Small Angle Scattering
of neutrons and x-rays

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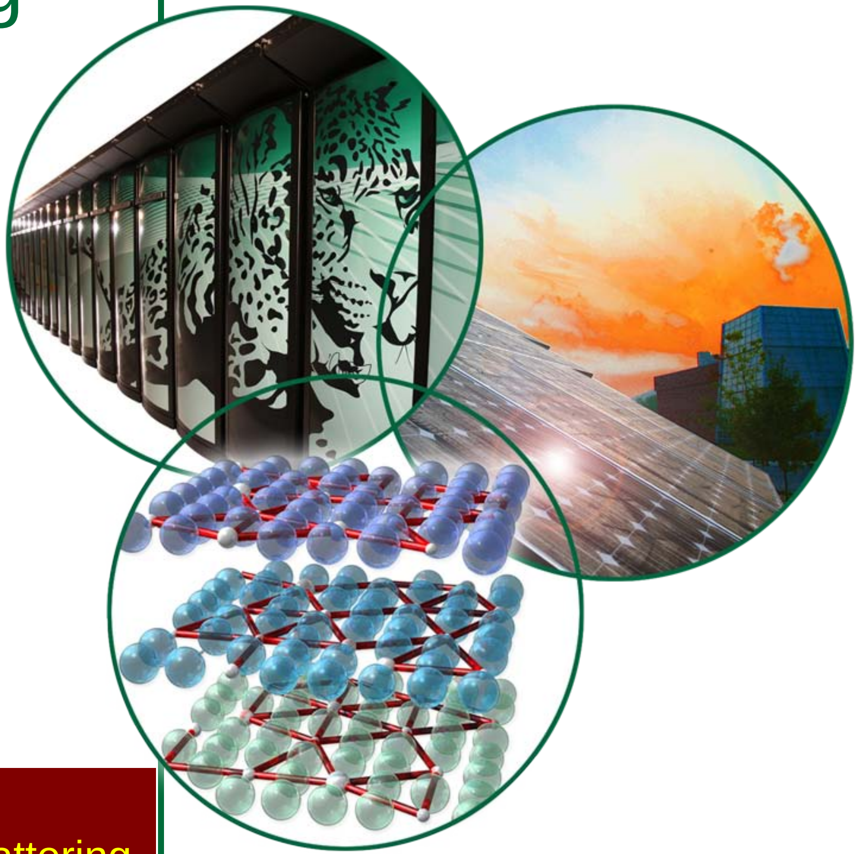

National School on Neutron and X-ray Scattering

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY

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- Applications – is SAS for you?
- Comparison with microscopy and diffraction
- Basic concepts of the technique
- SANS instrumentation
- Planning a SAS experiment and data reduction
- SAS data analysis and interpretation

SAS of x-rays, neutrons, laser light

- SAXS & SANS: structural information 1nm-1μm
- X-rays
  - Rotating anode / sealed tube: ~ 400 k$
  - Synchrotron: high flux, very small beams
- Neutrons
  - Isotope contrast, high penetration, magnetic contrast
- Laser Light scattering
  - Bench top technique, static and dynamic
- Applications in …
  - Important for polymers, soft materials, (biology)
  - Particulate and non-particulate
  - Pretty much anything 1nm-1μm

…really anything?

SAS applications A to Z

But what about SEM, TEM, AFM …?

Alzheimer's disease, aerogel, alloys

Bio-macromolecular assemblies, bone

Colloids, complex fluids, catalysts

Detergents, dairy (casein micelles)

Earth science, emulsions

Fluid adsorption in nanopores, fuel cells, food science (chocolate)

Gelation, green solvents

High pressure, high temperature…, hydrogen storage, helium bubble growth in fusion reactors

Implants (UHDPE)

Jelly

Kinetics (e.g. of polymerization or protein folding), keratin

Liquid Crystals

Magnetic flux lines, materials science

Nano-anything

Orientational order

Polymers, phase behavior, porosity

Quantum dots (GISAXS)

Rubber, ribosome

Soft matter, surfactants, switchgrass

Time-resolved, thermodynamics

Uranium separation

Vesicles, virus

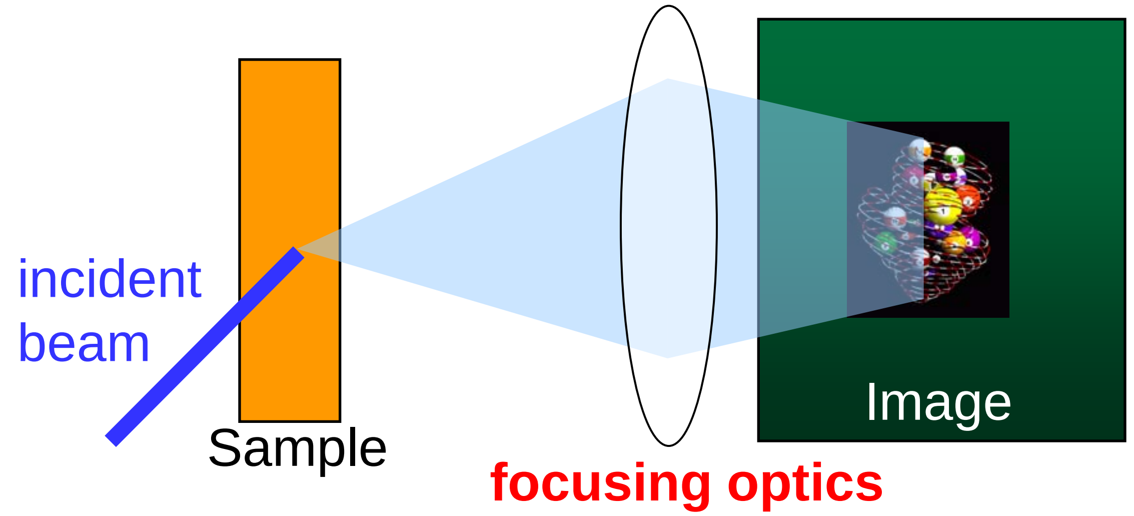
Wine science

Xylose isomerase

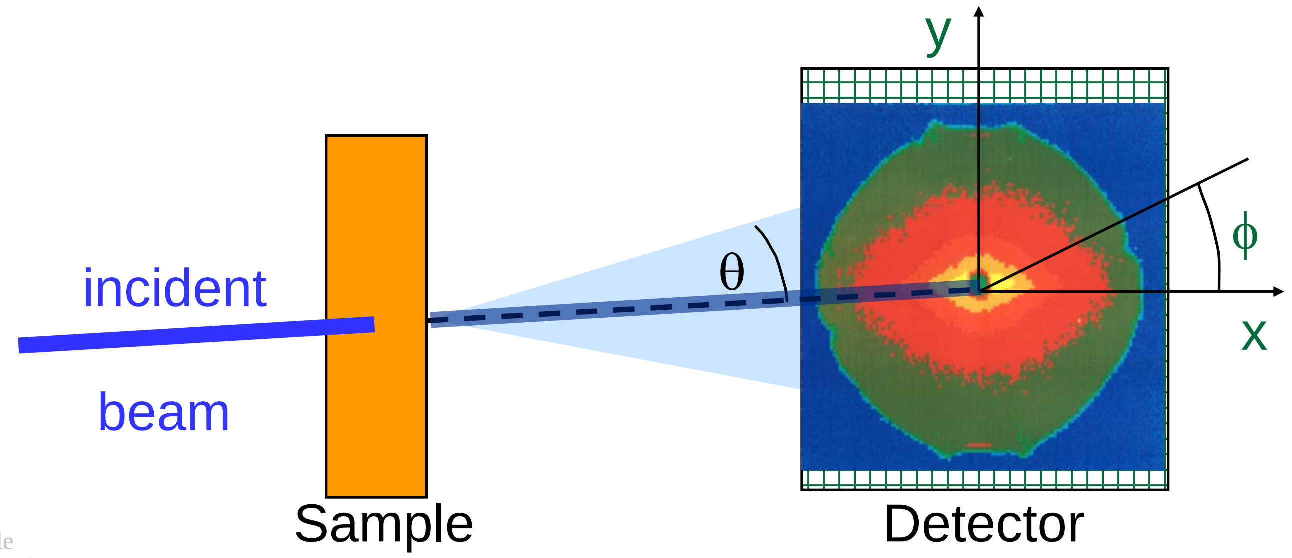
Yttrium-stabilized zirconia (YSZ)

Zeolites

Microscopy : enlarged image



SAS : interference pattern

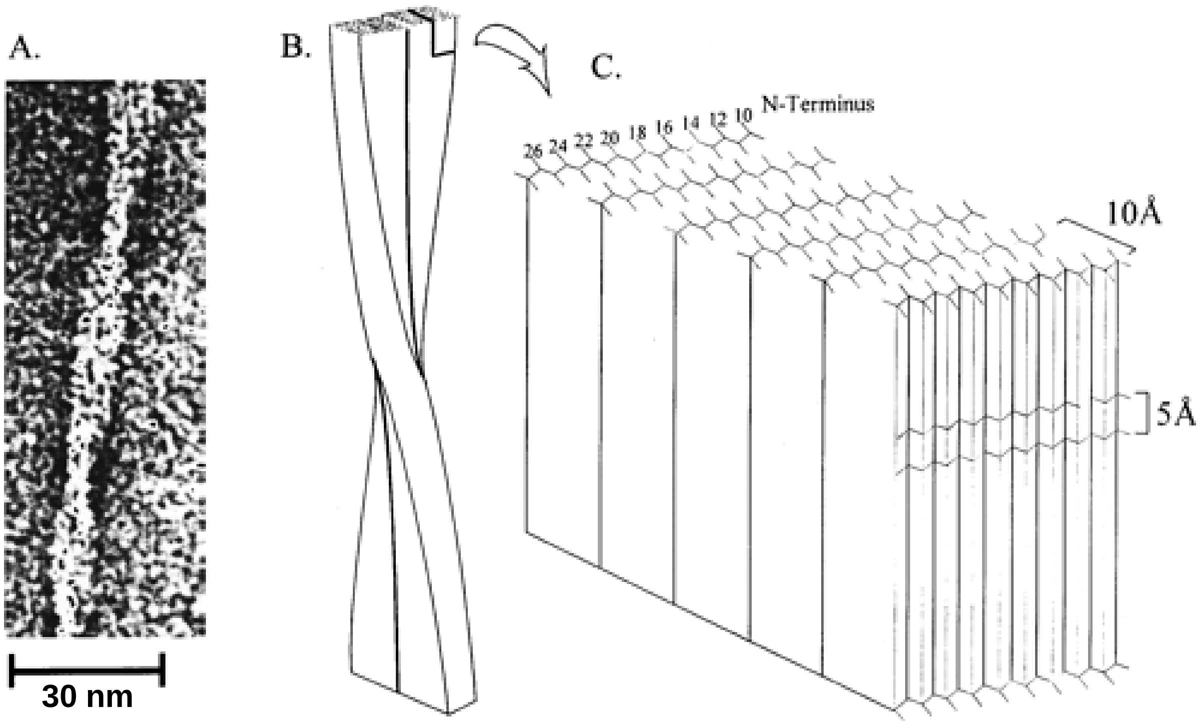


Neutron Scattering and Microscopy

- Common features
  - Size range 1nm-1μm
  - Contrast labeling options (stains / isotope labels)
- SAS practical aspects
  - No special sample preparation such as cryo-microtome
  - Sample environments control (p, T, H)
  - Non-destructive (exception: radiation damage in synchrotron beam)
  - In-situ, time-resolved
- Fundamental difference
  - "Real space" image with certain resolution
  - Scattering pattern, averaged over volume
- Complementarity

Alzheimer's Disease – β-Amyloid

- Among leading causes of death
- Miss-folded peptides form hierarchical ordered fibril structures & plaques
- Structure established using synthetic model peptides and complementary methods NMR, SANS, EM



- **NMR**
  - **β-fold**
- **SANS**
  - **Fiber shape**
  - **Diameter**
  - **6 sheet stack**
- **EM**
  - **Overall morphology**
  - **Twist**

T.S. Burkoth et al. *J. Am. Chem. Soc.* **2000,** *122,* 7883-7889

Comparing SAXS and SANS

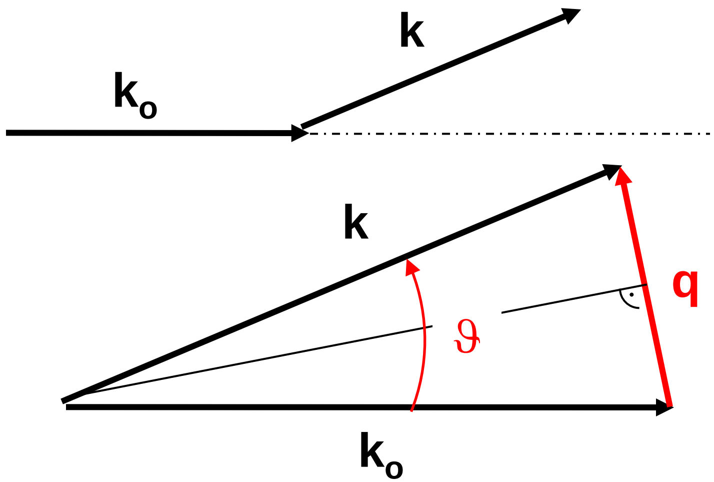
- SAXS & SANS
  - nm scale structural analysis (~1nm-1μm)
  - Non-destructive (radiation damage in synchrotron SAXS can be an issue)
  - In-situ
- Synchrotron X-rays
  - High throughput
  - Time-resolution (ms – ps)
  - Tiny beams – microfocus: e.g. scanning of cells
- Neutrons
  - ‘see’ light atoms: polymers, biology, soft condensed matter, hydrogen in metals
  - Isotope labeling
  - High penetration
    - bulky specimens, e.g. residual stress in motor block
    - complicated environments (P,T), e.g. ^{4}He cryostat
  - Magnetic contrast
  - No radiation damage

Scattering and Diffraction (Crystallography)

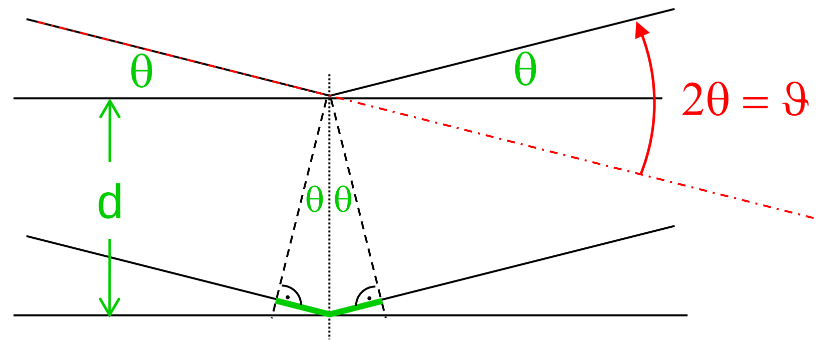
- Diffraction from crystals, Scattering from anything else (less ordered)
- Same basic physics: interactions of radiation with matter
  - SAXS/WAXS, SAND/WAND
  - Instruments: resolution (D) / flux (S)
  - Diffraction needs crystals, scattering does not.
  - Analysis?!
- At small *Q* (small angles, large λ): observe nm-sized volume elements, "blobs" NOT atoms
  - Scattering length $\rightarrow$ **scattering length density (SLD)**
  - SAS is sensitive to spatial non-uniformity of SLD:
    ΔSLD = Contrast $\rightarrow$ **contrast variation!**

Scattering Vector, *q* or momentum transfer, *Q*, *h*, *k*, *s*

Wave vector k: $|k| = k = 2\pi/\lambda$



Bragg: waves with wavelength λ reflected by sets of lattice planes



$\Delta = 2d \sin(\theta)$

if $\Delta = \mathbf{n}\,\lambda$ then reflection, else extinction

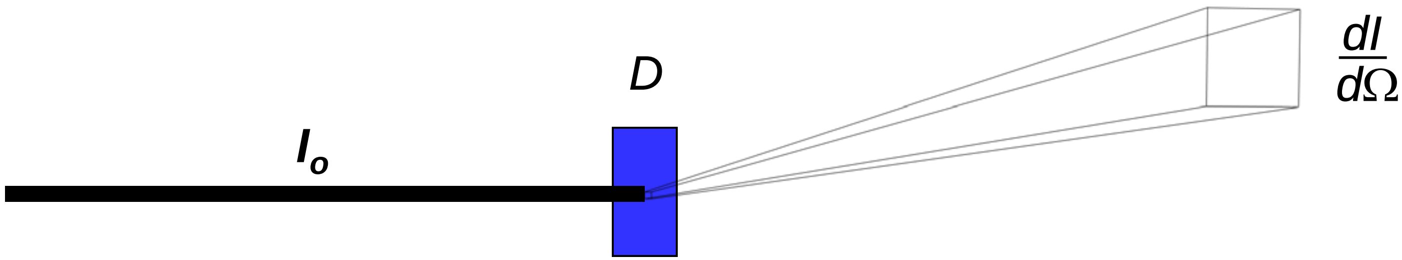
$$q = 2k\sin\left(\frac{\vartheta}{2}\right) = \frac{4\pi}{\lambda}\sin\left(\frac{\vartheta}{2}\right)$$

$$\frac{1}{d} = \frac{2}{\lambda}\sin\left(\frac{\vartheta}{2}\right)$$

$$d = \frac{2\pi}{q}$$

q in nm^{-1} or $Å^{-1}$

Absolute Intensity / Scattering Cross Section – cm^{-1}?



$$\frac{dI}{d\Omega} = TI_oD\frac{d\Sigma}{d\Omega} \longleftrightarrow \frac{d\Sigma}{d\Omega} = \frac{1}{TI_oD}\frac{dI}{d\Omega}$$ **[cm^{-1}sterad^{-1}]**

dI/dΩ	= Scattered intensity per solid angle
Io	= Primary beam intensity
T	= Transmission (x-ray absorption, incoherent neutron scattering)
D	= Thickness
dΣ/dΩ	= Scattering **cross section per unit volume** [cm^{-1}sterad^{-1}]

Neutron Scattering Intensity

- Incoming waves scatter off individual nuclei according to scattering length b (can be + or -).
- Interference of wavelets from distribution of nuclei (= structure) adds up to “net scattering” amplitude (Fourier transform of structure).
- Measured intensity is the magnitude square of amplitude.
- Measured intensity is also the Fourier transform of pair correlation function P(r).

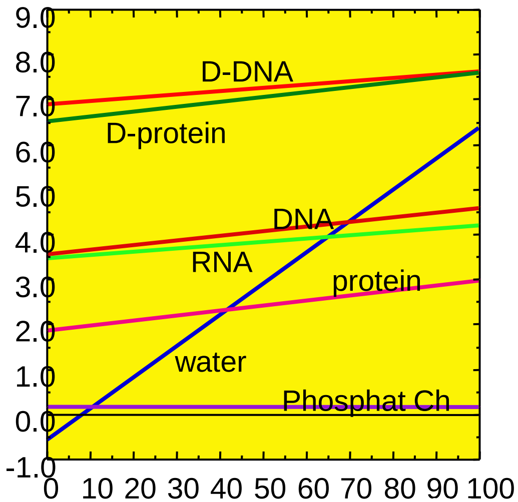
$$I(q) = \left| \int_V (\rho(\vec{r}) - \rho_s) e^{-i\vec{q} \bullet \vec{r}} d^3 r \right|^2$$

Contrast – Atomic Scattering Lengths

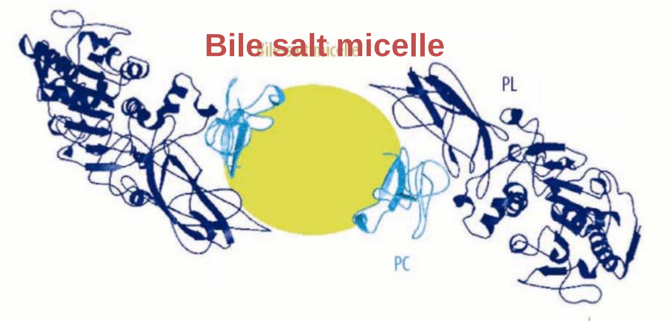
Element	Neutrons (10^{-12} cm)	X-rays (10^{-12} cm)	Electrons
^{1}H	**-0.374**	0.28	**1**
^{2}H (D)	0.667	0.28	**1**
C	**0.665**	**1.67**	**6**
N	**0.940**	**1.97**	**7**
O	**0.580**	**2.25**	**8**
P	**0.520**	**4.23**	**15**

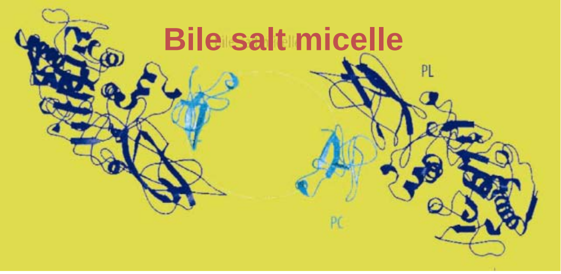
For SAS: SL → **SLD** → ΔSLD

SANS – Contrast Variation



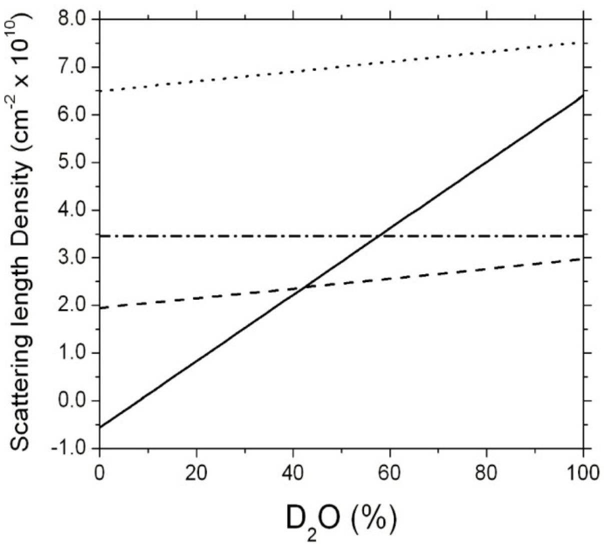
D_2O/H_2O contrast variation

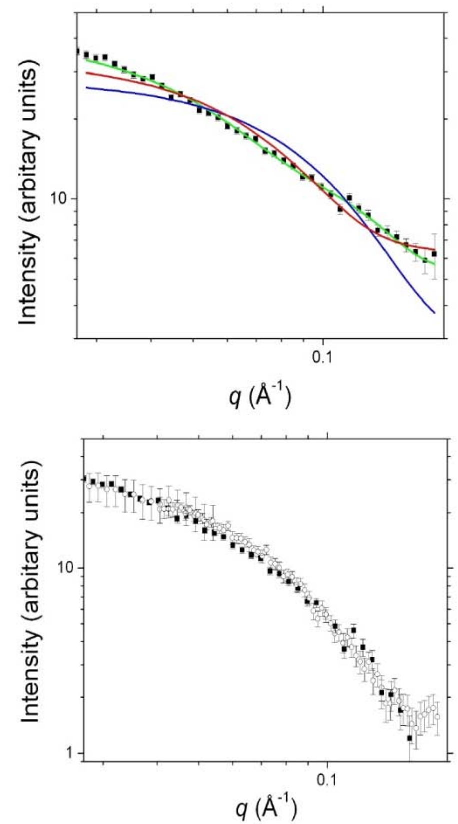


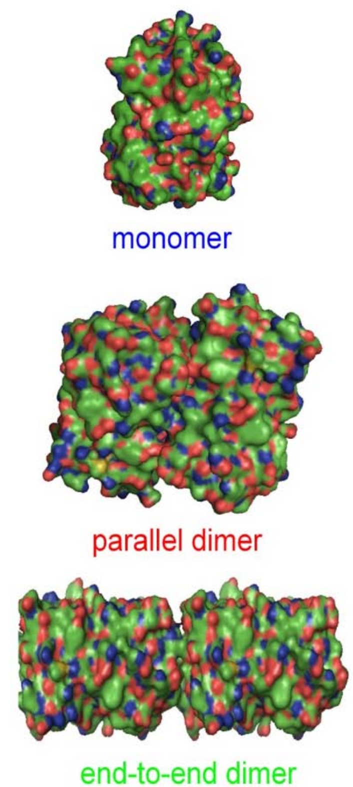


Visualizing Proteins in Inorganic Hydrogels

- Entrapment of bio-macromolecular assemblies is an emerging theme: bio-composite, biomimetic, bio-inspired for catalysts, sensors, functional materials – e.g., light harvesting antenna complexes for solar energy (PARC-EFRC)
- SANS shows that green fluorescent protein, an enzyme with potential applications in energy transfer and sensor development, is homogeneously dispersed in a silica gel matrix as a functional end-to-end dimer.
- **SANS with contrast variation shows structure of proteins in a complex gel matrix**



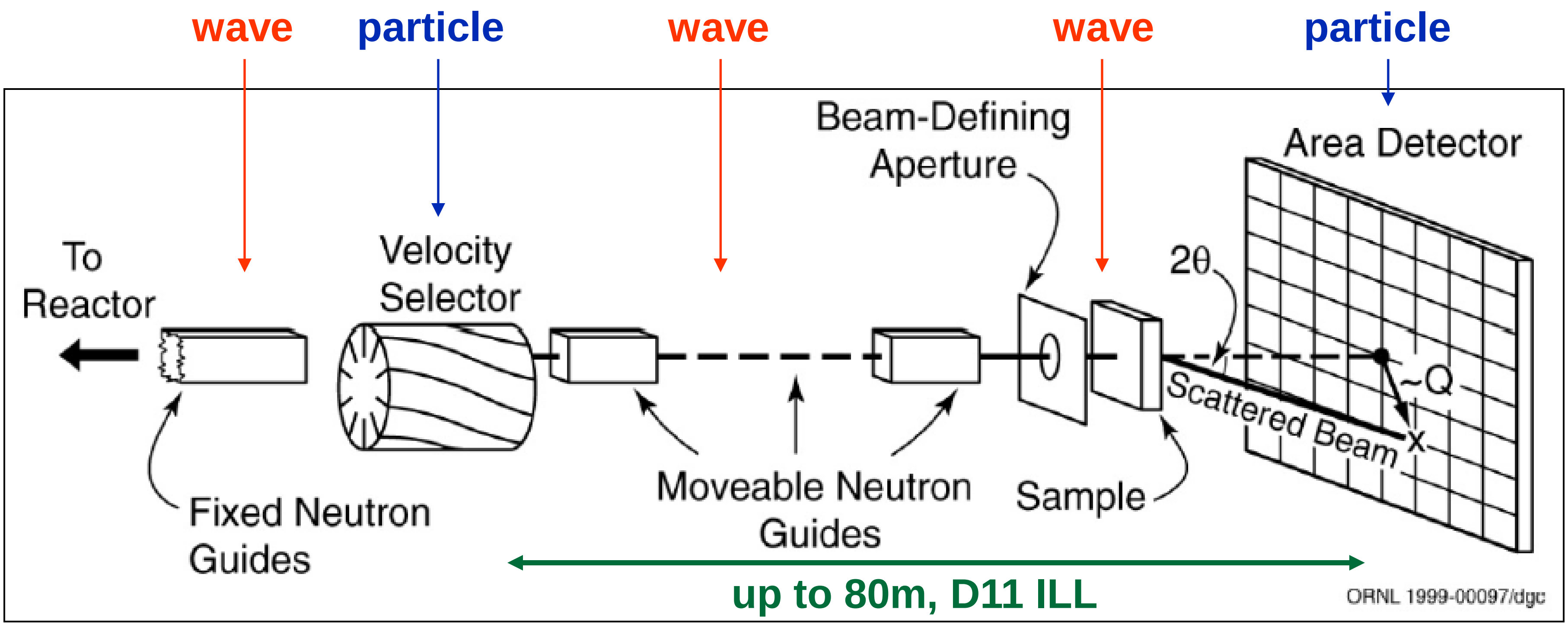




Luo, G., Zhang, Q., Del Castillo, A. R., Urban, V. and O'Neill, H., *ACS Appl. Mater. Interfaces* **1**: 2262-2268 (2009).

SANS guide hall (HFIR) a few years ago

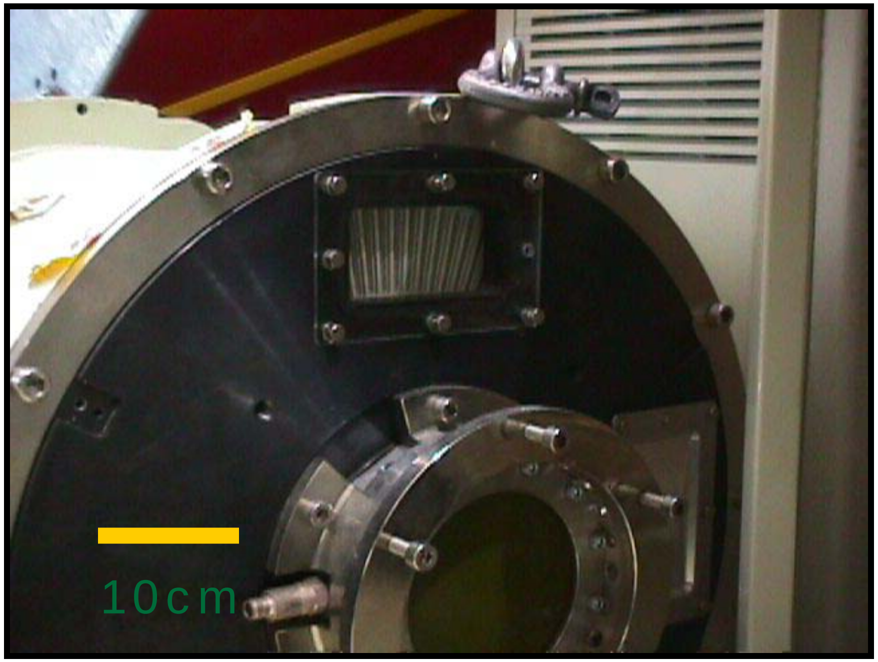
Layout of a SANS instrument



Typical layout at a continuous (reactor) source

"particle – wave proof machine"

Monochromator – Velocity Selector
neutron wavelength – neutron momentum



De Broglie: $$\lambda = \frac{h}{p} = \frac{h}{mv}$$

	Cold	Thermal
T (K)	20	300
v (m/s)	574	2224
E (meV)	1.7	25.9
λ (Å)	6.89	1.78

Practical Considerations at SANS and SAXS User Facilities

- Plan your experiment well!
- What Q-range would I like, and what must I have?
- For how long should I measure my samples? – *counting statistics, sample size (~ 10 x 10 x 1 mm^3)*
- How will I correct for backgrounds?
- How can I optimize my sample quality?
- Less is often more: Do fewer things but those do right! (especially with neutrons)
- Ask your local contact / instrument scientist for advice well ahead of time!

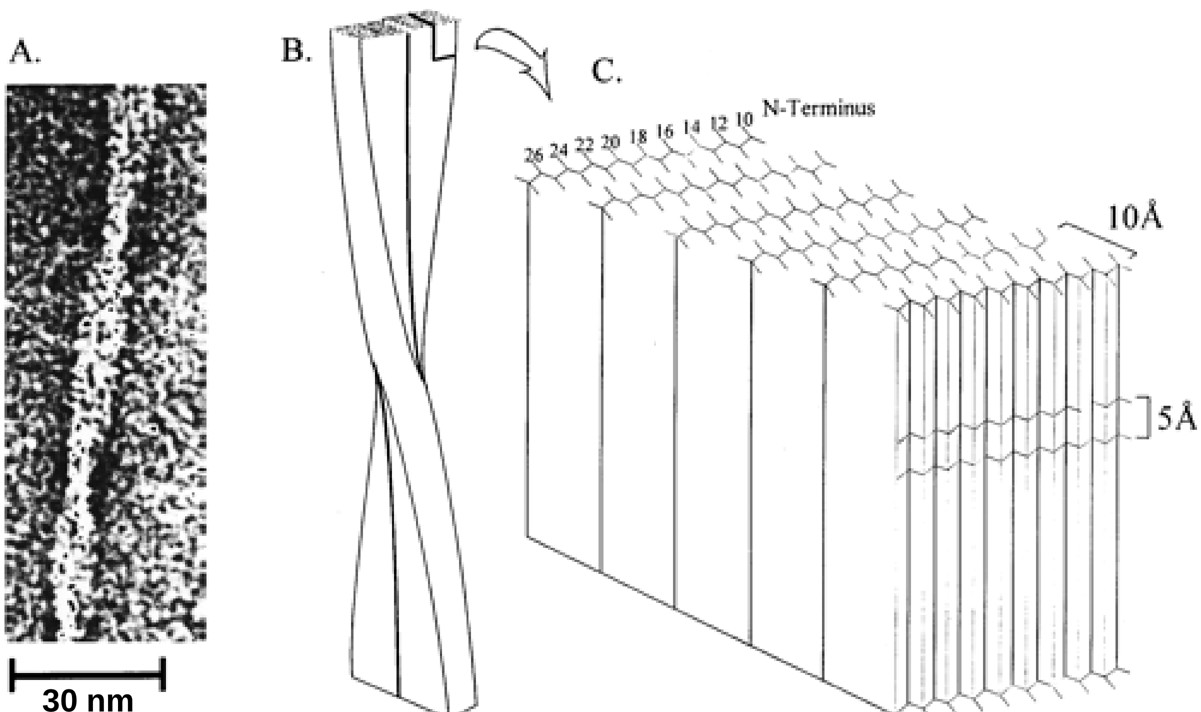
Data Reduction, Processing, Correction

- Normalization to monitor or time
- Backgrounds
- Transmission
- Azimuthal averaging
- Absolute intensity scale (cm^{-1})

- **Measure and subtract background very carefully!**
- **Do the absolute calibration – it's worth the extra effort!**

Alzheimer's Disease – β-Amyloid

- Among leading causes of death
- Miss-folded peptides form hierarchical ordered fibril structures & plaques
- Structure established using synthetic model peptides and complimentary methods NMR, SANS, EM



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- **NMR**
  - **β-fold**
- **SANS**
  - **Fiber**
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  - **Overall morphology**
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SAS Analysis –
A spacewalk of sorts
Fourier, Q, reciprocal space

how to get your bearings…
baby steps

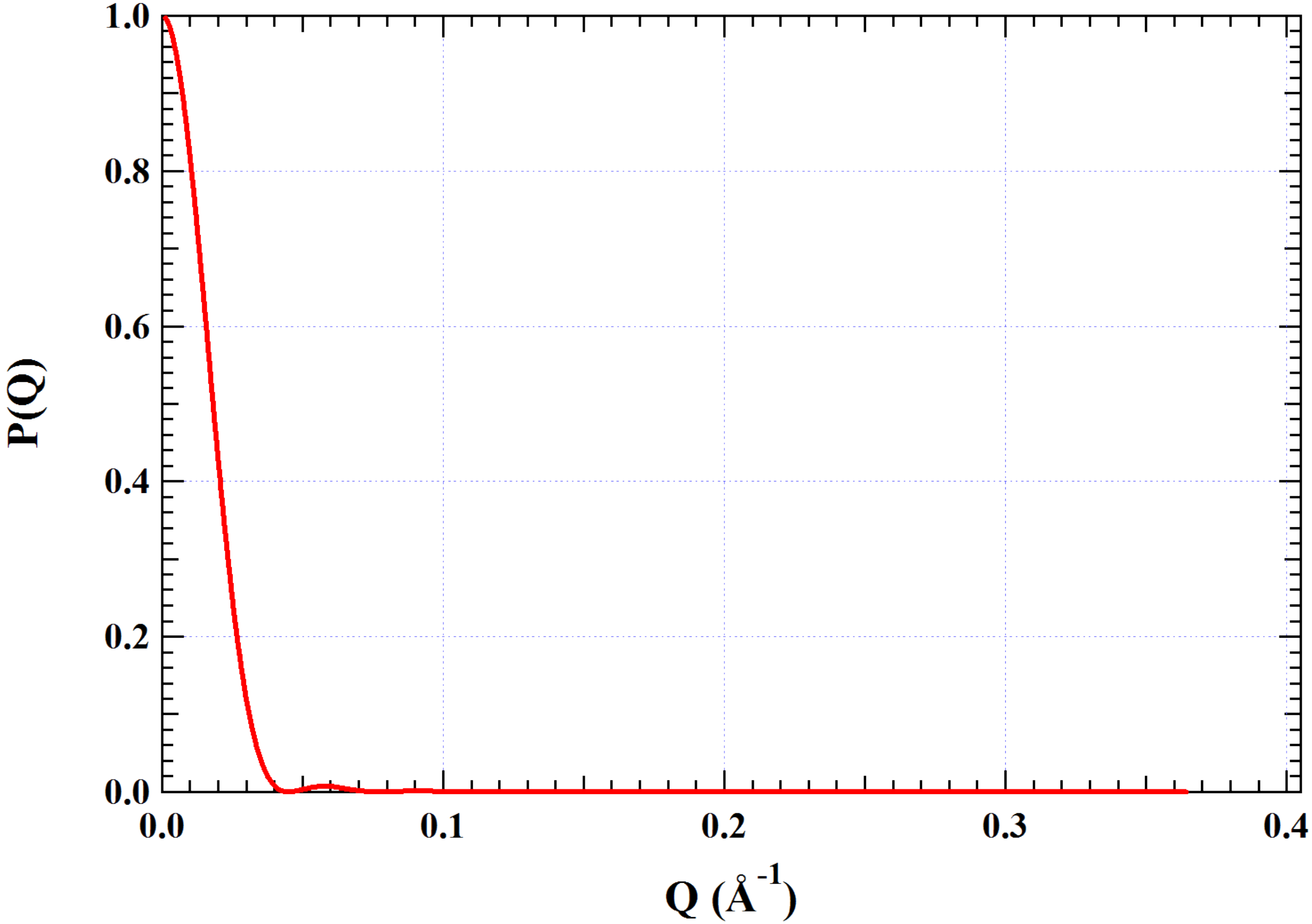
Carl Meade and Mark Lee rehearse spacewalk contingency plans in 1994

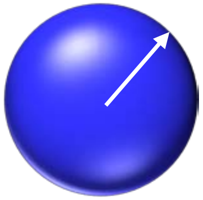
Bruce McCandless II took the first untethered space walk in February 1984. Here we see him from Challenger, floating above Earth.

Ed White, the first American to walk in space, hangs out during the Gemini 4 mission. He's attached to the craft by both umbilical and tether lines.

Sphere

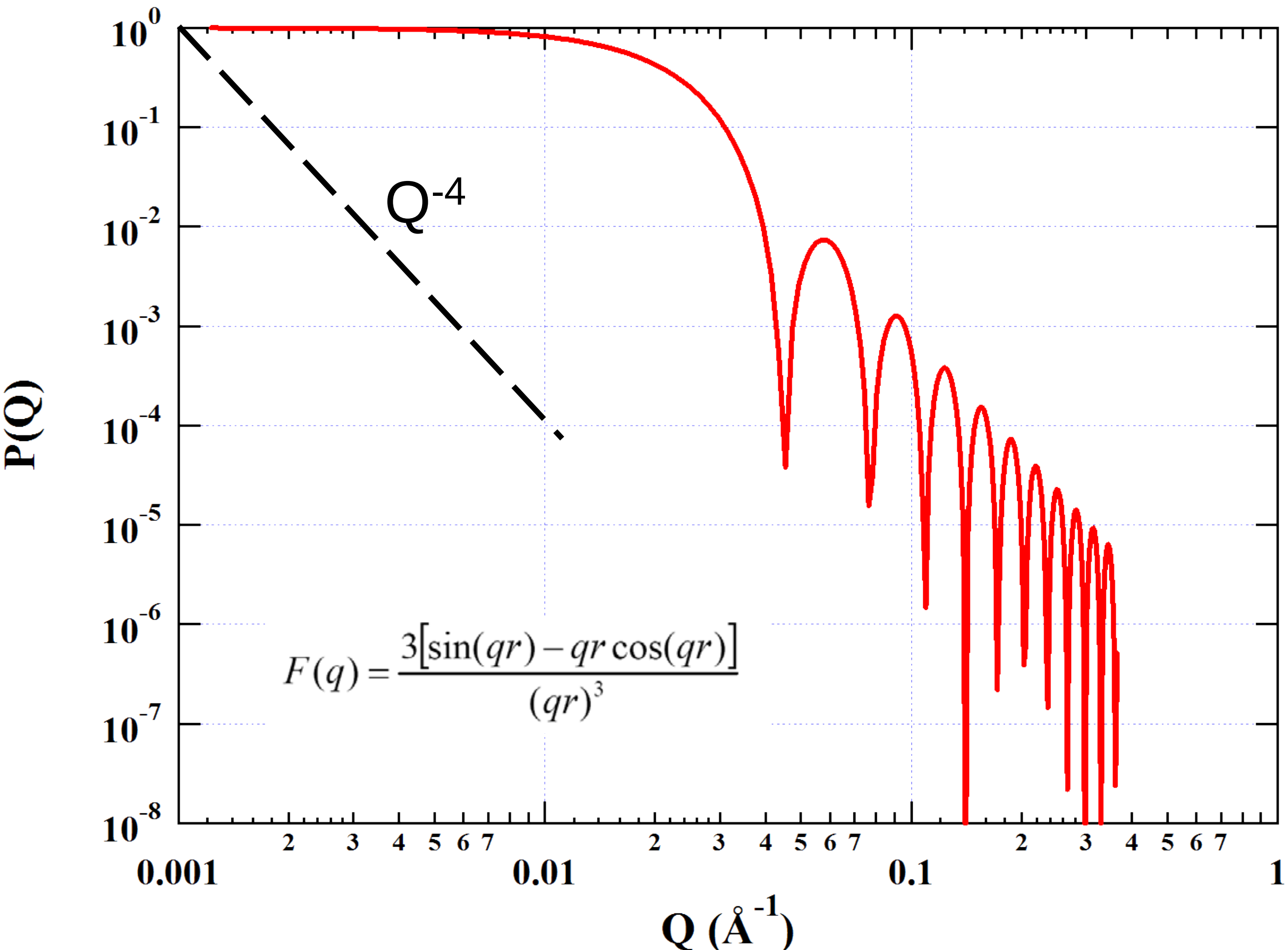
precisely: monodisperse sphere of uniform density with sharp and smooth surface



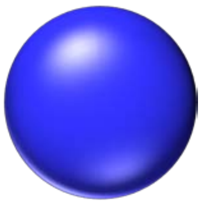


100 Å radius

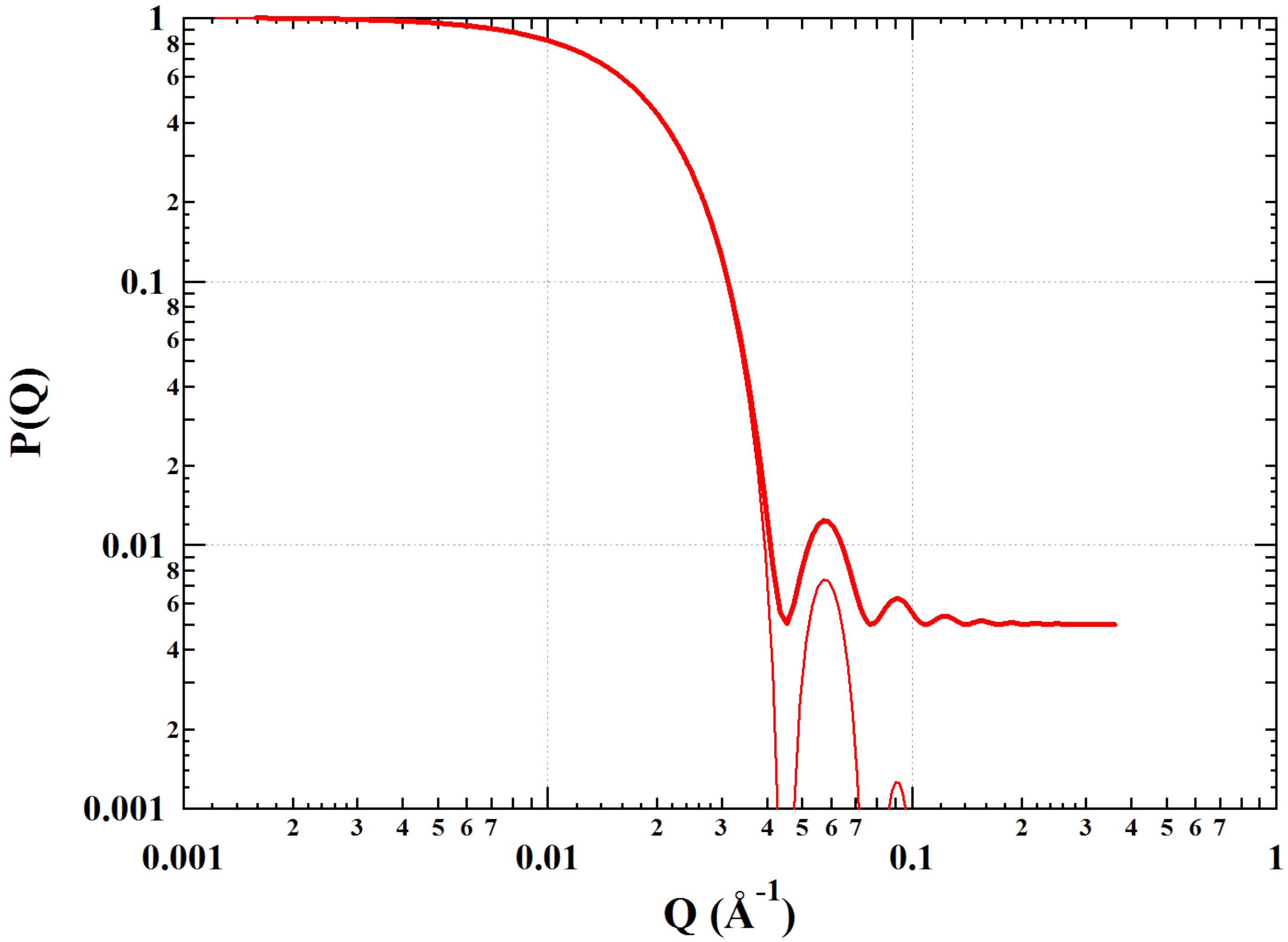
Sphere

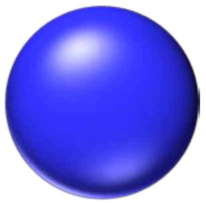


P(Q)
Q (Å^{-1})
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
0.001
0.01
0.1
1
Q^{-4}
$F(q) = \frac{3[\sin(qr) - qr\cos(qr)]}{(qr)^3}$

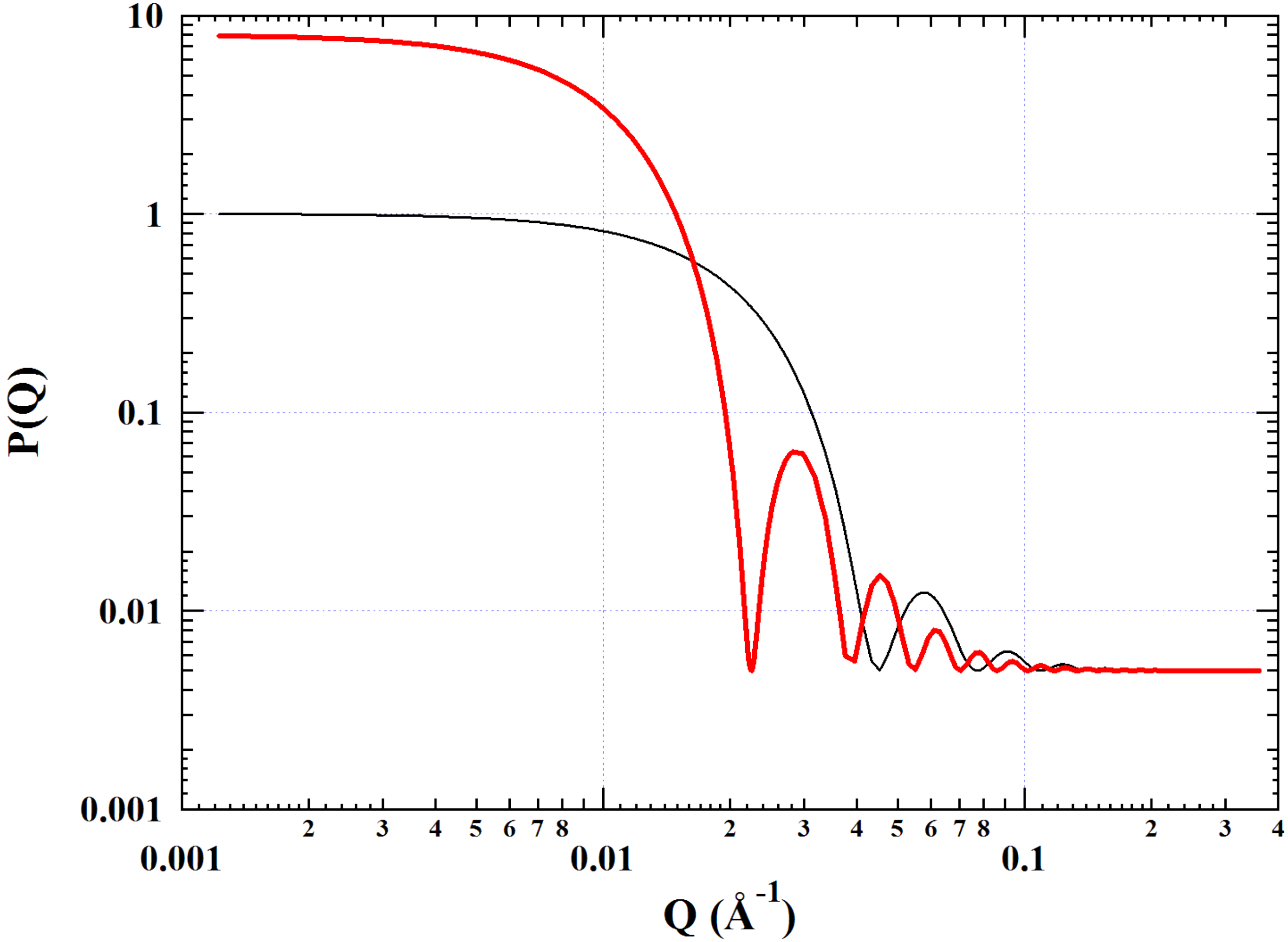


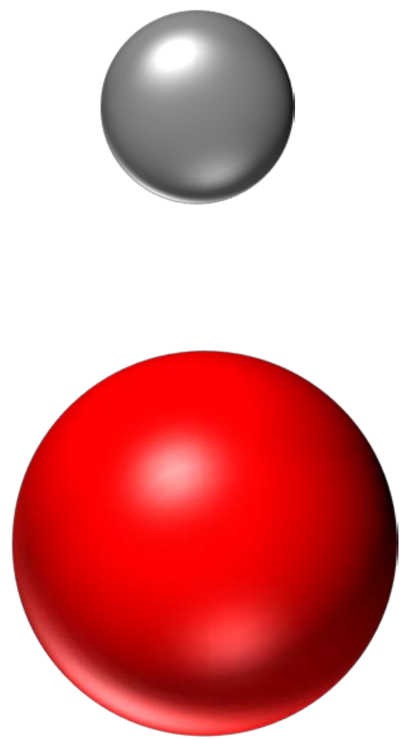
In practice: sphere + constant background



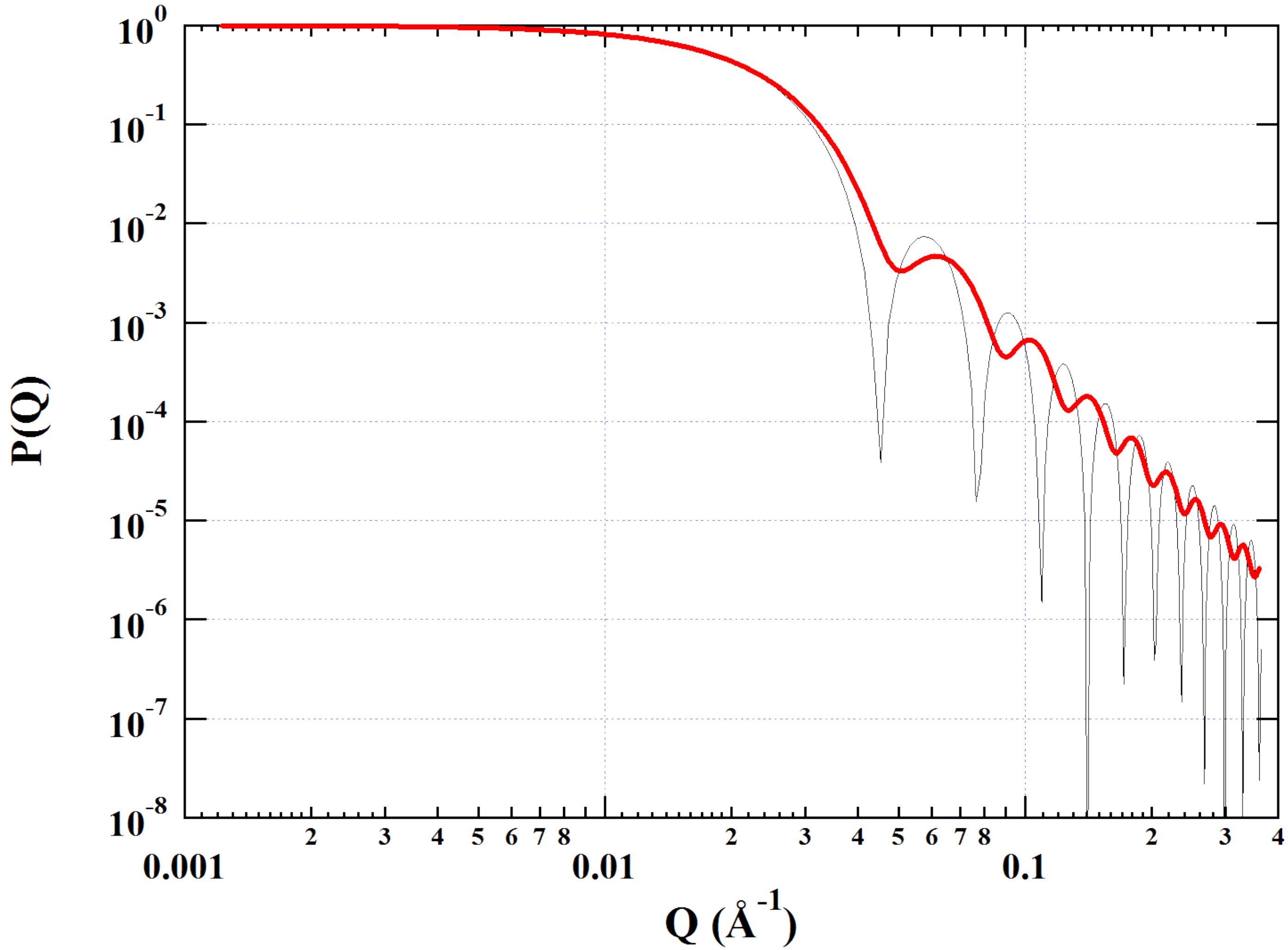


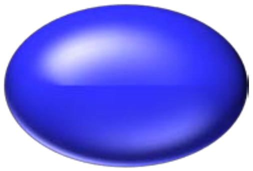
Spheres of different sizes



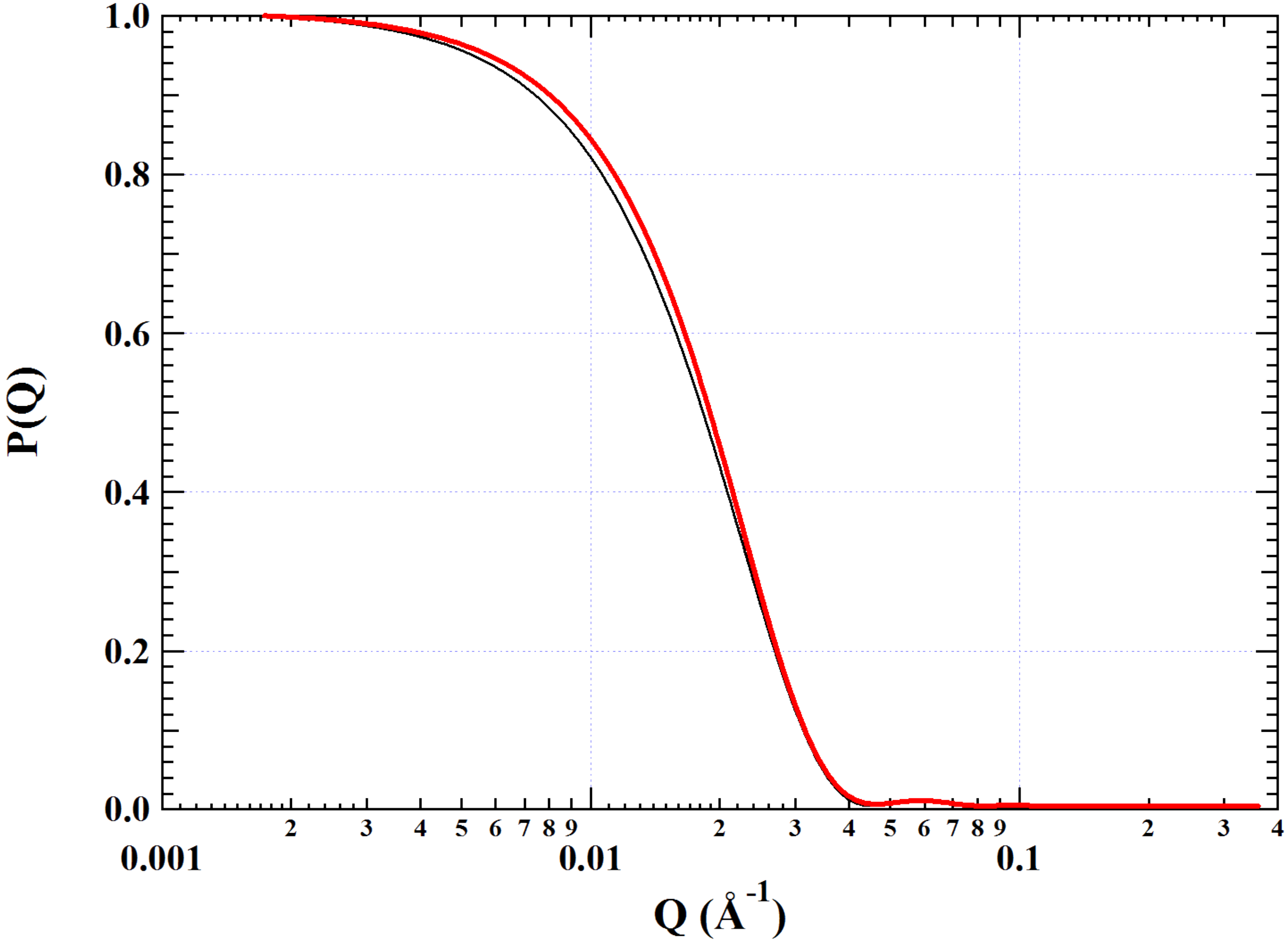


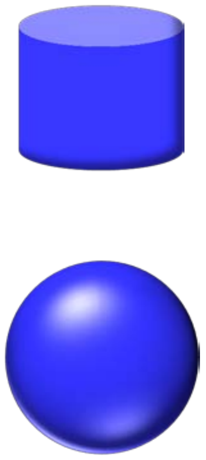
Ellipsoid
aspect ratio 1.5



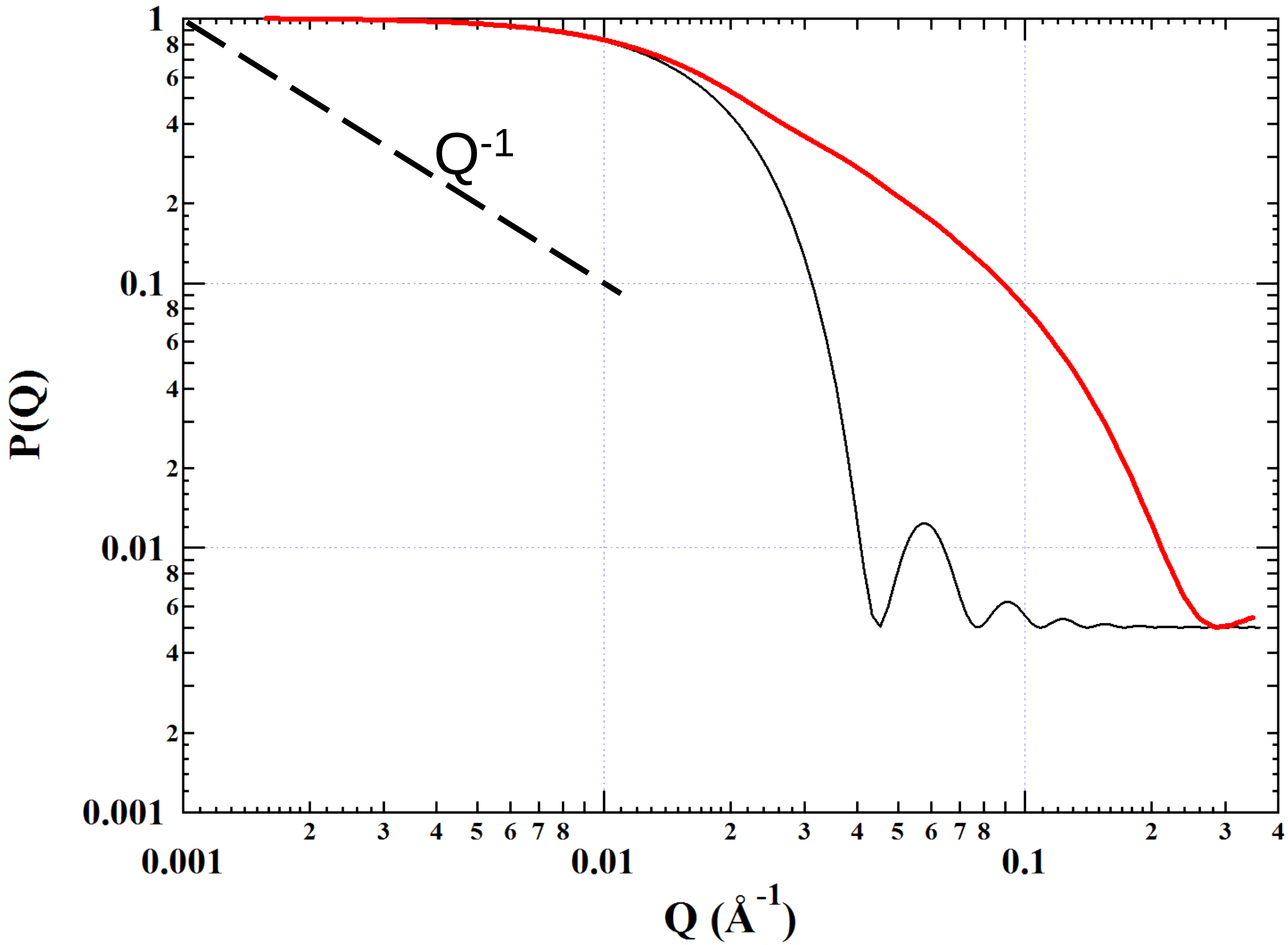


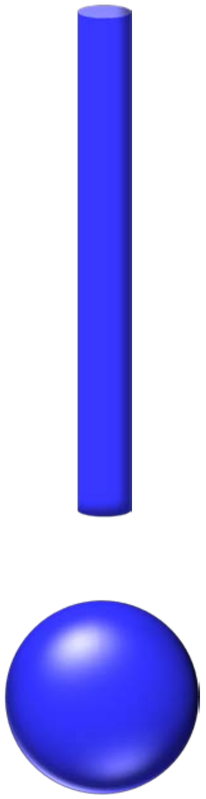
Circular Cylinder
with same Rg as the sphere



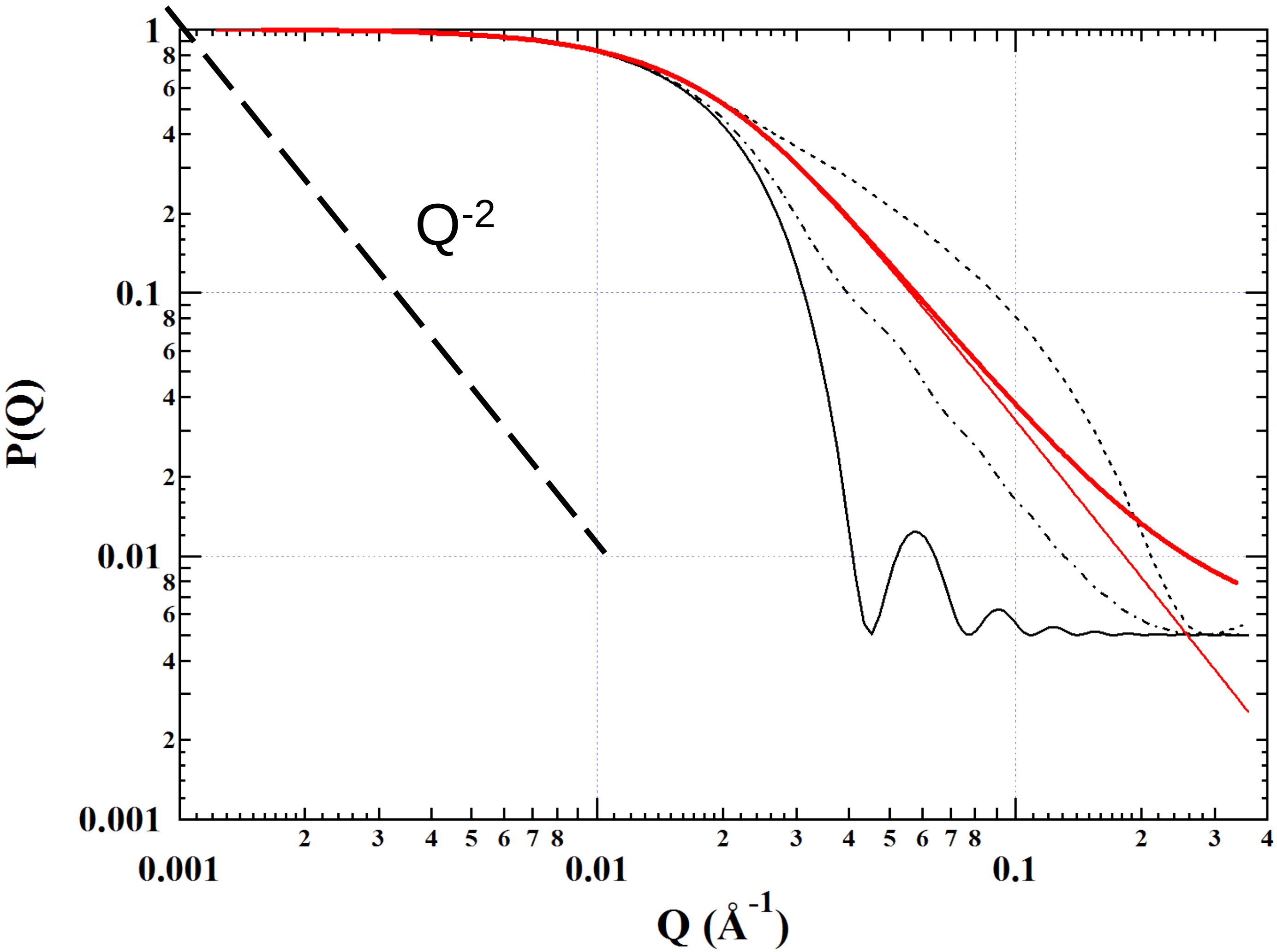


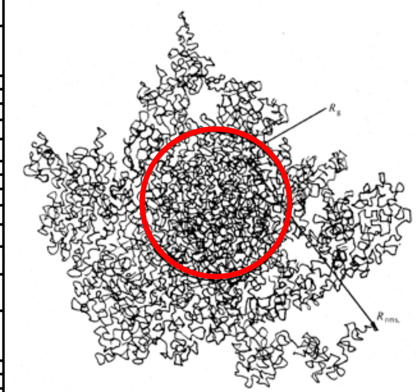
“Long & thin” cylinder

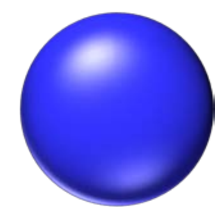




Polymer coil







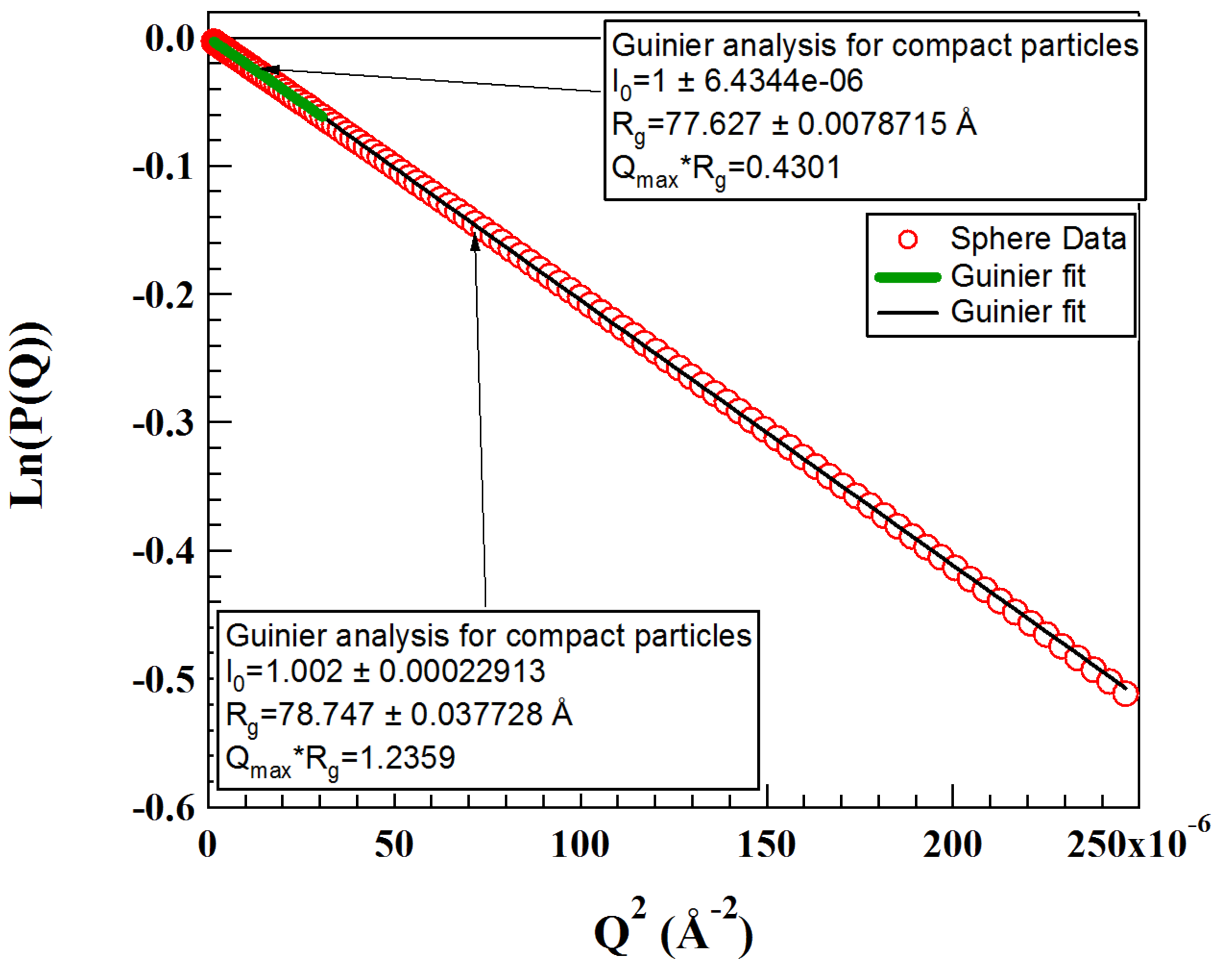
Guinier Analysis
size of any kind of object

- At small Q anything that could reasonably be considered an object follows Guinier approximation.

$$\ln[I(q)] \propto q^2 R_g^2 / 3 \quad qR_g < 1; \quad \text{sphere}: R = \sqrt{\frac{5}{3}} R_g$$

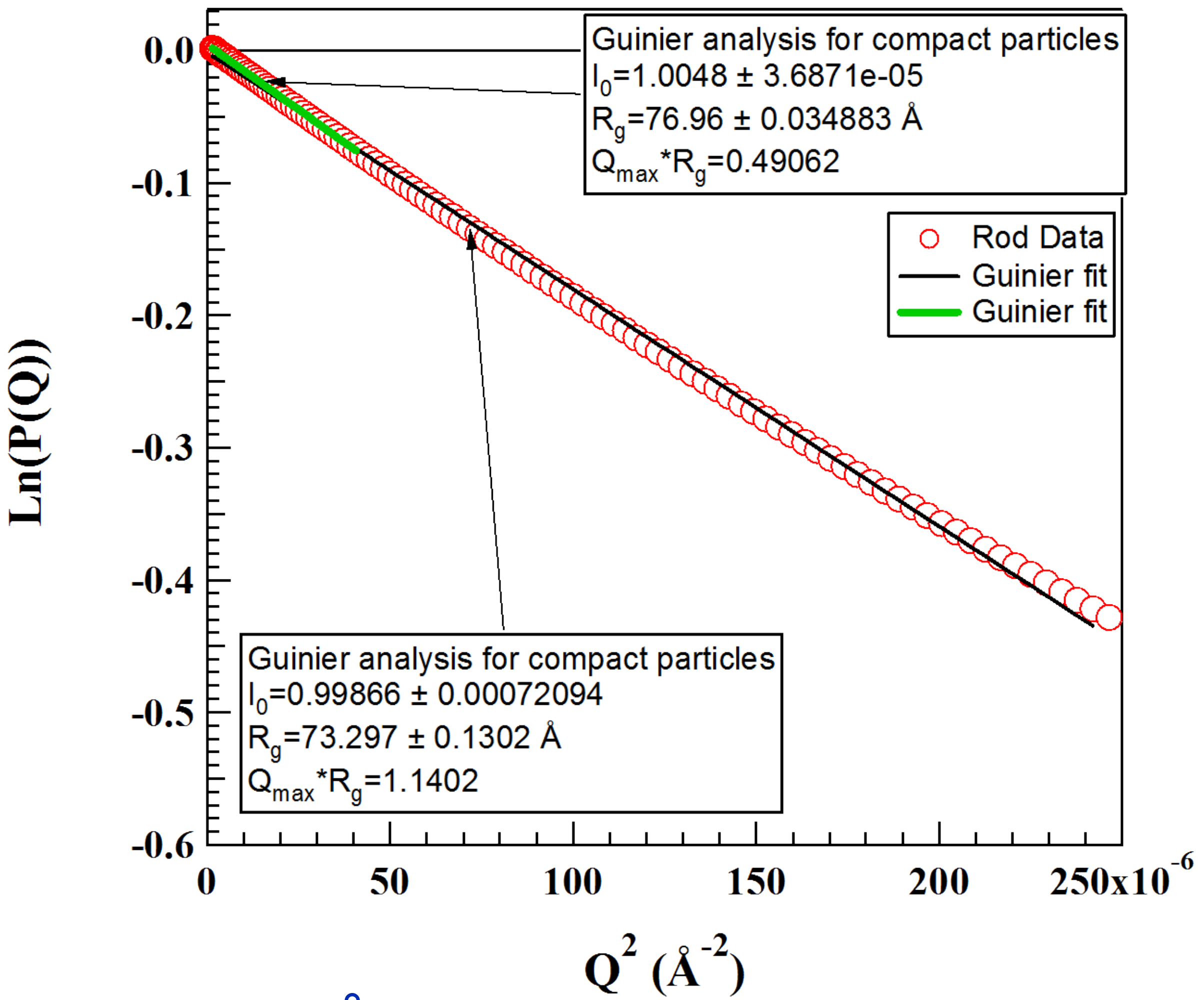
- Modified Guinier approximations exist to determine cross sectional radius of rods or thickness of sheets

Guinier Analysis
size of any kind of object



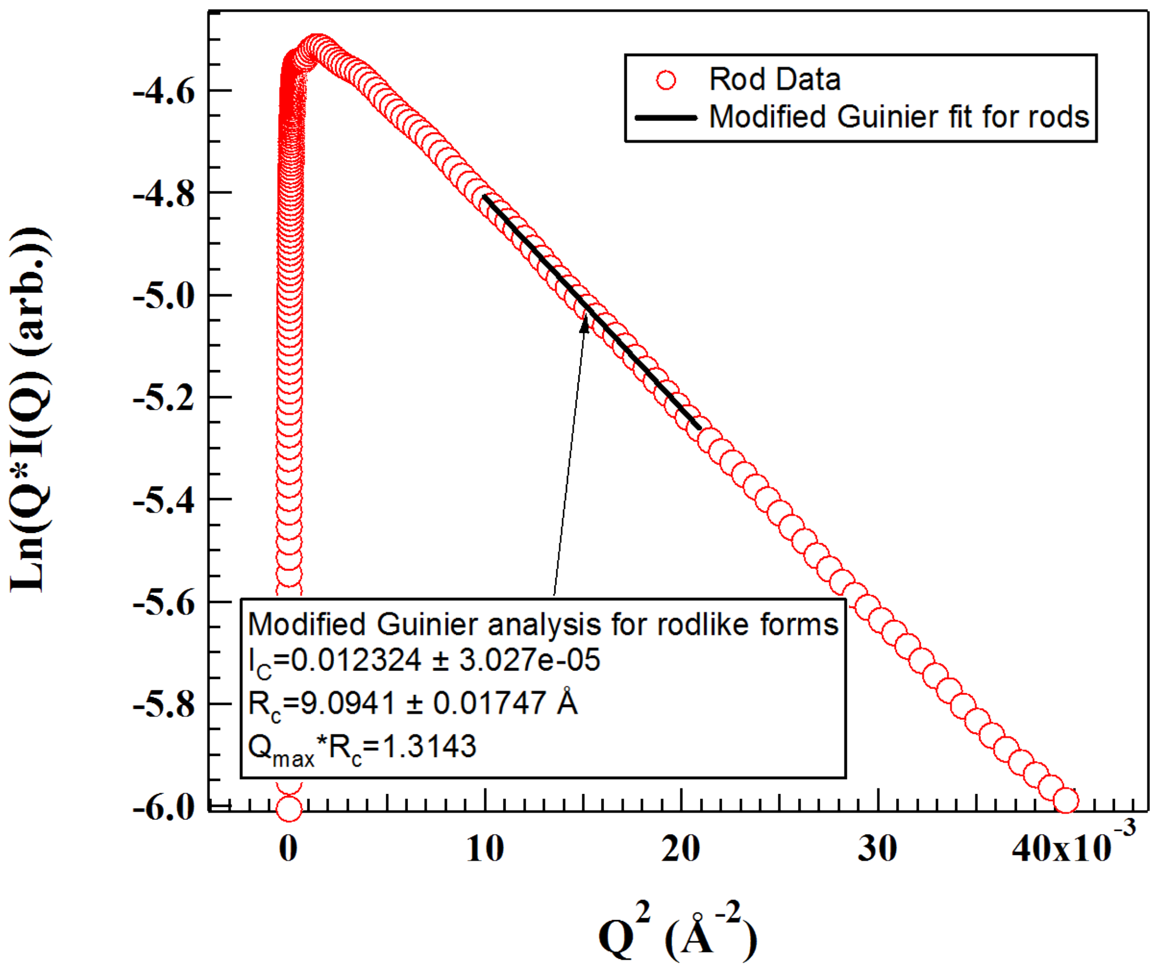
Precise R_g is 77.46 Å

Guinier Analysis
size of any kind of object



Precise R_g is 77.46 Å

Modified Guinier Analysis
for object extended in 1 dimension

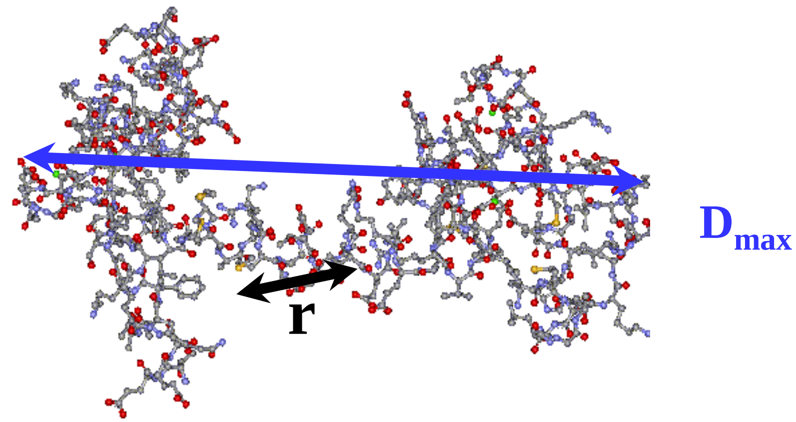


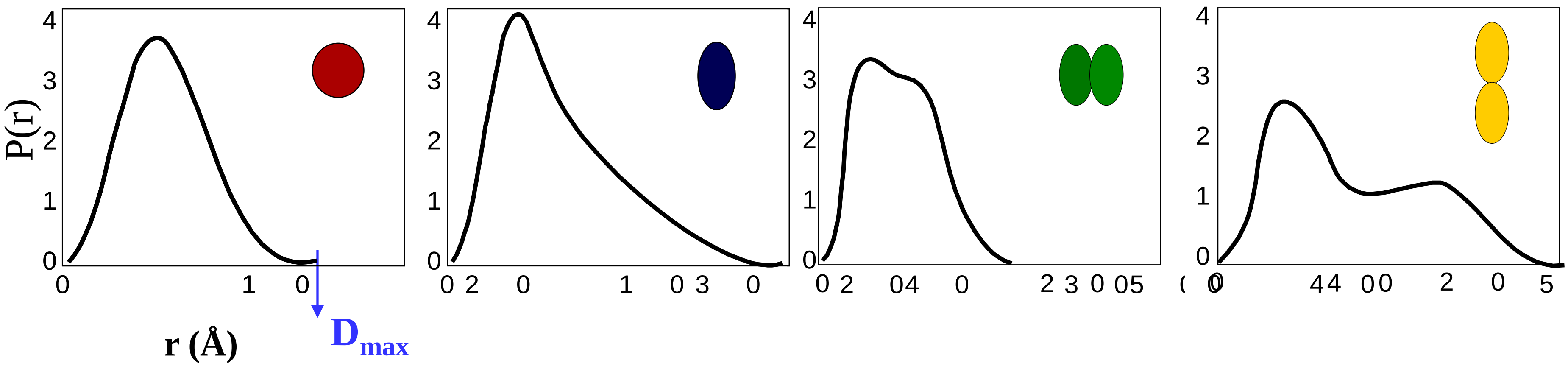
Rod radius = $\sqrt{2}$ * R_c = 12.9 Å, exact radius = 13.3 Å

A similar approach exists for thickness of (2d) sheet-like structure.

Pair correlation function and shape

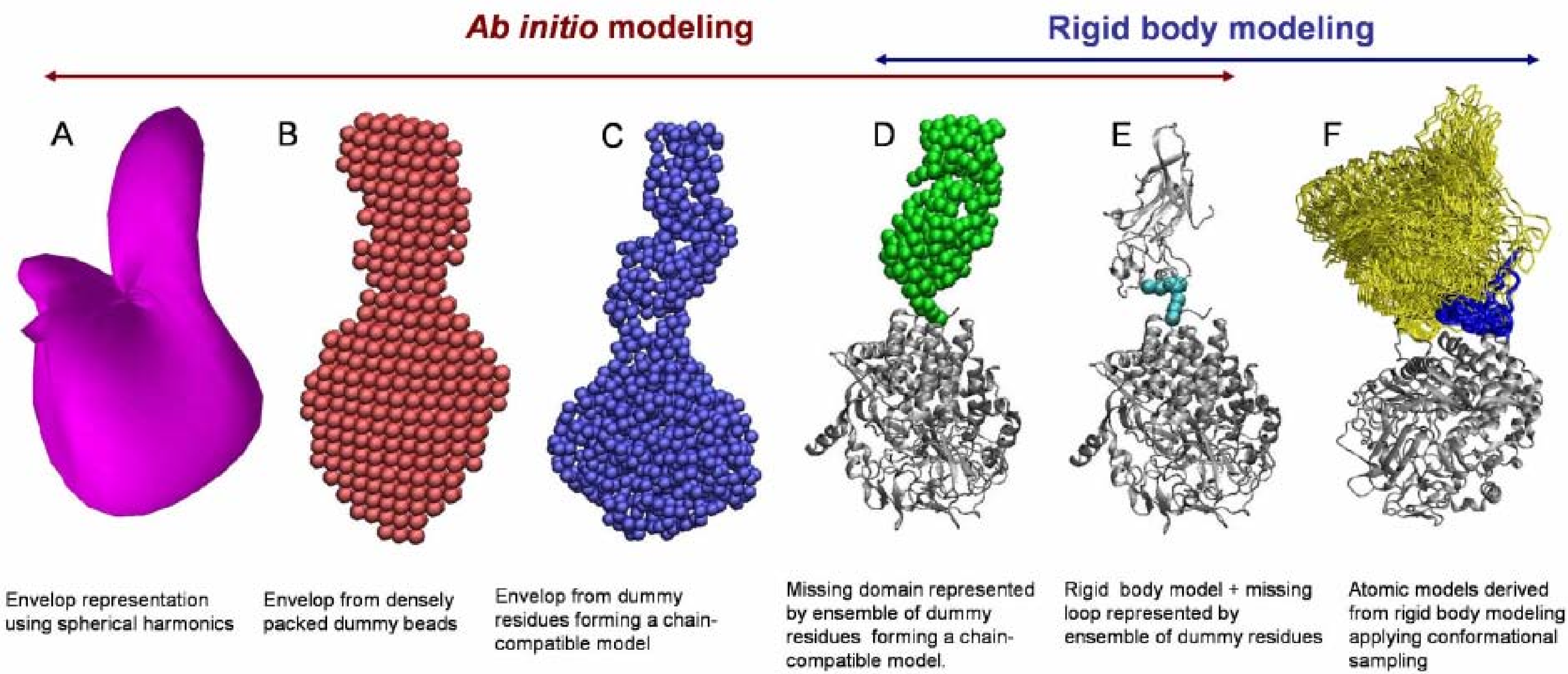
P(r) : inverse Fourier transform of scattering function : Probability of finding a vector of length r between scattering centers within the scattering particle.





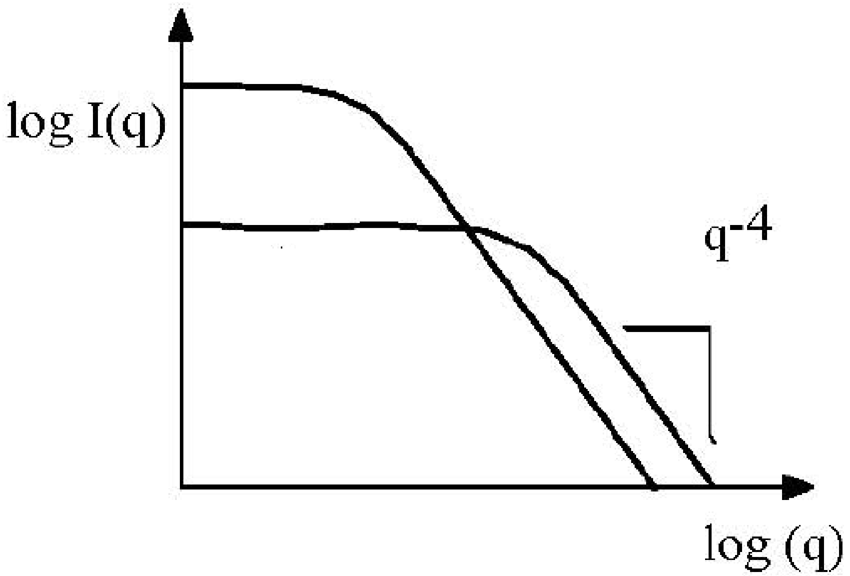
Shape : Modeled as a uniform density distribution that best fits the scattering data.

SAS Form Factor Modeling
of great use in biology



- Spherical Harmonics (Svergun, Stuhrmann, Grossman …)
- Aggregates of Spheres (Svergun, Doniach, Chacón, Heller …)
- Sets of High-resolution Structures (Svergun, Heller, Grishaev, Gabel …)
- Simple Shapes and Custom Approaches (Henderson, Zhao, Gregurick, Heller …)

Surface Scattering - *Porod*



At large q:

$I(q) \propto q^{-4}$

Specific Surface Area, S_V

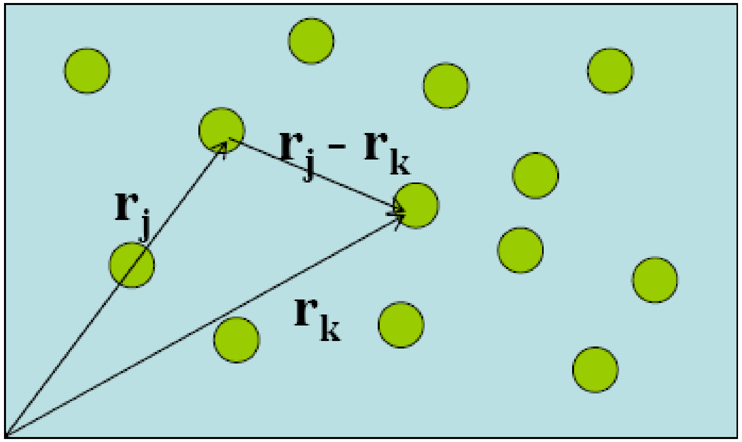
$$\lim_{q \to \infty} I(q) = 2\pi S_V |\Delta\rho|^2 q^{-4}$$

But, fractal rough interfaces: Q^{-x} , $3 < x < 4$

Interparticle Structure Factor S(Q)

$$I(q) = \frac{N}{V}(\Delta\rho)^2 V_p^2 P(q) S(\vec{q}) \text{ where } P(q) = \left|F(q)\right|^2$$

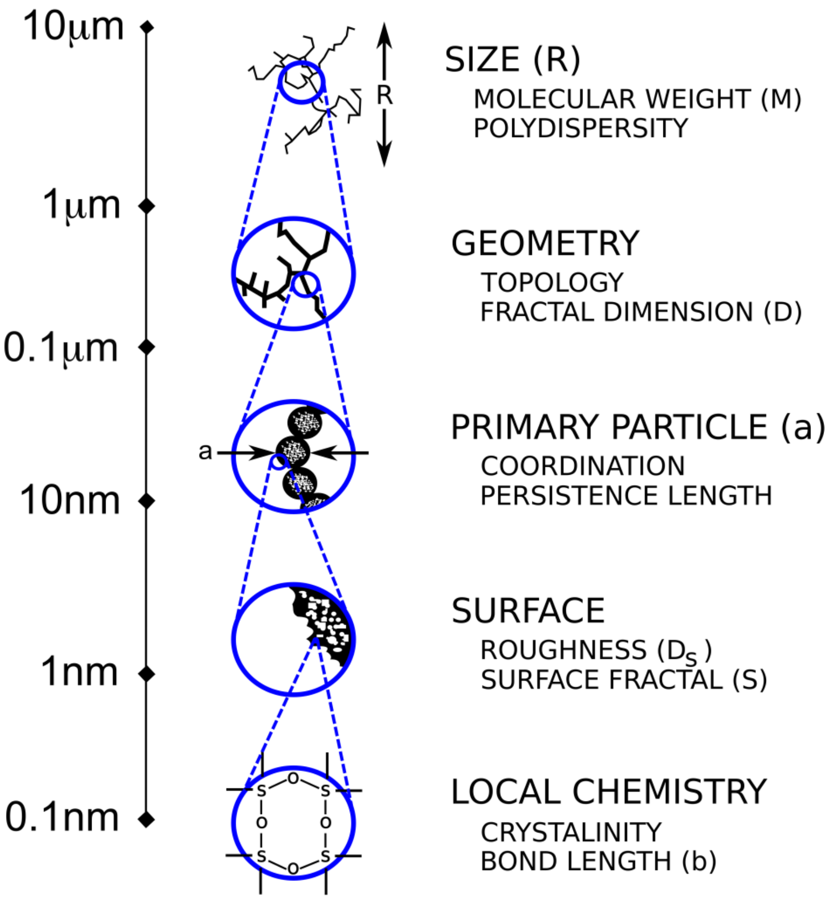
$$S(\vec{q}) = 1 + \left\langle \sum_{k=1}^{N} \sum_{\substack{j=1 \\ j\neq k}}^{N} e^{i\vec{q}\cdot(\vec{r}_k - \vec{r}_j)} \right\rangle$$

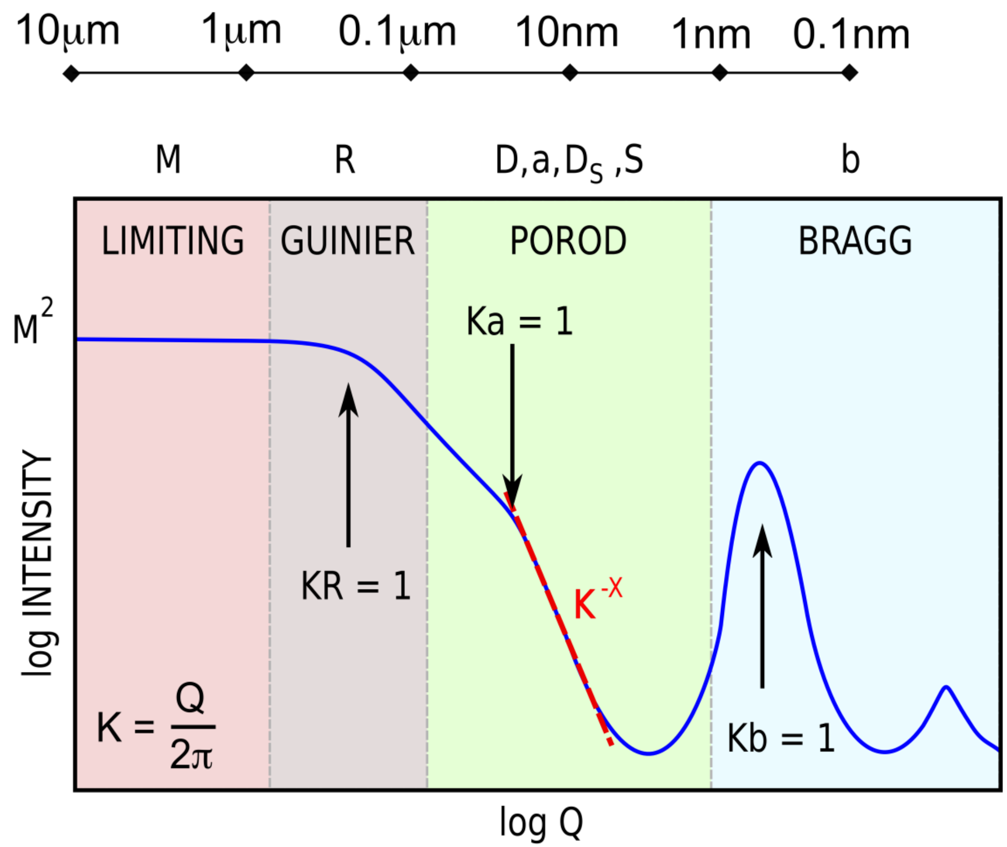


I(q) is modulated by interference effects between radiation scattered by different scattering bodies.

S(q) examples: hard sphere potential, sticky sphere etc.

Structural Hierarchy (particulate)





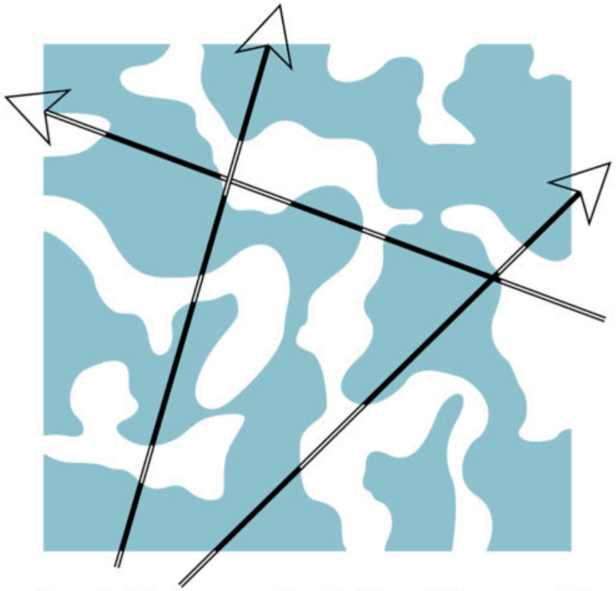
Adapted from DW Schaefer *MRS Symposium Proceeding* 1987

Structural information viewed on five length scales. Structural features at larger length scales are observed at smaller Q.

Scattering analysis that describes hierarchical structures: Mass Fractal (Teixeira), Unified Fit (Beaucage) *combine power law scattering ranges with R_g transitions*

Non-particulate Scattering

Debye Bueche Model for Two-Phase System, Each with Random Shape, Uniform Electron or Scattering Length Density and Sharp Boundaries



Physical Concept of the Mean Chord or Inhomogeneity Length

Mean Chord Intercepts:

$$L_1 = \frac{a}{\phi}$$

$$L_2 = \frac{a}{(1-\phi)}$$

The fluctuations in scattering power at two points A and B, distance r apart, can be characterized by $\gamma(r) \langle\eta^2\rangle_{AV} = \langle\eta_A\eta_B\rangle_{AV}$. For random two phase system: $\gamma(r) = e^{-r/a}$

$$\frac{d\Sigma}{d\Omega}(Q) = \frac{A}{[1 + Q^2a^2]^2}$$

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SAS Summary

- SAS applications are in the nm to μm range and otherwise only limited by imagination.
- SAS is used alone, but often complementary to other methods, e.g. microscopy.
- Scattering is similar to diffraction (but different).
- SAS data analysis can be tough math, or make use of readily available approximations, models and software.
- SAS does not see atoms but larger, interesting features over many length scales.
- Precision of structural parameters can be 1Å or better.