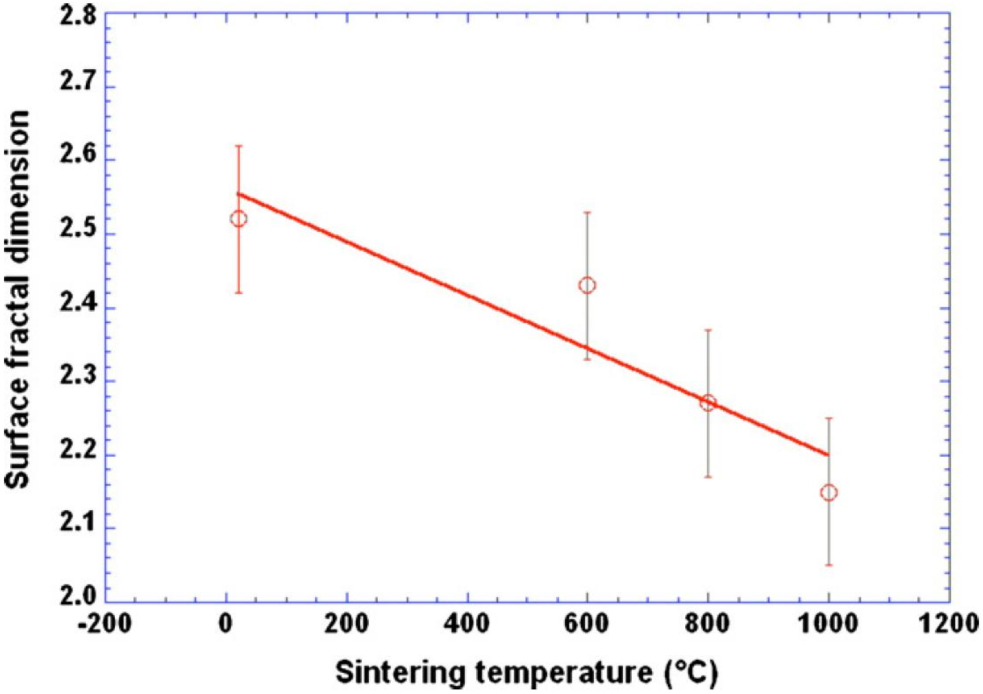
- Composites prepared from Al2O3 powder (99.95% purity, average grain size 960nm), covered by Ni-P by electroless method.
- The ceramic powder covered by metal was pressed under high pressure (7 GPa) at different temperatures (RT, 600°C, 800°C, 1000°C)





$Q^2(d\Sigma/d\Omega)$ vs. Q maximum at $Q = \sqrt{3}/R_G$, R_G = Guinier radius

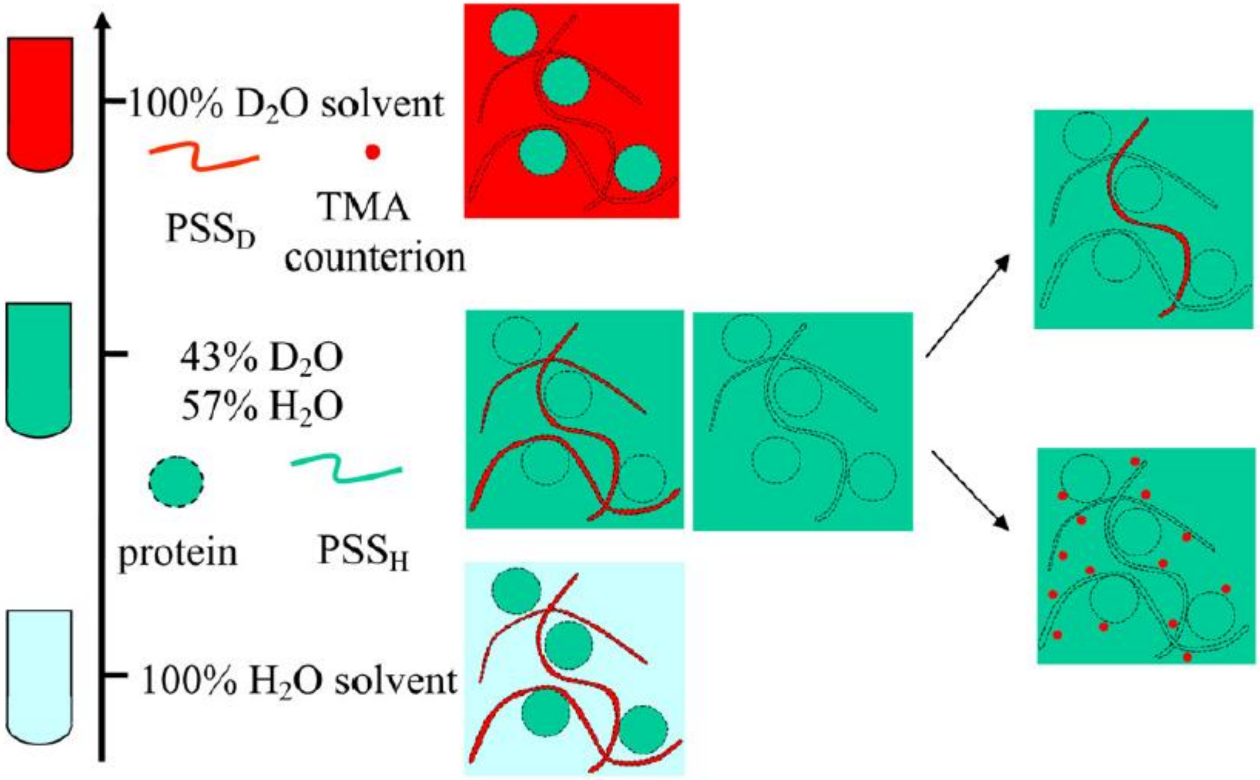

10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
$d\Sigma/d\Omega$ (cm^{-1})
10^{-2}
10^{-1}
Q ($Å^{-1}$)
1000°C
800°C
600°C
RT
Q^{Ds-6}; Ds = 2.15
Q^{Ds-6}; Ds = 2.27
Q^{Ds-6}; Ds = 2.43
Q^{Ds-6}; Ds = 2.52


2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
Surface fractal dimension
-200
0
200
400
600
800
1000
1200
Sintering temperature (°C)

Contrast variation - Mixtures

- two species A and B in a solvent S, with value ρ_A different enough from ρ_B.
- if we match one species with the appropriate mixture of deuterated (D) and non-deuterated (H) solvents, we have access to the contribution of the other species only.

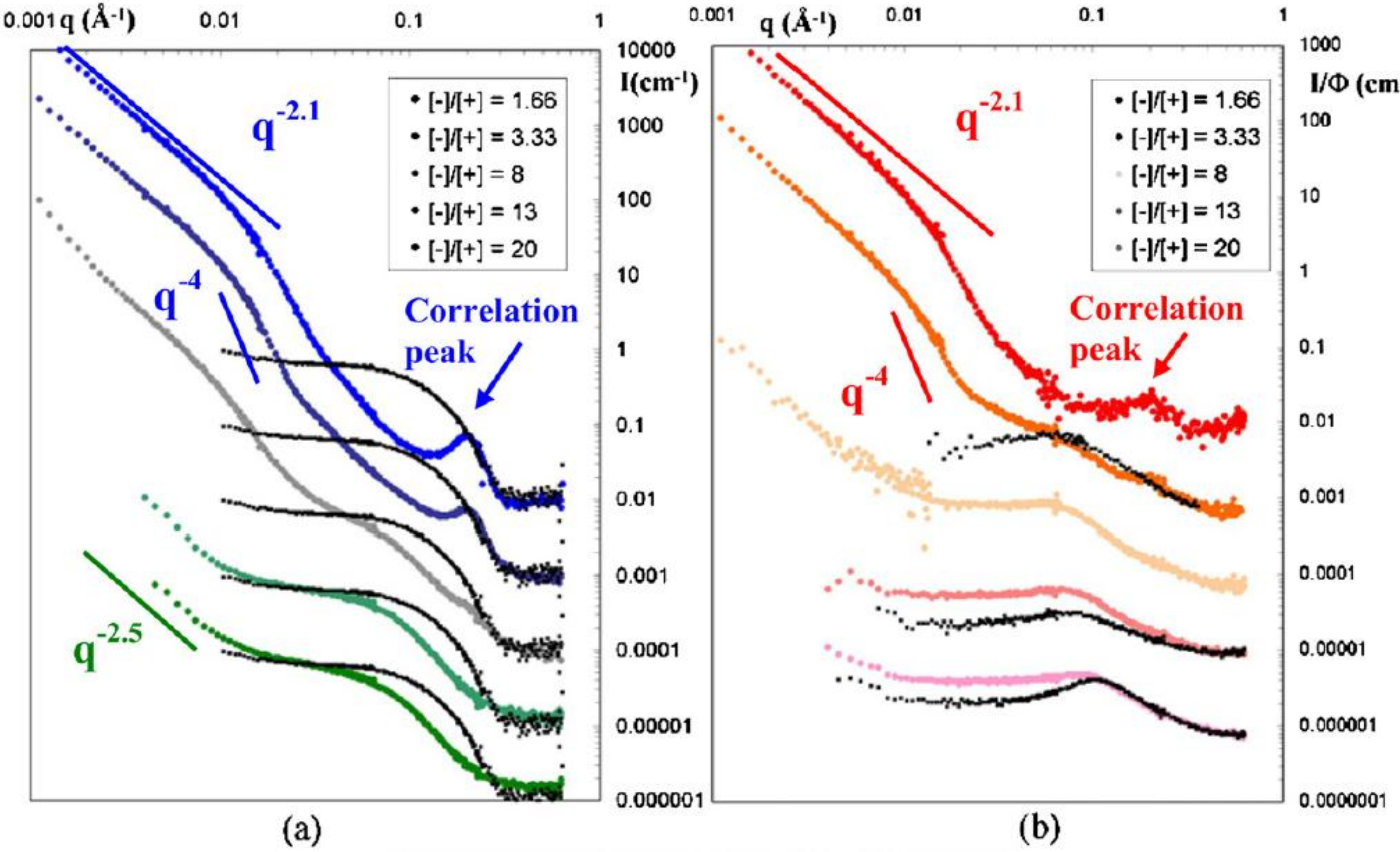
Lysozyme + Sodium Poly(styrenesulfonate) (PSSNa) + TetraMethylAmmonium counterions (TMA+), and matching solvents



If the cross section (or SANS intensity) scales with q^{-n} over a wide range of q, the “possible” structure can be obtained with some knowledge of the systems.

particles	**n**
Long Rigid rod	1
Smooth 2-D Objects	2
Linear Gaussian Chain	2
Chain with Excluded Volume	5/3
Interfacial Scattering from 3-D Objects	
with Smooth Surface (Porod regime)	4
with fractal Surface	3 ~ 4

Lysozyme + Sodium Poly(styrenesulfonate) (PSSNa)



SANS curves as a function of the introduced charge ratio [−]/[+] :
(a) scattering of lysozyme (40 g/L). Each curve is shifted by a factor 10, and compared to that of diluted lysozyme (10 g/L) measured in same contrast conditions, multiplied by a factor 4, and plotted in black points.
(b) Scattering of polyelectrolyte for the same five charge ratios (shifted each by 10), and compared to the one of pure PSS Na solutions measured in same contrast conditions and plotted in black points.

Lysozyme + Sodium Poly(styrenesulfonate) (PSSNa)

- at large q, the scatterings from the two species are different from each other. As in pure PSS solutions, the PSS signal is that of a semi-flexible individual chain, approaching progressively the signal of a rod (q^{-1}) at the largest q's. In this same large q range, the protein signal is also identical to that of an individual protein, displaying a q^{-4} law. But at intermediate q, a new effect is visible: a pronounced maximum can be seen at $q \sim 2\pi/R_{lys}$. This is characteristic of close contact between two proteins inside the complexes;

- at low q, the signals of lysozyme (when PSS is matched) and of PSS (when lysozyme is matched) display an identical variation with q. When going from large to low q, we first see an increase, corresponding to a q^{-4} law (massive globules with sharp surface).
Looking at a slightly lower q (upper curves), we see that the signal bends down and follows a rounded curve: this corresponds to the Guinier law for this compact globule, which we can call 'primary aggregate'. We can actually fit the signal in such Guinier range and in the q^{-4} regime to the scattering calculated for spherical 'globules' of radius R_{comp} of order 10 nm.

General requirements

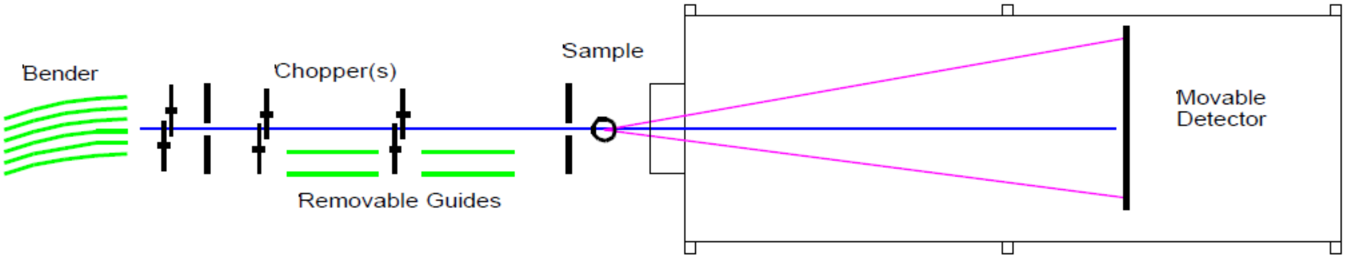


Fig. 1: Generic SANS instrument for ESS. Curved guide and/or bender removes beam from direct view of moderator. Large area detector (at least 1m x1m) moves in vacuum tank, and may be offset sideways. Substantial beam line and vacuum tank shielding will be required.

- Single "figure of merit" comparison of pulsed SANS with reactor SANS is NOT possible , as neutrons are used in different ways , and conclusions depend on the system under study and the science involved.

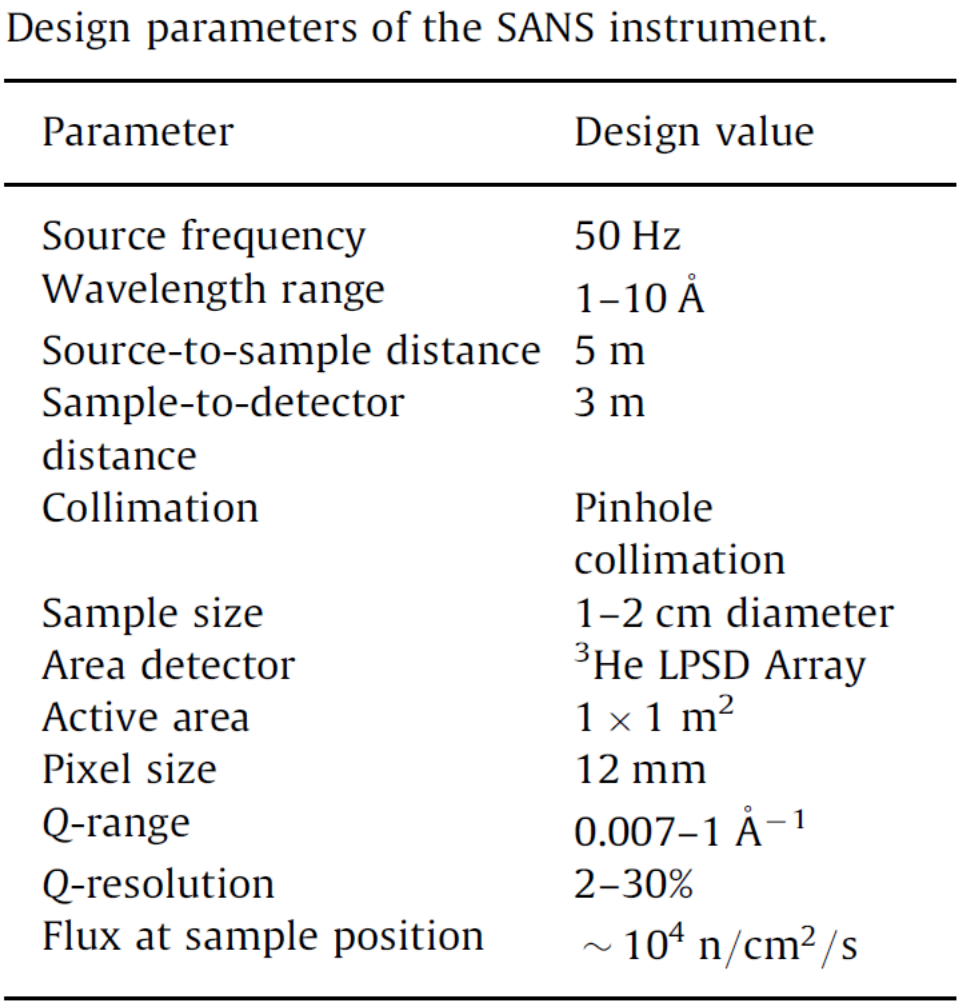
- Some experiments need to optimise the instrument for highest flux in a given Q-range, other experiments might optimise for highest resolution (dQ/Q), and others may optimise for maximum available Q-range, even using the low-flux limits. Dynamical studies require a large Q range in a single shot.

- Incident collimation will require choppers to select wavelengths, as well as the usual movable guide sections to change collimation length.

- Flexible instrument, with as a ~$1m^2$ square detector, eventually moving within a range of a some meters from the sample in a vacuum tank, in order to optimise λ range, Q range, and geometric resolution to suit particular experiments.

General requirements

TOF SANS instrument to be built at the Compact Pulsed Hadron Source (CPHS) of Tsinghua University, China



Design parameters of the SANS instrument.

Parameter	Design value
Source frequency	50 Hz
Wavelength range	1–10 Å
Source-to-sample distance	5 m
Sample-to-detector distance	3 m
Collimation	Pinhole collimation
Sample size	1–2 cm diameter
Area detector	^{3}He LPSD Array
Active area	1×1 m^2
Pixel size	12 mm
Q-range	0.007–1 Å^{-1}
Q-resolution	2–30%
Flux at sample position	$\sim 10^4$ n/cm^2/s