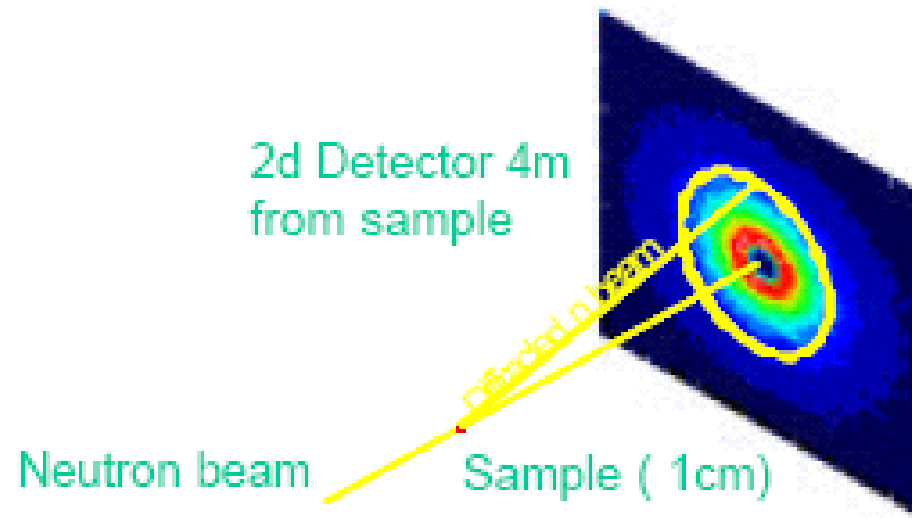


# SANS

Scattering (or diffraction) of X-rays, light, or neutrons at **small angles** is used to examine objects that are **large** compared to the wavelength ( $\lambda$ ) of the radiation used.

## LOQ at ISIS

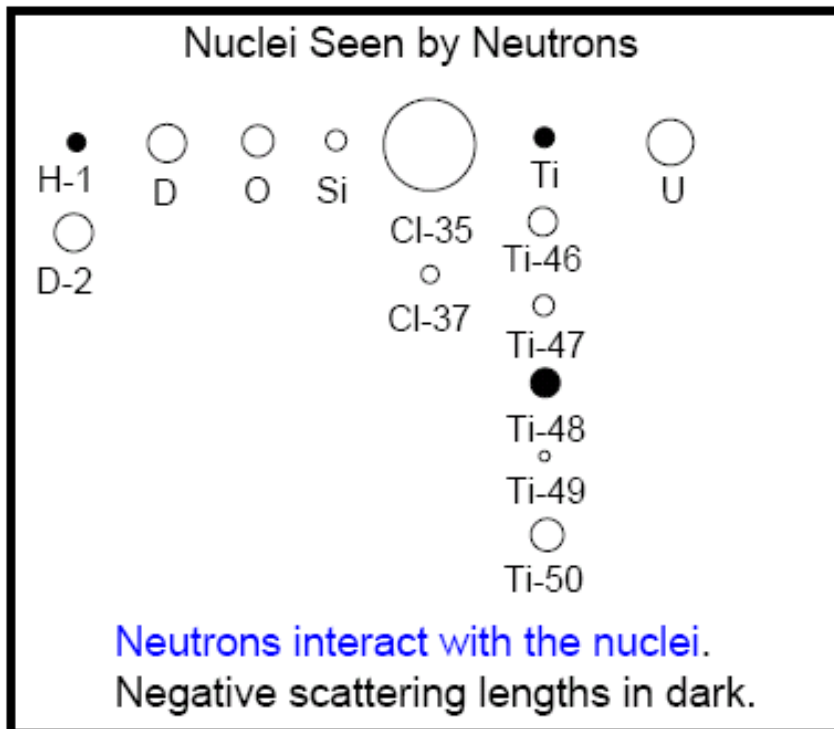
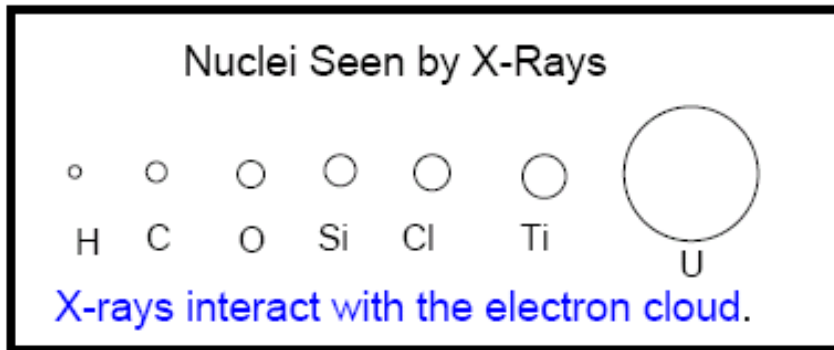


Sizes of interest = “large scale structures” = 1 – 300 nm or more

- Mesoporous structures
- Biological structures (membranes, vesicles, proteins in solution)
- Polymers
- Colloids and surfactants (micelles and more)
- Magnetic films and nanoparticles
- Voids and Precipitates

## WHY USE NEUTRONS?

- Neutrons interact through short-range nuclear interactions. They have no charge and are **very penetrating** and **do not destroy samples**.
- **Neutron wavelengths** are comparable to **atomic sizes** and interdistance spacings.
- Neutrons interactions with **hydrogen** and **deuterium** are widely different making the **deuterium labeling method** an advantage.



In the case of light or X-rays, the scattering cross-section of an atom (a concept which may be likened to the collision cross-section encountered in the classical derivation of chemical kinetic theory) increases in direct proportion to the number of electrons present; that is, it increases with increasing atomic number,  $Z$ . However, the strength of the neutron-nucleus interaction varies completely irregularly with  $Z$ ; not even isotopes of the same element have the same *neutron scattering cross-section*,  $\sigma$ . The most significant isotopic variation occurs when  $Z = 1$ . Hydrogen has a (coherent)  $\sigma_{coh}$  of  $1.75 \times 10^{-24} \text{ cm}^2$  (or, in physicists units, 1.75 barns) which is roughly the same as that of manganese. On the other hand, for deuterium  $\sigma_{coh} = 5.6$  barns, similar to the value for carbon-12. Thus, and unlike X-rays, not only can neutrons "see" hydrogen isotopes, but they can differentiate between them.

For neutrons,  $b_i$  depends on nucleus (isotope, spin relative to neutron ( $\uparrow\uparrow$  or  $\downarrow\uparrow$ )), etc. Even for one type of atom,

$$b_i = \langle b \rangle + \delta b_i \leftarrow \text{random variable}$$

- **Neutron “contrast variation” provides powerful and often unique insights.**
- **Carefully designed experiments provide information on much more than “structure” alone.**

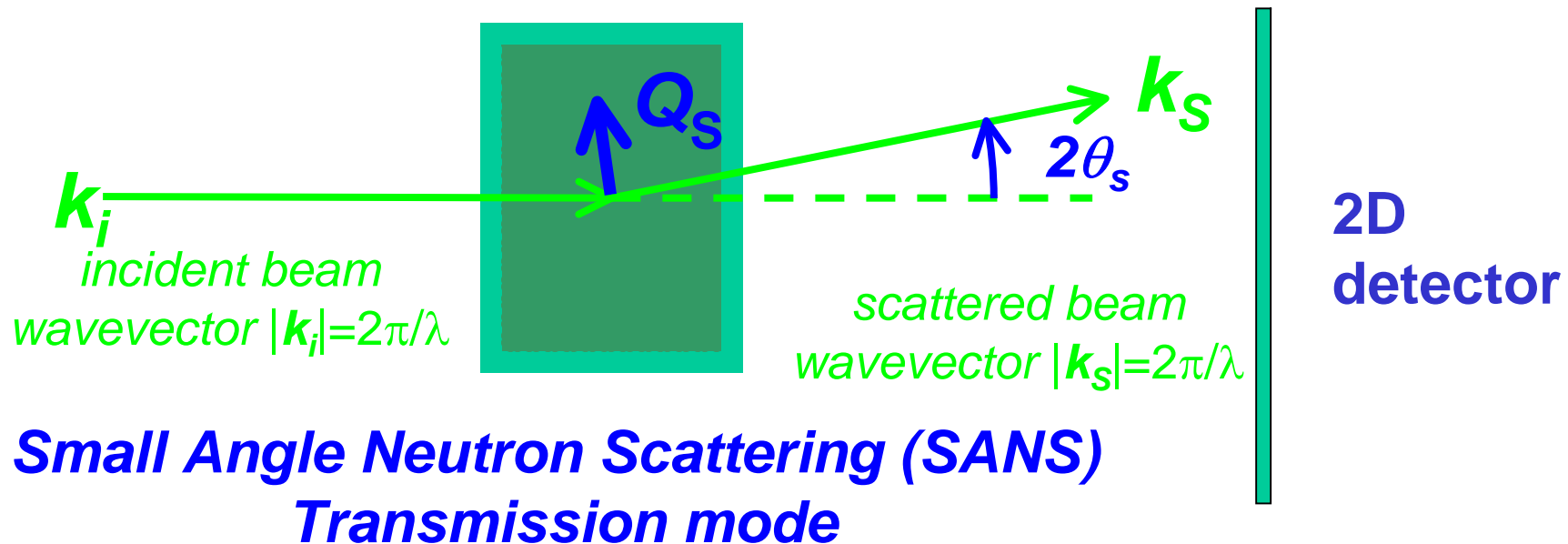
## The Neutron has Both Particle-Like and Wave-Like Properties

- Mass:  $m_n = 1.675 \times 10^{-27}$  kg
- Charge = 0; Spin =  $\frac{1}{2}$
- Magnetic dipole moment:  $\mu_n = -1.913 \mu_N$
- Nuclear magneton:  $\mu_N = eh/4\pi m_p = 5.051 \times 10^{-27}$  J T<sup>-1</sup>
- Velocity (v), kinetic energy (E), wavevector (k), wavelength ( $\lambda$ ), temperature (T).
- $E = m_n v^2/2 = k_B T = (hk/2\pi)^2/2m_n$ ;  $k = 2\pi/\lambda = m_n v/(h/2\pi)$

	<u>Energy (meV)</u>	<u>Temp (K)</u>	<u>Wavelength (nm)</u>
<b>Cold</b>	<b>0.1 – 10</b>	<b>1 – 120</b>	<b>0.4 – 3</b>
<b>Thermal</b>	<b>5 – 100</b>	<b>60 – 1000</b>	<b>0.1 – 0.4</b>
<b>Hot</b>	<b>100 – 500</b>	<b>1000 – 6000</b>	<b>0.04 – 0.1</b>

$$\lambda \text{ (nm)} = 395.6 / v \text{ (m/s)}$$

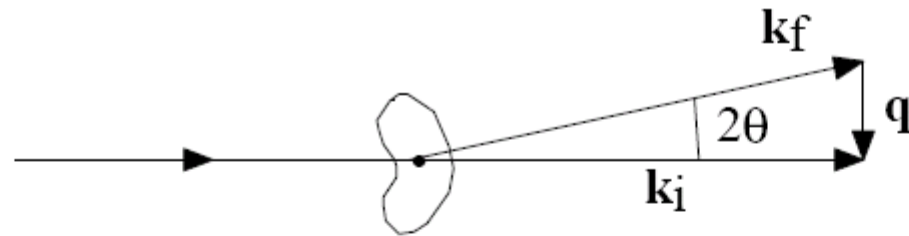
$$E \text{ (meV)} = 0.02072 k^2 \text{ (k in nm}^{-1}\text{)}$$



(elastic scattering)  $k_s = k_i + Q_s$   
 $Q_s = |Q_s| = 4\pi \sin\theta_s / \lambda$

A **diffraction pattern** is obtained (not a direct image)

- Rather than use scattering angle  $2\theta_s$  to show the diffraction pattern we use the **scattering vector Q** (in “reciprocal space”)



Constructive interference from structures in the direction of  $\mathbf{q}$

$$\text{Diffraction length scale } d \approx \frac{2\pi}{q}$$

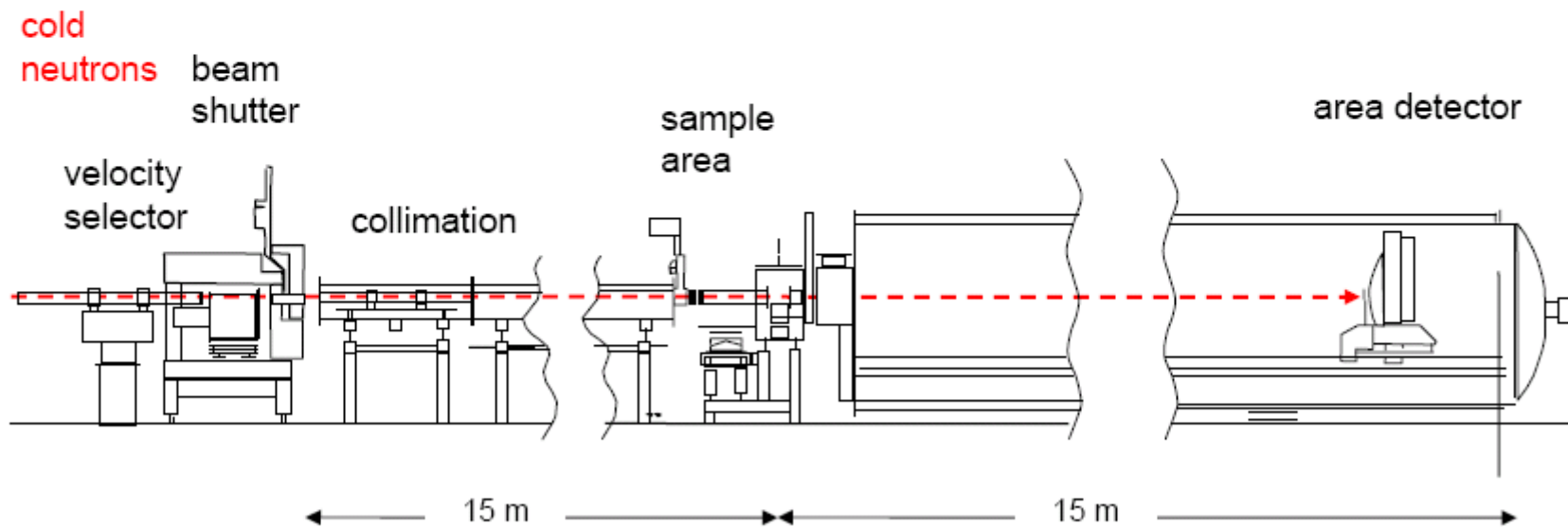
$$2\theta \approx \frac{\lambda}{d} \approx \frac{6\text{\AA}}{60 \text{ to } 1000\text{\AA}}$$

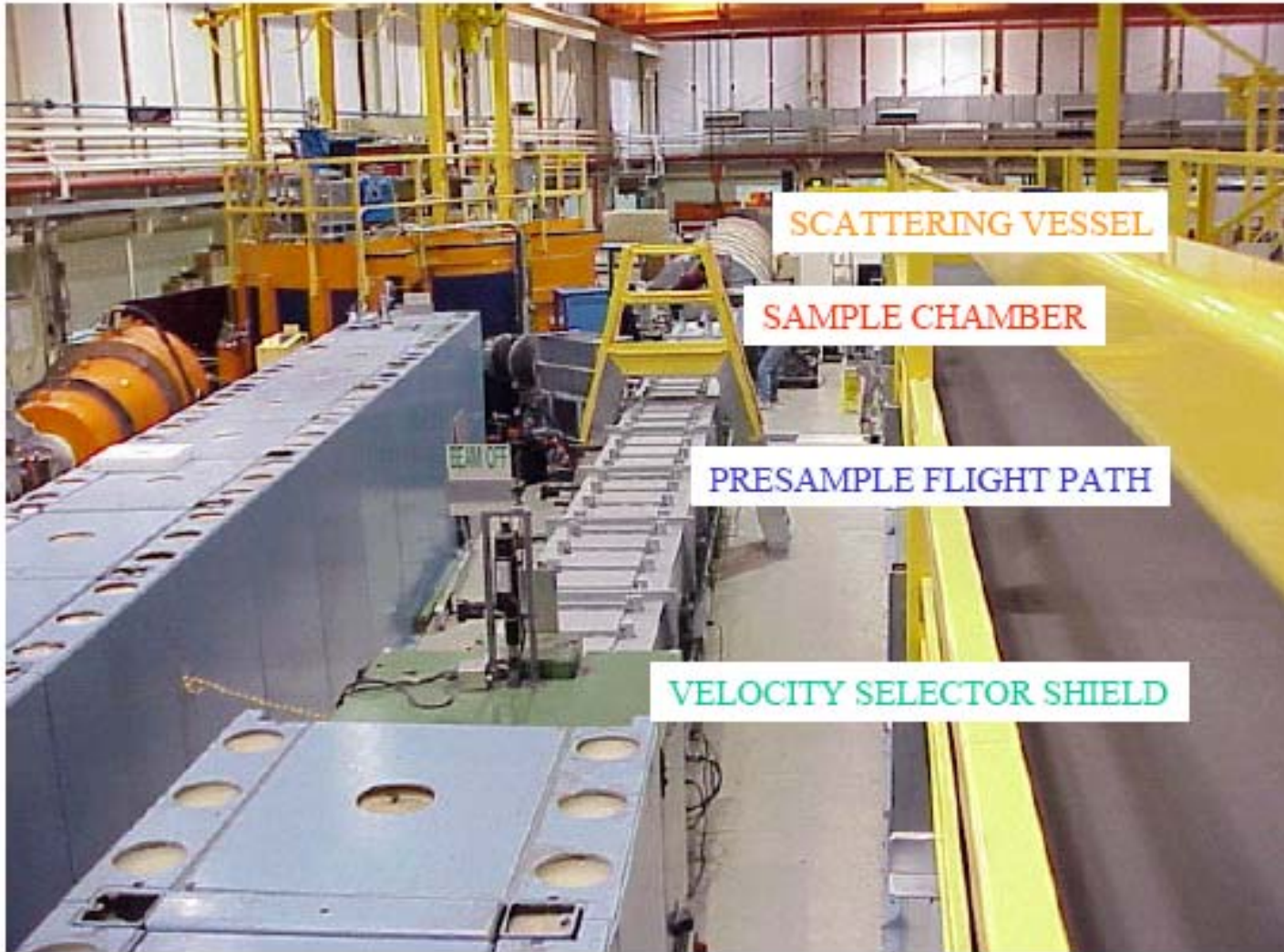
$$2\theta \approx 0.3^\circ \text{ to } 5^\circ$$

Scattering is at small angles - non-zero but smaller than classical diffraction angles



# The NG3 30 m NIST-SANS Instrument





SCATTERING VESSEL

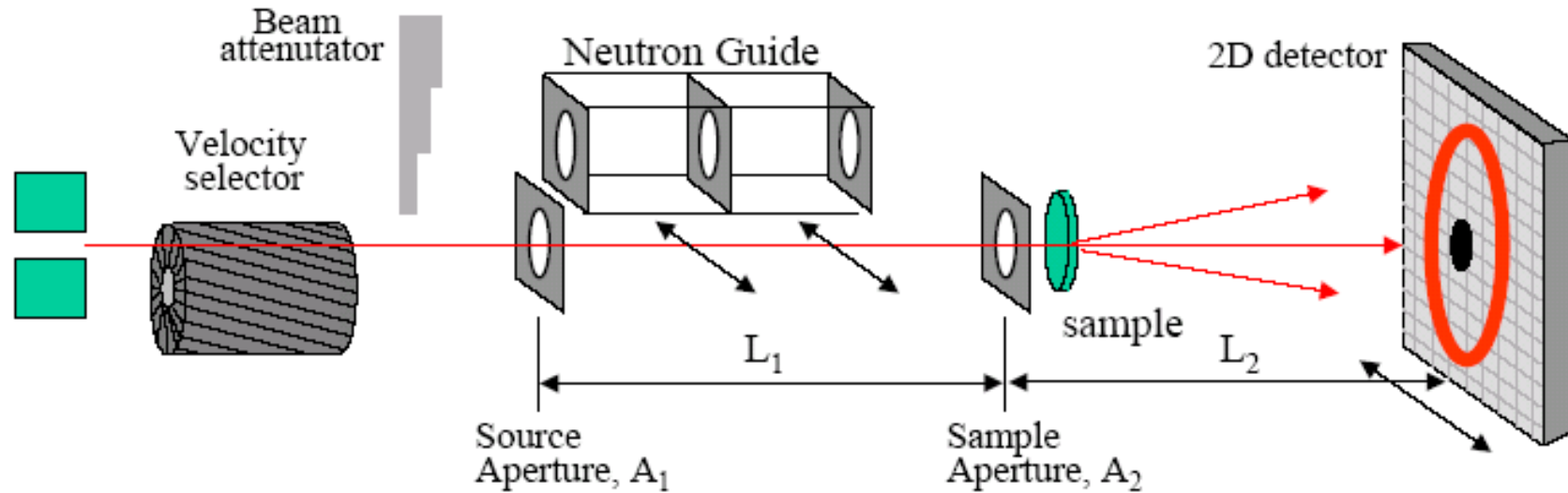
SAMPLE CHAMBER

PRESAMPLE FLIGHT PATH

VELOCITY SELECTOR SHIELD

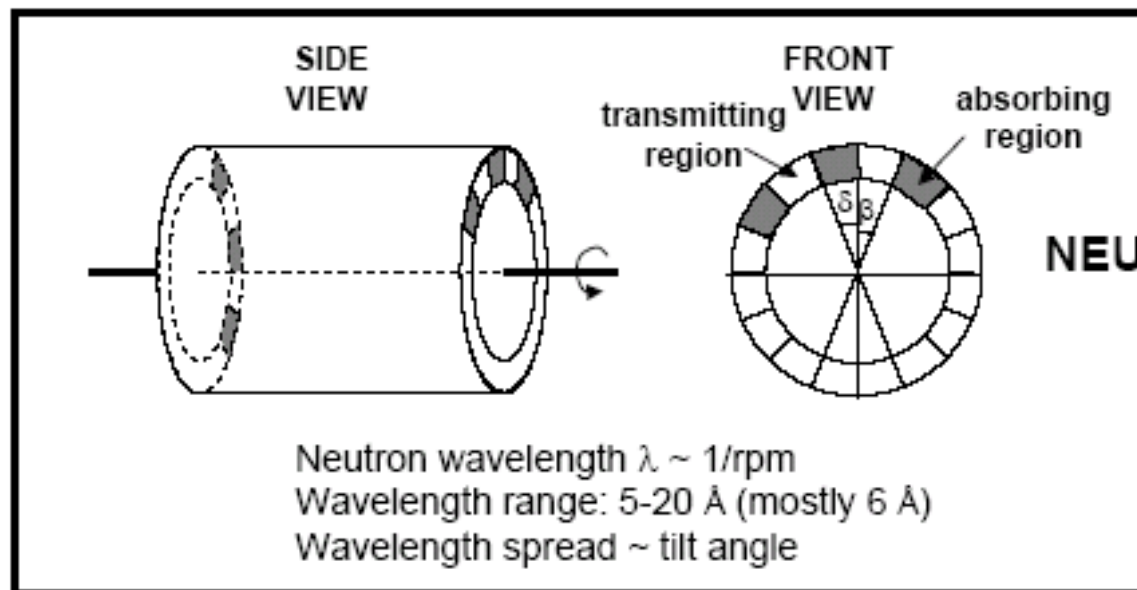
## 30 m NIST-SANS Instrument Characteristics

Source:	neutron guide (NG3), 6 x 6 cm <sup>2</sup>
Monochromator:	mechanical <a href="#">velocity selector</a> with variable speed and pitch
<a href="#">Wavelength Range:</a>	variable from 5 Å to 20 Å
Wavelength Resol.:	10% to 30% for $\Delta\lambda/\lambda$ (FWHM)
Source-to-Sample Dist.:	3.5 to 15m in 1.5m steps via insertion of neutron guides
Sample-to-Detector Dist.:	1.3 to 13.2 m continuously variable for NG3
Collimation:	circular pinhole collimation
Sample Size:	0.5 to 2.5 cm diameter
Q-range:	0.001 to 0.6 Å <sup>-1</sup>
<a href="#">Size Regime:</a>	<a href="#">10 Å to 6000 Å</a>
Detector:	64 x 64 cm <sup>2</sup> He-3 position-sensitive <a href="#">area detector</a> proportional counter (0.5 cm <sup>2</sup> resolution).



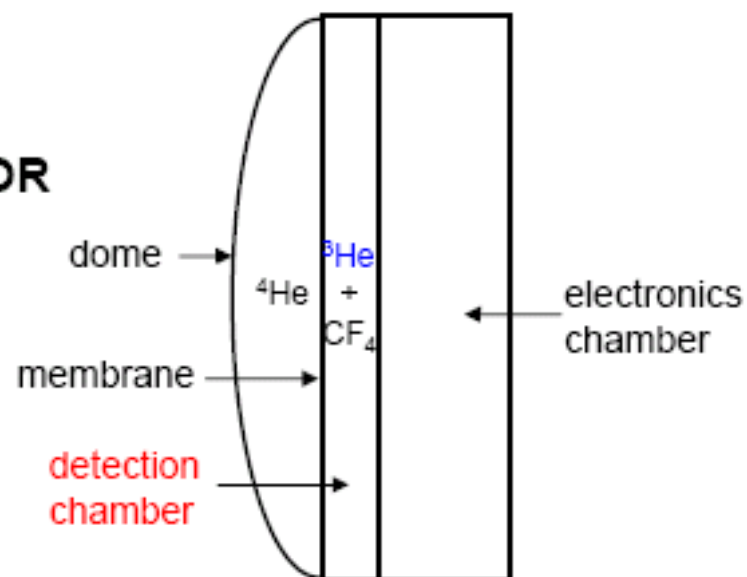
Why such a long instrument ?

When you perform an experiment you'll always try to have as much intensity as possible with a good resolution ( $\delta Q$ ). Essentially  $L_1 \approx L_2$



## NEUTRON VELOCITY SELECTOR

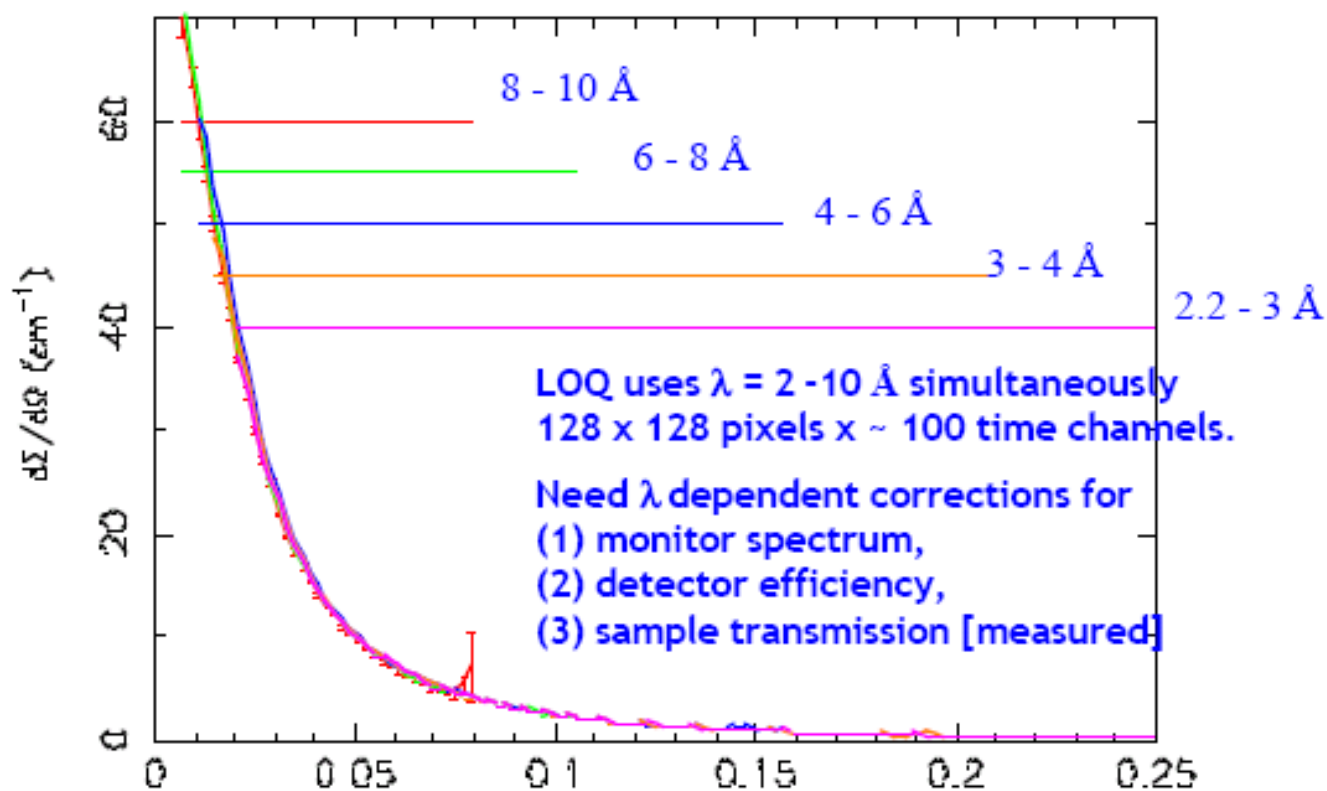
## NEUTRON AREA DETECTOR



neutron + He-3  $\rightarrow$  proton + tritium  
 Detector resolution =  $0.5 \times 0.5 \text{ cm}^2$

# TOF instruments

LOQ data reduction, (e.g. for 49% d-PS/ h-PS)



$$Q = \frac{4\pi}{\lambda} \sin(\theta/2)$$

## Small Angle Samples

### Neutrons –

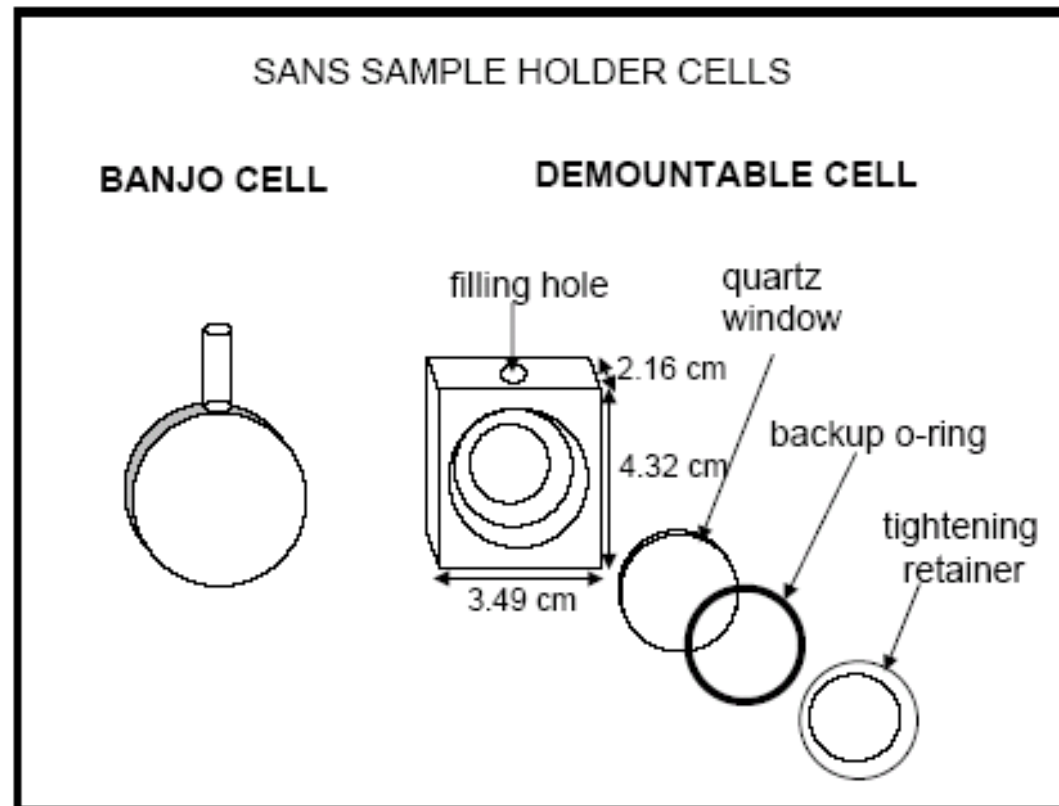
- 8-12 mm diameter beam
- 1mm thick ( 2mm in D<sub>2</sub>O)
- Quartz glass cells  
(as for UV spectroscopy, no Boron which adsorbs neutrons, as does Cadmium)
- Pressure, shear cells, cryostat, furnace etc, fairly easy

### X-Rays –

- $\ll$  1mm beam
- Thin samples
- Mica window cells
- Radiation damage and/or heating ?
- Powerful synchrotron X-ray beams do now allow more complex sample environment – but samples still fry!

## SANS SAMPLES AND CELL HOLDERS

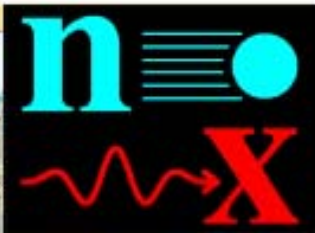
SANS samples can be **solid**, **gels**, **solutions** or powders.  
Sample **thicknesses** are **1 mm** to **2 mm**.  
Sample diameter can vary between **0.5 cm** and **2 cm**.

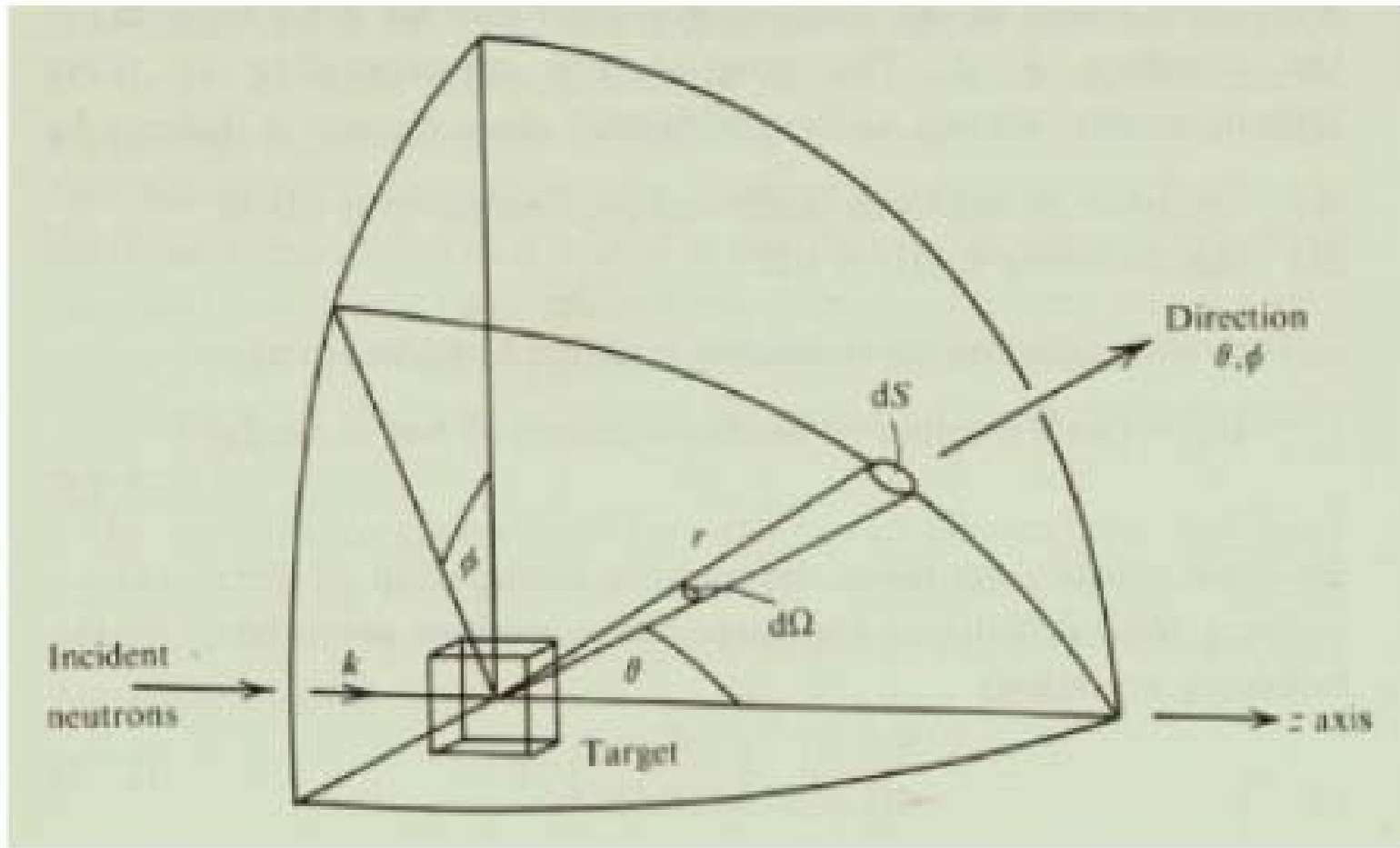






**Synchrotron-  
and Neutron  
Scattering  
Places**



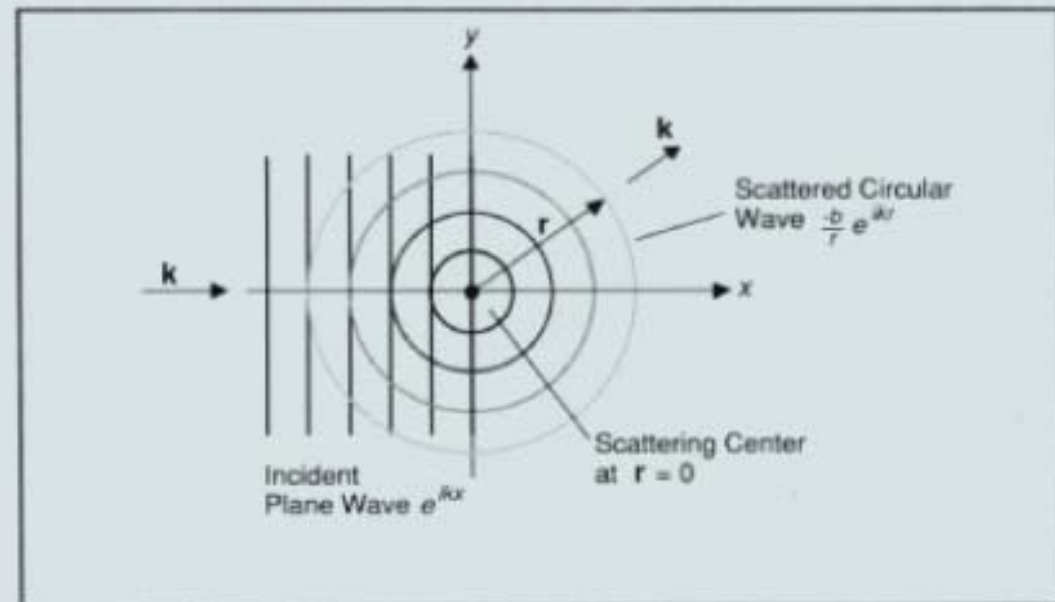


$\Phi$  = number of incident neutrons per  $\text{cm}^2$  per second

$\sigma$  = total number of neutrons scattered per second /  $\Phi$

$$\frac{d\sigma}{d\Omega} = \frac{\text{number of neutrons scattered per second into } d\Omega}{\Phi d\Omega}$$

# Scattering by a Single (fixed) Nucleus



- range of nuclear force ( $\sim 1$  fm) is  $\ll$  neutron wavelength so scattering is “point-like”
- energy of neutron is too small to change energy of nucleus & neutron cannot transfer KE to a fixed nucleus  $\Rightarrow$  scattering is elastic
- we consider only scattering far from nuclear resonances where neutron absorption is negligible

If  $v$  is the velocity of the neutron (same before and after scattering), the number of neutrons passing through an area  $dS$  per second after scattering is :

$$v dS |\psi_{\text{scat}}|^2 = v dS b^2/r^2 = v b^2 d\Omega$$

Since the number of incident neutrons passing through unit area is :  $\Phi = v |\psi_{\text{incident}}|^2 = v$

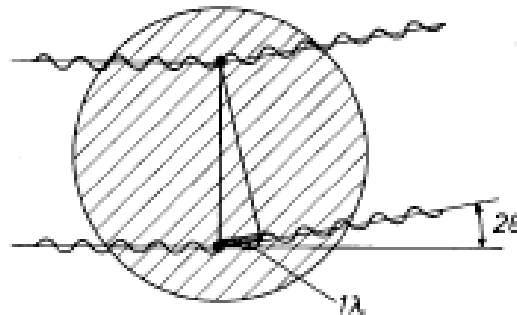
$$\frac{d\sigma}{d\Omega} = \frac{v b^2 d\Omega}{\Phi d\Omega} = b^2$$

$$\text{so } \sigma_{\text{total}} = 4\pi b^2$$

## Diffraction theory for SAS:

DO NOT PANIC if you are not good at maths ....

For a rotationally averaged or centro-symmetric particle:



Scattered waves from pairs of points in the sample interfere with each other.

Whole number of wavelengths  
“constructive interference” = Bragg condition.

Mathematically we sum the amplitudes and phases of the interfering waves over all possible “pairs of points”.

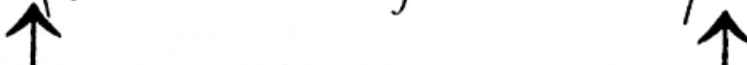
(“Points” could be individual atoms, but in SANS we do not usually know where the atoms are, so we average them out):

$$\frac{d\sigma}{d\Omega}(\vec{q}) = \frac{1}{N} \left| \sum_i^N b_i e^{i\vec{q}\cdot\vec{r}_i} \right|^2$$

$$V(\underline{r}) = \frac{2\pi\hbar^2}{m_n} \sum_i b_i \delta(\underline{r} - \underline{R}_i)$$

$$A(\underline{Q}) = \sum_i b_i e^{i\underline{Q} \cdot \underline{R}_i}$$

$$\frac{d\sigma}{d\Omega}(\underline{Q}) = |A(\underline{Q})|^2 = \left\langle \sum_i b_i e^{i\underline{Q} \cdot \underline{R}_i} \cdot \sum_j b_j^* e^{-i\underline{Q} \cdot \underline{R}_j} \right\rangle$$


  
 average over the random distribution

$$= \sum_i \sum_j \langle b_i b_j^* \rangle e^{i\underline{Q}(\underline{R}_i - \underline{R}_j)}$$

$$\langle b_i b_j \rangle = \begin{cases} \langle b \rangle \langle b \rangle = \langle b \rangle^2 & i \neq j \\ \langle b^2 \rangle = \langle b \rangle^2 + \langle (b - \langle b \rangle)^2 \rangle & i = j \end{cases}$$

$\uparrow$   
 $\langle (b - \langle b \rangle)^2 \rangle = \langle b^2 - 2b\langle b \rangle + \langle b \rangle^2 \rangle = \langle b^2 \rangle - \langle b \rangle^2$

$$\frac{d\sigma}{d\Omega}(\underline{Q}) = \langle b \rangle^2 \left| \sum_i e^{i\underline{Q} \cdot \underline{R}_i} \right|^2 \quad \text{"coherent"}$$

$$+ N \langle (b - \langle b \rangle)^2 \rangle \quad \text{"incoherent"}$$

---


$$\frac{d\sigma}{d\Omega}(\vec{q}) = \frac{1}{N} \left| \sum_i^N b_i e^{i\vec{q}\cdot\vec{r}} \right|^2$$

- We can replace the sum over atoms with integral over the scattering length density

$$\sum_i^N b_i \rightarrow \int_V \rho(\vec{r}) d\vec{r}$$

- Normalizing by sample volume and introducing scattering length density:

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{N}{V} \frac{d\sigma}{d\Omega}(\vec{q}) = \frac{1}{V} \left| \int_V \rho(\vec{r}) e^{i\vec{q}\cdot\vec{r}} d\vec{r} \right|^2$$

- Inhomogeneities in  $\rho(\vec{r})$  give rise to small angle scattering
- $\Sigma = \sigma/V$  is the “macroscopic cross section”

- Easier to think in terms of material properties rather than atomic properties
- Define a “Scattering Length Density”

$$\rho(\vec{r}) = b_i \delta(\vec{r} - \vec{r}_i)$$

or

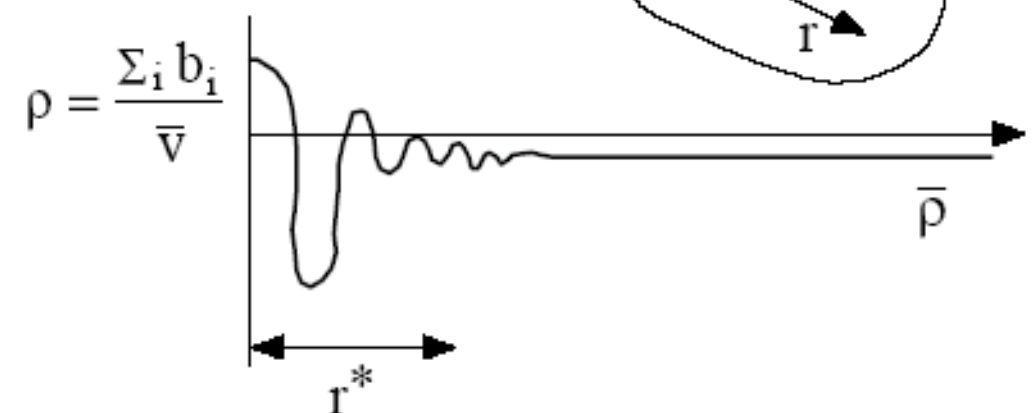
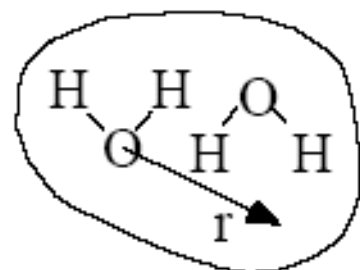
$$\rho = \frac{\sum_i^n b_i}{\bar{V}}$$

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



- Can we really use scattering length densities?

- consider  $\text{H}_2\text{O}$  :  $\bar{v} \approx 30 \text{ \AA}^3$   $r \approx 2 \text{ \AA}$



$$\frac{1}{q} > r^* \quad r^* \approx 10 \text{ \AA} \quad q \leq 0.1 \text{ \AA}^{-1}$$

$\approx 100$  molecules

- We can use material properties rather than atomic properties when doing small-angle scattering

## Neutron scattering length densities

$$\rho = \frac{\sum n_i b_i}{V} \quad \text{V can be any suitable volume, e.g. one molecule} \quad V_{MOLAR} = \frac{\rho_{BULK} N_A}{M}$$

$$\text{e.g. water} \quad V = \frac{1.0 \text{ g cm}^{-3} 6.023 \times 10^{23}}{18.0152 \text{ g mol}^{-1}} = 29.915 \times 10^{-24} \text{ cm}^3 = 29.915 \text{ \AA}^3$$

$$\text{H}_2\text{O} \quad \rho = \frac{(2 \times (-0.3739) + 0.580) \times 10^{-12} \text{ cm}}{29.915 \times 10^{-24} \text{ cm}^3} = -0.56 \times 10^{10} \text{ cm}^{-2}$$

$$\text{D}_2\text{O} \quad \rho = \frac{(2 \times 0.667 + 0.580) \times 10^{-12} \text{ cm}}{29.915 \times 10^{-24} \text{ cm}^3} = 6.40 \times 10^{10} \text{ cm}^{-2}$$

**NOTE** units of length per unit volume!

$\times 10^{10} \text{ cm}^{-2}$  is the same as  $\times 10^6 \text{ \AA}^{-2}$ ,  $1 \text{ \AA} = 10^{-8} \text{ cm} = 0.1 \text{ nm}$

$^1\text{H}$  ( $^7\text{Li}$ ,  $^{62}\text{Ni}$ ,  $^{48}\text{Ti}$  etc) have a **negative**  $b$  due to phase shift via neutron spin interaction.

## Digression - useful units!

Distances in **Angstrom**,  $1 \text{ \AA} = 10^{-10} \text{ m} = 10^{-8} \text{ cm} = 0.1 \text{ nm}$

Scattering lengths are in **femtometres**,  $1 \text{ fm} = 10^{-15} \text{ m}$

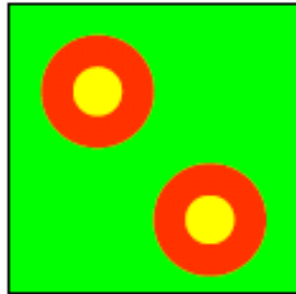
Total and absorption cross sections in **“barns”**,  $1 \text{ barn} = 10^{-24} \text{ cm}^2$

Neutron wide angle diffraction scattering cross sections are often **“barns per molecule”** or **“barns per atom”**

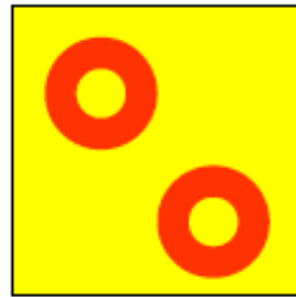
To go from SANS type  $\text{cm}^{-1}$  to **barns per molecule** (both have implied “per steradian” for scattering probability per unit solid angle)  
multiply by  $V_{\text{MOLAR}}$  in  $\text{\AA}^3$ .

$$\begin{aligned}(\partial\Sigma/\partial\Omega) [\text{cm}^{-1}] \times V [\text{\AA}^3] &= (\partial\Sigma/\partial\Omega) [\text{cm}^{-1}] V [10^{-24} \text{ cm}^3] \\ &= (\partial\Sigma/\partial\Omega)' [10^{-24} \text{ cm}^2] \\ &= (\partial\Sigma/\partial\Omega)' [\text{barns}]\end{aligned}$$

- Contrast Matching
  - reduce the number of phases 'visible'

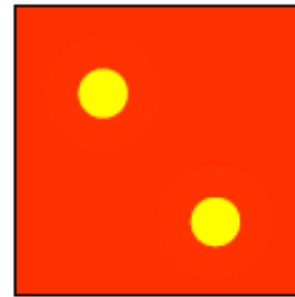


becomes...



$\rho$  solvent =  $\rho$  core  
(shell visible)

or



$\rho$  solvent =  $\rho$  shell  
(core visible)

- The two distinct two-phase systems can be easily understood

$$\frac{d\sigma}{d\Omega}(\vec{q}) = \text{differential cross section}$$

- normalize by scattering volume

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{N}{V} \frac{d\sigma}{d\Omega}(\vec{q}) = \text{scattering per unit volume}$$

- Two contributions to measured signal:

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{d\Sigma_{\text{coh}}}{d\Omega}(\vec{q}) + \frac{d\Sigma_{\text{inc}}}{d\Omega}$$

- Incoherent scattering is not q-dependent and contributes only to the noise level, while absorption reduces the overall signal

$$\frac{d\Sigma}{d\Omega}(\vec{q}) \propto I(q) = \begin{array}{l} \text{"Scattered Intensity"} \\ \text{(measured quantity)} \end{array}$$

## **Small Angle Neutron Scattering (SANS)**

*Macromolecular structures: polymers, micelles, complex fluids,  
precipitates, porous media, fractal structures*

*Measure: Scattered Intensity => Macroscopic cross section  
= (Scattered intensity(Q) / Incident intensity) T d*

$$\frac{d\Sigma}{d\Omega} [\vec{Q}_s] = \frac{\left| \iiint_{V_s} \Delta\rho[\vec{r}] \exp[i\vec{Q}_s \cdot \vec{r}] d^3\vec{r} \right|^2}{V_s}$$

*|3-D Fourier Transform of scattering contrast|<sup>2</sup>  
normalized to sample scattering volume*

*Reciprocity in diffraction:*

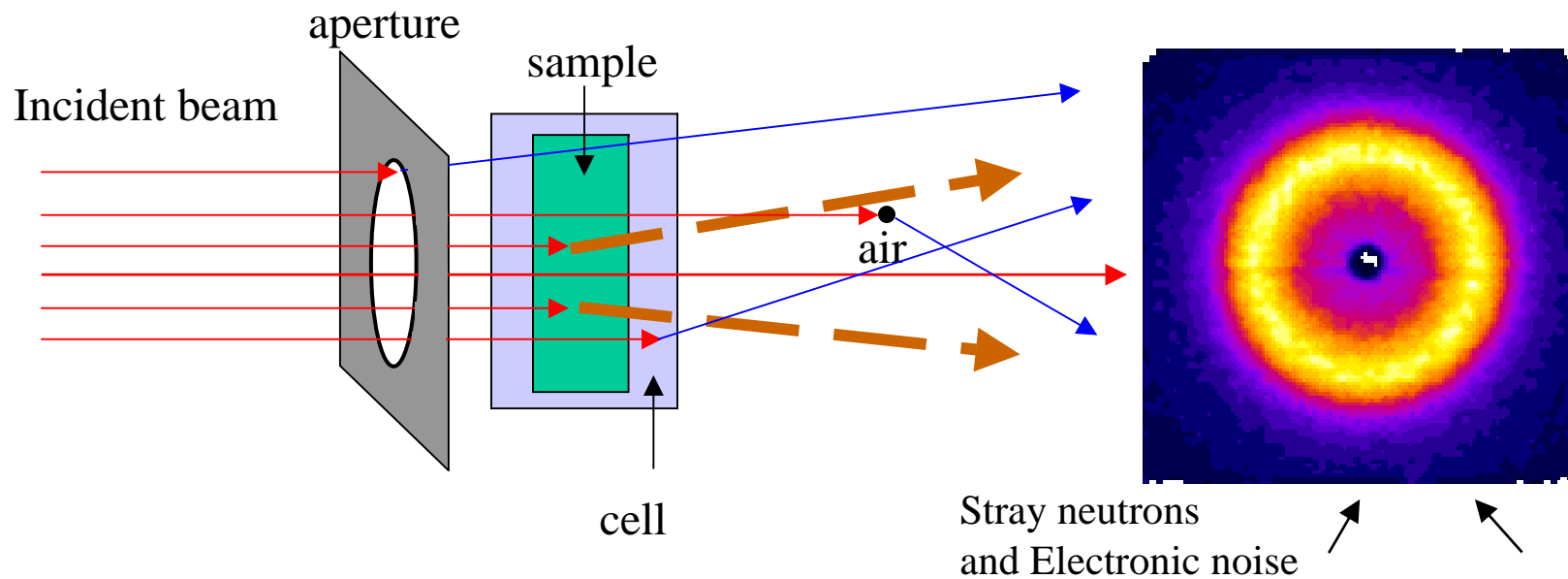
*Fourier features at  $Q_s$  => size  $d \sim 2\pi/Q_s$*

*Intensity at smaller  $Q_s$  (angle) => larger structures*

# Sample Scattering

- Contribution to detector counts

- 1) Scattering from sample
- 2) Scattering from other than sample (neutrons still go through sample)
- 3) Stray neutrons and electronic noise (neutrons don't go through sample)



$$I_{\text{meas}}(\mathbf{i}) = \Phi t A \varepsilon(\mathbf{i}) \Delta\Omega T_{c+s} [(d\Sigma/d\Omega)_s(\mathbf{i}) d_s + (d\Sigma/d\Omega)_c(\mathbf{i}) d_c] + I_{\text{bgd}} t$$

## SANS DATA ACQUISITION

- Choose **neutron wavelength** ( $\lambda = 6 \text{ \AA}$ ) and **wavelength spread** ( $\Delta\lambda/\lambda = 15\%$ ).
- Choose **source-to-sample distance**  $L_1$  and **sample-to-detector distance**  $L_2$ .
- Choose counting time.
- Measure scattering:
  - Empty cell** scattering
  - Sample** scattering
  - Blocked beam** scattering
- Measure **transmission**:
  - Cell transmission
  - Empty cell transmission
- Neutron transmission is the ratio of the transmitted beam to the incident beam.



## SANS DATA REDUCTION

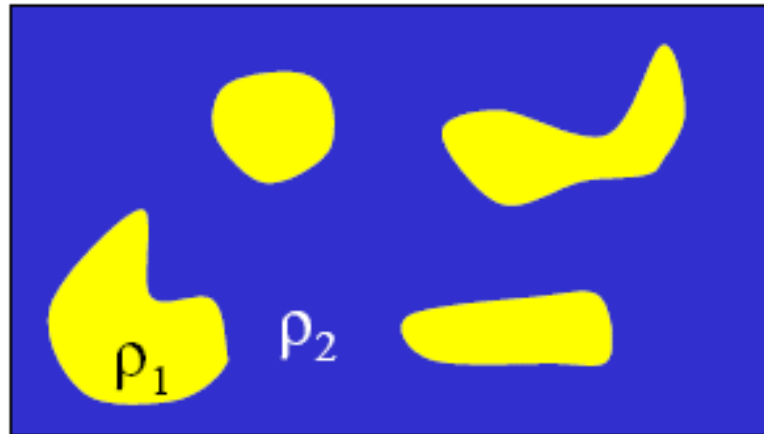
Correct for **empty cell** and **blocked beam** scattering.

$$I(Q) = [I_{\text{sample+cell}} - I_{\text{blocked beam}}] / T_{\text{sample+cell}} - [I_{\text{cell}} - I_{\text{blocked beam}}] / T_{\text{cell}}$$

Rescale the SANS **intensity** to an **absolute** scale (units of  $\text{cm}^{-1}$ ).

Perform the radial averaging for isotropic scattering to obtain the Q-dependent macroscopic **cross section**  $I(Q) = d\Sigma(Q)/d\Omega$ .

# General Two-Phase System



- Incompressible phases of scattering length density  $\rho_1$  and  $\rho_2$

$$V = V_1 + V_2$$

$$\rho(\mathbf{r}) = \begin{cases} \rho_1 & \text{in } V_1 \\ \rho_2 & \text{in } V_2 \end{cases}$$

- break the total volume into two sub-volumes

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{1}{V} \left| \int_{V_1} \rho_1 e^{i\vec{q}\cdot\vec{r}} d\vec{r}_1 + \int_{V_2} \rho_2 e^{i\vec{q}\cdot\vec{r}} d\vec{r}_2 \right|^2$$

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{1}{V} \left| \rho_1 \int_{V_1} e^{i\vec{q}\cdot\vec{r}} d\vec{r}_1 + \rho_2 \left\{ \int_V e^{i\vec{q}\cdot\vec{r}} d\vec{r} - \int_{V_1} e^{i\vec{q}\cdot\vec{r}} d\vec{r}_1 \right\} \right|^2$$

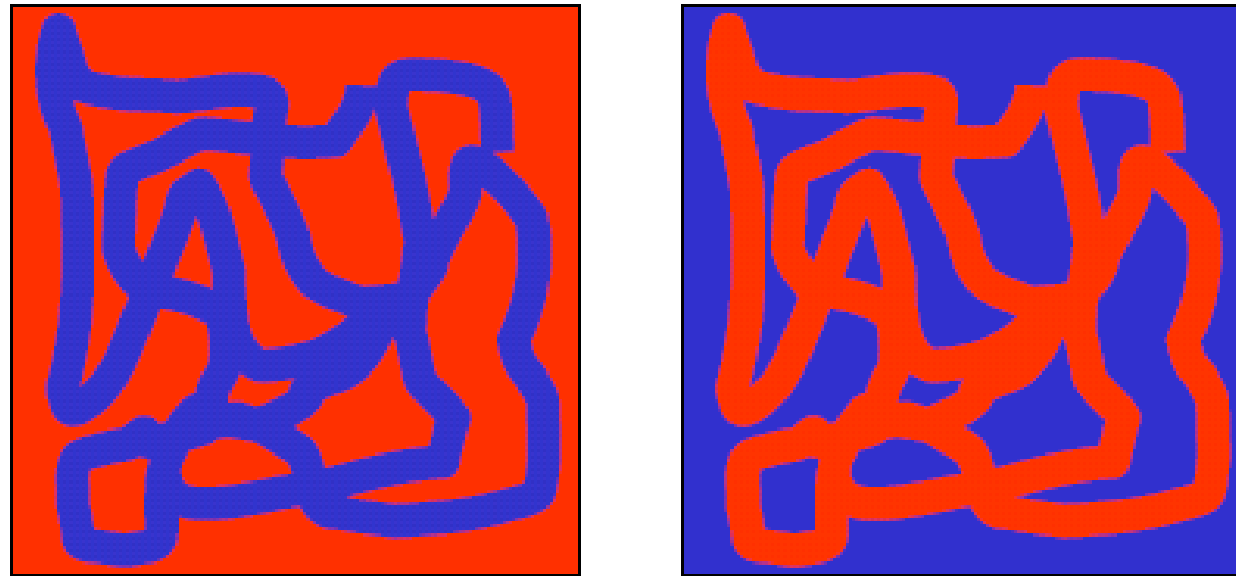
- So at non-zero q-values:

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{1}{V} (\rho_1 - \rho_2)^2 \left| \int_{V_1} e^{i\vec{q}\cdot\vec{r}} d\vec{r}_1 \right|^2$$

Material Properties  
+  
Radiation Properties

Spatial Arrangement  
of Material

# Babinet's Principle

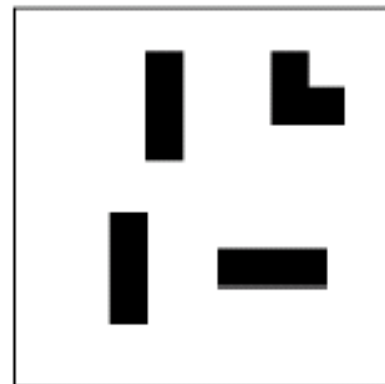
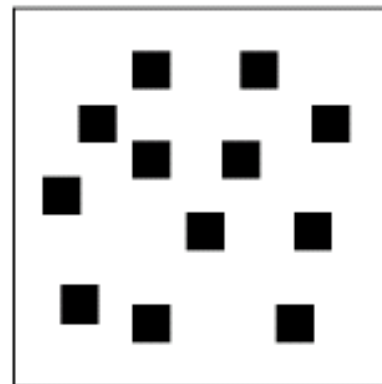


Two structures give the same scattering

$$\frac{d\Sigma}{d\Omega}(\vec{q}) \propto (\rho_1 - \rho_2)^2$$

\*incoherent scattering may be different

# Scattering Invariant



10 % black  
90 % white  
in each square

- Scattered intensity for each would certainly be different

$$Q_I \equiv \int_0^\infty q^2 \frac{d\Sigma}{d\Omega}(q) dq$$

- For an incompressible, two-phase system:

$$Q_I = 2\pi^2 \Delta\rho^2 \phi(1 - \phi)$$

- Domains can be in any arrangement

**Dilute particles – subtract uniform solvent & sum over one particle:**

$$\begin{aligned} P(Q) &= N \int_V \int_V (\rho(\underline{r}_1) - \rho_s)(\rho(\underline{r}_2) - \rho_s) \exp\{-iQ(\underline{r}_1 - \underline{r}_2)\} dV_1 dV_2 \\ &= NV^2 (\Delta\rho)^2 F^2(Q) \quad \text{Note } NV = \phi \text{ volume fraction} \end{aligned}$$

**Randomly oriented or centro-symmetric particle, ONLY gives information on average radial density distribution  $\rho(r)$  or  $g(r)$  :**

$$F(Q) = \int 4\pi r^2 \rho(r) \frac{\sin(Qr)}{Qr} dr$$

[ This is a Fourier transform: **small Q is for large  $r$ , high Q for small  $r$**  ]

## SANS from Dilute (i.e. Independent) Particles

"Dilute" means:

- no correlation between positions or orientations of particles

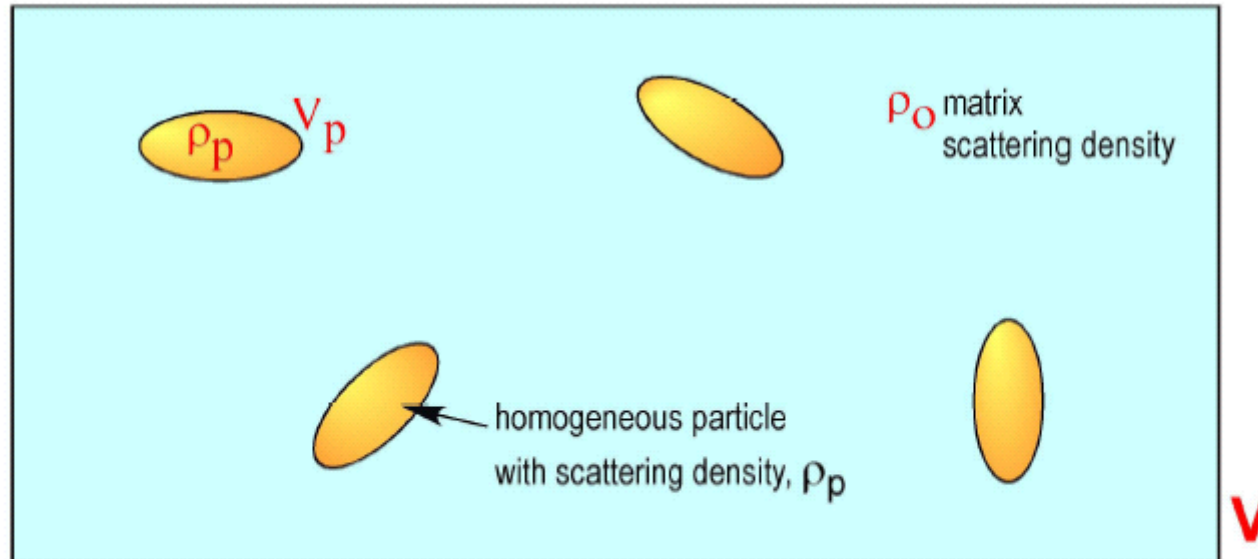
"Particle" means:

- any discrete submicron scale material inhomogeneity

### Simple (uniform) Particles

- macromolecules, e.g., proteins, polymer chains
- single phase precipitates in metal alloys
- voids, pores, microcracks, etc.
- simple colloids, e.g., latex

## Scattering from Dilute, Homogeneous Particles



$$I(\vec{Q}) \propto \frac{d\Sigma(\vec{Q})}{d\Omega} = \frac{1}{V} \left| \int_V \rho(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r} \right|^2$$



for identical particles

$$\frac{d\Sigma(\vec{Q})}{d\Omega} = \frac{N}{V} (\rho_p - \rho_o)^2 V_p^2 \left| \frac{1}{V_p} \int e^{i\vec{Q}\cdot\vec{r}} d\vec{r} \right|^2$$

Contrast Factor

Particle Shape

$|F_p(\vec{Q})|^2$  Form Factor

# SANS From Randomly Oriented Particles

## - Guinier Approximation for Low-Q Scattering

average over orientations

$$I_p(Q) \propto \frac{d\Sigma(Q)}{d\Omega} = \frac{1}{V} \left\langle \left| \int_V \rho(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d\vec{r} \right|^2 \right\rangle$$

$$\frac{d\Sigma(Q)}{d\Omega} = \frac{1}{V} \iint_V \rho(\vec{r}) \rho(\vec{r}') \langle e^{i\vec{Q}\cdot(\vec{r}-\vec{r}')} \rangle d\vec{r} d\vec{r}'$$

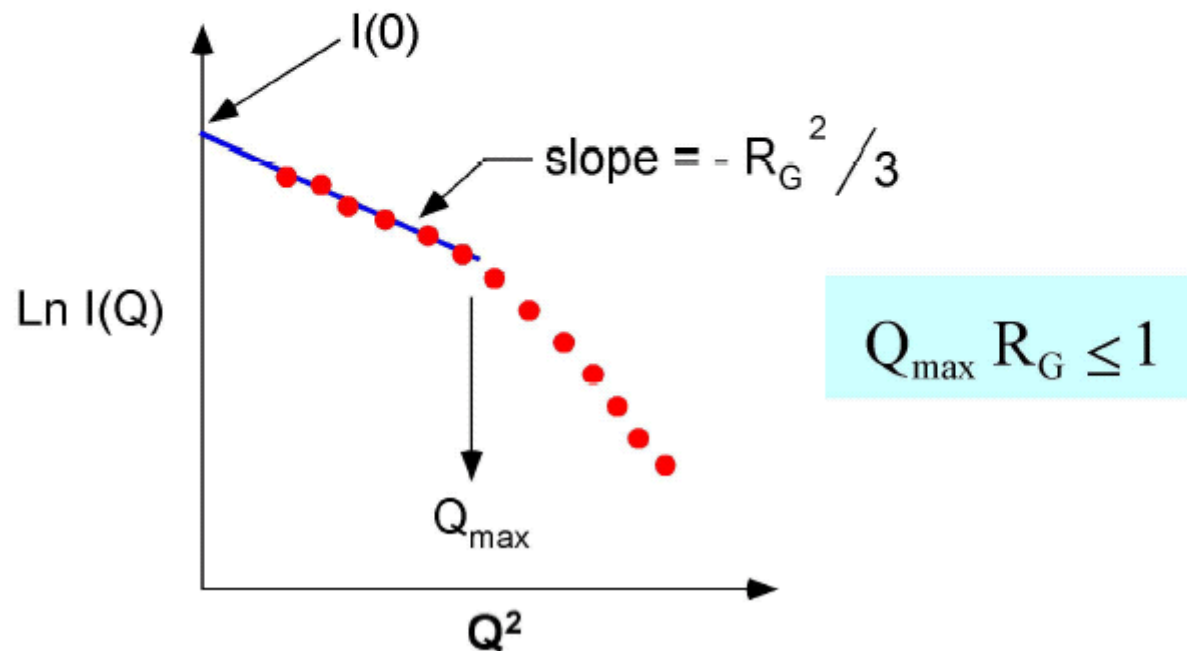
$$\frac{\sin(Q|\vec{r}-\vec{r}'|)}{Q|\vec{r}-\vec{r}'|} \sim 1 - \frac{1}{6}(Q|\vec{r}-\vec{r}'|)^2 + \dots$$

$$\frac{d\Sigma(Q)}{d\Omega} = \frac{1}{V} \left( \int_V \rho(\vec{r}) d\vec{r} \right)^2 \left[ 1 - \frac{1}{3} Q^2 R_G^2 + \dots \right]$$

$$I_p(Q) \cong I_p(0) e^{-\frac{1}{3} Q^2 R_G^2} \quad \text{when } QR_G \leq 1, \quad \text{Guinier law}$$

**Guinier Approximation:**  $I(Q) \cong I(0)e^{-\frac{1}{3}R_G^2 Q^2}$

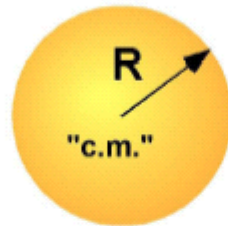
**Guinier Plot**  $\ln[I(Q)] = \ln[I(0)] - Q^2 R_G^2 / 3$



## Guinier Radius, $R_G$

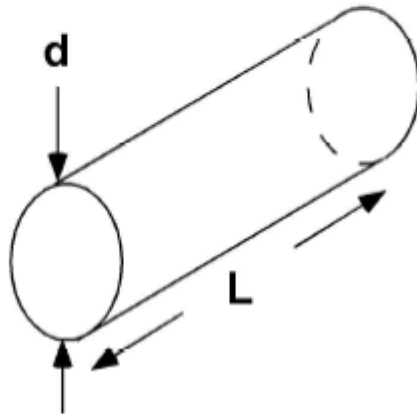
- rms distance from "center of scattering density"

### 1) Spherical Particles



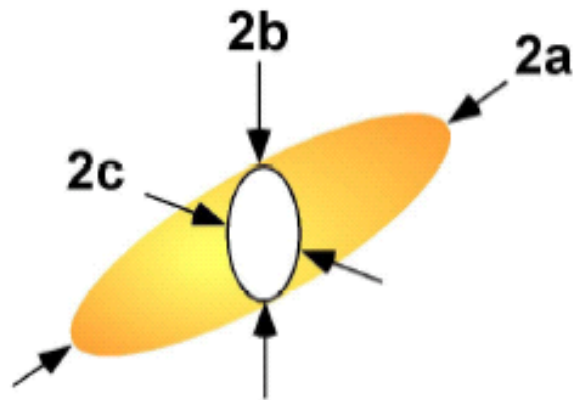
$$R_G^2 = \langle r^2 \rangle = \frac{\int \eta(\vec{r}) r^2 d\vec{r}}{\int \eta(\vec{r}) d\vec{r}} = \frac{3}{5} R^2$$

### 2) Cylinders (Rods or Disks)



$$R_G^2 = \frac{L^2}{12} + \frac{d^2}{8}$$

3) Ellipsoids (major axes 2a, 2b, 2c)



$$R_G^2 = \frac{1}{5}(a^2 + b^2 + c^2)$$

4) Gaussian chain



$$R_G^2 = \frac{1}{6} \overline{L^2} \quad \overline{L^2} = \text{average square of the end-to-end distance}$$

From Scattering Extrapolated to  $Q=0$

$$I(0) \propto \frac{d\Sigma(0)}{d\Omega} = \frac{1}{V} \left( \int_V \rho(\vec{r}) d\vec{r} \right)^2$$

$$\frac{d\Sigma(0)}{d\Omega} = \frac{N}{V} (\rho_p - \rho_o)^2 V_p^2 \quad \leftarrow \text{for } N \text{ uniform particles}$$

in volume,  $V$ , each with  
sld  $\rho_p$  and volume,  $V_p$

in terms of:

$$\begin{aligned} c(\text{particle concentration}) [\text{mg/ml}] &= \frac{N \rho V_p}{V} \\ M_w (\text{particle molecular weight}) &= \rho V_p N_A \end{aligned}$$

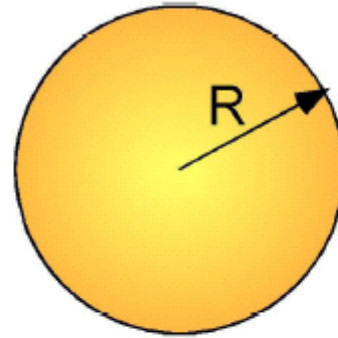
$$\frac{d\Sigma(0)}{d\Omega} = \frac{c M_w}{\rho N_A} (\rho_p - \rho_o)^2$$

$N_A$  = Avogadro's number

$\rho$  = mass density

## Form Factors for Some Simple Particle Shapes:

1) Spheres



$$\langle |F(Q, R)|^2 \rangle = \left\langle \left| \frac{1}{V_p} \int_{V_p} e^{i\vec{Q} \cdot \vec{r}} d\vec{r} \right|^2 \right\rangle$$

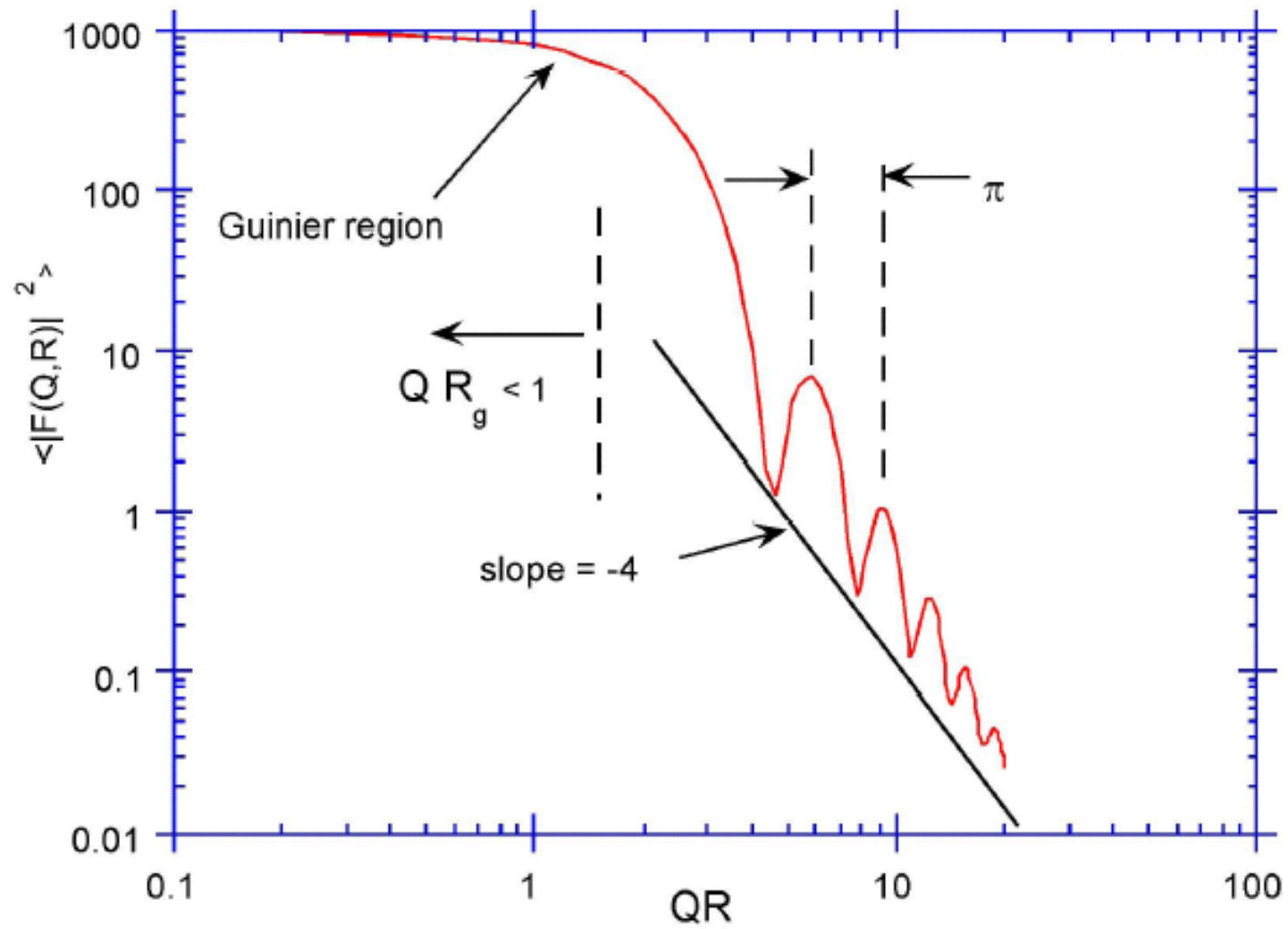
$$\langle |F(Q, R)|^2 \rangle = 9 \left[ \frac{\sin(QR) - QR \cos(QR)}{(QR)^3} \right]^2$$

$$I(Q) = NV^2 (\Delta\rho)^2 P(Q) + BKG$$

$$P(Q) = F^2(Q, r) \rightarrow 1 \text{ as } Q \rightarrow 0$$



### (Form Factor) <sup>2</sup> for Monodispersed Spheres



## Cylinder (rod or disc)

$$I(Q) = N(\Delta\rho)^2 V^2 \int_0^{\pi/2} F^2(Q) \sin(\gamma) d\gamma$$

$$F(Q) = \frac{\sin(\frac{1}{2}QL \cos \gamma)}{\frac{1}{2}QL \cos \gamma} \frac{2J_1(QR \sin \gamma)}{QR \sin \gamma}$$

Randomly oriented rods full length  $L$ , radius  $R$ ,  $V = \pi R^2 L$

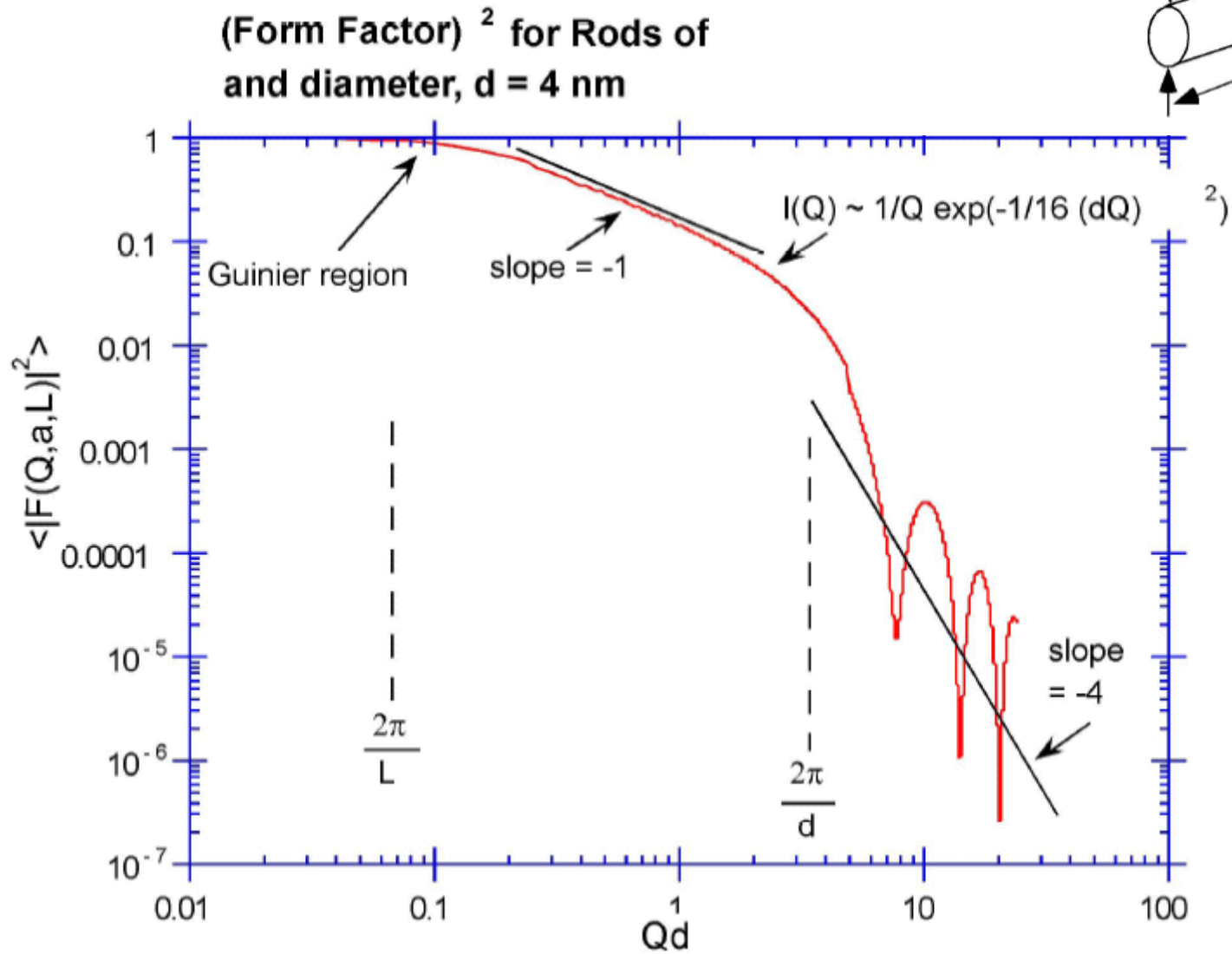
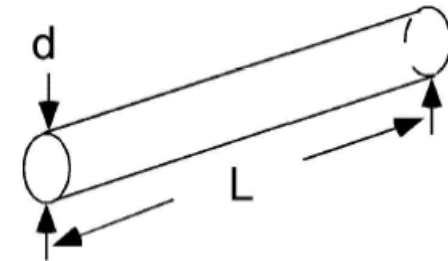
$J_1(x)$  = “first order Bessel function of the first kind”  
is **NOT** same as  $j_1(x)$  on next slide!

As  $x \rightarrow 0$ ,  $J_1(x)/x \rightarrow \frac{1}{2}$  &  $\sin(x)/x \rightarrow 1$  so  $P(Q \rightarrow 0) = 1$

**Integrate numerically** over  $\gamma$  = angle between  $\underline{Q}$  and rod axis.

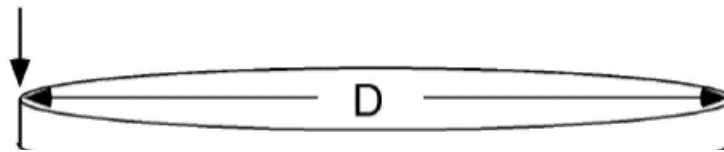
# Form Factors for Some Simple Particle Shapes:

## 2) Long Rods:

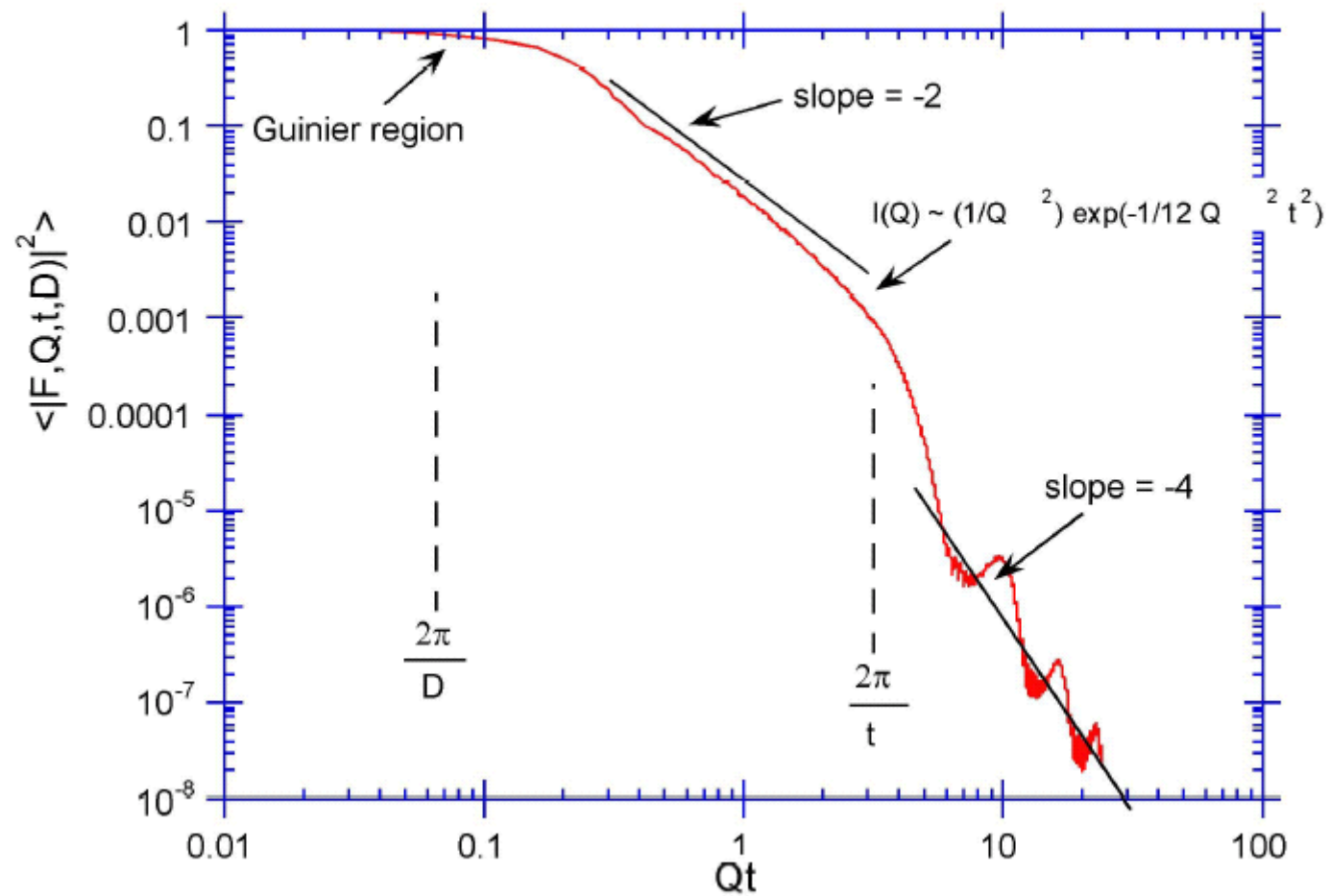


## Form Factors for Some Simple Shapes:

### 3) Thin Disks



**(Form Factor)<sup>2</sup> for Thin Disks of Diameter,  $D = 80$  nm,  
and Thickness,  $t = 4$  nm**



## Ellipsoid

ellipsoid radii  $R$ ,  $R$ , and  $XR$

$X > 1$  prolate (~ rugby ball),

$X < 1$  oblate (~ pumpkin),  $X = 1$  sphere.

$$V = \frac{4\pi}{3} XR^3$$

$$I(Q) = N(\Delta\rho)^2 V^2 \int_0^{\pi/2} F^2(u) \sin(\gamma) d\gamma$$

$$F(u) = \frac{j_1(u)}{u} = \frac{3(\sin(u) - u \cos(u))}{u^3} \quad u = QR(\sin^2 \gamma + X^2 \cos^2 \gamma)^{1/2}$$

Note  $F(u)$  is same as  $F(QR)$  for sphere!

Change of variable to  $\mu = \cos(\gamma)$  makes computation simpler:

$$I(Q) = N(\Delta\rho)^2 V^2 \int_0^1 F^2(u) d\mu \quad u = QR((1 - \mu^2) + X^2 \mu^2)^{1/2}$$

Can be hard to distinguish  $X < 1$  and  $X > 1$ , and also polydisperse spheres - absolute intensities, shape at high  $Q$ , and  $S(Q)$  may help.

## Gaussian coil (ideal polymer)

$$I(Q) = I_0 \cdot \left\{ 2(y - 1 + \exp(-y)) / y^2 \right\}$$

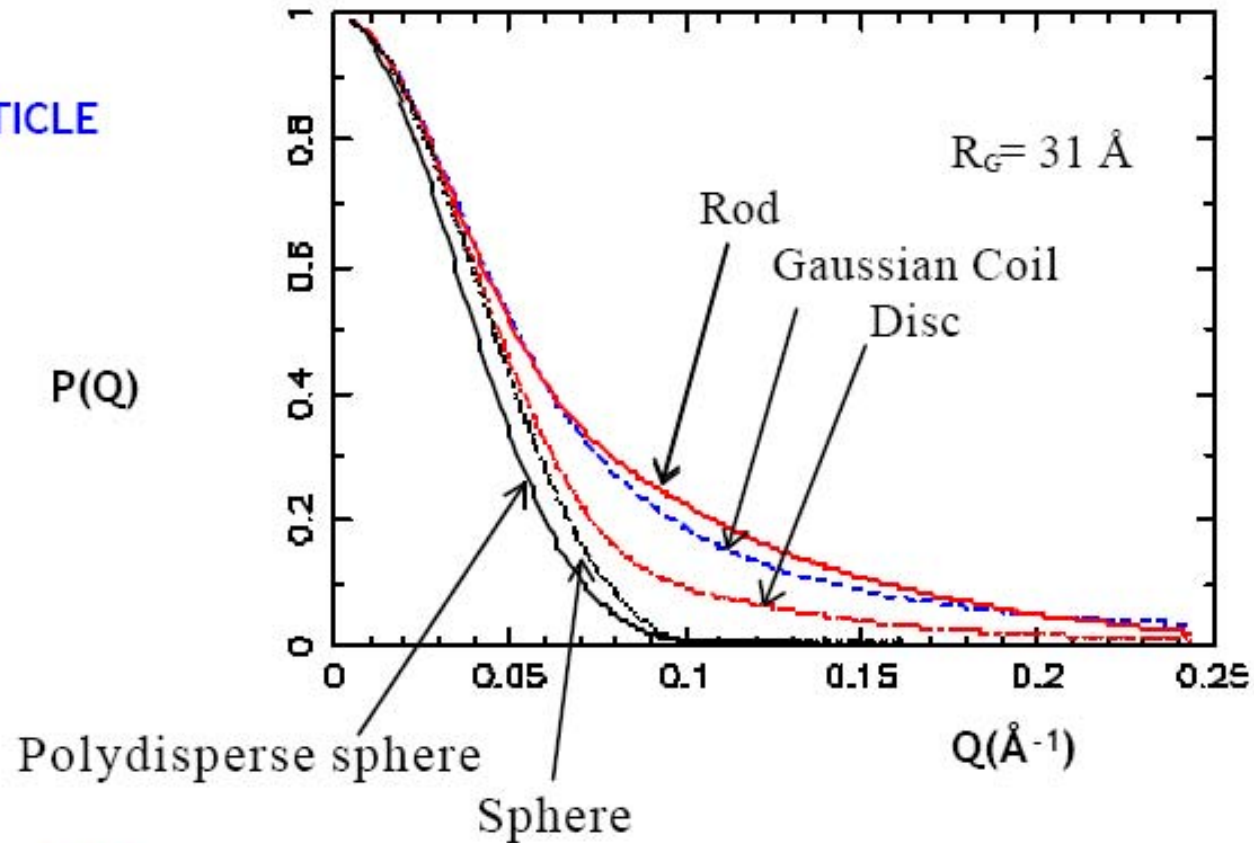
$$y = (QR_G)^2$$

$R_G$  = radius of gyration, the rms (root mean square) radius – same as in Guinier plot.

For dilute polymer, as usual

$$I_0 = NV^2 (\Delta\rho)^2$$

DILUTE PARTICLE  
SHAPE



$R_G = 31 \text{ \AA}$  (i.e. are same at small Q)

Rod  $R = 10 \text{ \AA}$ ,  $L = 104.5 \text{ \AA}$

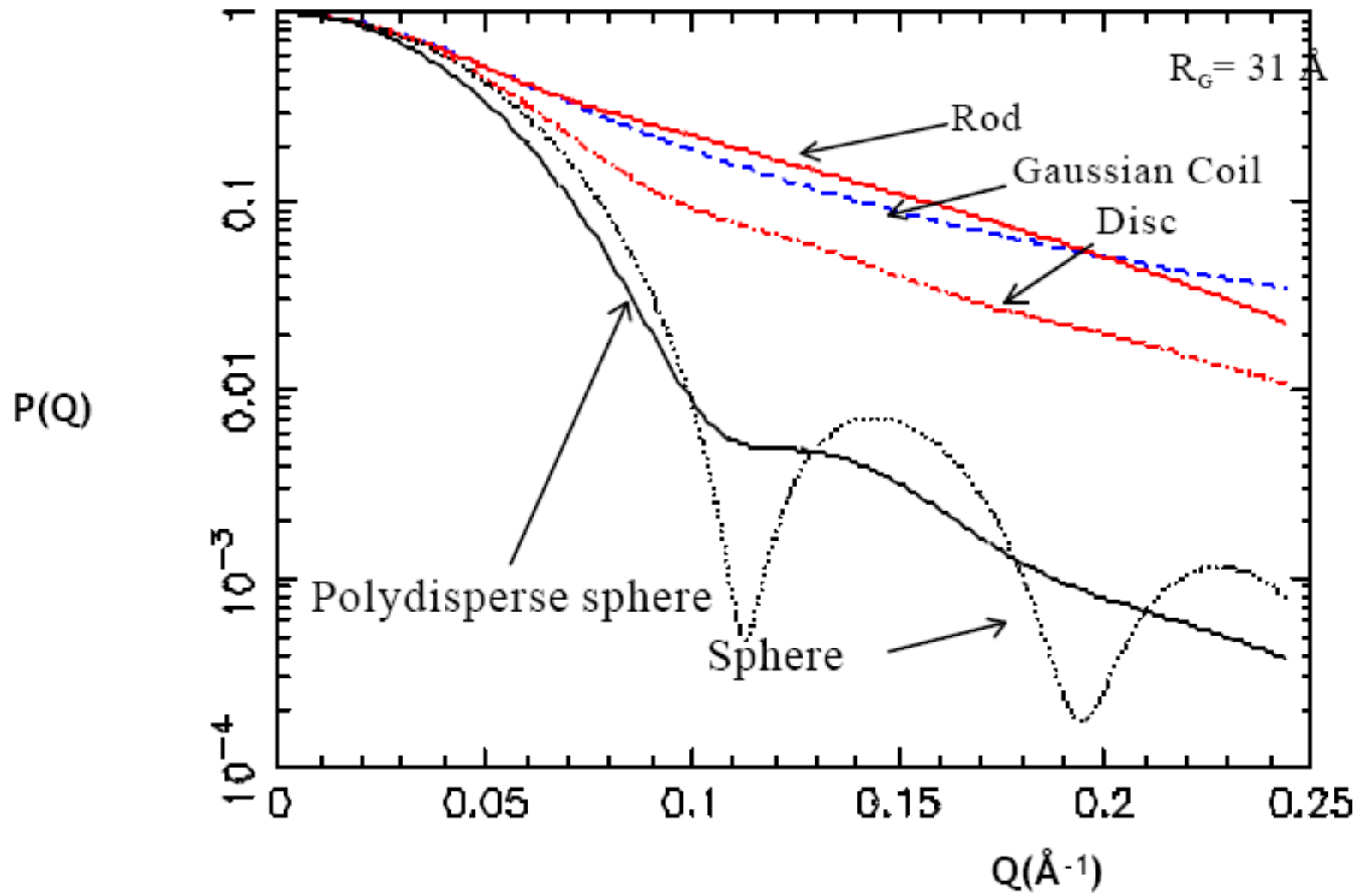
Disc  $R = 43.6$ ,  $L = 10$

Gaussian coil  $R_G = 31$

Monodisperse sphere  $R = 40$  has  $R_G = 40 \times \sqrt{3/5} = 31 \text{ \AA}$ , has resolution smearing.

Polydisperse (Schultz)  $R_{\text{bar}} = 40 \text{ \AA}$ ,  $\sigma/R_{\text{bar}} = 0.15$ , is steeper at small Q

# DILUTE PARTICLE SHAPE log-linear plot





## Absolute intensity of non-dilute samples & polymers

For dilute and concentrated (solid or melt) polymers and other particles:

$$I_0 = \phi(1 - \phi)V(\Delta\rho)^2 = \frac{c}{d}\left(1 - \frac{c}{d}\right)\frac{M}{dN_A}(\Delta\rho)^2$$

$\phi$  = volume fraction

$V$  = particle volume

$(\Delta\rho)^2$  = scattering length density difference

$c$  = concentration ( g.cm<sup>-3</sup>),

$M$  = molecular weight ( g.mol<sup>-1</sup>),

$N_A$  = Avogadro's number,

$d$  = bulk density ( g.cm<sup>-3</sup>).

**NOTE at 50%vol,  $f(1-f)$  halves the usual intensity.**

Polymer equations - often “disguised” with

(polymerisation index) × (monomer molecular weight,

segment length etc.)

For micelles  $M$  gives the aggregation number.

**POROD'S LAW - surface to volume ratio from high Q limit**

**Well defined, sharp interface**

$$I(Q) \rightarrow \frac{2\pi(\Delta\rho)^2 S}{Q^4}$$

**If a plot of  $Q^4 I(Q)$  will has a plateau value  $y$  [units  $\text{\AA}^4 \text{ cm}^{-1}$ ] then**

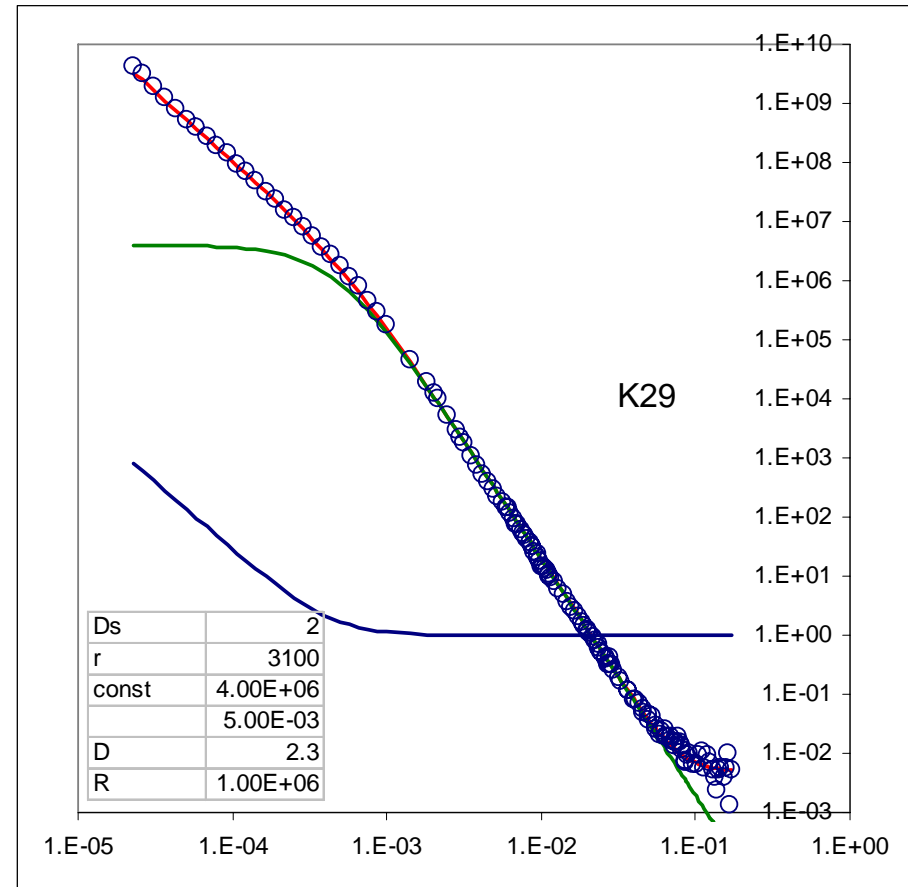
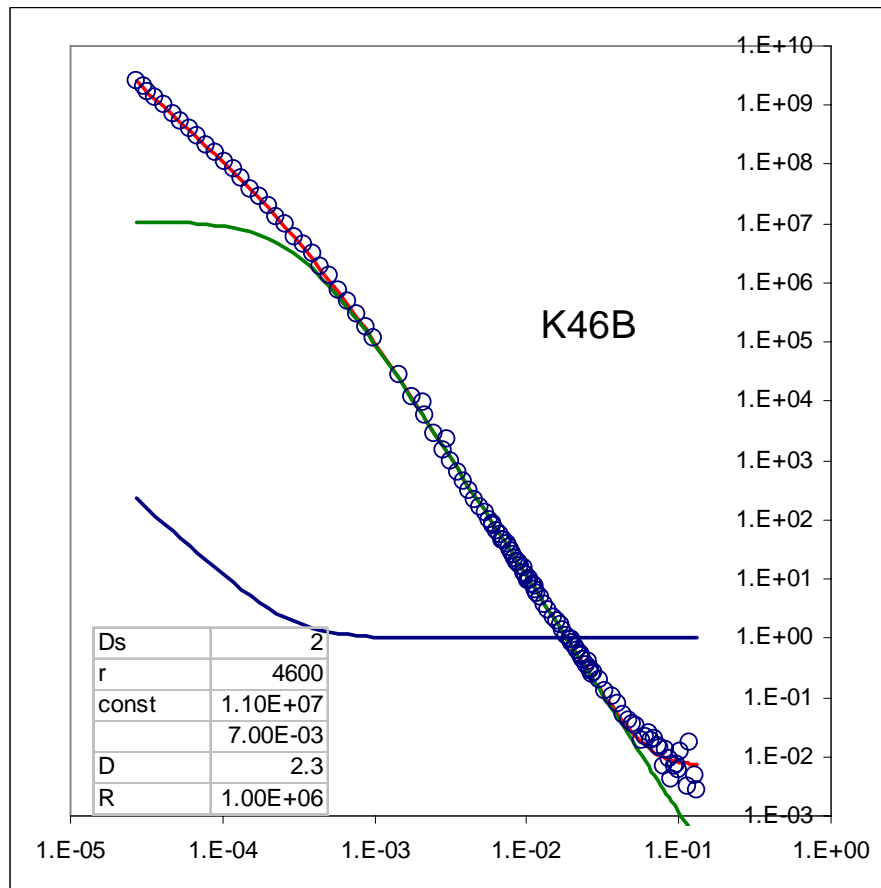
$$S(\text{cm}^2 / \text{cm}^3) = \frac{10^{32} y}{2\pi(\Delta\rho)^2} \quad \Delta\rho \text{ in cm}^{-2}$$

**A good “incoherent” background subtraction is vital !**

**Can try FIT to  $Q^{-4}$  and additional flat background.**

**[ Other “power laws” may (or may not) relate to “fractal” materials or rough surfaces, thin sheets, thin rods etc. ]**

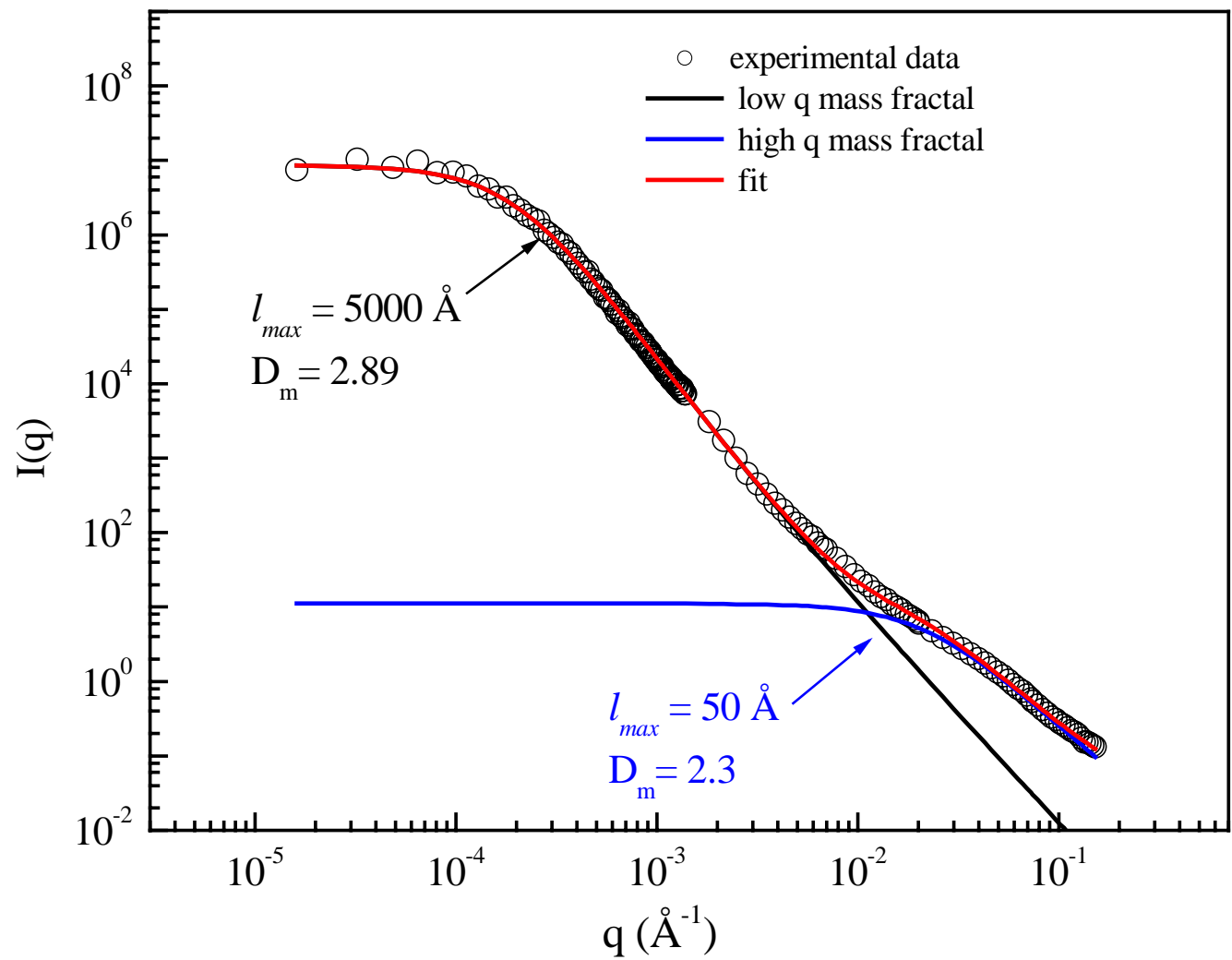
# White marbles from Carrara (Italy)

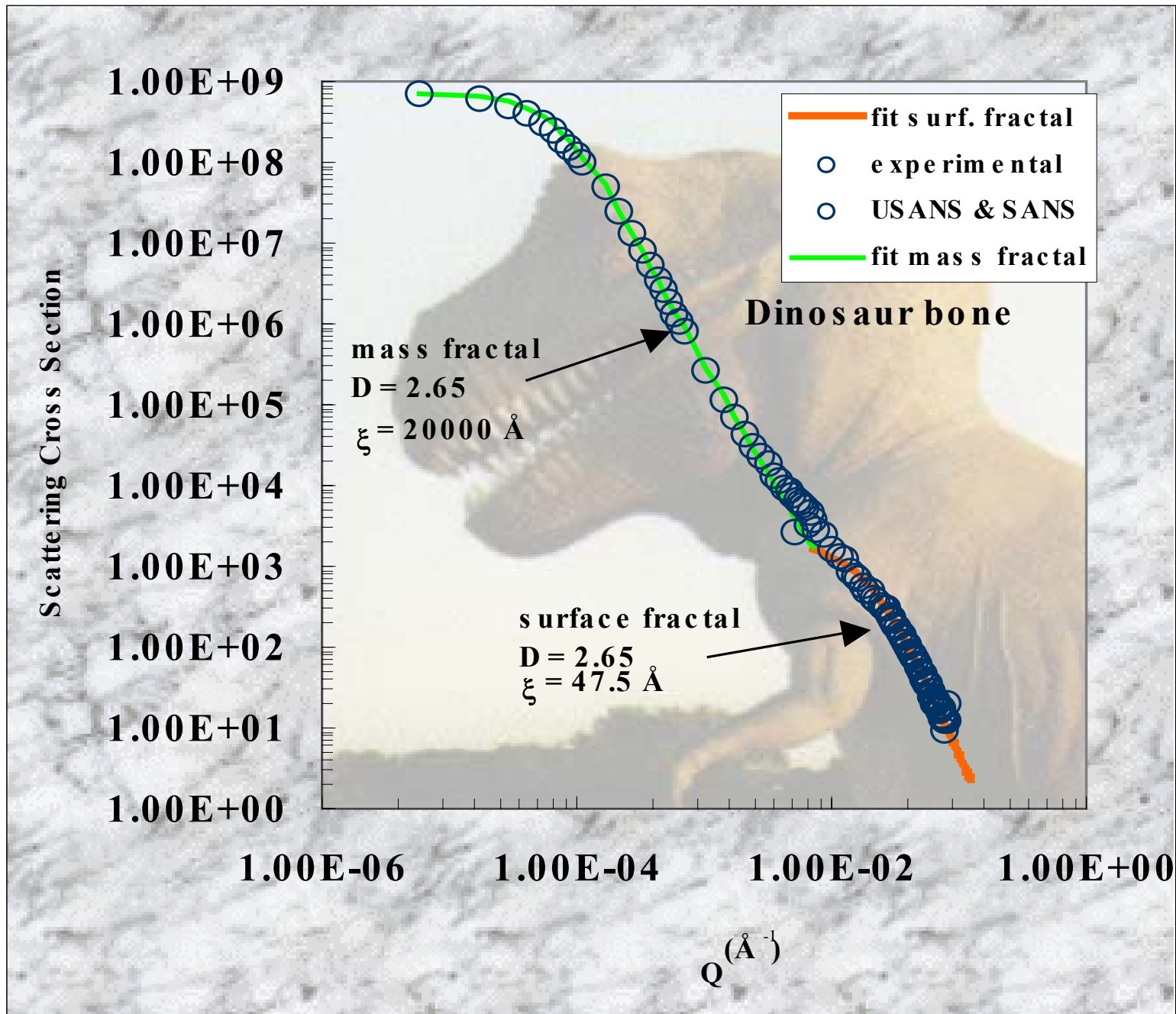


$$\mathbf{I}(\mathbf{q}) \propto \mathbf{P}(\mathbf{q}, \mathbf{r}, \mathbf{D}_s) \cdot \mathbf{S}(\mathbf{q}, \mathbf{r}, \mathbf{D}, \mathbf{R})$$

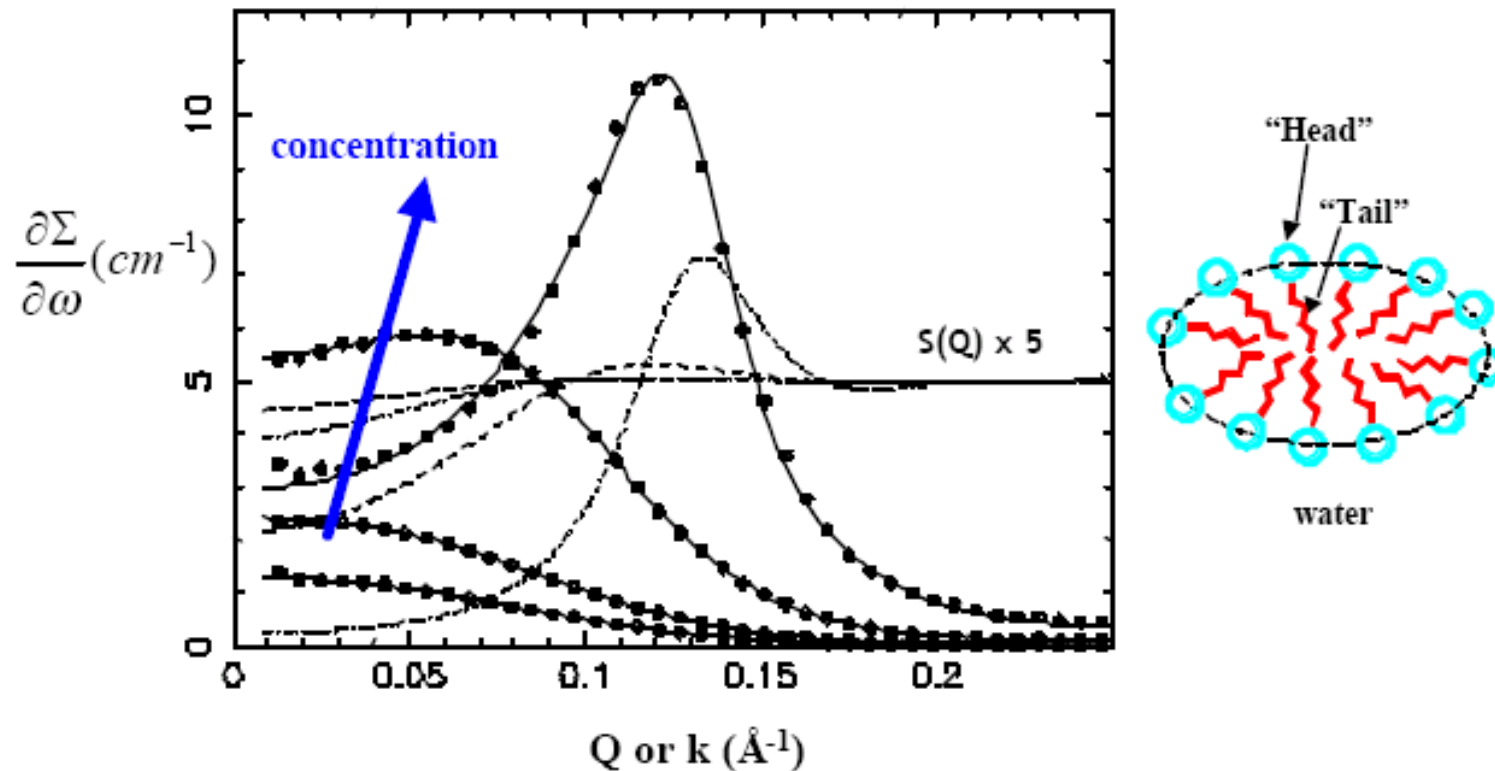
$$\mathbf{P}(\mathbf{q}, \mathbf{r}, \mathbf{D}_s) = \left( \mathbf{1} + \frac{\sqrt{2}}{3} \mathbf{q}^2 \mathbf{r}^2 \right)^{\frac{\mathbf{D}_s - 6}{2}}$$

$$\mathbf{S}(\mathbf{q}, \mathbf{r}, \mathbf{D}, \mathbf{R}) = \mathbf{1} + \frac{\mathbf{D} \Gamma(\mathbf{D} - 1)}{\mathbf{q} \mathbf{r}^{\mathbf{D}}} \left( \mathbf{1} + \frac{\mathbf{1}}{\mathbf{q} \mathbf{R}^2} \right)^{\frac{1 - \mathbf{D}}{2}} \sin[(\mathbf{D} - 1) \arctan(\mathbf{q} \mathbf{R})]$$





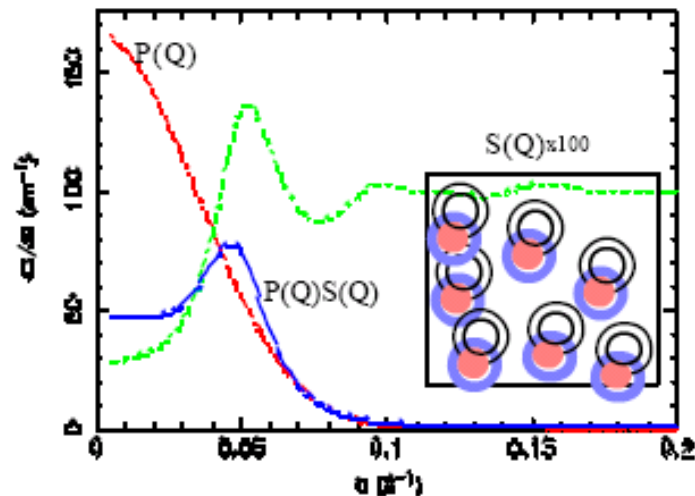
SANS data (circles) for particles (surfactant micelles) in solution in D<sub>2</sub>O, with increasing concentration (ignore the dashed lines, will see this again later when we explain the fits) Data for 0.9, 1.8, 7 and 29 % vol.



Does not look like Bragg scatter from a crystal, except for peak at the highest concentration – “Bragg peak” from a very disordered array of micelles !  
 SANS fits give size, shape (aggregation number) and charge on the micelle. Particle radius  $\sim 19 \text{ \AA}$ , axial ratio  $X \sim 1.7$

D.J.Barlow, M.J.Lawrence, T.Zuberi, S.Zuberi & R.K.Heenan, *Langmuir* **16**(2000)10398-10403.

## Example: interacting spheres:



10%  $R=40 \text{ \AA}$  radius spheres, in  
 “core” contrast,  
 (polydispersity  $\sigma/R_{\text{bar}}=0.15$ ,  
 $\Delta\rho=6 \times 10^{10} \text{ cm}^{-3}$ ).  
 plus another 16% in invisible  $15 \text{ \AA}$   
 coating gives hard sphere  
 $S(Q)$  of 26 % vol &  $R = 55 \text{ \AA}$   
 $S(Q) \rightarrow 1$  at high  $Q$

At higher volume fractions we start to see interference from waves scattered by adjacent particles ( it was there all along, but at smaller  $Q$ , inside the beam stop!).  
 $I(Q=0)$  is now decreased!

To first approximation we multiply  $P(Q)$  by an “inter-particle structure factor”  $S(Q)$  which depends on “long range” interparticle interactions.  $S(Q)$  comes from a Fourier transform of interparticle  $g(r)$  & hence interaction potential for colloids or Bragg  $d = 2\pi/Q_{\text{peak}}$  in “liquid crystal”.

$$\frac{\partial \Sigma}{\partial \omega} = I(Q) = NV^2 (\Delta\rho)^2 P(Q)S(Q) + BKG$$

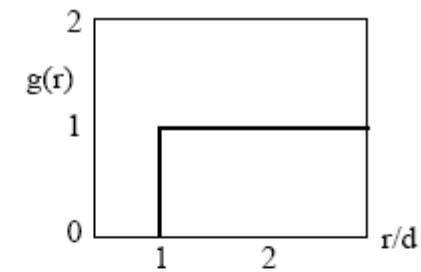
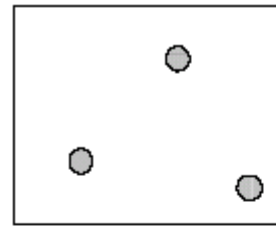


$$\langle S(\bar{q}) \rangle = S(q) = 1 + 4\pi n_p \int_0^{\infty} [g(r) - 1] \frac{\sin qr}{qr} r^2 dr$$

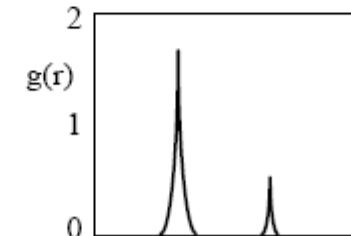
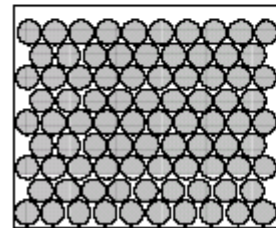
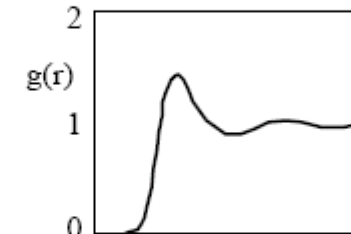
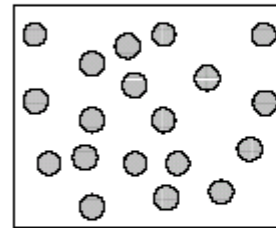
Note:

- $S(q)$  is proportional to the number density of particles
- $S(q)$  depends on  $g(r)$ , the pair correlation function

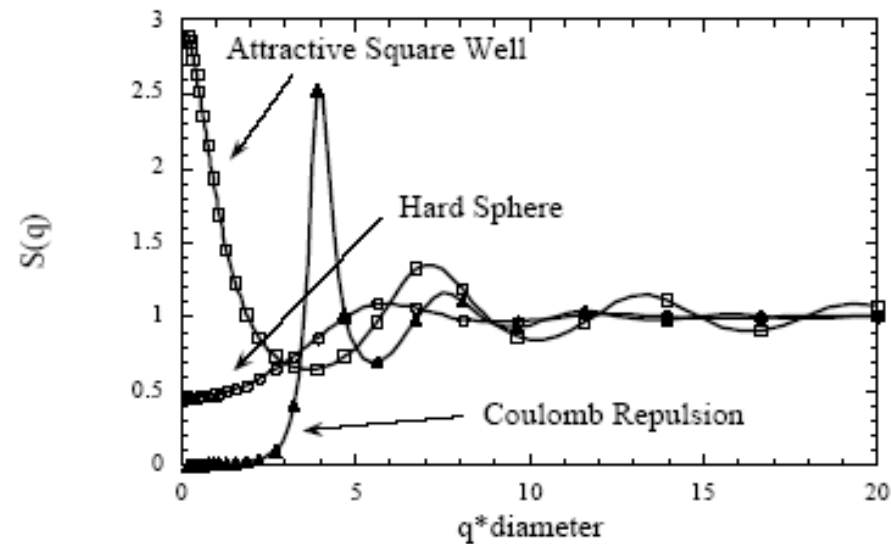
➤  $n_p g(r)$  is a “local” density of particles



➤ Spatial arrangement set by interparticle interactions and indirect interactions



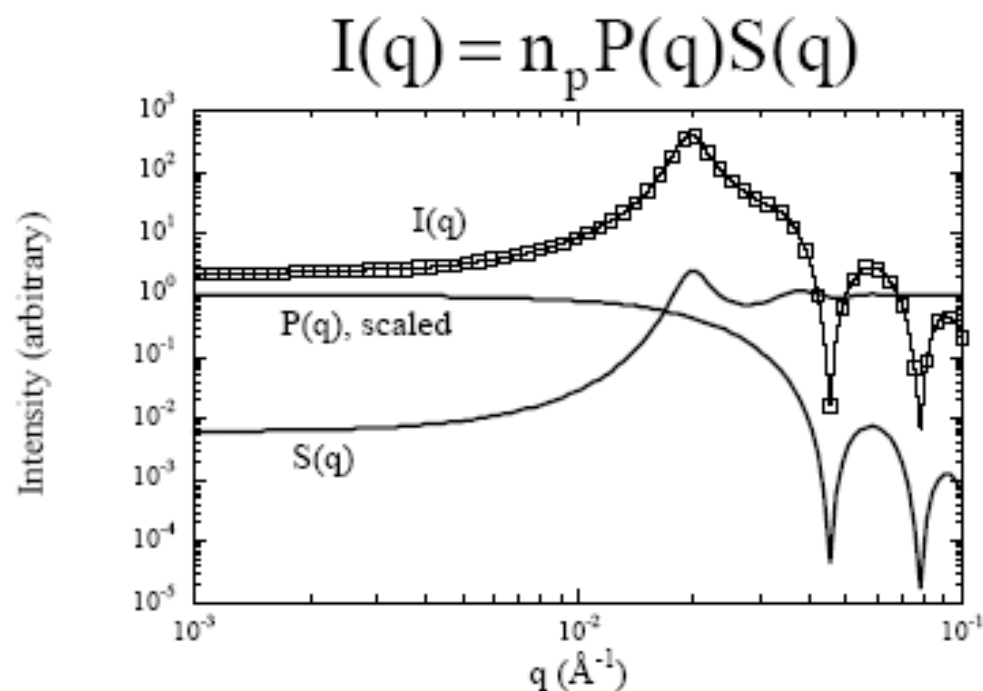
- The form of the interparticle potential has a great effect on the low  $q$  value of  $S(q)$



- The low  $q$  limit is proportional to the osmotic compressibility

$$S(q = 0) = kT \left( \frac{\partial n}{\partial \pi} \right)$$

- Attractive interactions  $\Rightarrow$  more compressible
- Repulsive interactions  $\Rightarrow$  less compressible



- The form of the interparticle potential has a great effect on the low  $q$  value of  $S(q)$
- Example of charged spheres:
  - development of “interaction peak”
  - change in low- $q$  slope and  $I(0)$
- Must fit model to data
  - know  $P(q)$
  - ?calculate  $S(q)$ ?

➤ Ornstein Zernicke Equation:

$$h(\mathbf{r}) = g(\mathbf{r}) - 1 = c(\mathbf{r}) + n \int c(|\vec{r} - \vec{x}|) h(\mathbf{x}) d\vec{x}$$

- $c(\mathbf{r})$  = direct correlation function
- Integral = all indirect interactions

➤ A second relation is necessary to relate  $c(\mathbf{r})$  and  $g(\mathbf{r})$

➤ Percus-Yevick Closure - an approximation

$$c(\mathbf{r}) = g(\mathbf{r}) [1 - e^{\beta u(\mathbf{r})}]$$

- correct closure gives correct results
- in general a difficult problem

$$\langle S(\vec{q}) \rangle = S(q) = 1 + 4\pi n_p \int_0^{\infty} [g(r) - 1] \frac{\sin qr}{qr} r^2 dr$$

## POLYDISPERSITY

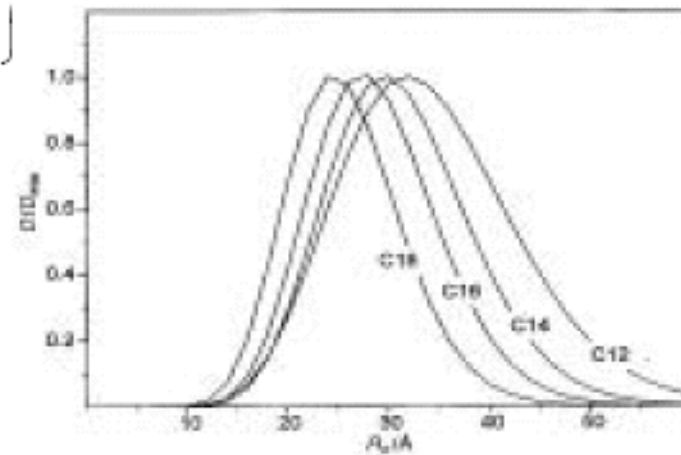
Sum SANS over size distribution - Gaussian, log-normal, uniform, etc. “Schultz distribution” is similar to log-normal but  $I(Q)$  is analytic. Generally SANS is only sensitive to mean  $R_{bar}$  and “polydispersity”  $\sigma(R)/R_{bar}$  where  $\sigma(R)$  is the standard deviation.

Schultz distribution:

$$N(r) = \left[ \frac{(Z+1)}{R_{bar}} \right]^{Z+1} \frac{r^Z}{\Gamma(Z+1)} \exp \left\{ -\frac{(Z+1)r}{R_{bar}} \right\}$$

$$\frac{\sigma}{R_{bar}} = \frac{1}{(Z+1)^{1/2}}$$

$$Z = \left( \frac{R_{bar}}{\sigma} \right)^2 - 1$$

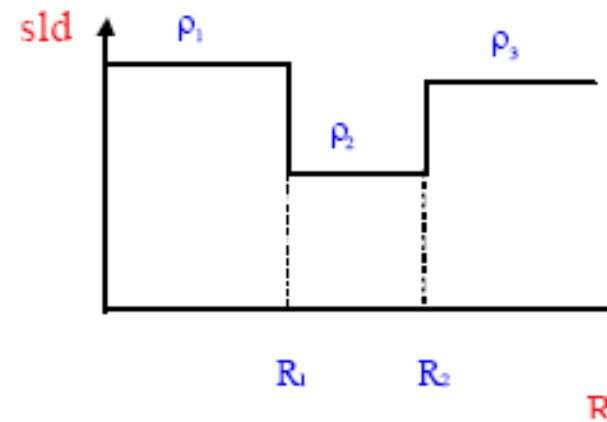
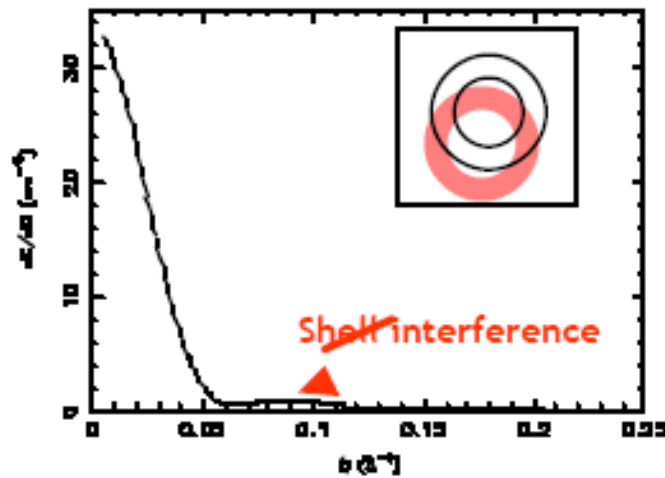


**NOTE:** at large  $\sigma$  the Schultz is very skewed and has significant numbers of small particles. Gamma function  $\Gamma(n) = (n-1)!$  Care is needed in numerical calcs as  $Z$  may be large.

## Contrast variation - introduction

For core plus shell spherical particle

e.g. Spherical Shell  $R_1 = 40 \text{ \AA}$  ( $R_2 - R_1 = 15 \text{ \AA}$ ) (with 15% polydispersity)



$$I(Q) = N \left\{ (\rho_1 - \rho_2) V_1 F(Q, R_1) + (\rho_2 - \rho_3) V_2 F(Q, R_2) \right\}^2$$

$$F(Q, r) = \frac{3(\sin(Qr) - Qr \cos(Qr))}{(Qr)^3}$$

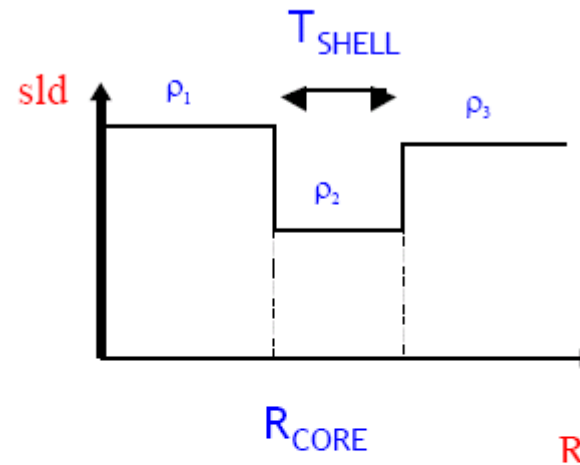
$I(Q=0)$  not so simple now !

At “contrast match”  $\rho_1 = \rho_3$ , then we see “hollow shell” with oscillation in  $I(Q)$  which is very sensitive to the details of the structure.

## Practical computations

Please note – the way that equations are presented in scientific papers may not be the best way to use them in a computer program.

There are many ways to re-arrange the equations, e.g. the core/shell sphere on the previous slide can become:



$$I(Q) = \frac{16\pi^2 N}{Q^6} \left\{ (\rho_1 - \rho_2) f(Q, R_{CORE}) + (\rho_2 - \rho_3) f(Q, R_{CORE} + T_{SHELL}) \right\}^2$$

$$f(Q, r) = (\sin(Qr) - Qr \cos(Qr))$$

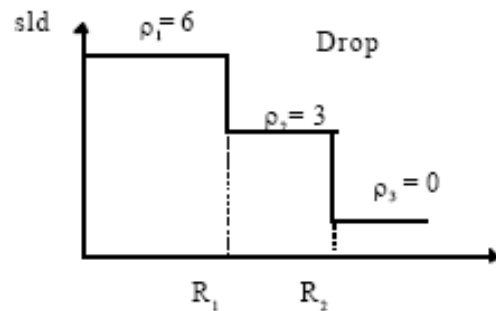
Where there are N particles per unit volume (usually per cm<sup>3</sup>).

Note that we may need to include a factor 10<sup>48</sup> to convert Q(Å<sup>-1</sup>)<sup>6</sup> to cm<sup>-6</sup>.

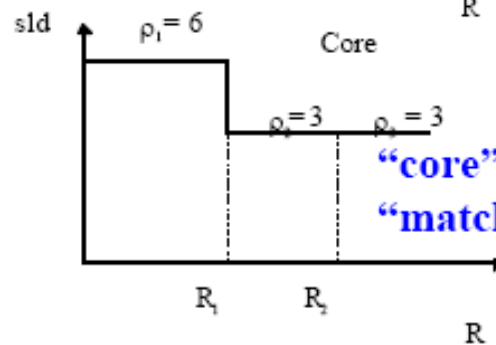


## CONTRAST VARIATION - CORE/SHELL PARTICLES

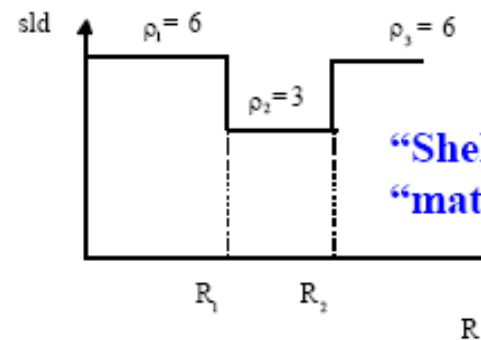
e.g. Core  $\rho_1 = 6 \times 10^{10} \text{ cm}^{-2}$ , mean  $R_1 = 40 \text{ \AA}$ ,  $\phi = 1\%$ ,  $\sigma/R_{\text{bar}} = 15\%$   
 $R_2 - R_1 = 15 \text{ \AA}$  shell  $\rho_2 = 3 \times 10^{10} \text{ cm}^{-2}$ .



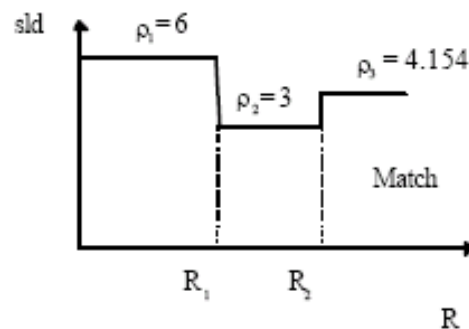
“drop” contrast sees whole particle  
 ( here some effect of the shell )



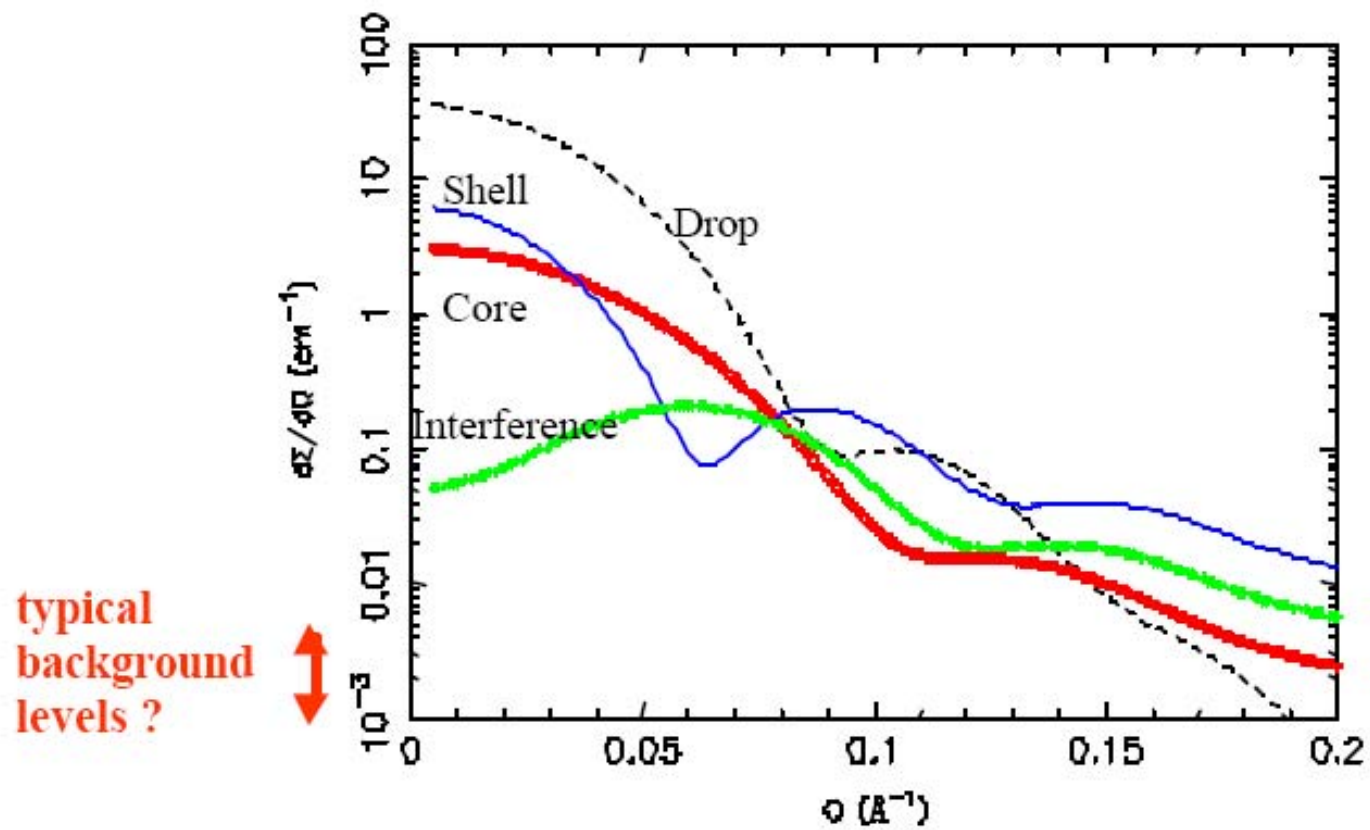
“core” - solvent  
 “matches” shell



“Shell” - solvent  
 “matches” core



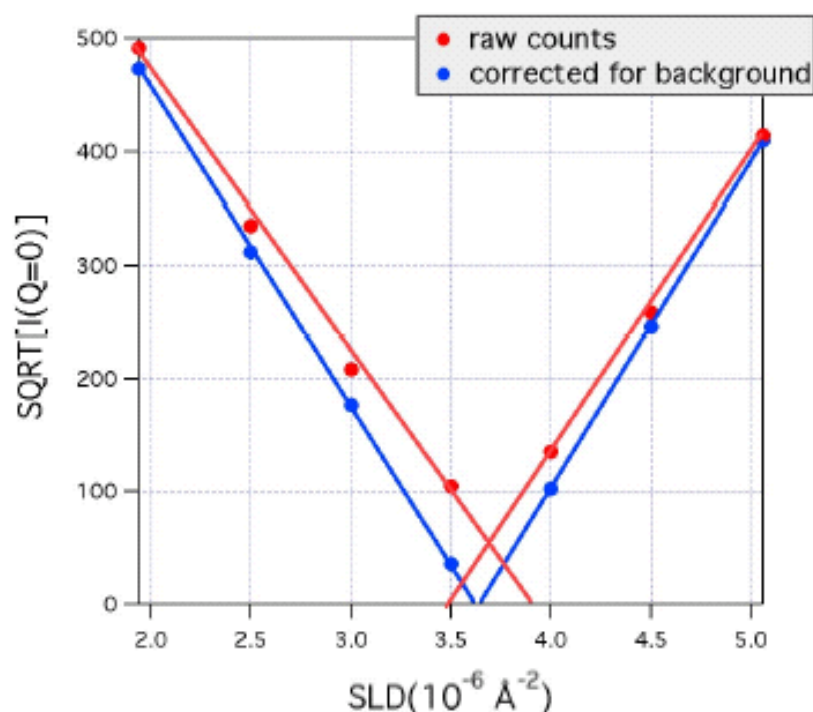
“interference” – rarely seen, but be aware! Solvent  
 between “core” & “shell” matches the average sld  
 of the whole particle.  
 Small Q, long dist. SANS ~ zero,  
 High Q, short distances some scatter!



**NOTE**  $I(Q)$  from “shell contrast” scales non-linearly with particle size and layer thickness - trial calculations are useful to plan experiments.

# Determining the Contrast Match Point

$$I(Q=0) = \frac{N}{V} (\rho_p - \rho_o)^2 V_p^2$$



\*\*Need "dilute" particles and "low" Q

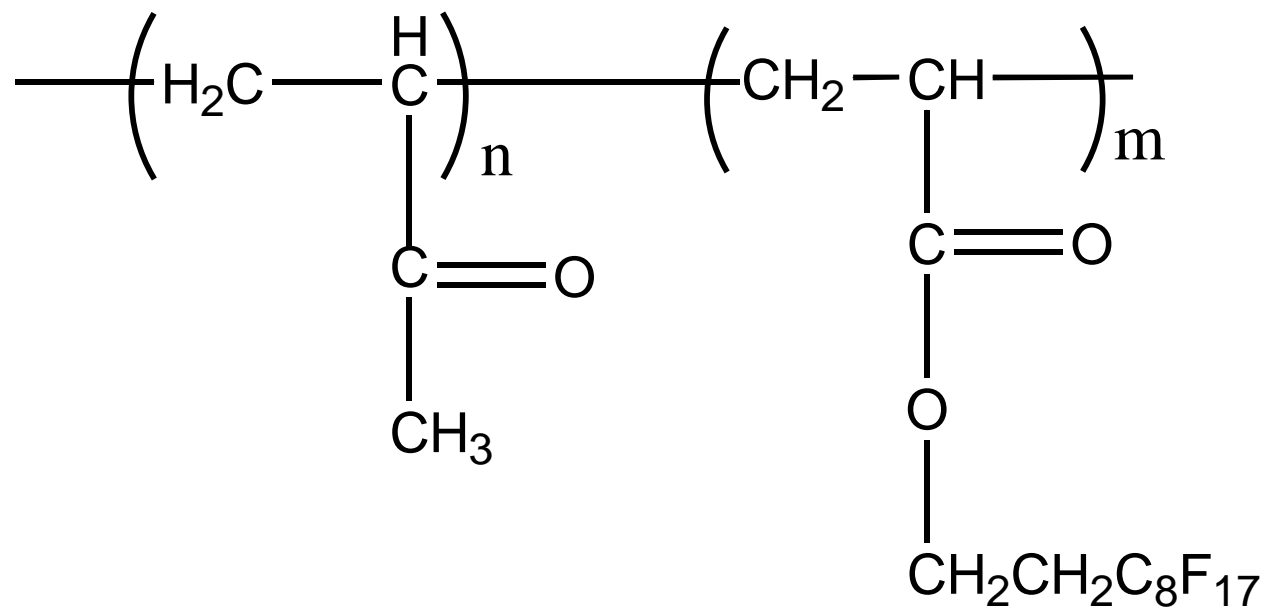
- Make several measurements at different solvent SLDs
- Keep the same concentration
- Extrapolate data to  $I(Q=0)$
- Plot  $\text{sqrt}(I(Q=0))$  vs. SLD
  
- Don't forget to correct for the incoherent background contribution
  
- For composite particles,  $I(Q=0)$  will never reach zero - but it will be a minimum at the average particle contrast

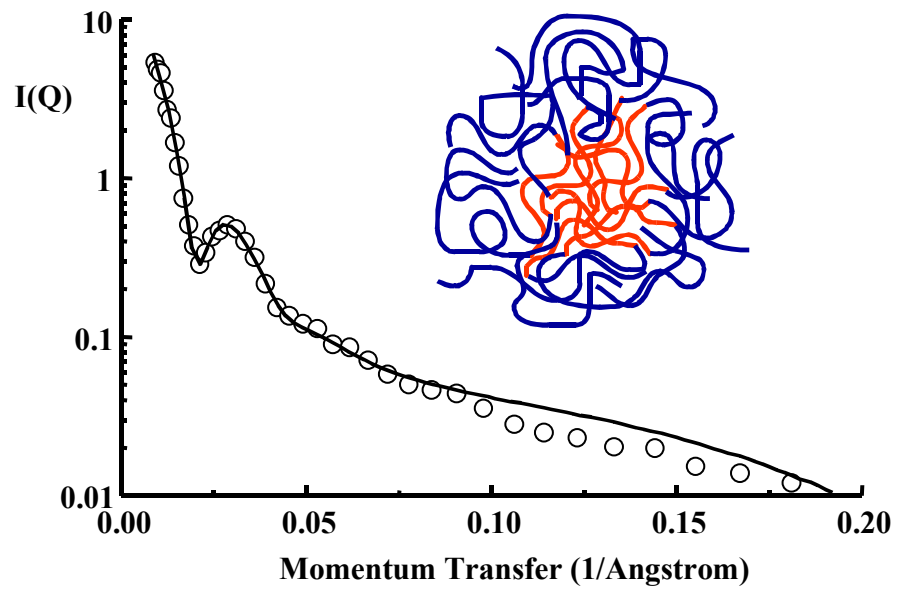
**scCO<sub>2</sub> is a very poor solvent for most high MW polymers, with the possible exception of fluoropolymers, silicones, and poly(ether-carbonate)**

**(T. Sarbu, T.Styranec and E.J. Beckman, Nature, vol. 405, 11 May 2000)**

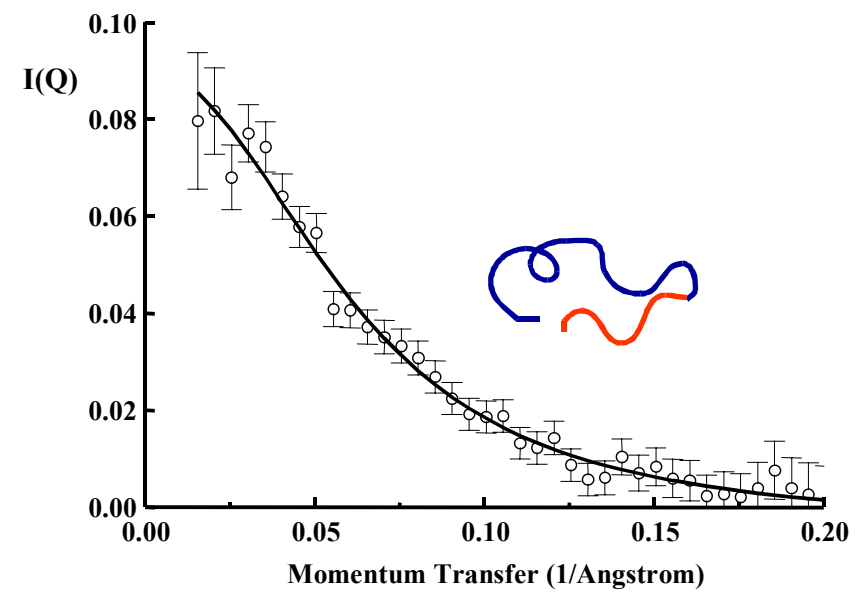
**It is then possible to design copolymers with a CO<sub>2</sub>-phobic and a CO<sub>2</sub>-philic portion that behave as surfactants, giving micellar-like aggregates in certain conditions**

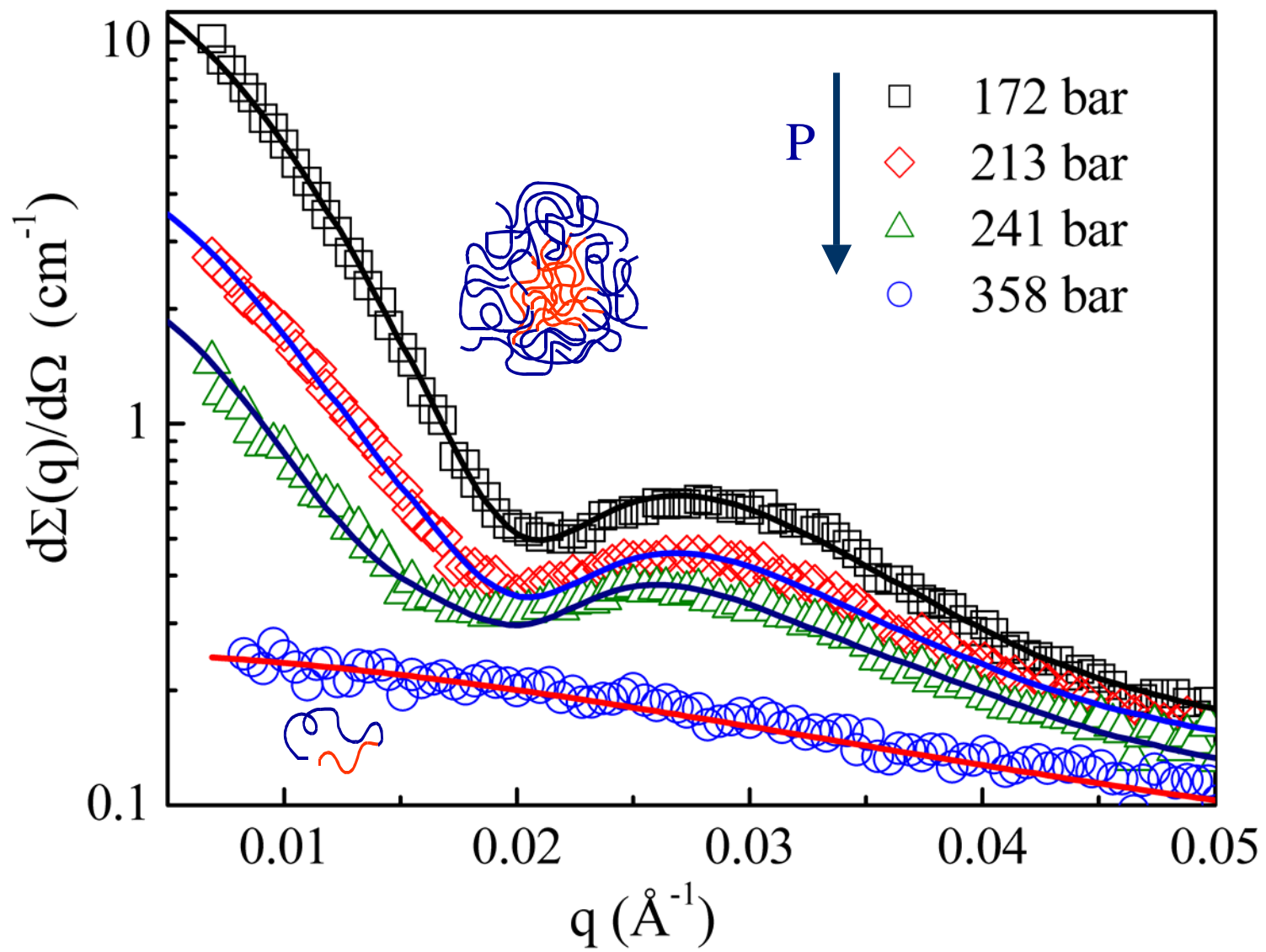
# PVAC-b-PTAN





High Pressure  
(High Density)





- Model

$$d\Sigma(Q)/d\Omega = N_p[d\Sigma(Q)/d\Omega]_{RC} + N_{Agg}[d\Sigma(Q)/d\Omega]_{Agg}$$

Random coils

+

Aggregates

$$2 N_p [(QR_g)^2 + \exp[-(QR_g)^2] - 1] / (QR_g)^4$$

P. Debye (1944)

+

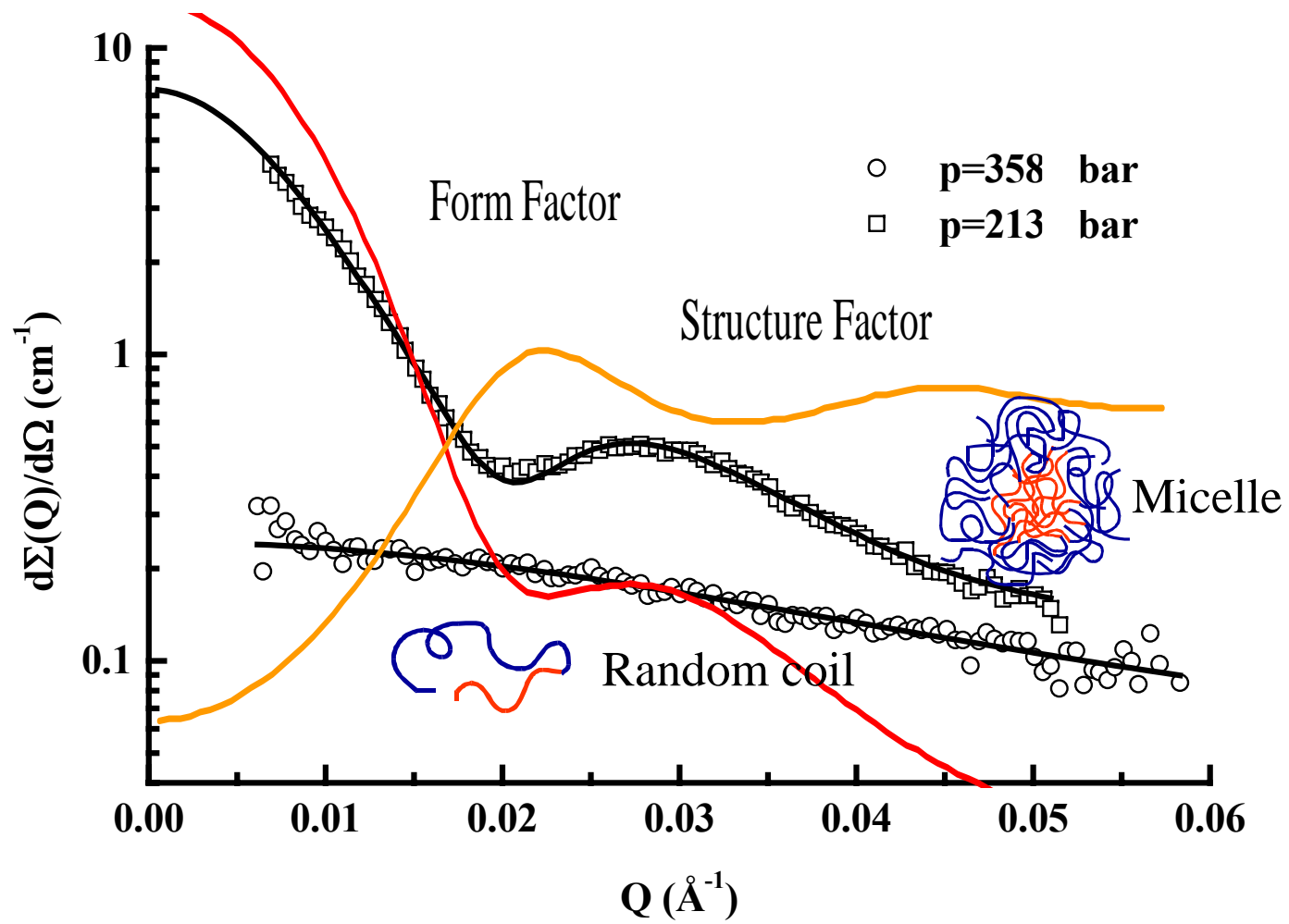
$$N_{agg} P(Q) S(Q)$$

Core+shell  
(polydisperse)  
spheres

+

PY hard spheres  
+  
ECF





<i>P</i>	(1-uom)	$\rho$	CS	Agg.	<i>Z</i>
172	0.925	0.821	1.00	29.5(1)	17.0(1)
179	0.925	0.830	1.0(1)	29.3(3)	17.0(1)
186	0.925	0.838	1.1(1)	29.2(5)	17.4(1)
199	0.900	0.849	1.1(1)	28.0(3)	19.5(3)
213	0.900	0.858	1.1(1)	24.8(5)	18.4(5)
227	0.875	0.868	1.1(2)	21.7(2)	18.0(2)
241	0.875	0.879	1.1(3)	19.4(2)	17.0(2)
255	0.850	0.889	1.1(1)	18.6(2)	17.0(2)
268	0.750	0.900	1.6(2)	14.8(3)	17.0(2)
282	0.65	0.909	1.8(2)	12.0(2)	10.0(2)
295		transition zone, 0.91 g/cm <sup>3</sup>			
310		transition zone, 0.92 g/cm <sup>3</sup>			
357		0.917	Random coil, R <sub>g</sub> 43.5 Å		

- Basic Equations
- Model-independent methods
  - Guinier, Porod, Invariant
- Non-Linear Model Fitting
  - Particles, Polymers, Materials
- Global Fitting
- Anisotropic Scattering
- Transforms
- Ab initio modeling

Easy

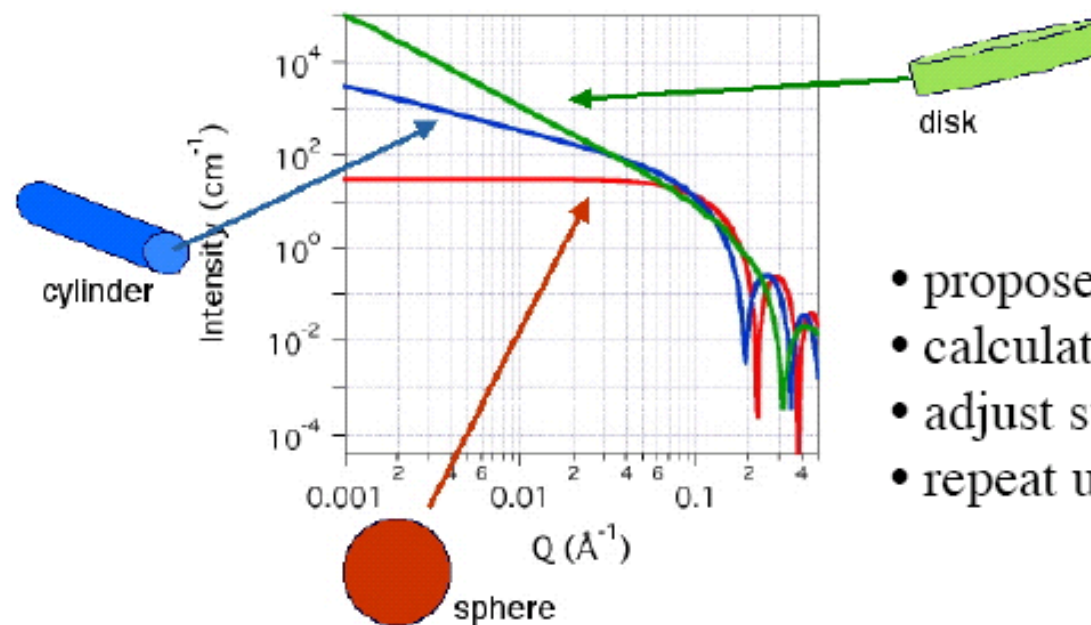


More involved

# Non-Linear Model Fitting

One of the most commonly used methods

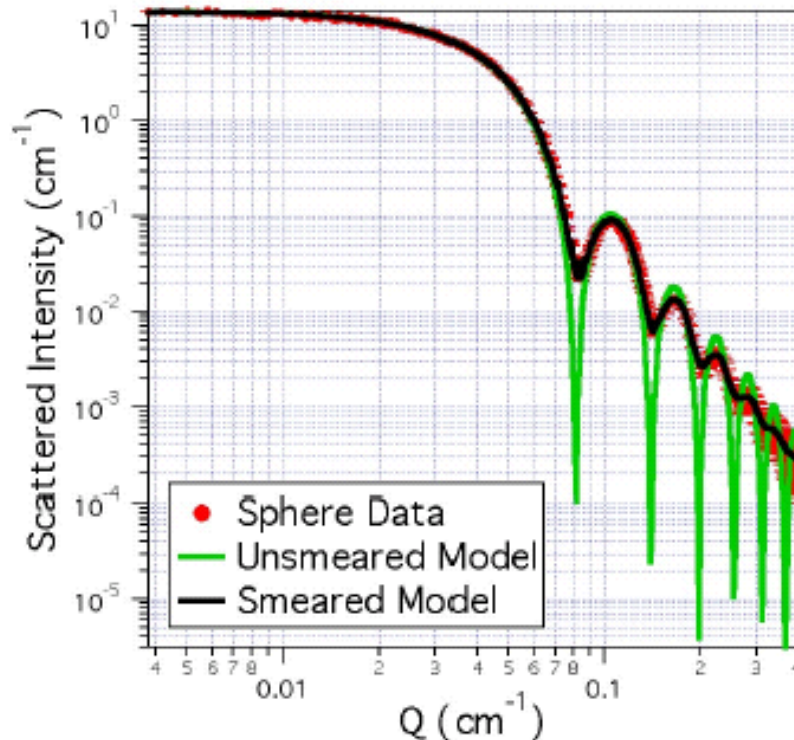
- a “forward” calculation
- many structures and interactions to choose from



- propose a structural model
- calculate  $I(Q)$
- adjust structural parameters
- repeat until done



# Non-Linear Model Fitting



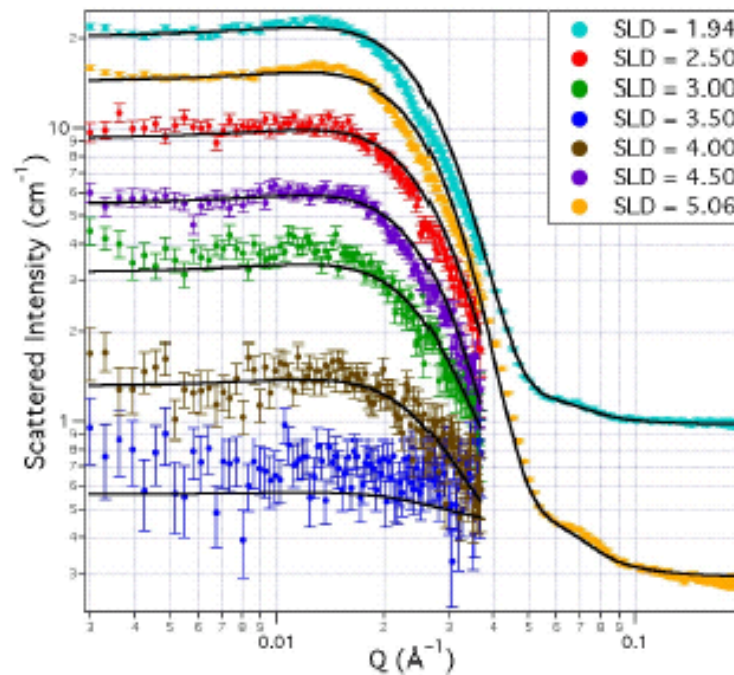
Point	parameters_sf	coef_sf	smear_coef_sf
0	scale	0.05	0.05
1	Radius (Å)	55	55
2	contrast ( $\text{\AA}^{-2}$ )	2e-06	2e-06
3	bkgd ( $\text{cm}^{-1}$ )	0	0

- Non-linear least squares fitting to experimental data
- Use all the information you can to reduce the number of free model parameters
  - SLD's
  - Concentrations
  - Lengths
- A “good” fit does not necessarily guarantee a perfect representation of the structure in the sample

# Global Fitting

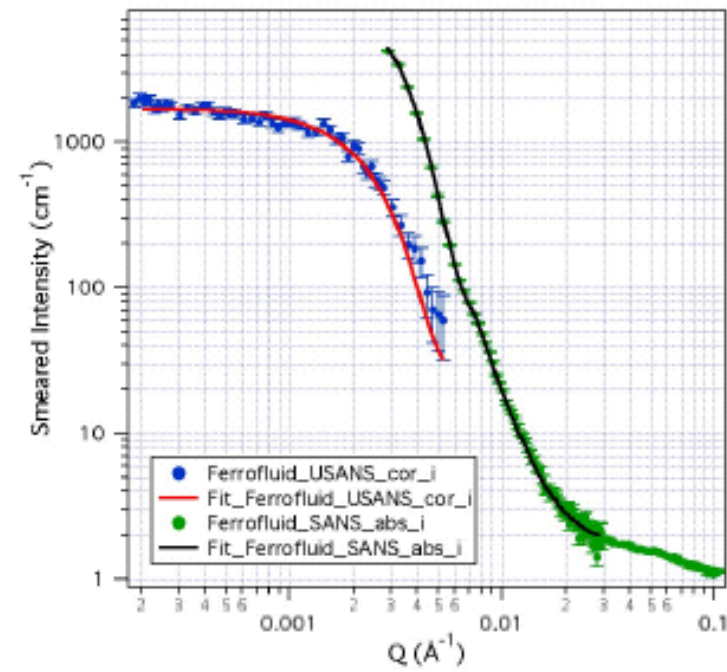
## Contrast variation

- same particles, different solvent
- $R$ ,  $\rho_p$ ,  $\phi$  are the same
- $\rho_{\text{solv}}$ , background are different



## SANS + USANS data

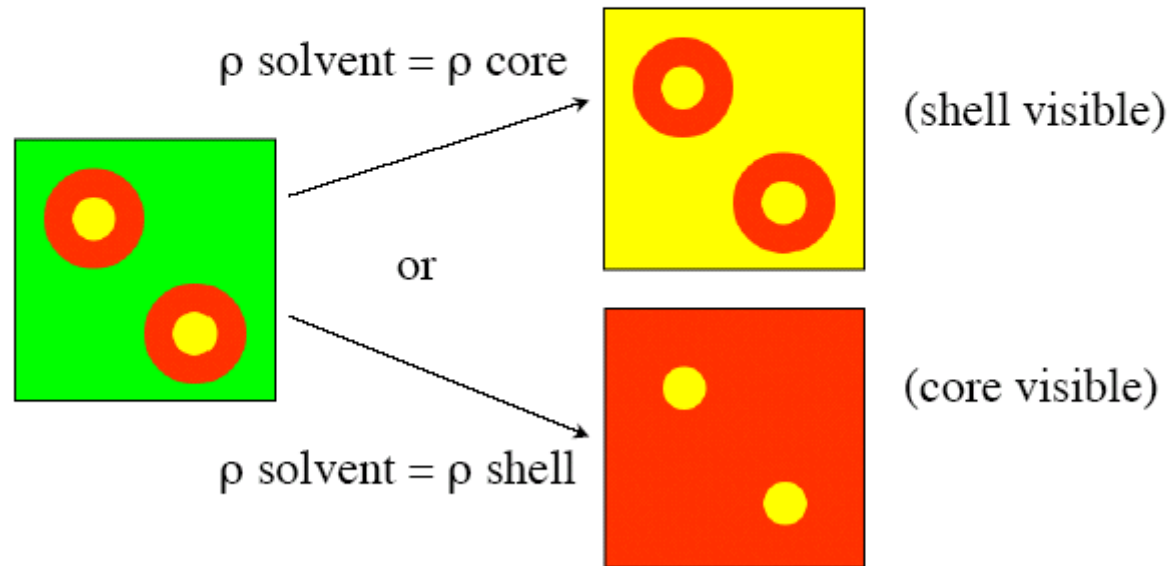
- same sample (same cell)
- all parameters are the same
- smearing, scaling different



# Contrast Variation

## Contrast Matching

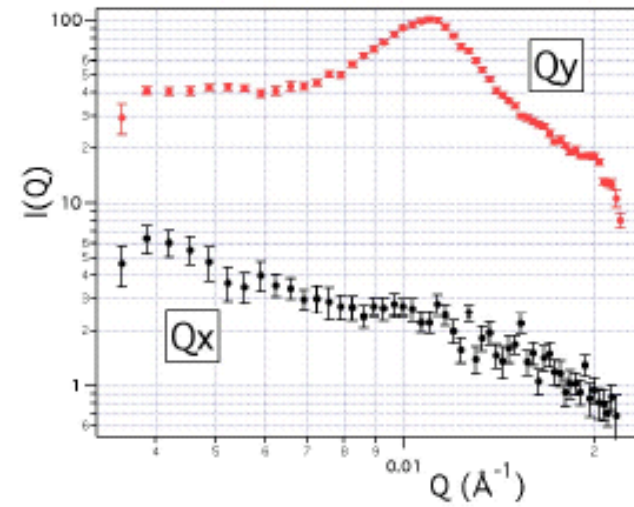
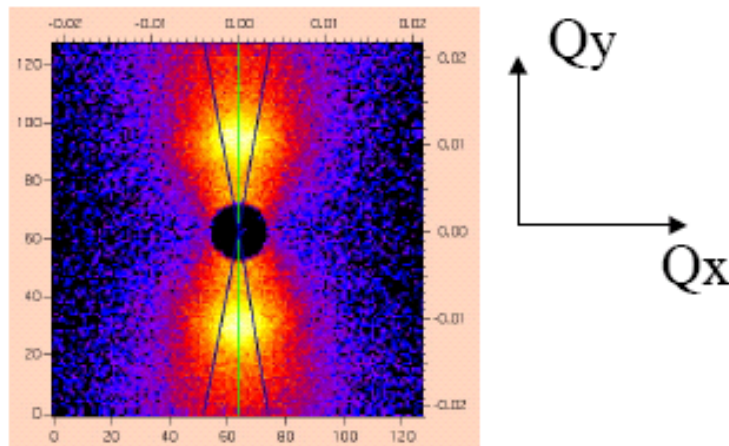
reduce the number of phases “visible”



- The two distinct two - phase systems can be easily understood

# Anisotropic Scattering

Elongated particles aligned by shear





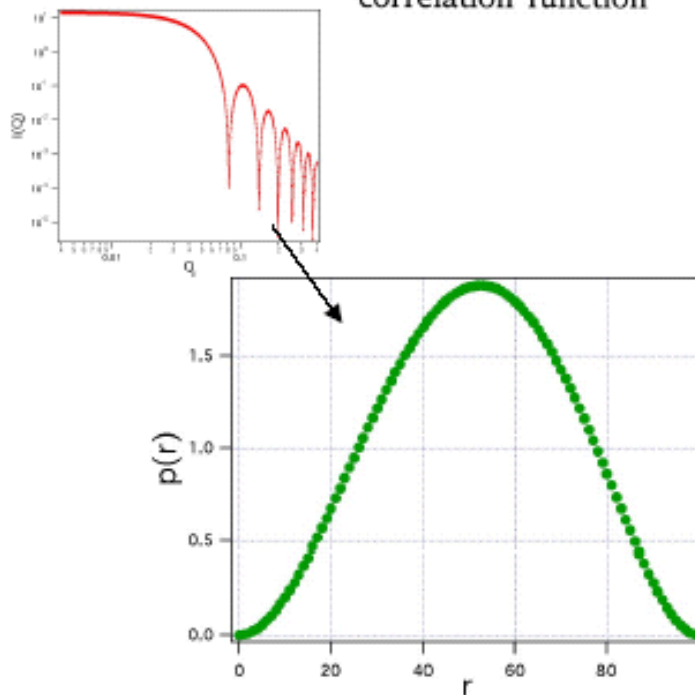
# Transforms - p(r)

Distance Distribution Function: p(r)

$$I_p(Q) \propto \left\langle \int \gamma(\vec{r}) e^{iQ \cdot \vec{r}} d\vec{r} \right\rangle = 4\pi \int r^2 \gamma(r) \frac{\sin(Qr)}{Qr} dr$$

↖ average over orientations  
↖ correlation function

p(r) is the probability that 2 randomly chosen points are at a distance r apart



If  $I(Q)$  is measured over a wide enough  $Q$ -range, then one can compute  $p(r)$  as the inverse transform:

$$p(r) = \frac{1}{2\pi^2} \int_0^{\infty} I(Q) (Qr) \sin(Qr) dQ$$

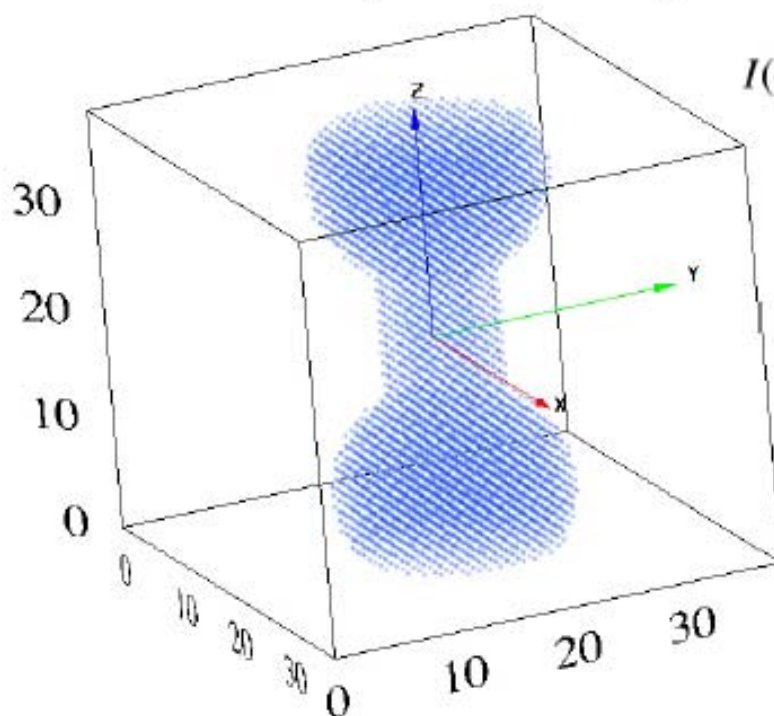
For a sphere:

$$p(r) = 12x^2(2 - 3x + x^3) \quad x = r/D$$

\*See: D. Svergun, O. Glatter

# Ab initio methods

- Calculate  $I(Q)$  for complex structures
  - Biological molecules made up of subunits
  - non-standard geometric shapes



$$I(Q) = \sum_{i=1}^n I_i(Q) + 2 \sum_{i \neq j} F_i(Q) F_j(Q) \frac{\sin(Qr_{ij})}{Qr_{ij}}$$

- fill volume with spheres on a grid
- need distance between every pair
- can be computationally intensive
- can optimize shape

- packages available (D. Svergun)

**\*\*Need “dilute” particles and “burly” computer**

## Interesting Links:

<http://scattering.tripod.com>

[\*\*http://www.isis.rl.ac.uk/LargeScale/LOQ/loq.htm\*\*](http://www.isis.rl.ac.uk/LargeScale/LOQ/loq.htm)

[\*\*http://www.ncnr.nist.gov/resources/simulator.html\*\*](http://www.ncnr.nist.gov/resources/simulator.html)