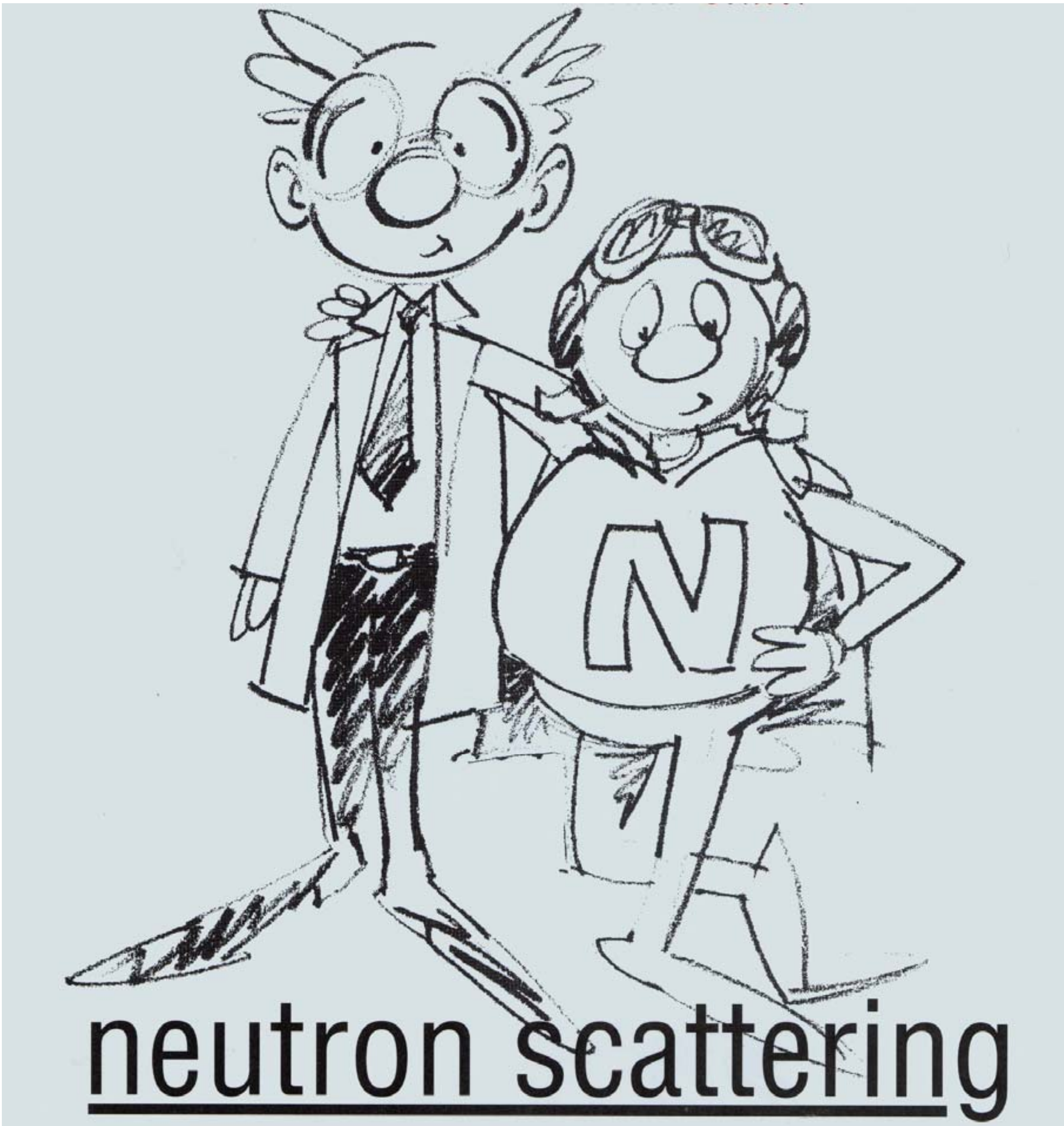
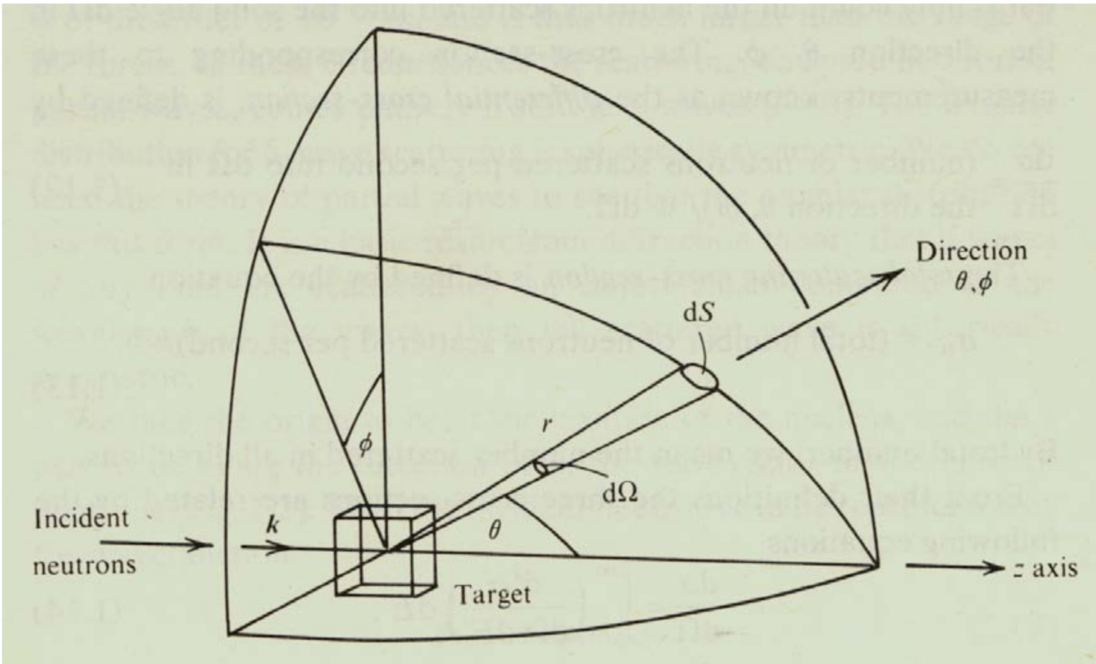


by

Roger Pynn

Basic Introduction to Small Angle Scattering

We Measure Neutrons Scattered from a Sample

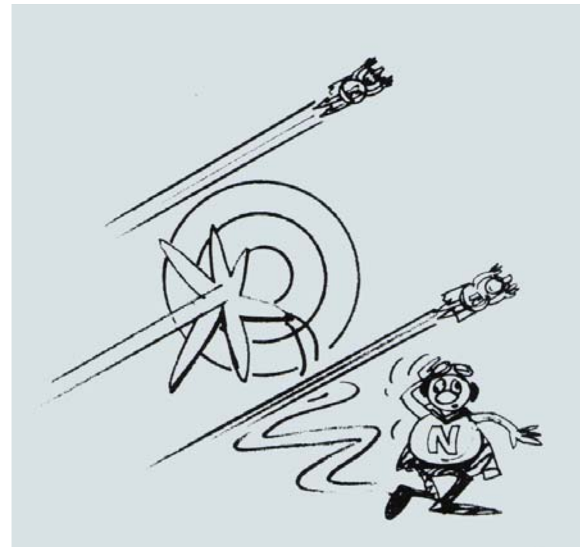


Φ = number of incident neutrons per cm^2 per second

σ = total number of neutrons scattered per second / Φ

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

$$\frac{d^2\sigma}{d\Omega dE} = \frac{\text{number of neutrons scattered per second into d}\Omega \text{ \& dE}}{\Phi \text{ d}\Omega \text{ dE}}$$



cross section

The effective area presented by a nucleus to an incident neutron. One unit for cross section is the barn, as in "can't hit the side of a barn!"

σ measured in barns:
1 barn = 10^{-24} cm^2

Attenuation = $\exp(-N\sigma t)$
N = # of atoms/unit volume
t = thickness

Scattering from Many Atoms

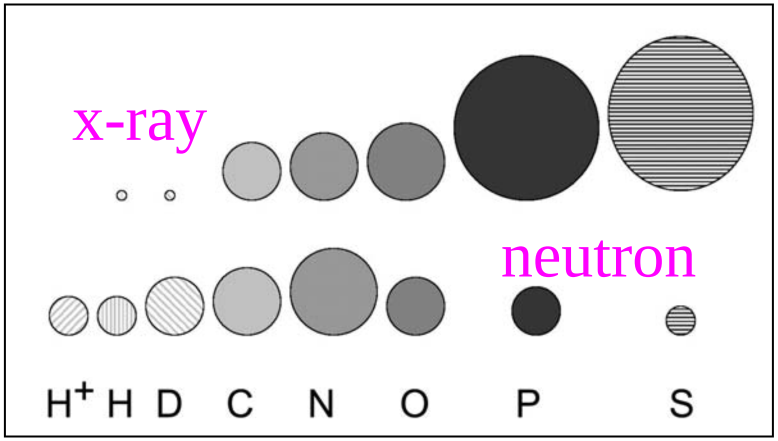
- Neutrons are scattered by nuclei
  - The range of nuclear forces is femtometers – much less than the neutron wavelength so the scattering is point like (ripples on a pond)
- Energy of (thermal) neutron is too small to change nuclear energy
  - If the nucleus is fixed, the scattering is elastic
- We can add up the (elastic) scattering from an assembly of nuclei:

$$\frac{d\sigma}{d\Omega} = \sum_{i,j} b_i b_j e^{i(\vec{k}_0 - \vec{k}').(\vec{R}_i - \vec{R}_j)} = \sum_{i,j} b_i b_j e^{-i\vec{Q}.(\vec{R}_i - \vec{R}_j)}$$

where the wavevector transfer Q is defined by $\vec{Q} = \vec{k}' - \vec{k}_0$

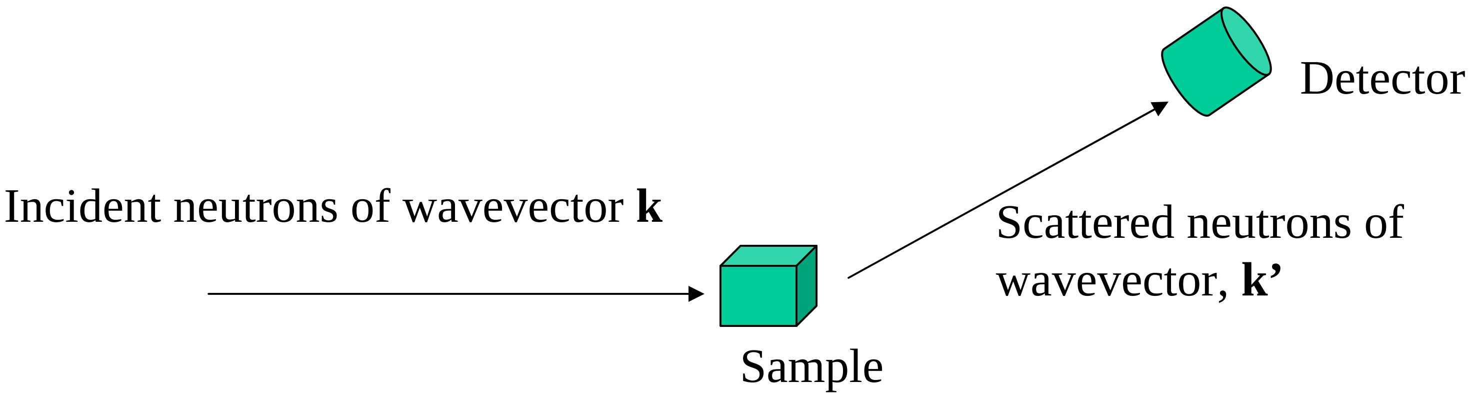
  - b_i is called the coherent scattering length of nucleus *i*
  - ***k*** is the incident neutron wavevector (2π/λ); ***k'*** is the scattered wavevector
  - The calculation assumes the scattering is weak (called Born Approximation)

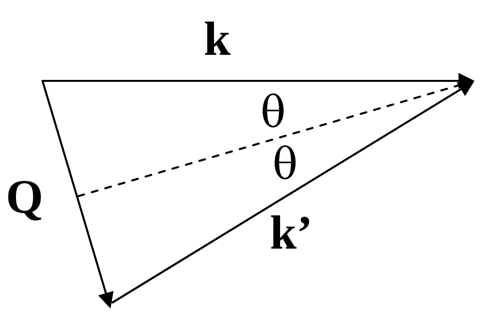
The Success of Neutron Scattering is Rooted in the Neutron's Interactions with Matter



- Interact with nuclei not electrons
- Isotopic sensitivity (especially D and H)
- Penetrates sample containment
- Sensitive to bulk and buried structure
- Simple interpretation – provides statistical averages, not single instances
- Wavelength similar to inter-atomic spacings
- Energy similar to thermal energies in matter
- Nuclear and magnetic interactions of similar strength

Scattering Triangle





Neutron diffraction measures the differential scattering cross section $d\sigma/d\Omega$ as a function of the scattering wavevector (**Q**)

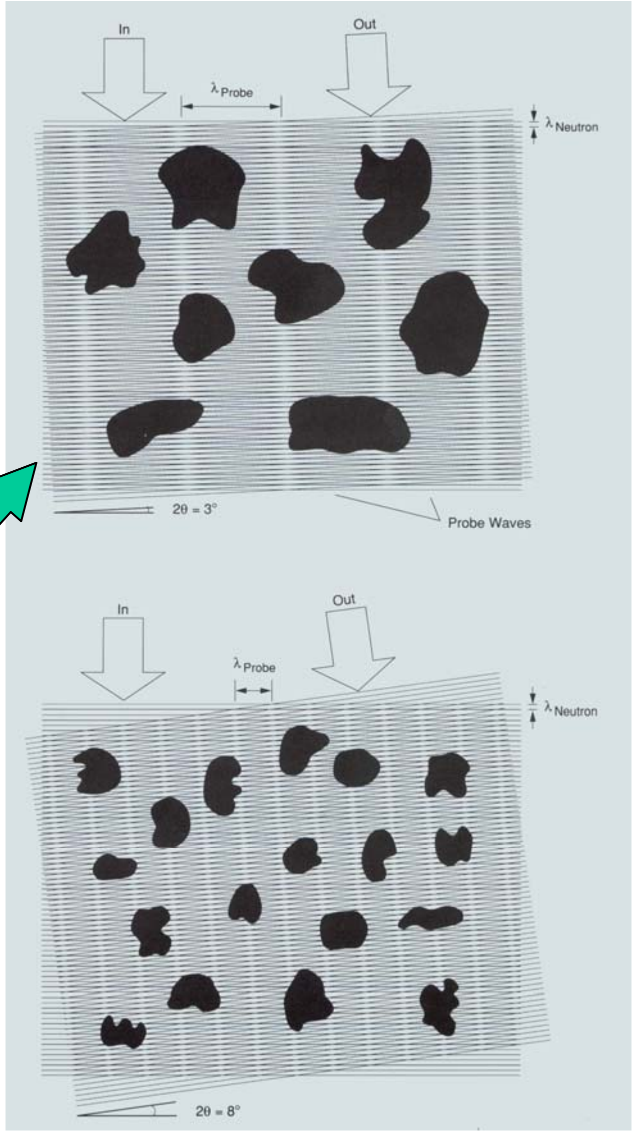
For elastic scattering, k = k' so $Q = 2\, k \sin\theta = (2\,\pi/\lambda)\sin\theta$
The distance probed in the sample is: $d = 2\pi / Q$
(Combining the two equations gives Bragg's Law: $\lambda = 2\, d \sin\theta$)

Small Angle Neutron Scattering (SANS) Is Used to Measure Large Objects (~10 nm to ~1 μm)

Small Q => large d (because $d=2\pi/Q$)

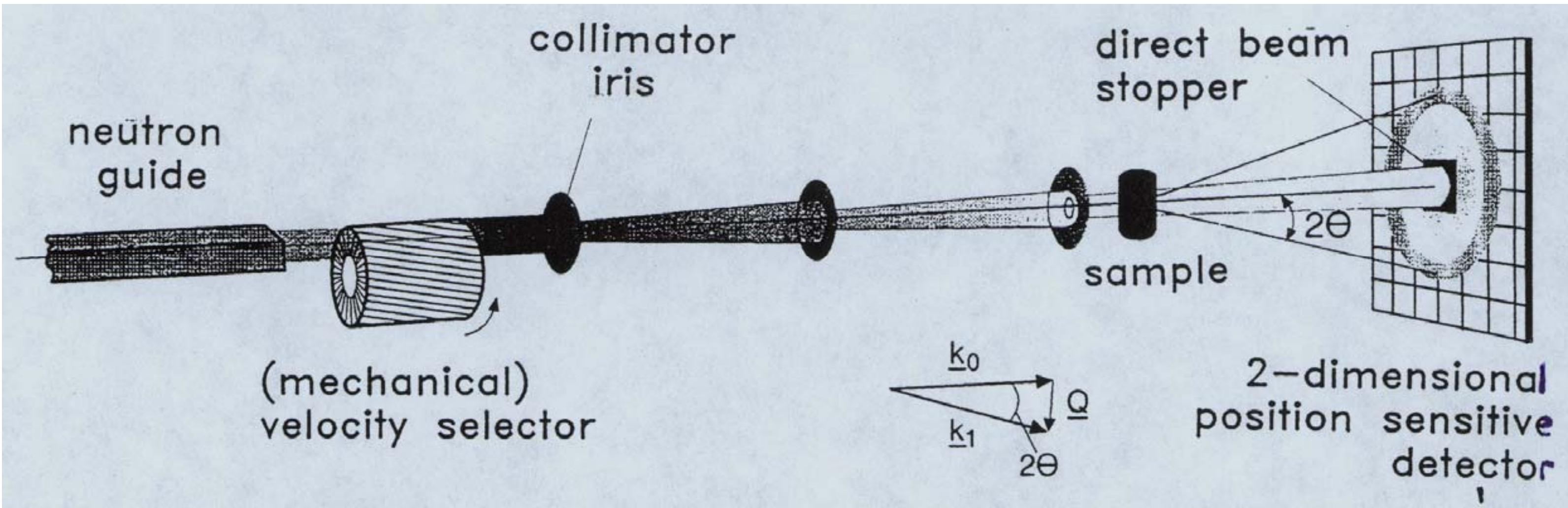
Large d => small θ (because $\lambda = 2 d \sin \theta$)

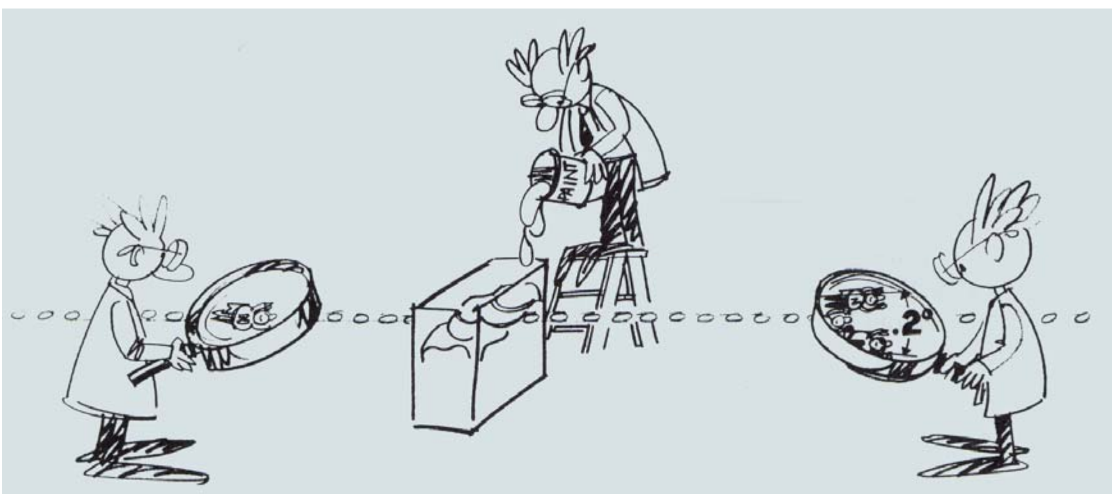
Scattering at small angles probes large length scales



Typical scattering angles for SANS are ~ 0.3º to 5º

Two Views of the Components of a Typical Reactor-based SANS Diffractometer

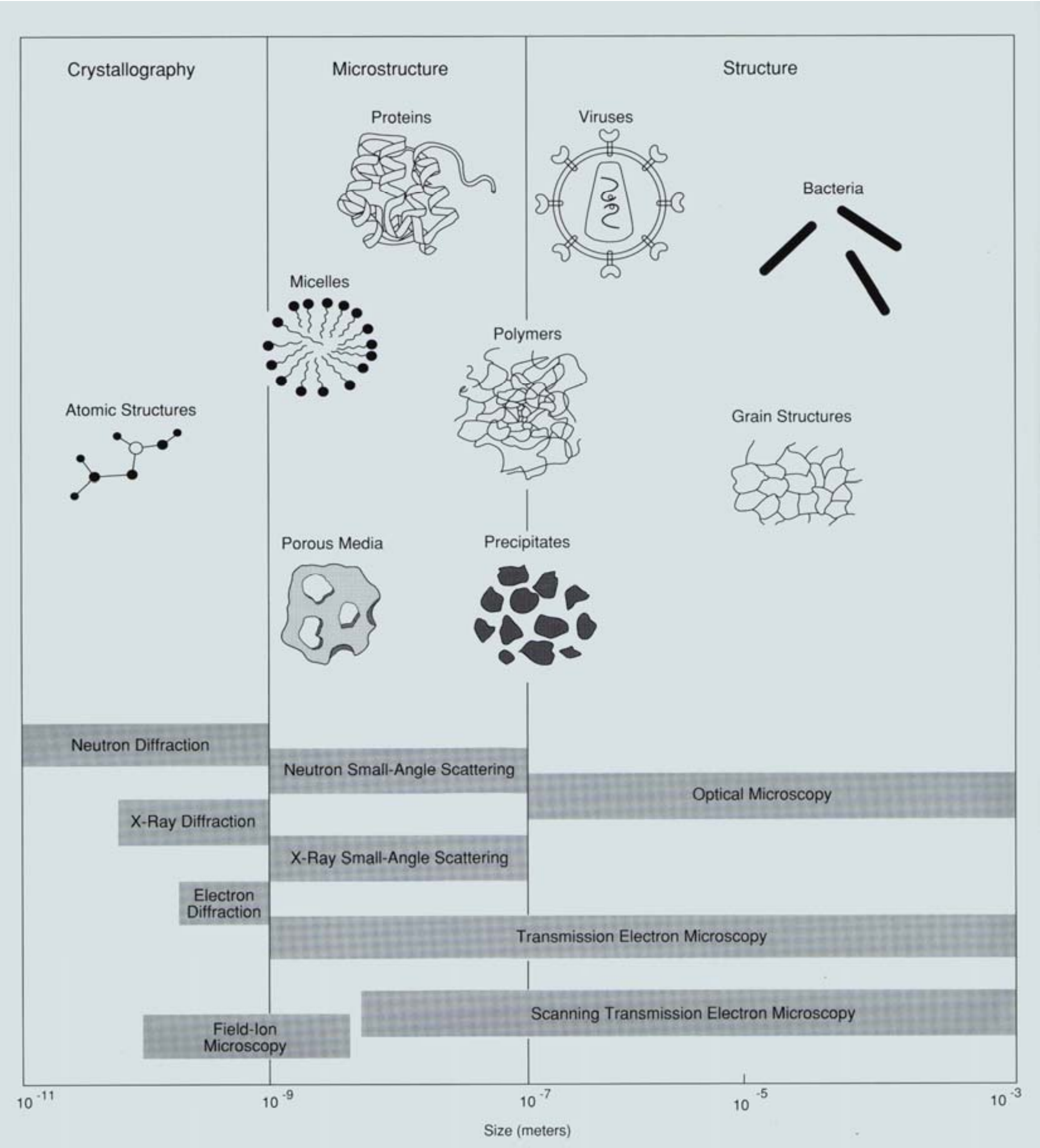




Note that SANS, like other diffraction methods, probes material structure in the direction of (vector) $\vec{Q}$

The NIST 30m SANS Instrument Under Construction

Where Does SANS Fit As a Structural Probe?



Typical SANS Applications

- Biology
  - Organization of biomolecular complexes in solution
  - Conformation changes affecting function of proteins, enzymes, protein/DNA complexes, membranes etc
  - Mechanisms and pathways for protein folding and DNA supercoiling

- Polymers
  - Conformation of polymer molecules in solution and in the bulk
  - Structure of microphase separated block copolymers
  - Factors affecting miscibility of polymer blends

- Chemistry
  - Structure and interactions in colloid suspensions, microemeulsions, surfactant phases etc
  - Mechanisms of molecular self-assembly in solutions

Scattering Length Density

- Remember $$\frac{d\sigma}{d\Omega} = b_{coh}^2 \left\langle \left| \int d\vec{r}.e^{-i\vec{Q}.\vec{r}} n_{nuc}(\vec{r}) \right|^2 \right\rangle$$
- What happens if Q is very small?
  - The phase factor will not change significantly between neighboring atoms
  - We can average the nuclear scattering potential over length scales ~2π/10Q
  - This average is called the scattering length density and denoted $\rho(\vec{r})$
- How do we calculate the SLD?
  - Easiest method: go to www.ncnr.nist.gov/resources/sldcalc.html
  - By hand: let us calculate the scattering length density for quartz – SiO_2
  - Density is 2.66 $gm.cm^{-3}$; Molecular weight is 60.08 gm. $mole^{-1}$
  - Number of molecules per $Å^3$ = N = $10^{-24}(2.66/60.08)*N_{avagadro}$ = 0.0267 molecules per $Å^3$
  - SLD=Σb/volume = $N(b_{Si} + 2b_O)$ = 0.0267(4.15 + 11.6) 10^{-5} $Å^{-2}$ = 4.21 $x10^{-6}$ $Å^{-2}$
- A uniform SLD causes scattering only at Q=0; spatial variations in the SLD cause scattering at finite values of Q

SLD Calculation

- www.ncnr.nist.gov/resources/sldcalc.html
- Need to know chemical formula and density

Enter →	Compound	C6H12
Enter →	Density (g/cm^3)	0.86
Not relevant for SLD →	Wavelength (A)	6
		Calculate
	Neutron SLD	-3.07E-7 (A^-2)
X-ray values →	Cu Ka SLD	8.34E-6 +9.36E-9i (A^-
X-ray values →	Mo Ka SLD	8.33E-6 +2.08E-9i (A^-
Background →	Neutron Inc. XS	5.93; 33.4 (cm^-1)
	Neutron Abs. XS	0.0823 (cm^-1)
Determine best sample thickness →	Neutron 1/e length	0.166 (cm)

Note units of the cross section – this is cross section per unit volume of sample

SANS Measures Particle Shapes and Inter-particle Correlations

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 \int_{space} d^3r \int_{space} d^3r' n_N(\vec{r}) n_N(\vec{r}').e^{i\vec{Q}.(\vec{r}-\vec{r}')}$$

$$= \int_{space} d^3R \int_{space} d^3R' \langle n_P(\vec{R}) n_P(\vec{R}') \rangle e^{i\vec{Q}.(\vec{R}-\vec{R}')} \left\langle \left| (\rho - \rho_0) \int_{particle} d^3x.e^{i\vec{Q}.\vec{x}} \right|^2 \right\rangle_{orientation}$$

$$\frac{d\sigma}{d\Omega} = (\rho - \rho_0)^2 \left| F(\vec{Q}) \right|^2 V_p^2 N_P \int_{space} d^3R.G_P(\vec{R}).e^{i\vec{Q}.\vec{R}}$$

where G_P is the particle - particle correlation function (the probability that there is a particle at $\vec{R}$ if there's one at the origin) and $|F(\vec{Q})|^2$ is the particle form factor :

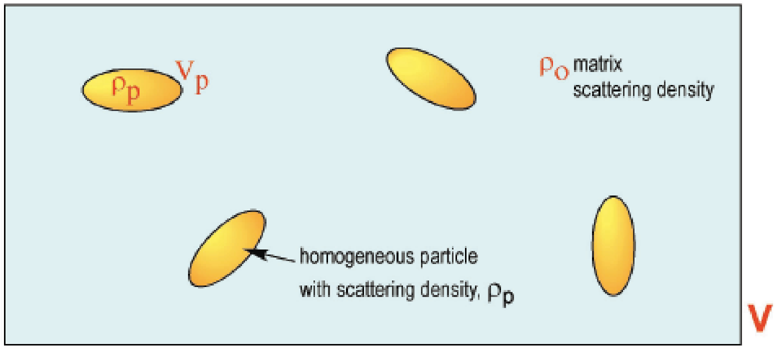
$$\left| F(\vec{Q}) \right|^2 = \frac{1}{V_p^2} \left\langle \left| \int_{particle} d^3x.e^{i\vec{Q}.\vec{x}} \right|^2 \right\rangle_{orientation}$$

Scattering from Independent Particles

Scattered intensity per unit volume of sample = $I(\vec{Q}) = \frac{1}{V}\frac{d\sigma}{d\Omega} = \frac{1}{V}\left\langle \left| \int \rho(\vec{r}) e^{i\vec{Q}.\vec{r}} d\vec{r} \right|^2 \right\rangle$

For identical particles

$$I(Q) = \frac{N}{V}(\rho_p - \rho_0)^2 V_p^2 \left\langle \left| \frac{1}{V_p} \int_{particle} e^{i\vec{Q}.\vec{r}} d\vec{r} \right|^2 \right\rangle$$



contrast factor

particle form factor $\left|F(\vec{Q})\right|^2$

Note that $I(0) = \frac{N}{V}(\rho_p - \rho_0)^2 V_p^2$

Particle concentration $c = NV_p / V$ and particle molecular weight $M_w = \rho V_p N_A$

where ρ is the particle mass density and N_A is Avagadro's number

so $I(0) = \frac{cM_w}{\rho N_A}(\rho_p - \rho_0)^2$ provides a way to find the particle molecular weight

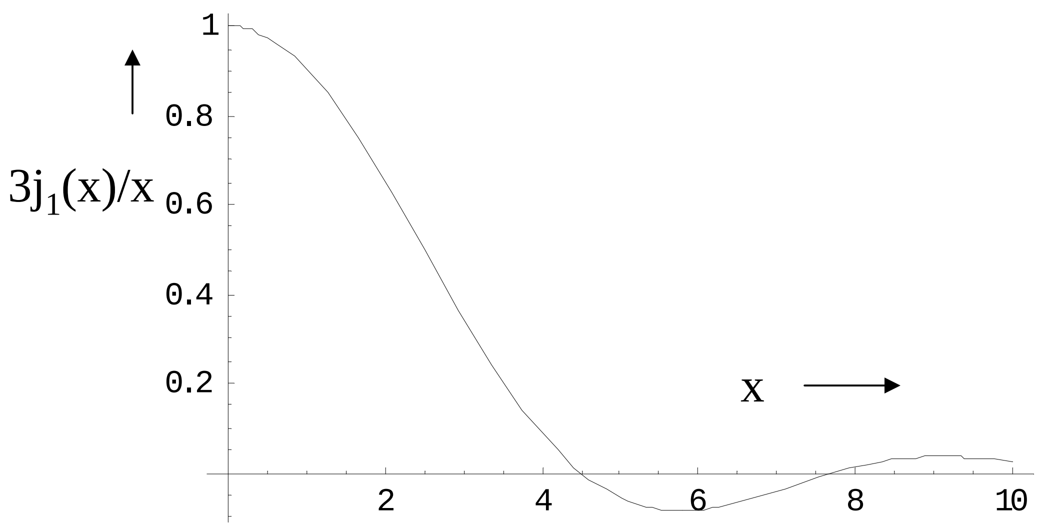
Scattering for Spherical Particles

The particle form factor $\left|F(\vec{Q})\right|^2 = \left|\int_V d\vec{r}\, e^{i\vec{Q}.\vec{r}}\right|^2$ is determined by the particle shape.

For a sphere of radius R, F(Q) only depends on the magnitude of Q:

$$F_{sphere}(Q) = 3V_0\left[\frac{\sin QR - QR\cos QR}{(QR)^3}\right] \equiv \frac{3V_0}{QR} j_1(QR) \;\to V_0 \text{ at } Q = 0$$

Thus, as $Q \to 0$, the total scattering from an assembly of uncorrelated spherical particles [i.e. when $G(\vec{r}) \to \delta(\vec{r})$] is proportional to the square of the particle volume times the number of particles.



Radius of Gyration Is the Particle "Size" Usually Deduced From SANS Measurements

If we measure $\vec{r}$ from the centroid of the particle and expand the exponential in the definition of the form factor at small Q:

$$F(Q) = \int_V d\vec{r} e^{i\vec{Q}.\vec{r}} \approx V_0 + i\int_V \vec{Q}.\vec{r} d^3r - \frac{1}{2}\int_V (\vec{Q}.\vec{r})^2 d^3r + ...$$

$$= V_0\left[1 - \frac{Q^2}{2}\frac{\int_0^\pi \cos^2\theta \sin\theta . d\theta}{\int_0^\pi \sin\theta . d\theta}\frac{\int_{V_0} r^2 d^3r}{\int_{V_0} d^3r} + ...\right] = V_0\left[1 - \frac{Q^2 r_g^2}{6} + ...\right] \approx V_0 e^{-\frac{Q^2 r_g^2}{6}}$$

where r_g is the radius of gyration is $r_g = \int_V R^2 d^3r / \int_V d^3r$. It is usually obtained from a fit to SANS data at low Q (in the so-called Guinier region) or by plotting ln(Intensity) v Q^2. The slope of the data at the lowest values of Q is $r_g^2/3$. It is easily verified that the expression for the form factor of a sphere is a special case of this general result.

Incoherent Background and Absorption

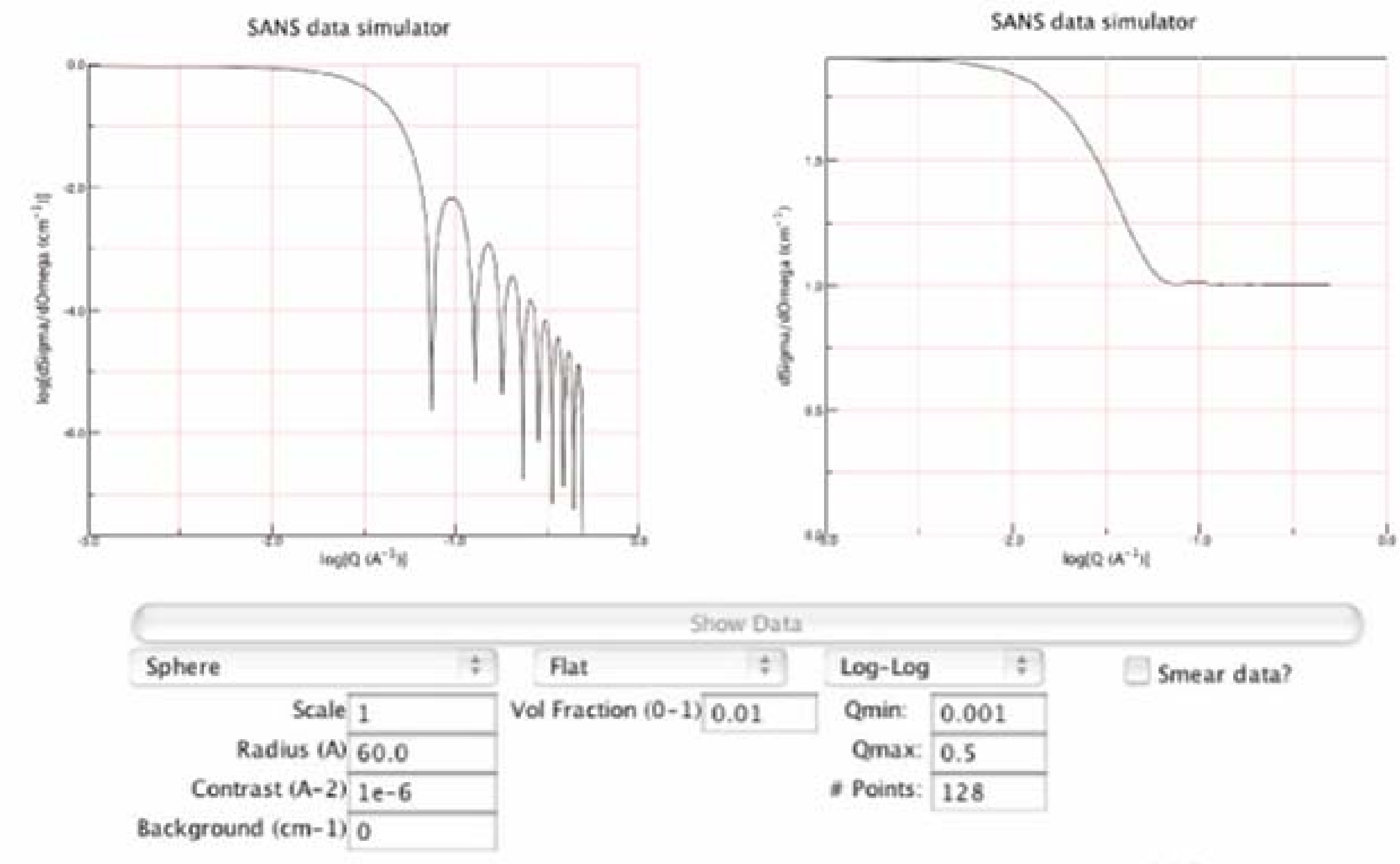
- In addition to coherent (Q-dependent) scattering, neutrons may be scattered incoherently
- Incoherent scattering is not directionally (Q) dependent
  - In SANS (or reflectometry) measurements it is a uniform background
- Incoherent scattering arises from two sources:
  - Spin incoherent scattering (the neutron-nucleus state can be singlet or triplet and these have different scattering lengths)
  - Isotopic incoherent scattering
- Look up incoherent scattering lengths (included in NIST SLD calculator – see next VG)
- Neutrons may also be absorbed by some nuclei

Calculating Form Factors

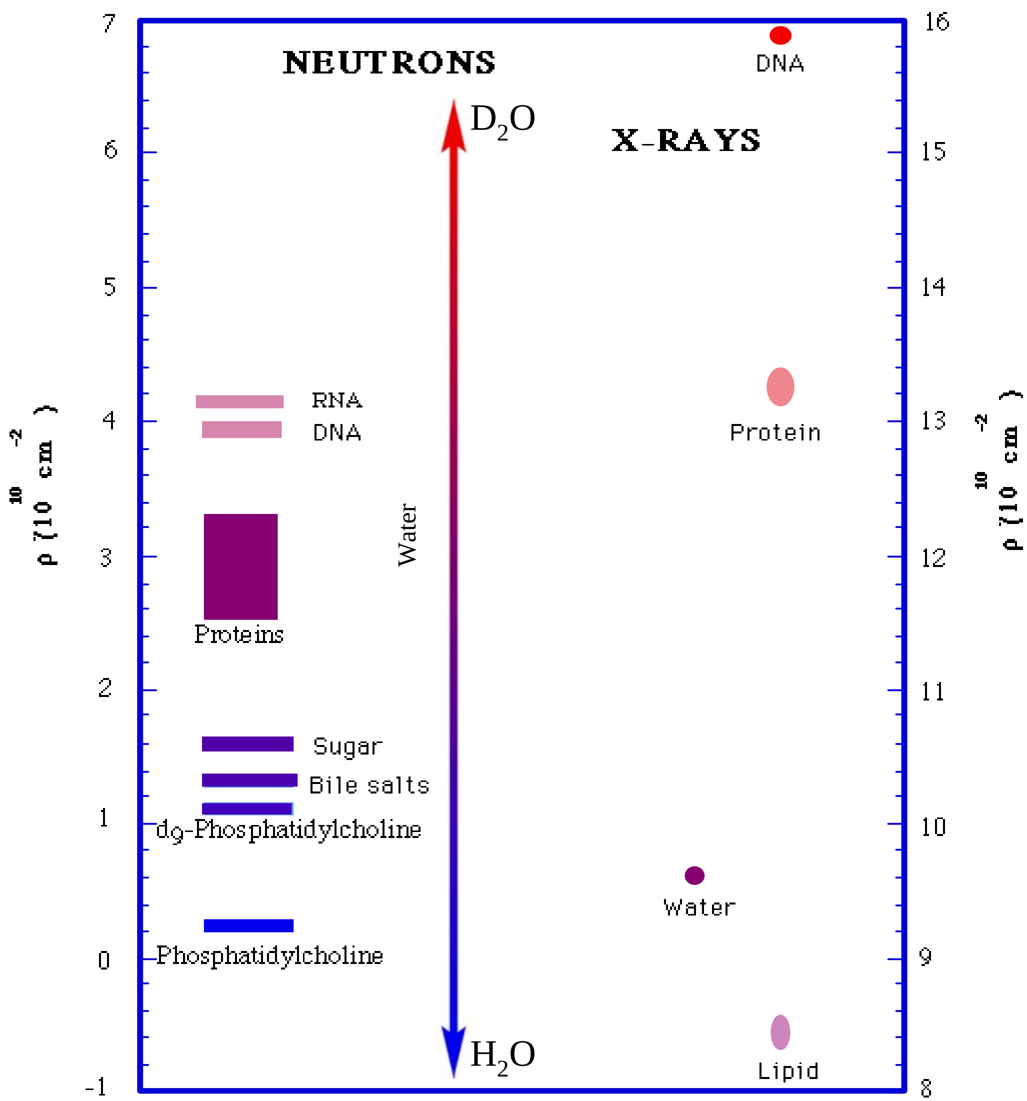
- www.ncnr.nist.gov/resources/simulator.html
- Note: T(1 mm H_2O) = 0.5; T(1 mm D_2O) = 0.9
  $d\sigma/d\Omega$ (H_2O) = 1 cm^{-1}; $d\sigma/d\Omega$ (D_2O) = 0.06 cm^{-1}

No background

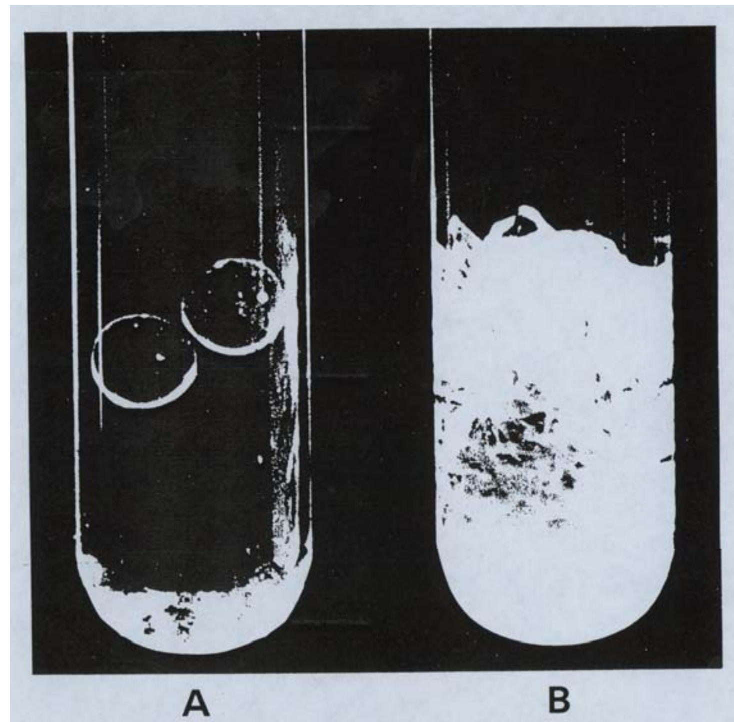
H_2O background



Contrast & Contrast Matching

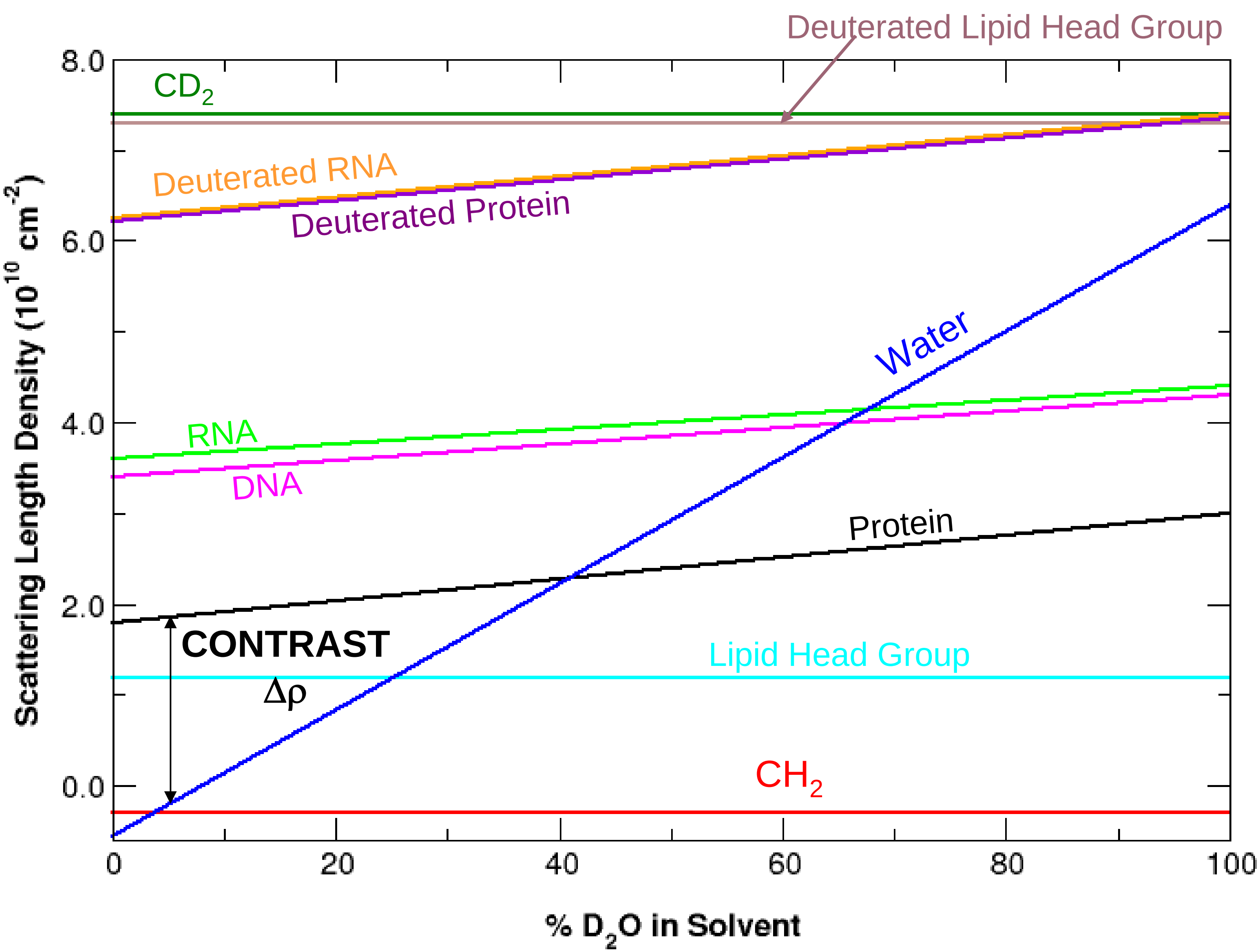


* Chart courtesy of Rex Hjelm



Both tubes contain borosilicate beads + pyrex fibers + solvent. (A) solvent refractive index matched to pyrex;. (B) solvent index different from both beads and fibers – scattering from fibers dominates

Contrast Variation



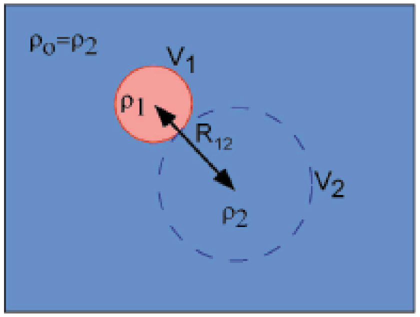
Isotopic Contrast for Neutrons

Hydrogen Isotope	Scattering Length b (fm)
^{1}H	-3.7409 (11)
^{2}D	6.674 (6)
^{3}T	4.792 (27)

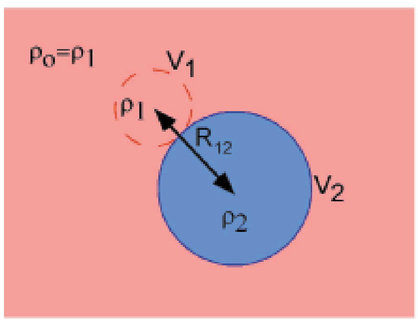
Nickel Isotope	Scattering Lengths b (fm)
^{58}Ni	15.0 (5)
^{60}Ni	2.8 (1)
^{61}Ni	7.60 (6)
^{62}Ni	-8.7 (2)
^{64}Ni	-0.38 (7)

Using Contrast Variation to Study Compound Particles

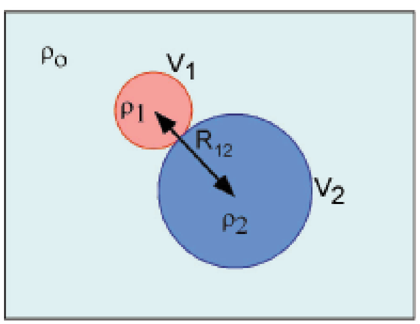
Examples include nucleosomes (protein/DNA) and ribosomes (poteins/RNA)



$$I_1(Q) = (\rho_1 - \rho_2)^2 F_1^2$$



$$I_2(Q) = (\rho_2 - \rho_1)^2 F_2^2$$



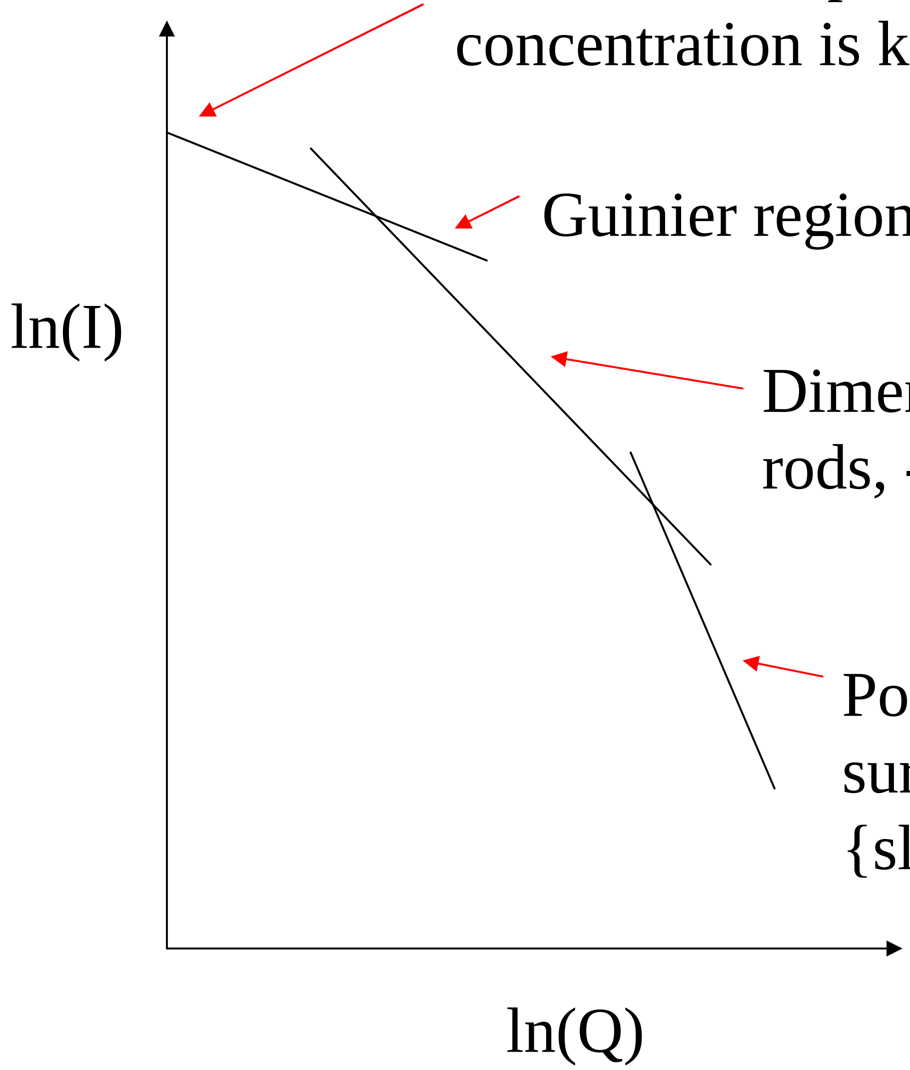
$$I_3(Q) - \frac{(\rho_1 - \rho_o)^2}{(\rho_1 - \rho_2)^2} I_1(Q) - \frac{(\rho_2 - \rho_o)^2}{(\rho_1 - \rho_2)^2} I_2(Q)$$

$$= \underbrace{2(\rho_1 - \rho_o)(\rho_2 - \rho_o) F_1 F_2 \frac{\sin(QR_{12})}{QR_{12}}}$$

$=0$ at $Q = \pi/R_{12}$

Viewgraph from Charles Glinka (NIST)

What can we Learn from SANS?



Zero Q intercept - gives particle volume if concentration is known

Guinier region (slope = $-r_g^2/3$ gives particle "size")

Dimensionality of particle (slope = -1 for rods, -2 for sheets, $-D_f$ for a mass fractal)

Porod region - gives surface area and surface fractal dimension {slope = $-(6-D_s)$}

Sample Requirements for SANS

- Monodisperse particles, non-interacting to measure shape
- Concentration: 1-5 mg/ml
- Volume: 350-700 μl per sample
- Data collection time: 0.5-6 hrs per sample
- Typical biology experiment: 2-4 days
- Deuterated solvent is highly desirable
- Multiple concentrations are usually necessary.
- Specific deuteration may be necessary.
- Multiple solvents of different deuteration are highly desirable → contrast variation.

References

- Viewgraphs describing the NIST 30-m SANS instrument
  - www.ncnr.nist.gov/programs/sans/tutorials/30mSANS_desc.pdf
- SANS data can be simulated for various particle shapes using the programs available at:
  - www.ncnr.nist.gov/resources/simulator.html
- To choose instrument parameters for a SANS experiment at NIST go to:
  - www.ncnr.nist.gov/resources/sansplan.html
- A very good description of SANS experiments can be found at:
  http://www.strubi.ox.ac.uk/people/gilbert/sans.html

END