

by

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Small Angle Scattering

This Lecture

- The size of objects measured with SANS
- Typical applications of SANS
- Instrumental resolution – how well can size be determined?
- Scattering length density
- Formal expression for scattering cross section
- Scattering from independent particles
- Radius of gyration and Guinier approximation
- Shapes of composite particles
- Particle correlations
- Contrast variation
- Porod scattering
- Scattering from fractals
- Sample requirements for SANS
- Tools for estimating scattering and interpreting data

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

Recall that :

$$\vec{Q} = \vec{k}' - \vec{k}_0 = 2k_0 \sin \theta \quad \text{for elastic scattering}$$

and that

$$\lambda = 2\pi / k = 2\pi / (Q / 2 \sin \theta) = 4\pi \sin \theta / Q$$

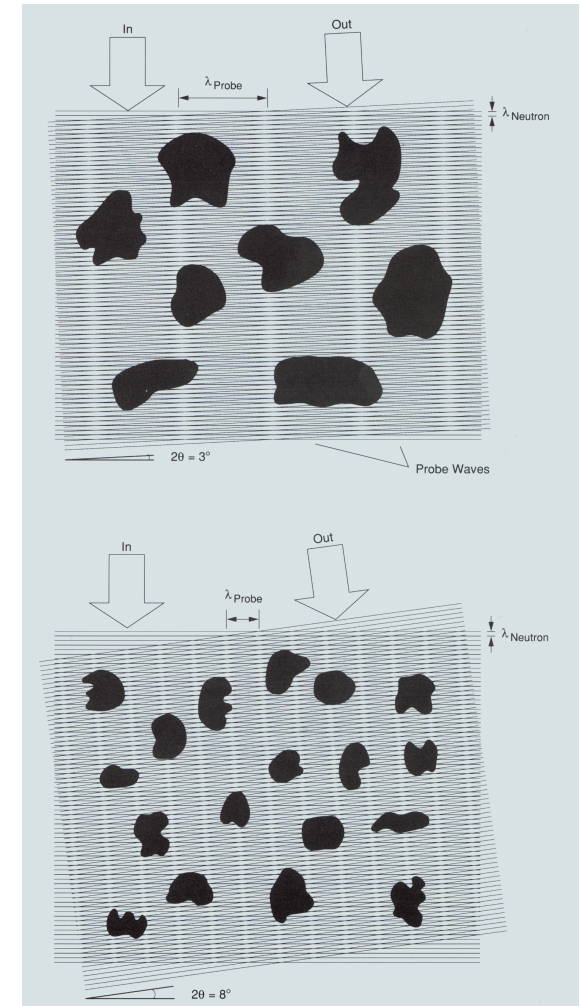
so we can rewrite Bragg's law $\lambda = 2d \sin \theta$ as

$$d = 2\pi / Q \quad \text{or for small } \theta \quad d \approx \lambda / 2\theta$$

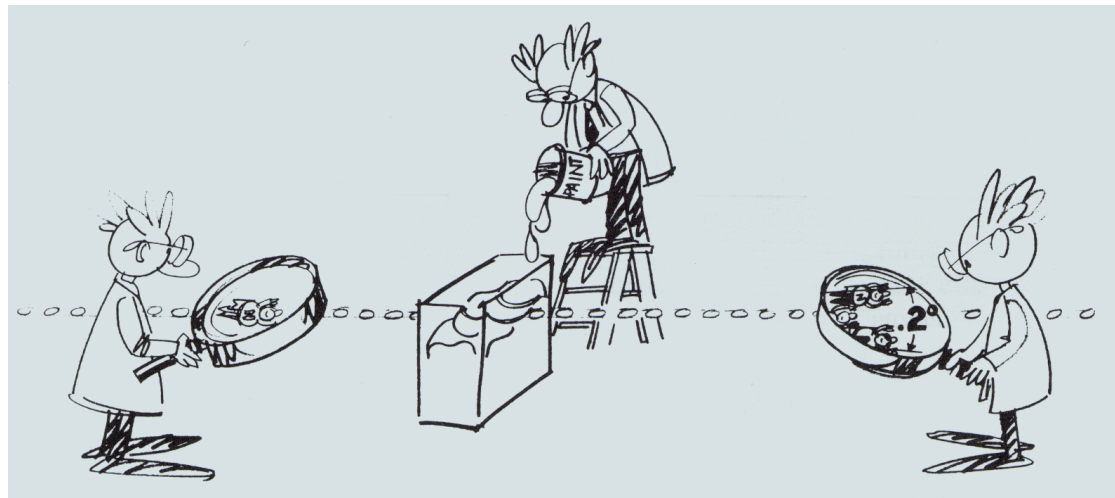
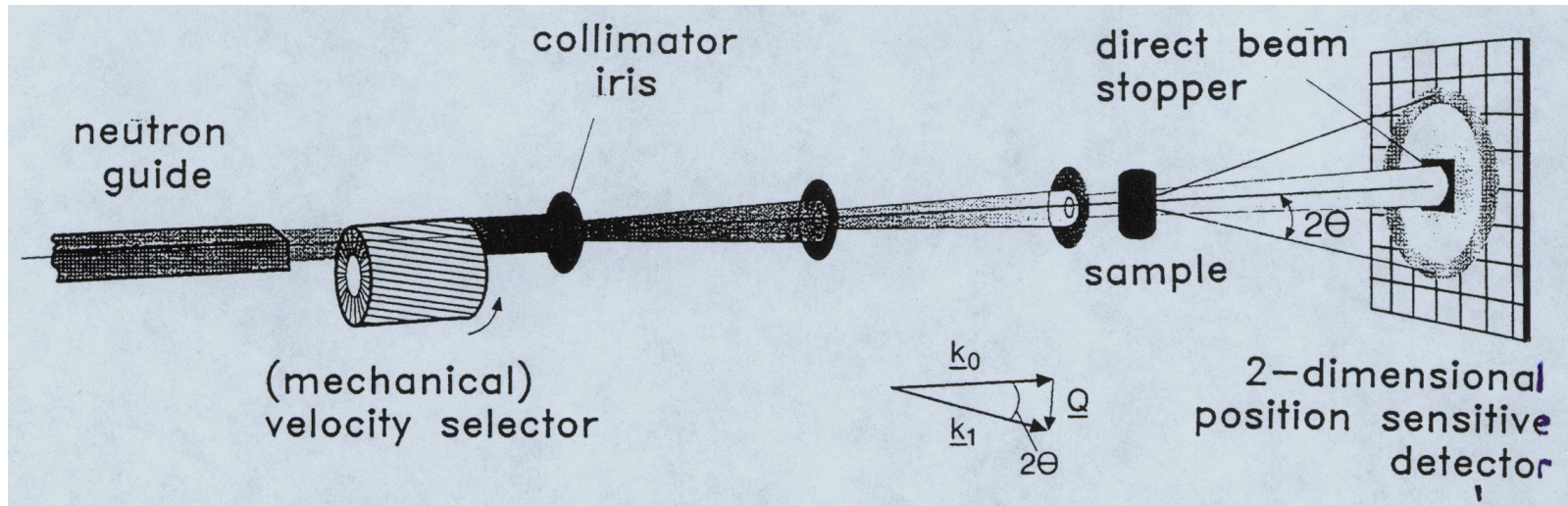
i.e. small $Q \Rightarrow$ large length scales

Scattering at small angles probes large length scales

Typical scattering angles for SANS are $\sim 0.3^\circ$ to 5°



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

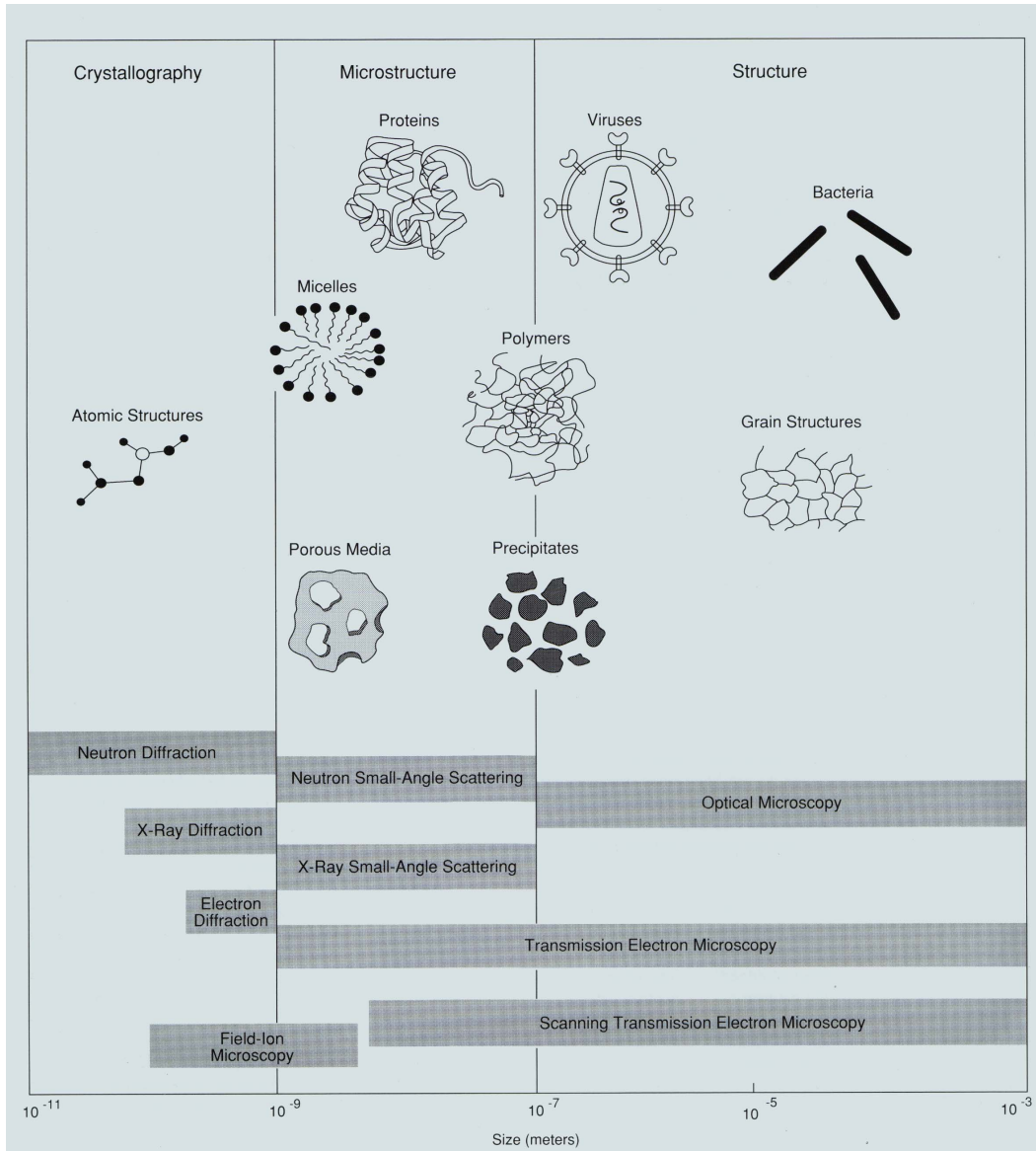


Note that SANS, like other diffraction methods, probes material structure in the direction of (vector) \vec{Q}

The NIST 30m SANS Instrument Under Construction



Where Does SANS Fit As a Structural Probe?



- SANS resolves structures on length scales of 1 – 1000 nm
- Neutrons can be used with bulk samples (1-2 mm thick)
- SANS is sensitive to light elements such as H, C & N
- SANS is sensitive to isotopes such as H and D

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, microemulsions, surfactant phases etc
 - Mechanisms of molecular self-assembly in solutions

Instrumental Resolution for SANS

$$Q = \frac{4\pi}{\lambda} \sin \theta \Rightarrow \left\langle \frac{\delta Q^2}{Q^2} \right\rangle = \left\langle \frac{\delta \lambda^2}{\lambda^2} \right\rangle + \left\langle \frac{\cos^2 \theta \cdot \delta \theta^2}{\sin^2 \theta} \right\rangle$$

For SANS, $(\delta \lambda / \lambda)_{rms} \sim 5\%$ and θ is small, so $\left\langle \frac{\delta Q^2}{Q^2} \right\rangle = 0.0025 + \left\langle \frac{\delta \theta^2}{\theta^2} \right\rangle$

For equal source - sample & sample - detector distances of L and equal apertures at source and sample of h , $\delta \theta_{rms} = \sqrt{5/12} h/L$.

The smallest value of θ is determined by the direct beam size: $2\theta_{min} \sim 1.5h/L$

At this value of θ , angular resolution dominates and

$$\delta Q_{rms} \sim (\delta \theta_{rms} / \theta_{min}) Q_{min} \sim \delta \theta_{rms} 4\pi / \lambda \sim (2\pi / \lambda) h / L$$

The largest observable object is $\sim 2\pi / \delta Q_{rms} \sim \lambda L / h$.

This achieves a maximum of about $5 \mu\text{m}$ at the ILL 40 m SANS instrument using 15 \AA neutrons.

Note that at the largest values of θ , set by the detector size and distance from the sample, wavelength resolution dominates.

Scattering Length Density

- Remember $\frac{d\sigma}{d\Omega} = b_{coh}^2 \left\langle \left| \int d\vec{r} \cdot e^{-i\vec{Q}\cdot\vec{r}} n_{nuc}(\vec{r}) \right|^2 \right\rangle$
- 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 $\sim 2\pi/10Q$
 - 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 – SiO₂
 - Density is 2.66 gm.cm⁻³; Molecular weight is 60.08 gm. mole⁻¹
 - Number of molecules per Å³ = N = 10⁻²⁴(2.66/60.08)*N_{avagadro} = 0.0267 molecules per Å³
 - SLD=Sb/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; 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
	→	Density (g/cm ³)	0.86
Not relevant for SLD	→	Wavelength (Å)	6
			Calculate
		Neutron SLD	-3.07E-7 (Å ⁻²)
X-ray values	→	Cu Ka SLD	8.34E-6 +9.36E-9i (Å ⁻¹)
	→	Mo Ka SLD	8.33E-6 +2.08E-9i (Å ⁻¹)
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

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 \int_{\text{space}} d^3r \int_{\text{space}} d^3r' n_N(\vec{r}) n_N(\vec{r}') e^{i\vec{Q}\cdot(\vec{r}-\vec{r}')} \\ = \int_{\text{space}} d^3R \int_{\text{space}} d^3R' \langle n_P(\vec{R}) n_P(\vec{R}') \rangle e^{i\vec{Q}\cdot(\vec{R}-\vec{R}')} \left\langle \left| (\rho - \rho_0) \int_{\text{particle}} d^3x e^{i\vec{Q}\cdot\vec{x}} \right|^2 \right\rangle_{\text{orientation}}$$

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

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 :

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

These expressions are the same as those for nuclear scattering except for the addition of a form factor that arises because the scattering is no longer from point-like particles

Scattering from Independent Particles

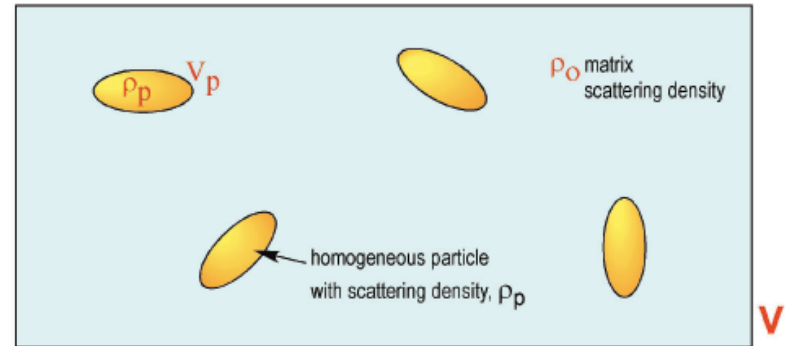
Scattered intensity per unit volume of sample = $I(\vec{Q}) = \frac{1}{V} \frac{d\sigma}{d\Omega} = \frac{1}{V} \left\langle \left| \int \rho(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d\vec{r} \right|^2 \right\rangle$

For identical particles

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

contrast factor

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



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

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

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

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

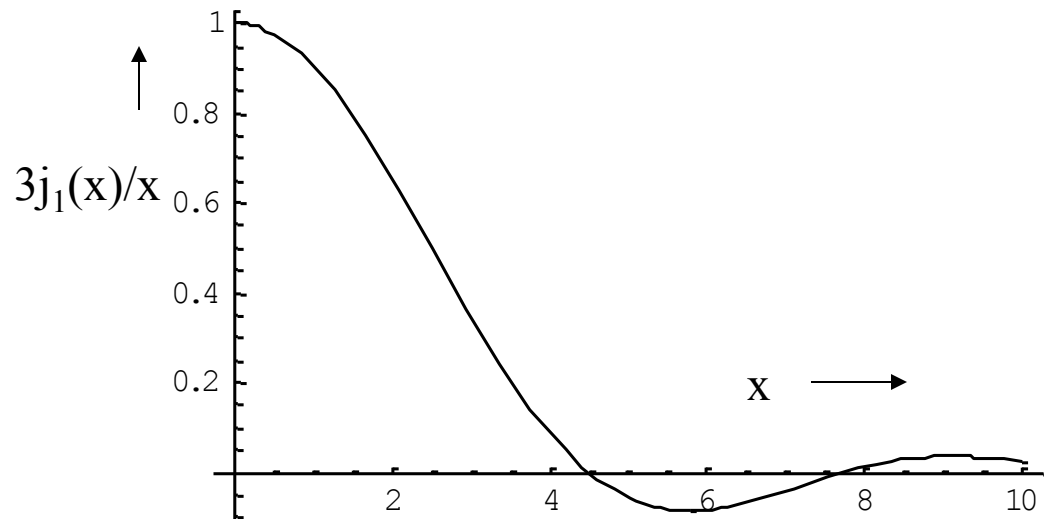
For elliptical particles

replace R by :

$$R \rightarrow (a^2 \sin^2 \vartheta + b^2 \cos^2 \vartheta)^{1/2}$$

where ϑ is the angle between

the major axis (a) and \vec{Q}



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

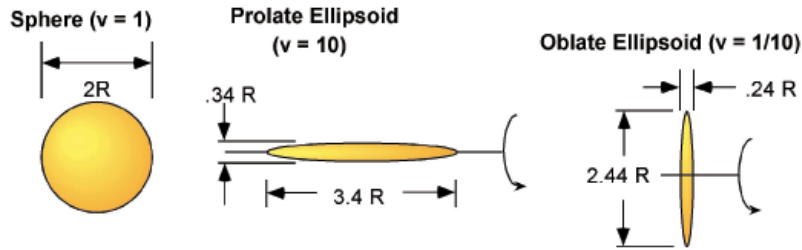
If we measure \vec{r} from the centroid of the particle and expand the exponential in the definition of the form factor at small Q :

$$\begin{aligned}
 F(Q) &= \int_V d\vec{r} e^{i\vec{Q}\cdot\vec{r}} \approx V_0 + i \int_V \vec{Q}\cdot\vec{r} d^3r - \frac{1}{2} \int_V (\vec{Q}\cdot\vec{r})^2 d^3r + \dots \\
 &= V_0 \left[1 - \frac{Q^2}{2} \frac{\int_0^\pi \cos^2 \theta \sin \theta d\theta \int_V r^2 d^3r}{\int_0^\pi \sin \theta d\theta \int_V d^3r} + \dots \right] = V_0 \left[1 - \frac{Q^2 r_g^2}{6} + \dots \right] \approx V_0 e^{-\frac{Q^2 r_g^2}{6}}
 \end{aligned}$$

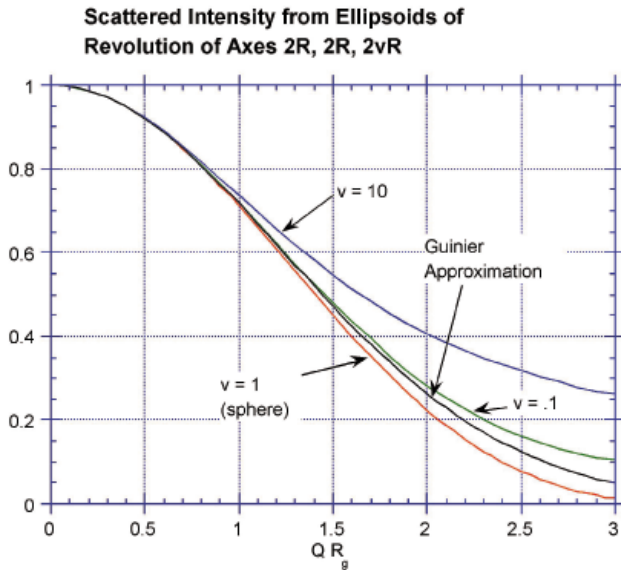
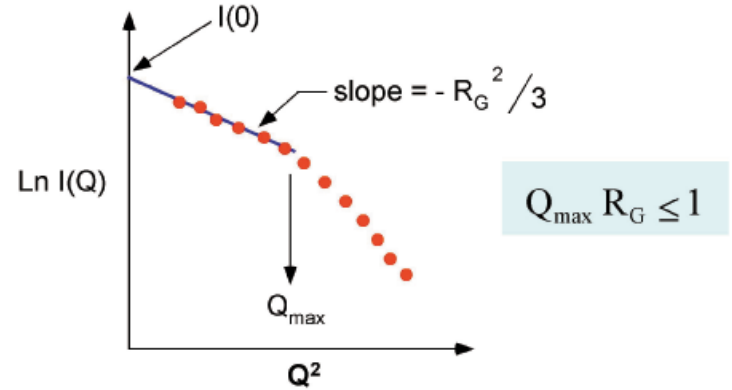
where r_g is the radius of gyration is $r_g = \sqrt{\int_V R^2 d^3r / \int_V d^3r}$. It is usually obtained from a fit to SANS data at low Q (in the so - called Guinier region) or by plotting $\ln(\text{Intensity})$ v Q^2 . The slope of the data at the lowest values of Q is $r_g^2/3$. It is easily verified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

Radii of Gyration for Various Shapes*

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



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



$$R_g = R \sqrt{\frac{2 + v^2}{5}}$$

Note that Guinier approximation works only when $QR_g < 1$

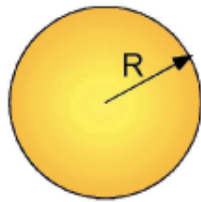
If particles are not mono-disperse, R_g is weighted towards larger particles

$$R_g^2 = \frac{3}{5} \frac{\langle R^8 \rangle}{\langle R^6 \rangle}$$

*Viewgraph from Charles Glinka

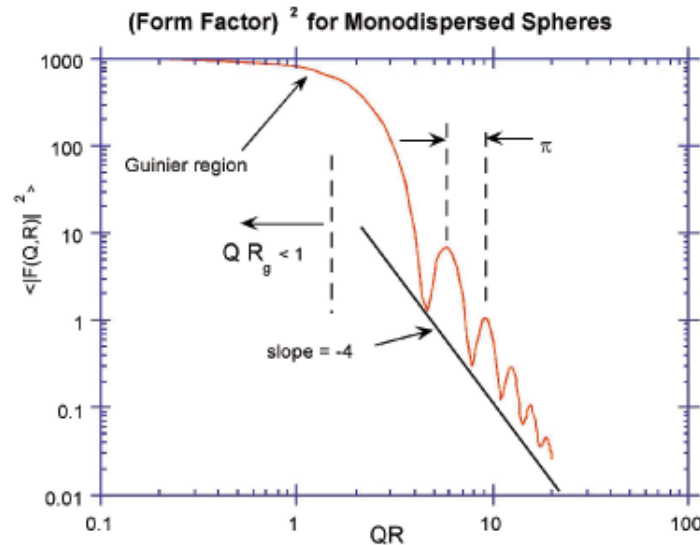
Beyond Guinier: Form Factors for Simple Shapes

1) Spheres

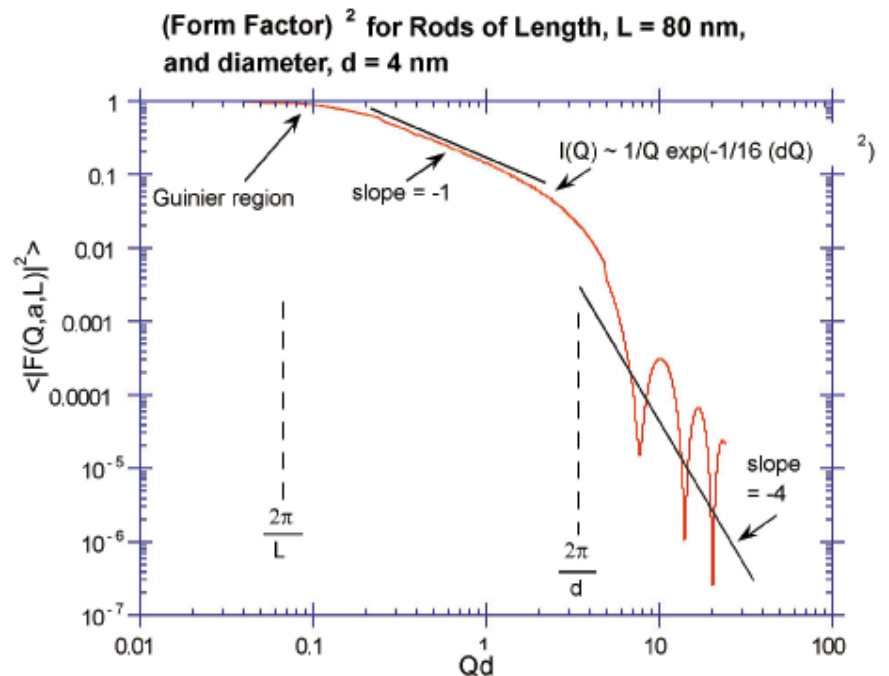
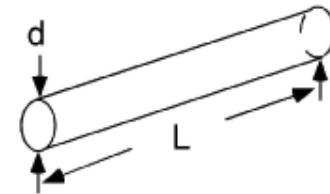


$$\langle |F(Q,R)|^2 \rangle = \left\langle \left| \frac{1}{V_p} \int_{V_p} e^{i\vec{Q}\cdot\vec{r}} d\vec{r} \right|^2 \right\rangle$$

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



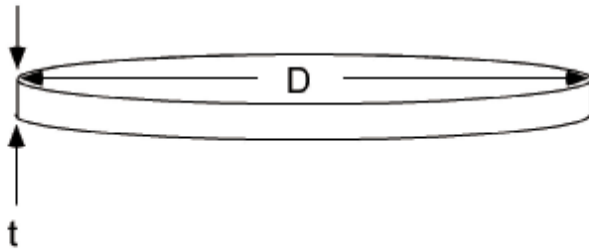
2) Long Rods:



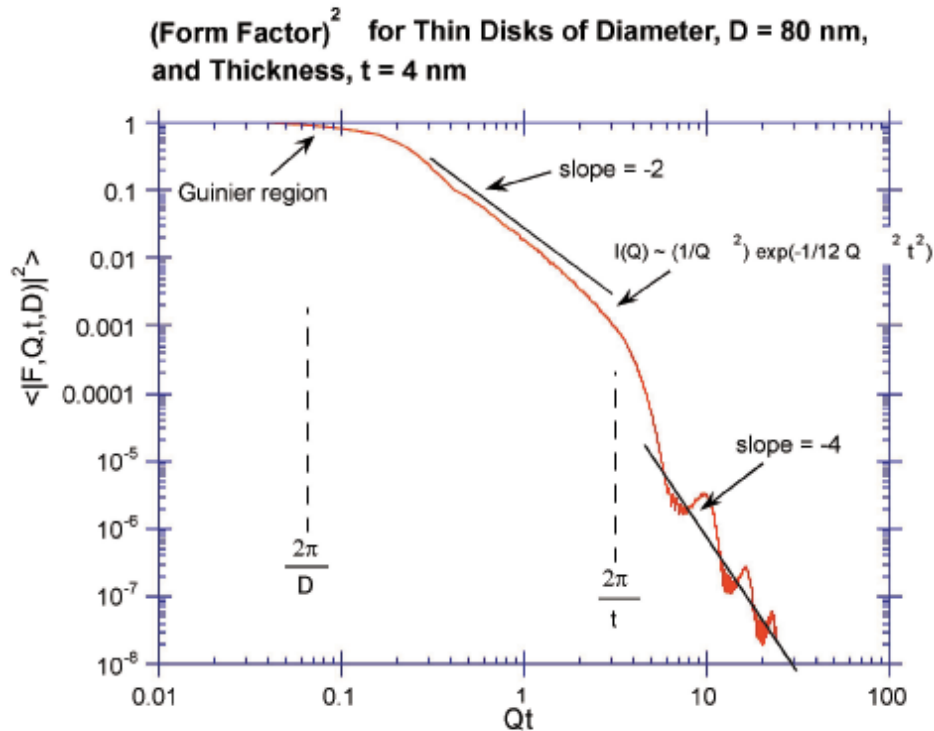
*viewgraph from Charles Glinka (NIST)

Form Factors (*cont' d*)

3) Thin Disks



Note that the slope of $I(Q) \nu Q$ that corresponds to the particle shape occurs over a region of Q bounded by the largest and smallest dimensions of the particles

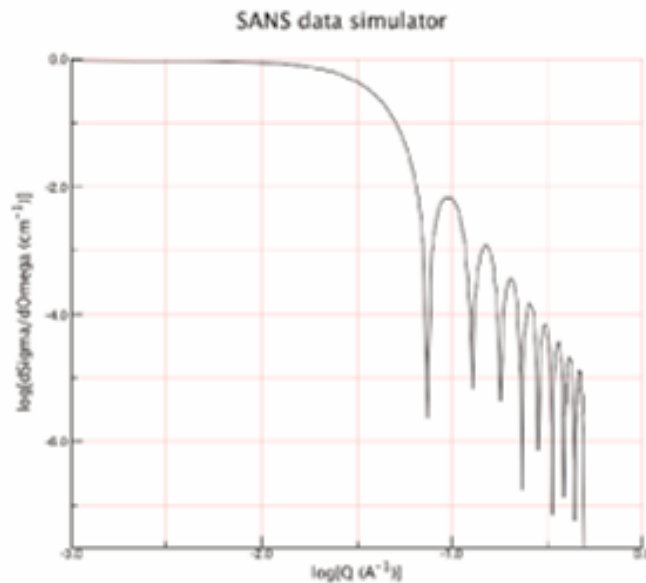


Note also that at large Q the average slope is -4. This is called the Porod region. We will discuss it later. The slope is a manifestation of a smooth 3-dimensional surface of the particles

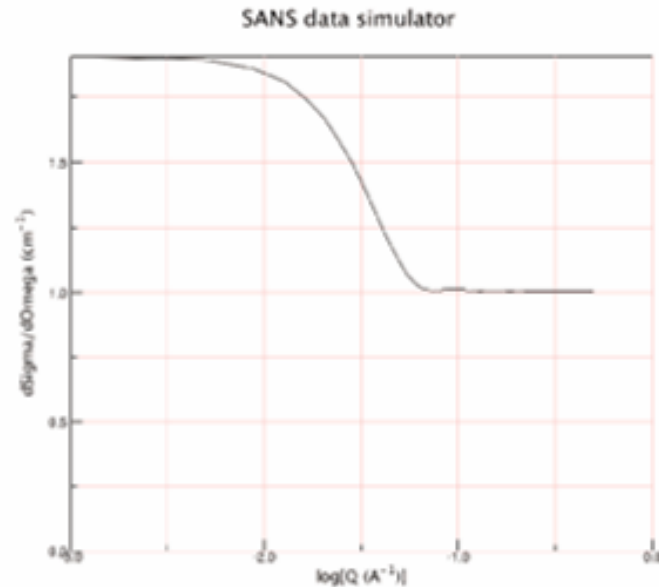
Calculating Form Factors

- www.ncnr.nist.gov/resources/simulator.html
- Note: $T(1 \text{ mm H}_2\text{O}) = 0.5$; $T(1 \text{ mm D}_2\text{O}) = 0.9$
 $ds/dW (\text{H}_2\text{O}) = 1 \text{ cm}^{-1}$; $ds/dW (\text{D}_2\text{O}) = 0.06 \text{ cm}^{-1}$

No background



H₂O background

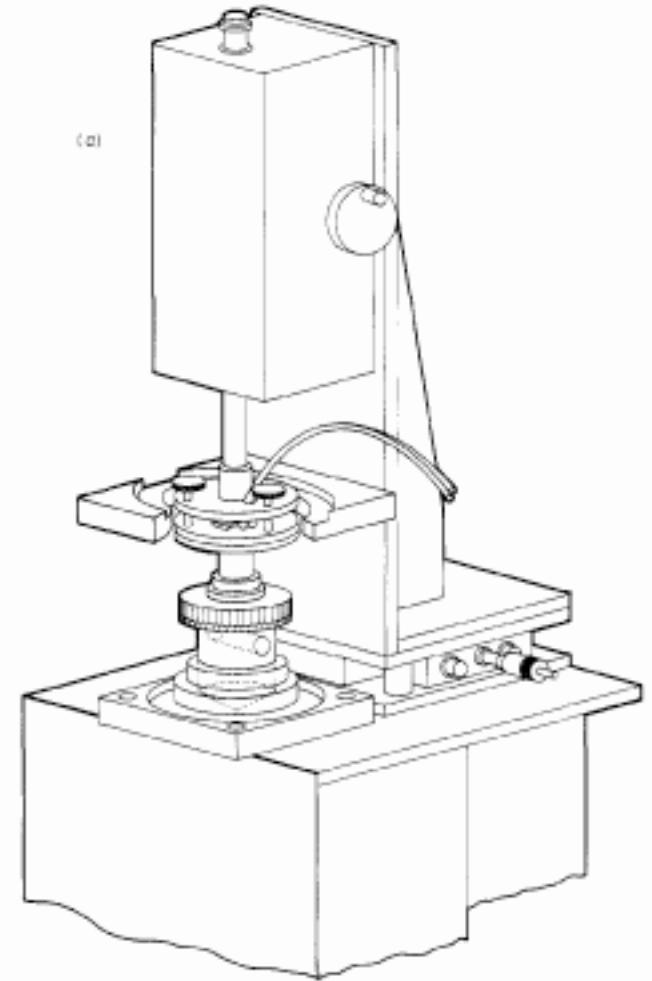
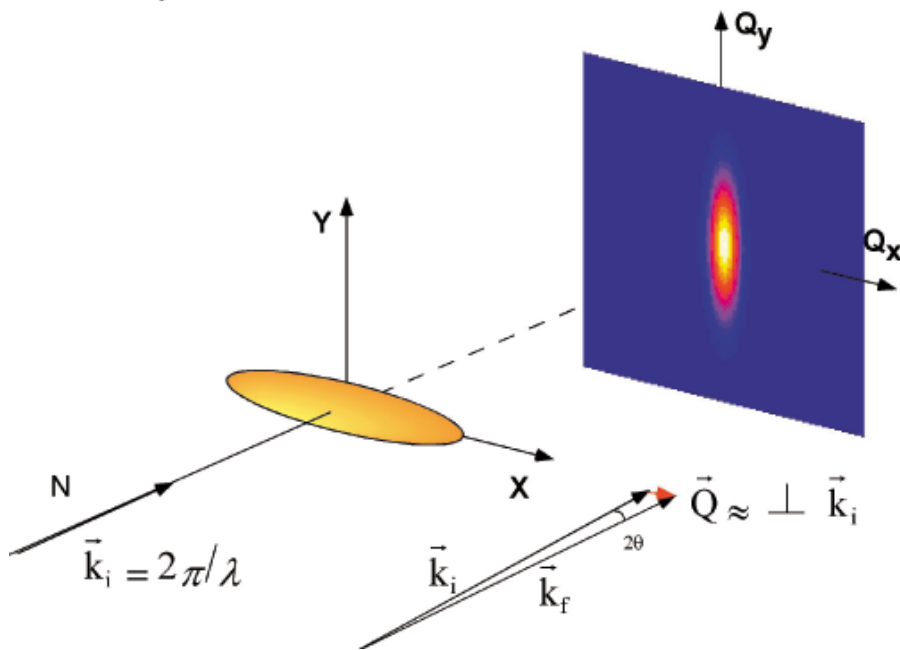


Show Data

Sphere	Flat	Log-Log	<input type="checkbox"/> Smear data?
Scale	Vol Fraction (0-1)	Qmin:	
Radius (A)	0.01	Qmax:	
Contrast (A ⁻²)		# Points:	
Background (cm ⁻¹)			

What Happens if Particles are Lined Up?

- Scattering probes structure in the direction of \vec{Q}



Couette shear cell

Determining Particle Size From Dilute Suspensions

- Particle size is usually deduced from dilute suspensions in which inter-particle correlations are absent
- In practice, instrumental resolution (finite beam coherence) will smear out minima in the form factor
- This effect can be accounted for if the spheres are mono-disperse
- For poly-disperse particles, maximum entropy techniques have been used successfully to obtain the distribution of particles sizes

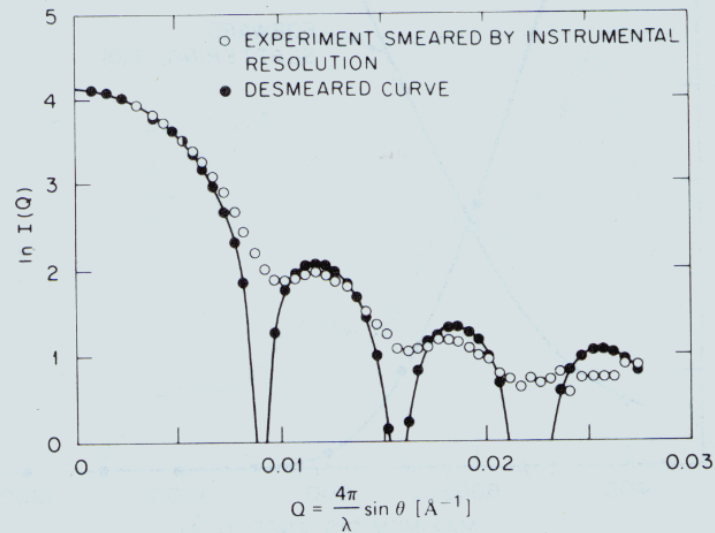


Fig. 4. Plot of $\ln I(Q)$ vs Q for 3.98 vol.% monodisperse PMMA-H spheres (core C1) in D_2O/H_2O mixtures.

Correlations Can Be Measured in Concentrated Systems

- A series of experiments in the late 1980's by Hayter et al and Chen et al produced accurate measurements of $S(Q)$ for colloidal and micellar systems
- To a large extent these data could be fit by $S(Q)$ calculated from the mean spherical model using a Yukawa potential to yield surface charge and screening length

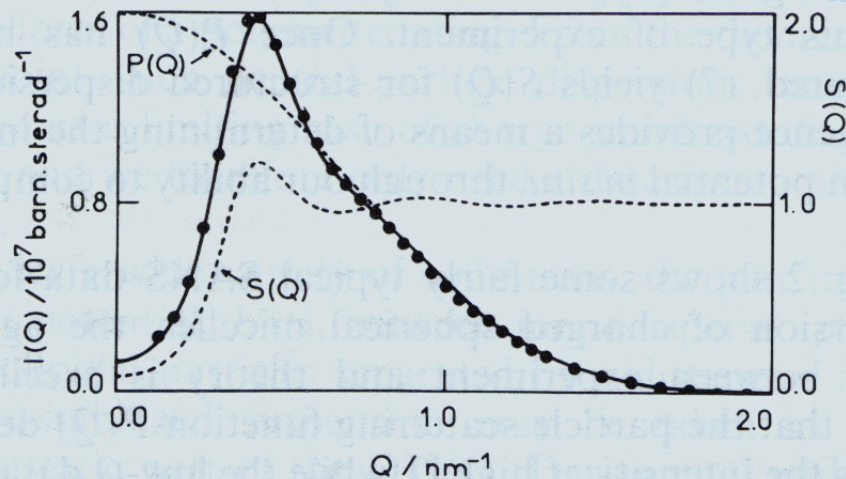


Fig. 2. Observed (●) and calculated (—) scattered intensity $I(Q)$ as a function of momentum transfer Q for a charged micellar dispersion: 0.03 mol dm^{-3} hexadecyltrimethylammonium chloride in D_2O at 313 K. The functions $P(Q)$ and $S(Q)$ are discussed in the text. ($1 \text{ barn sterad}^{-1} = 10^{-28} \text{ M}^2 \text{ sterad}^{-1}$).

Polymers Studied with SANS

For a Gaussian chain $R_g^2 = N\ell^2 / 6$ where ℓ is the segment length

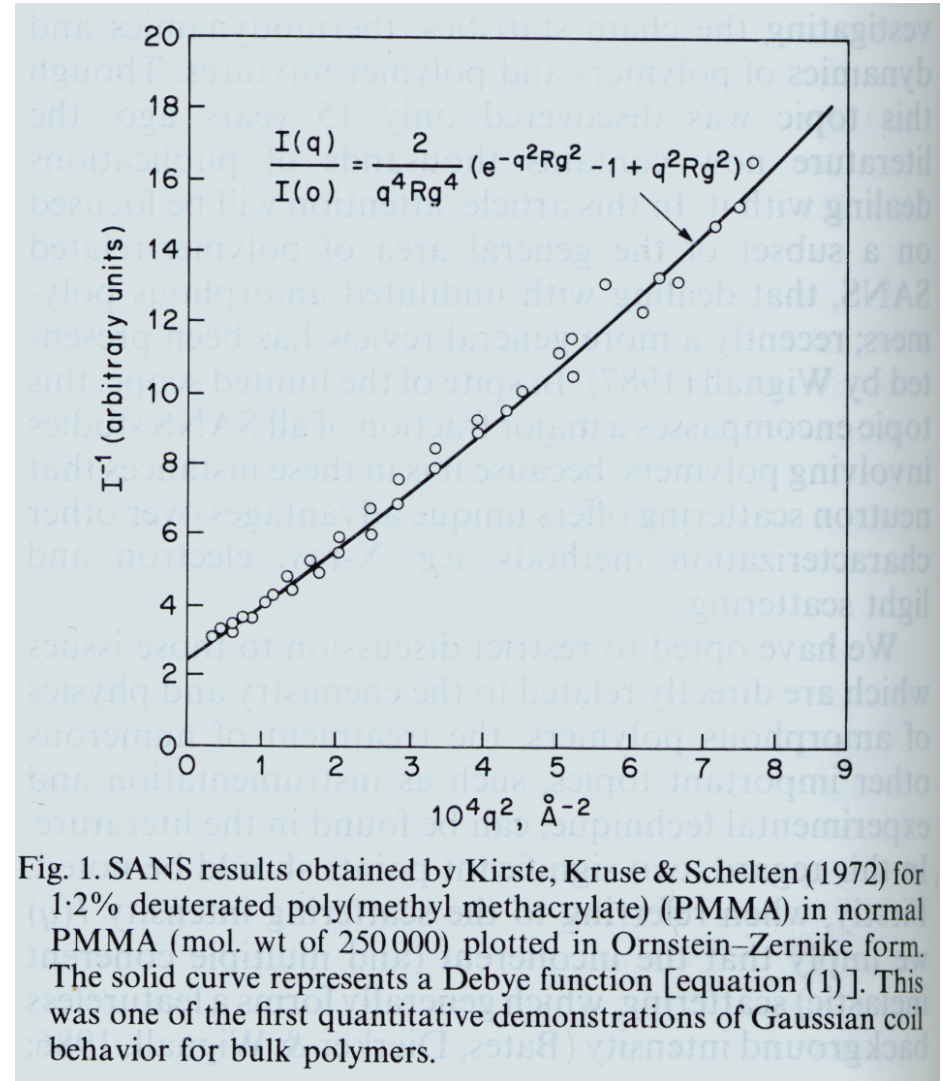
More generally, $R_g \sim N^\nu$ where

$\nu = 3/5$ for a good solvent; $\nu = 1/2$ for a theta solvent or a melt

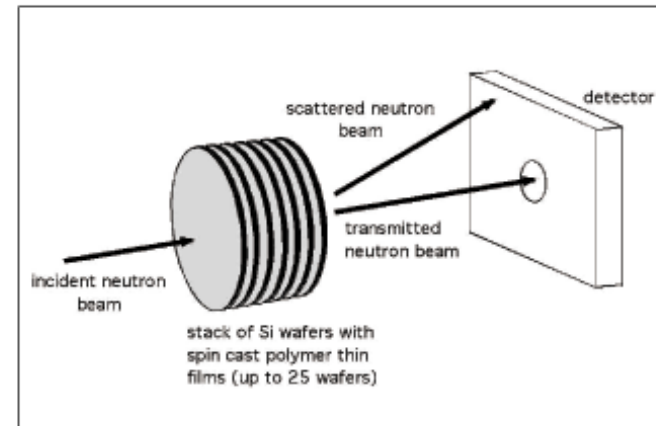
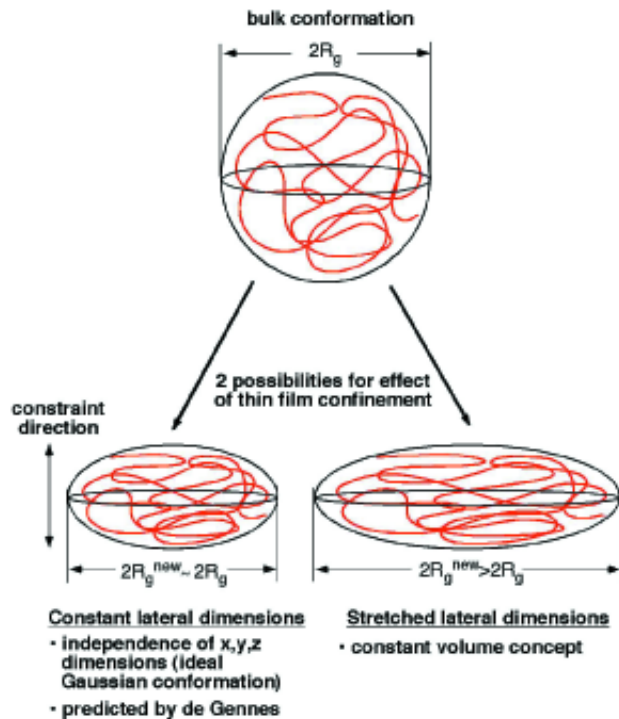
- Typically R_g is 5 - 50 nm for most polymers – good for SANS
- In addition to examining chain conformation, SANS has been used to probe thermodynamics (e.g. of blends and block copolymers) and to challenge various theories (e.g. random phase approximation)

Verification of of the Gaussian Coil Model for a Polymer Melt

- One of the earliest important results obtained by SANS was the verification of that $r_g \sim N^{-1/2}$ for polymer chains in a melt
- A better experiment was done 3 years later using a small amount of H-PMMA in D-PMMA (to avoid the large incoherent background) covering a MW range of 4 decades



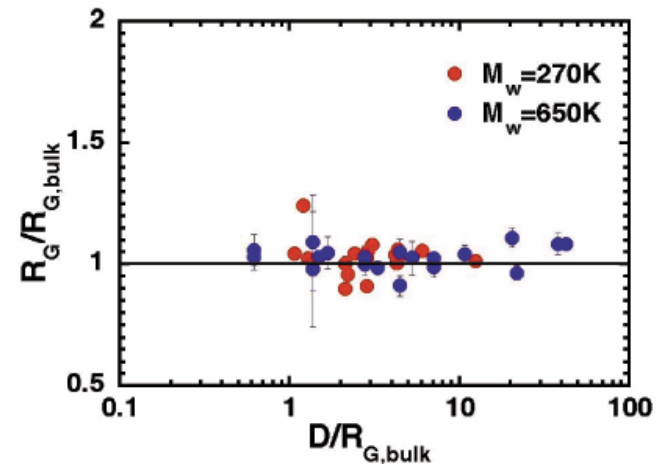
Probing Chain Conformation in Thin Films



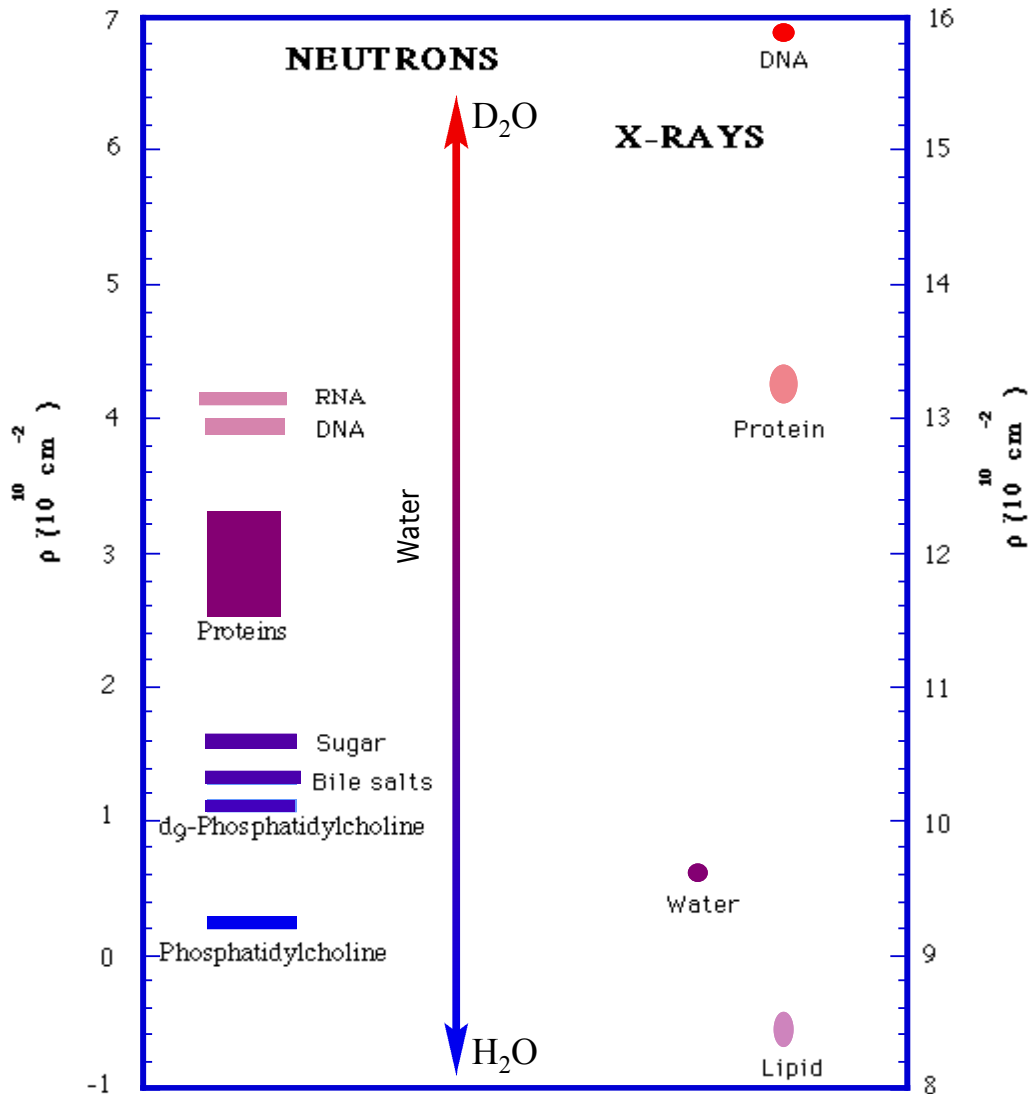
Thin films of 25% d-PS & 75% PS spun on to Si wafers. 25 wafers \Rightarrow 10 nm total polymer thickness – 0.2 mg

R.L. Jones, S.K. Kumar, D.L. Ho, R.M. Briber, T.P. Russell,
Nature, 1999, 400, 146

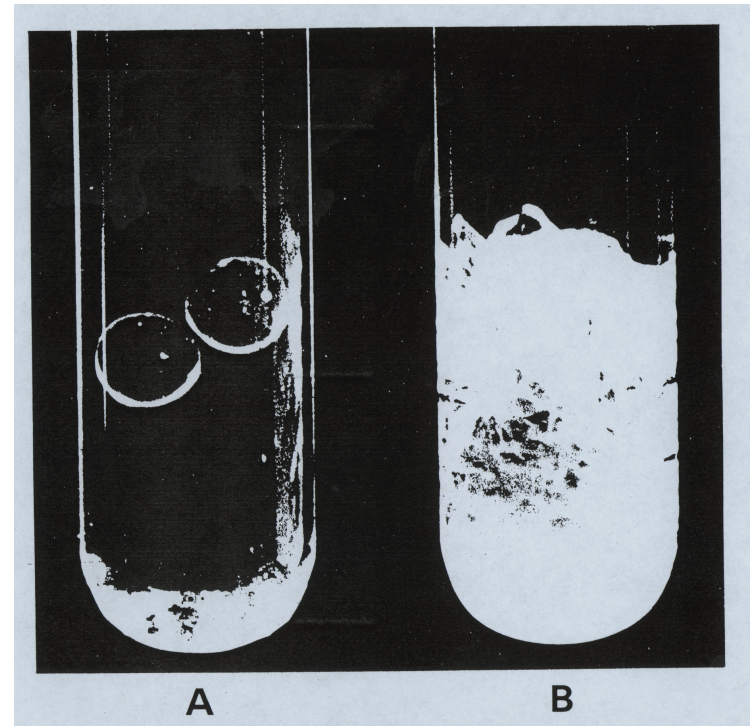
R_g in the plane of the film is unchanged down to film thickness of $R_g/2$



Contrast & Contrast Matching

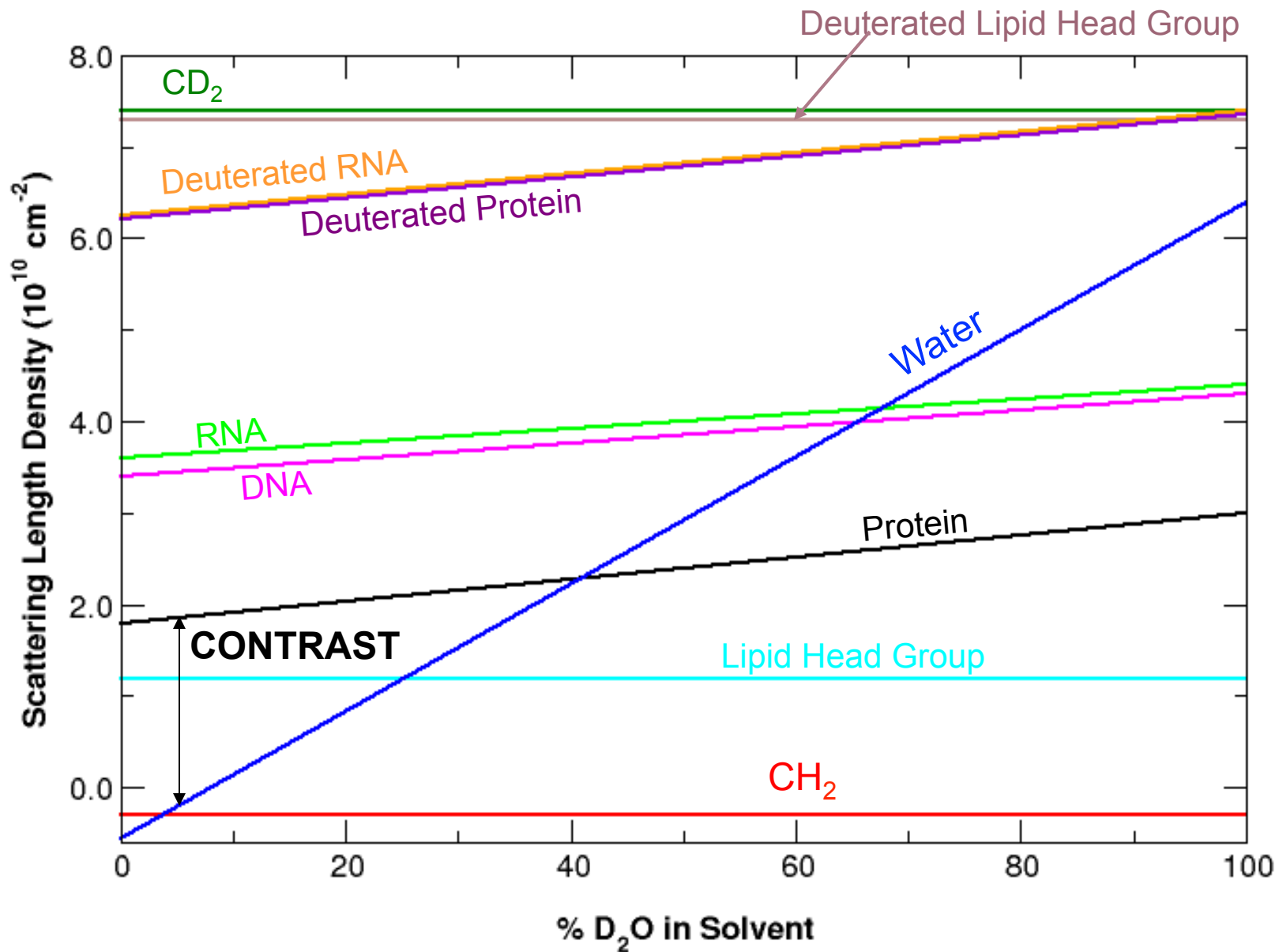


* Chart courtesy of Rex Hjelm



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

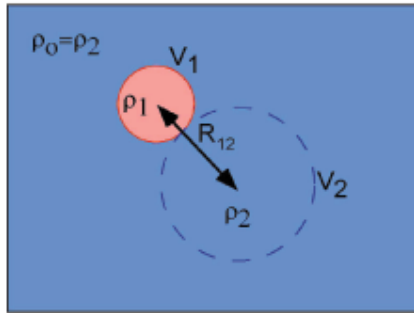


Isotopic Contrast for Neutrons

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

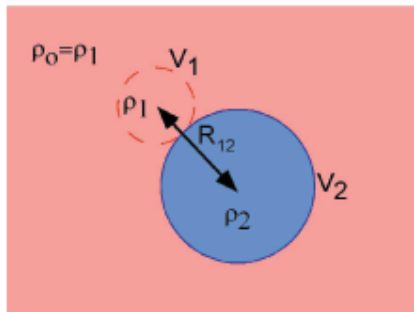
Nickel Isotope	Scattering Lengths b (fm)
^{58}Ni	15.0 (5)
^{60}Ni	2.8 (1)
^{61}Ni	7.60 (6)
^{62}Ni	-8.7 (2)
^{64}Ni	-0.38 (7)

Using Contrast Variation to Study Compound Particles



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

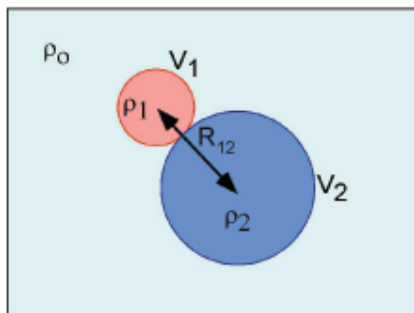
Examples include nucleosomes (protein/DNA) and ribosomes (proteins/RNA)



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

$$I(Q) = \frac{N}{V} \left\langle \left| \Delta\rho_1 \int_{V_1} e^{i\vec{Q}\cdot\vec{r}} d\vec{r}_1 + \Delta\rho_2 \int_{V_2} e^{i\vec{Q}\cdot\vec{r}} d\vec{r}_2 \right|^2 \right\rangle$$

$$I(Q) = \Delta\rho_1^2 \langle |F_1(Q)|^2 \rangle + \Delta\rho_2^2 \langle |F_2(Q)|^2 \rangle + \Delta\rho_1 \Delta\rho_2 |F_1(Q)| |F_2(Q)| \frac{\sin(QR_{12})}{QR_{12}}$$



$$I_3(Q) = \frac{(\rho_1 - \rho_0)^2}{(\rho_1 - \rho_2)^2} I_1(Q) - \frac{(\rho_2 - \rho_0)^2}{(\rho_1 - \rho_2)^2} I_2(Q)$$

$$= 2(\rho_1 - \rho_0)(\rho_2 - \rho_0) F_1 F_2 \frac{\sin(QR_{12})}{QR_{12}}$$

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

SANS Has Been Used to Study Bio-machines

- Capel and Moore (1988) used the fact that prokaryotes can grow when H is replaced by D to produce reconstituted ribosomes with various pairs of proteins (but not rRNA) deuterated
- They made 105 measurements of inter-protein distances involving 93 30S protein pairs over a 12 year period. They also measured radii of gyration
- Measurement of inter-protein distances is done by Fourier transforming the form factor to obtain $G(R)$
- They used these data to solve the ribosomal structure, resolving ambiguities by comparison with electron microscopy

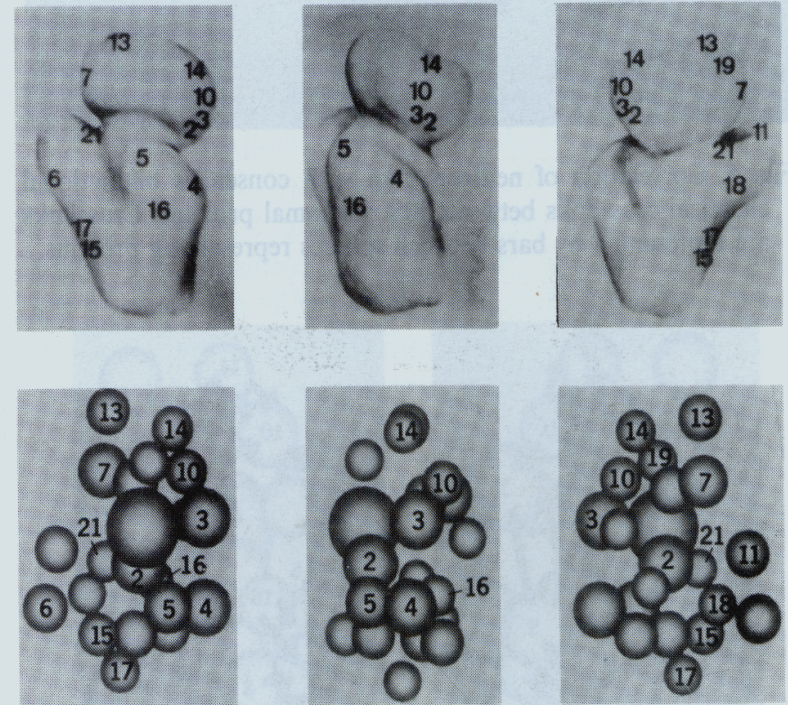


Fig. 4. Comparison of neutron map with a mapping of surface-exposed antigenic sites of ribosomal proteins of the 30S subunit obtained by immune-electron microscopy (Stoeffler & Stoeffler-Meilicke, 1986).

Porod Scattering

Let us examine the behavior of $|F(Q)|^2 (QR)^4$ at large values of Q for a spherical particle (i.e. $Q \gg 1/R$ where R is the sphere radius)

$$\begin{aligned} |F(Q)|^2 (QR)^4 &= 9V^2 \left[\frac{\sin QR - QR \cdot \cos QR}{(QR)^3} \right]^2 (QR)^4 = 9V^2 \left[\frac{\sin QR}{QR} - \cos QR \right]^2 \\ &\rightarrow 9V^2 \cos^2 QR \text{ as } Q \rightarrow \infty \\ &= 9V^2 / 2 \text{ on average (the oscillations will be smeared out by resolution)} \end{aligned}$$

Thus $|F(Q)|^2 \rightarrow \frac{9V^2}{2(QR)^4} = \frac{2\pi A}{Q^4}$ where A is the area of the sphere's surface.

This is Porod's law and holds as $Q \rightarrow \infty$ for any particle shape provided the particle surface is smooth.

Another way to obtain it is to expand $G(r) = 1 - ar + br^2 + \dots$ [with $a = A/(2\pi V)$] at small r and to evaluate the form factor with this (Debye) form for the correlation function.

Scattering From Fractal Systems

- Fractals are systems that are “self-similar” under a change of scale I.e. $R \rightarrow CR$
- For a mass fractal the number of particles within a sphere of radius R is proportional to R^D where D is the fractal dimension

Thus

$$4\pi R^2 dR.G(R) = \text{number of particles between distance } R \text{ and } R + dR = cR^{D-1} dR$$

$$\therefore G(R) = (c/4\pi)R^{D-3}$$

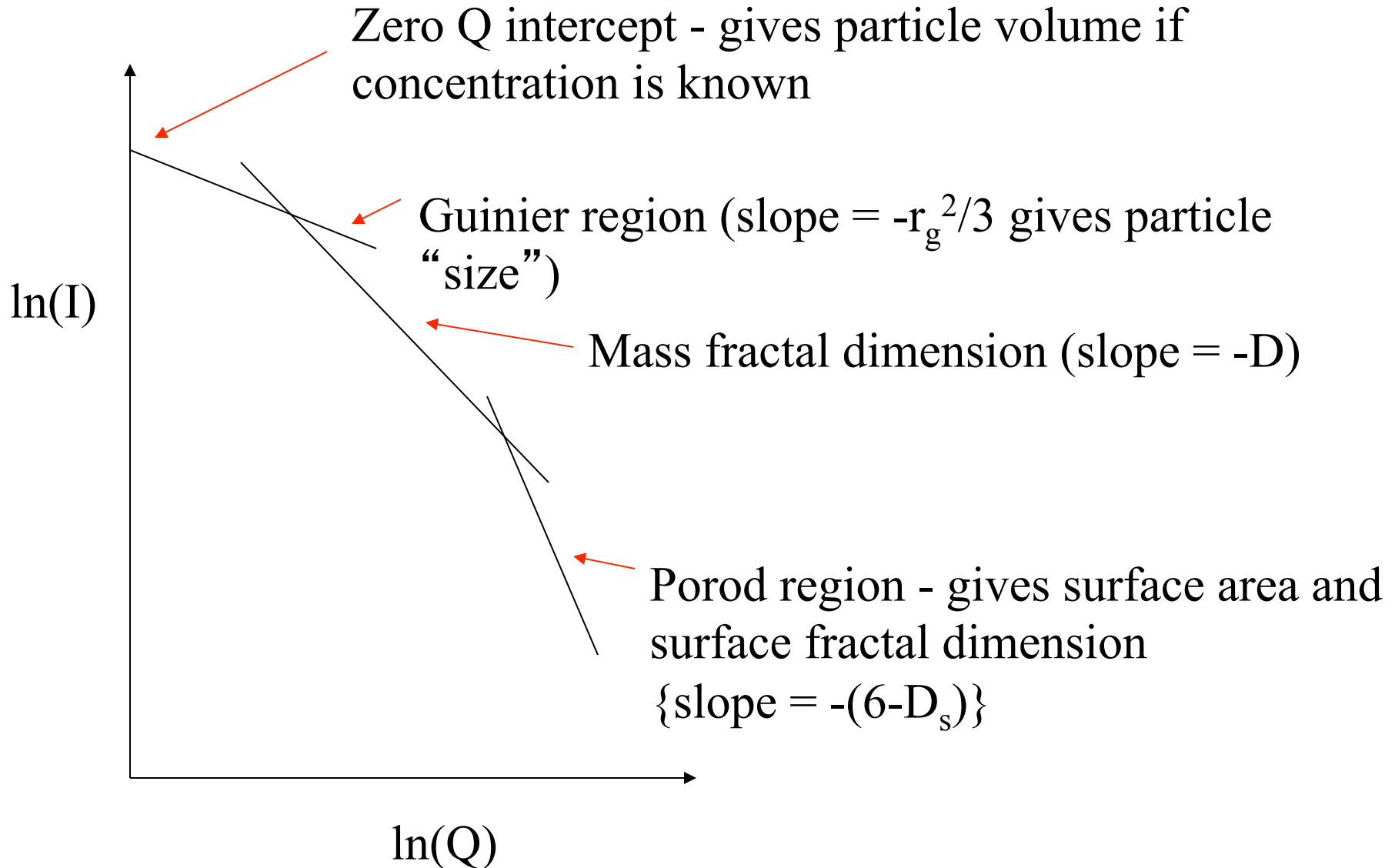
$$\text{and } S(\vec{Q}) = \int d\vec{R}.e^{i\vec{Q}.\vec{R}}G(R) = \frac{2\pi}{Q} \int dR.R.\sin QR.(c/4\pi)R^{D-3}$$

$$= \frac{c}{2} \frac{1}{Q^D} \int dx.x^{D-2}.\sin x = \frac{\text{const}}{Q^D}$$

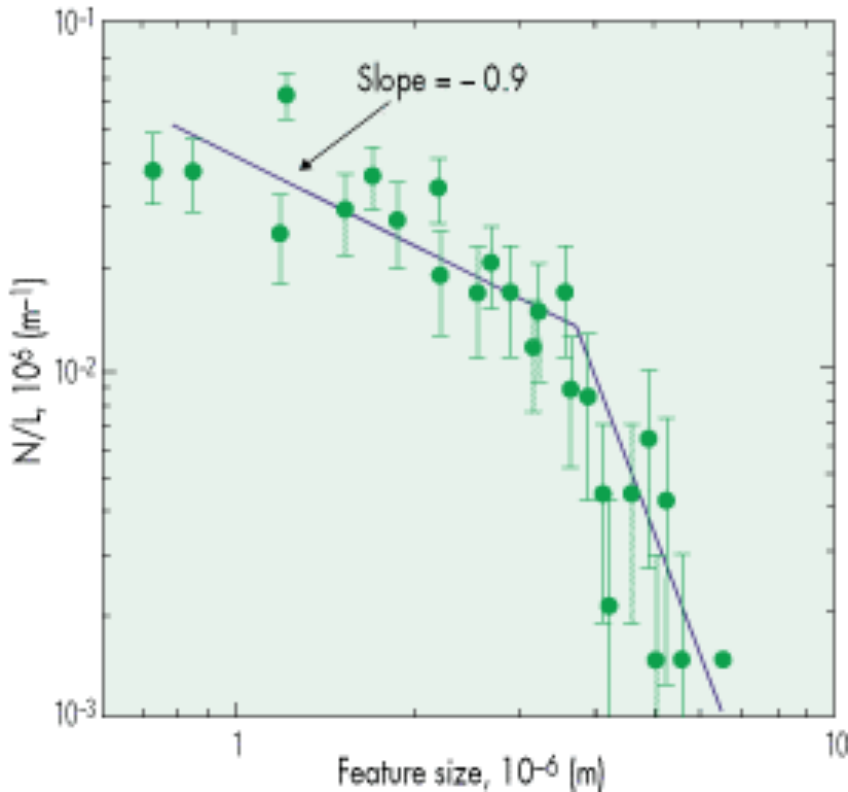
For a surface fractal, one can prove that $S(Q) \propto \frac{\text{const}}{Q^{6-D_s}}$ which reduces to the Porod

form for smooth surfaces of dimension 2.

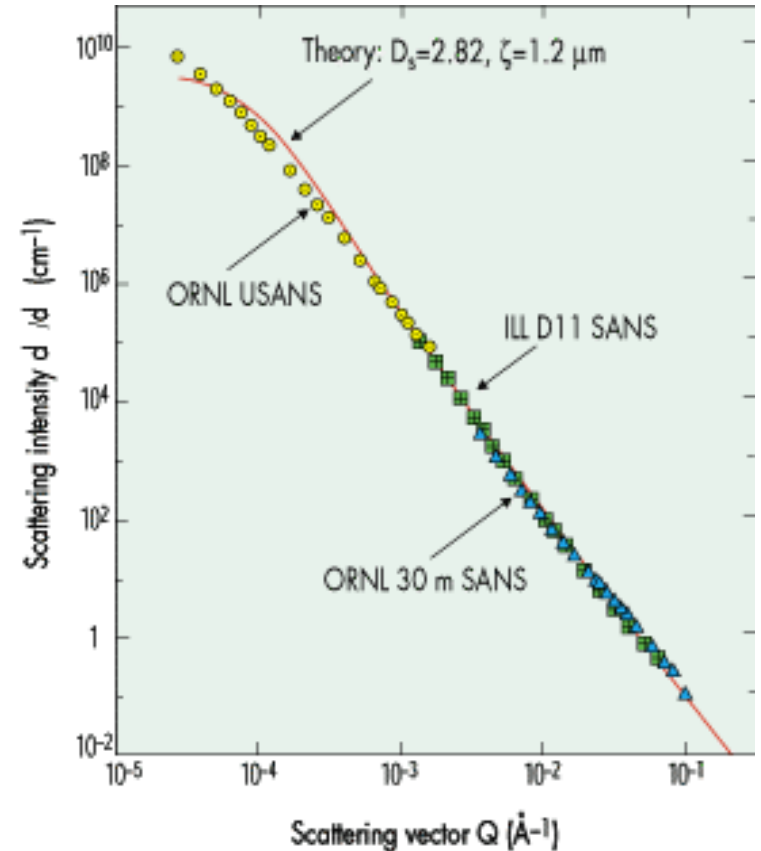
Typical Intensity Plot for SANS From Disordered Systems



Sedimentary Rocks Are One of the Most Extensive Fractal Systems*



Variation of the average number of SEM features per unit length with feature size. Note the breakdown of fractality ($D_s=2.8$ to 2.9) for lengths larger than 4 microns



SANS & USANS data from sedimentary rock showing that the pore-rock interface is a surface fractal ($D_s=2.82$) over 3 orders of magnitude in length scale

*A. P. Radlinski (Austr. Geo. Survey)

Sample Requirements for SANS

- Monodisperse, non-interacting (i.e. dilute)
- Concentration: 1-5 mg/ml
- Volume: 350-700 μ l 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 set of notes on SANS (the SANS Toolbox)
 - http://www.ncnr.nist.gov/staff/hammouda/the_SANS_toolbox.pdf