Small Angle Scattering
of neutrons and x-rays

Volker Urban

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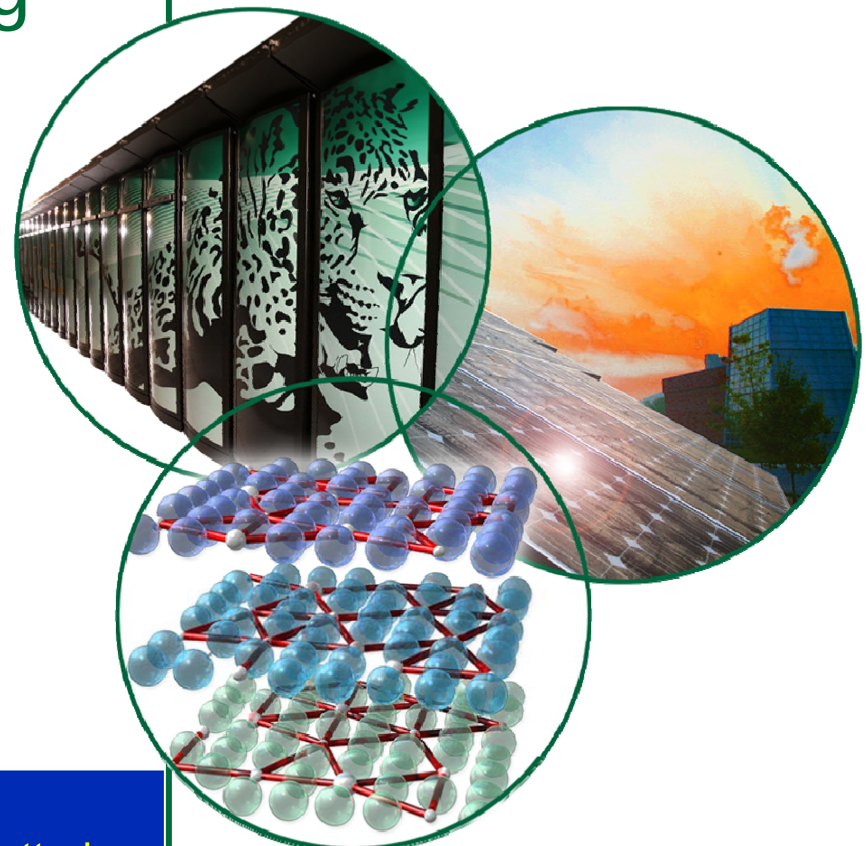


National School on Neutron and X-ray Scattering
May 30 – June 13, 2009


I am scattering like light…
Suzanne Vega – Small Blue Thing

Outline

- Applications – is SAS for you?
- Comparison with microscopy and diffraction
- Basic concepts of the technique
- At the beamline – SAS jargon
- Planning a SAS experiment and data reduction
- Break
- 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

SANS vs. Synchrotron SAXS

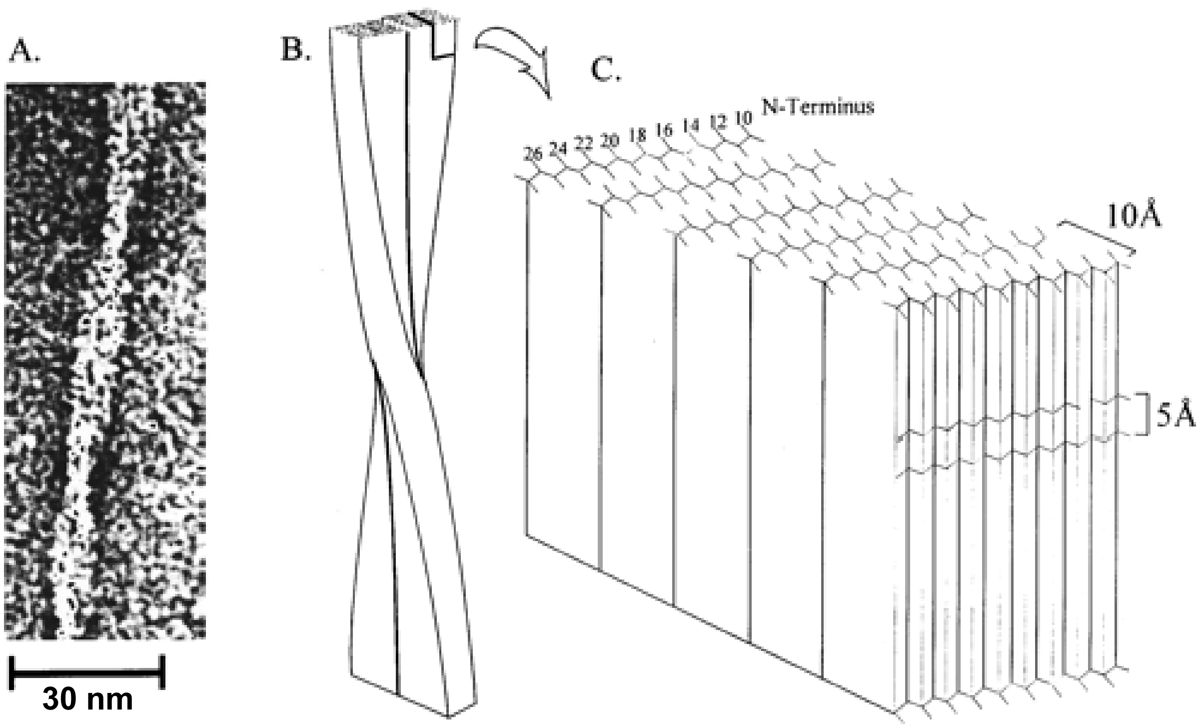
- SAXS & SANS
  - nm scale structural analysis (~1nm-1μm)
  - Non-destructive
  - In-situ
- Synchrotron X-rays
  - High throughput
  - Time-resolution (ms – ps)
  - Tiny beams – microfocus: e.g. scanning of cells
- Neutrons
  - ‘see’ light atoms: polymers, biology, soft condensed matter, hydrogen in 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

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
- Complimentarity

Alzheimer's Disease – β-Amyloid

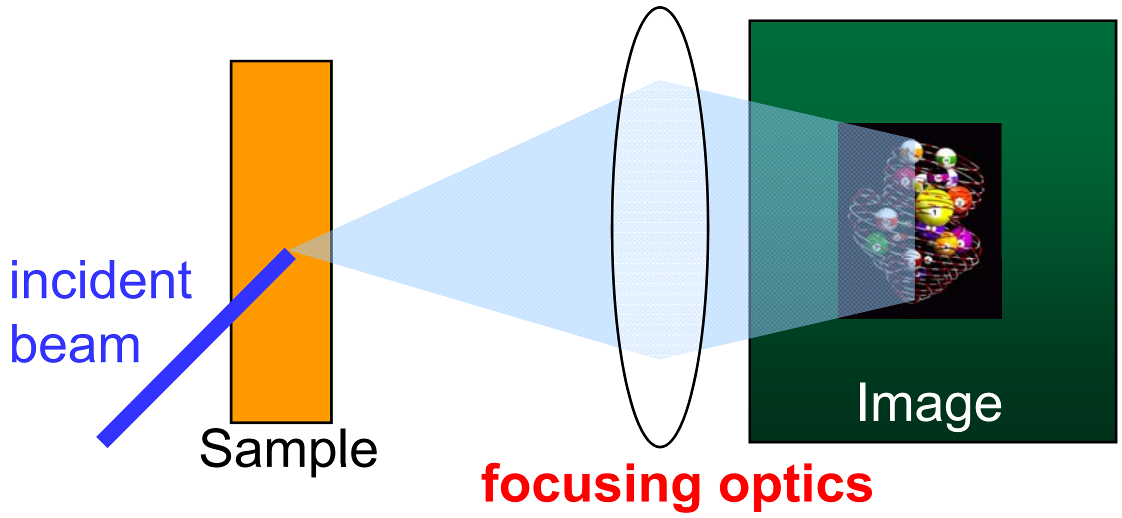
- Among leading causes of death
- Miss-folded peptides form hierarchical ordered fibril structures & plaques
- Structure established using synthetic model peptides and complimentary methods NMR, SANS, EM



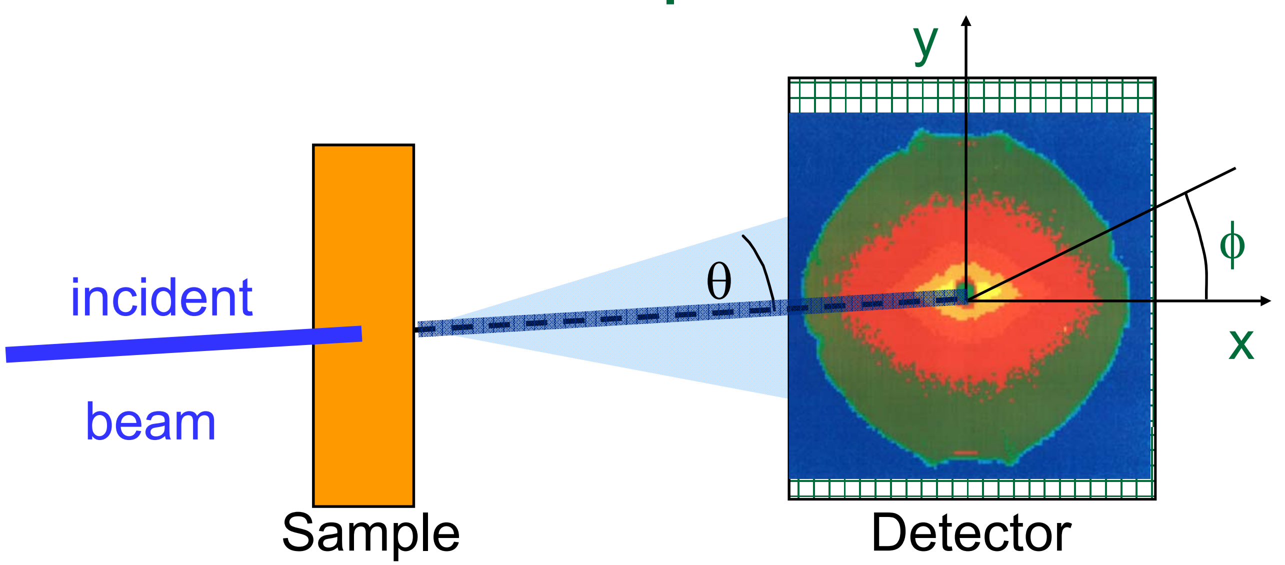
T.S. Burkoth et al. *J. Am. Chem. Soc.* **2000,** *122,* 7883-7889

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

Microscopy : enlarged image



SAS : interference pattern



Scattering and Diffraction (Crystallography)

- Strictly/historical: Scattering from individual electrons/nuclei, Diffraction through interference of primary waves
- Today's common language: Diffraction from crystals, Scattering from anything else (less ordered) > the difference is in the SAMPLE!
- 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 "blobs" NOT atoms – allows SLD contrast variation!

Diffraction (Crystallography)
here at Small Angles

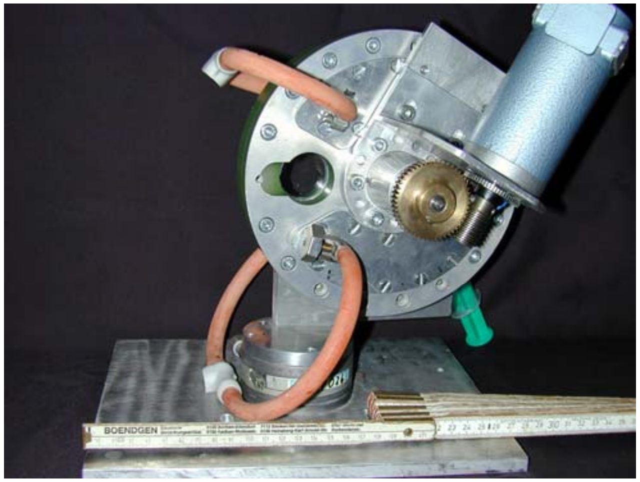
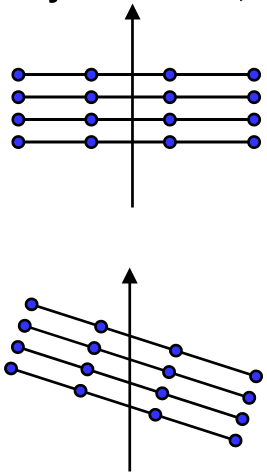
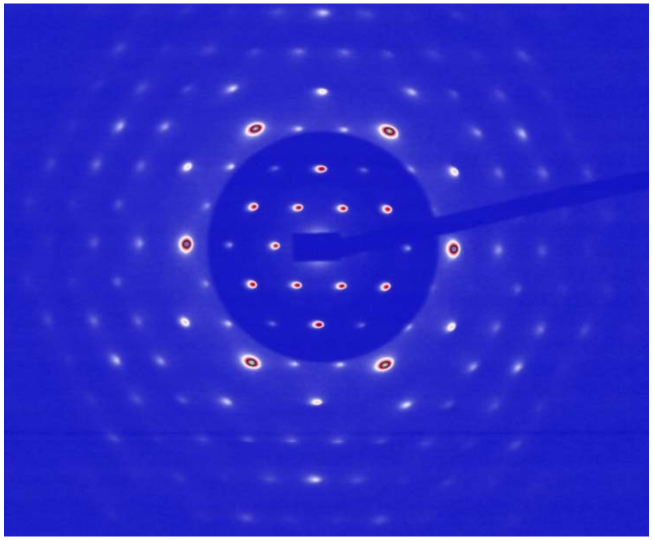


Plate Geometry - Versmold, Uni Aachen



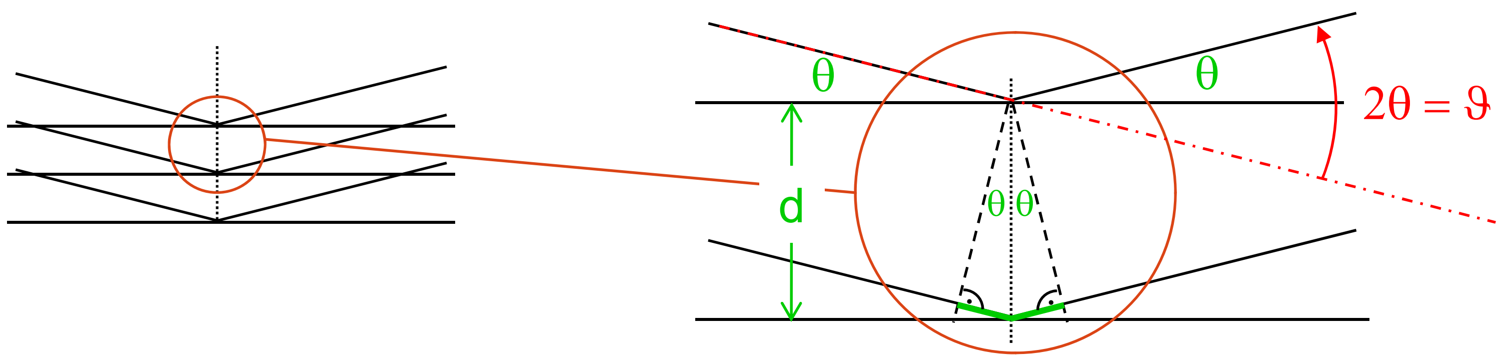
Shear ordered charge stabilized colloidal dispersion

Scattering along Bragg-rods of layered system > stacking sequence



Diffraction - Bragg's Law

Waves with wavelength λ are reflected by sets of lattice planes



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

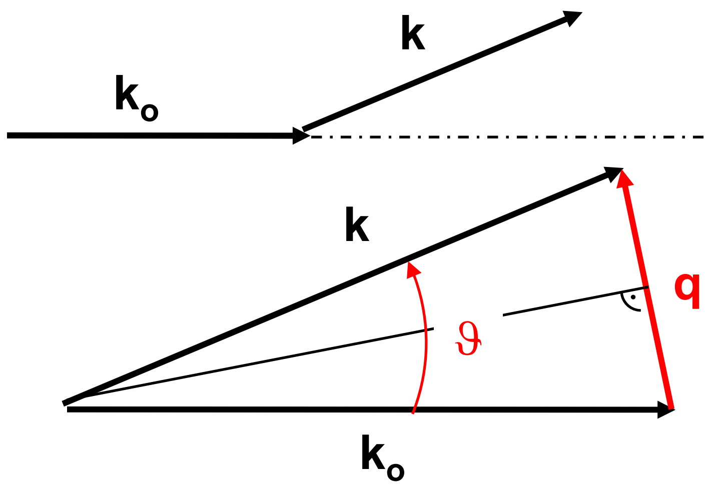
Phase shift = $2\pi\, \Delta/\lambda$

if $\Delta = n\, \lambda$ then reflection

otherwise extinction $\longrightarrow$ $\mathbf{n\lambda = 2d \sin(\theta)}$ $\quad 1/d = 2/\lambda \sin(\vartheta/2)$

Scattering Vector – q
aka momentum transfer, Q, h, k, s

Wave vector k: |k| = k = 2π/λ



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

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

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

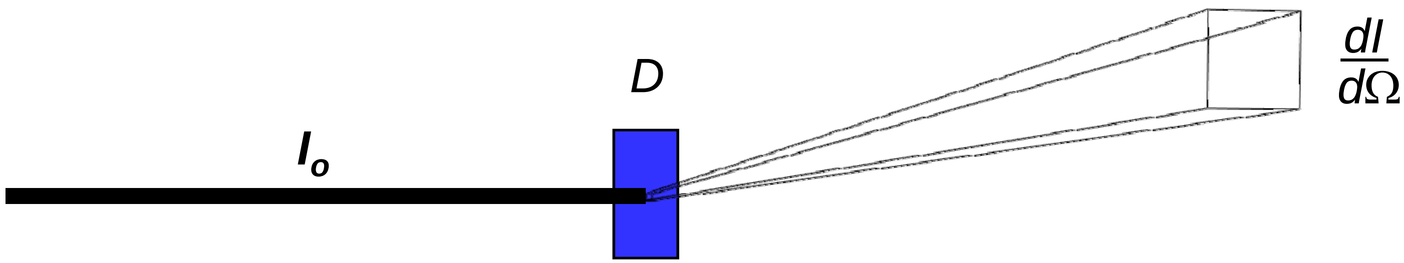
q in nm^{-1} or $Å^{-1}$

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).

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

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



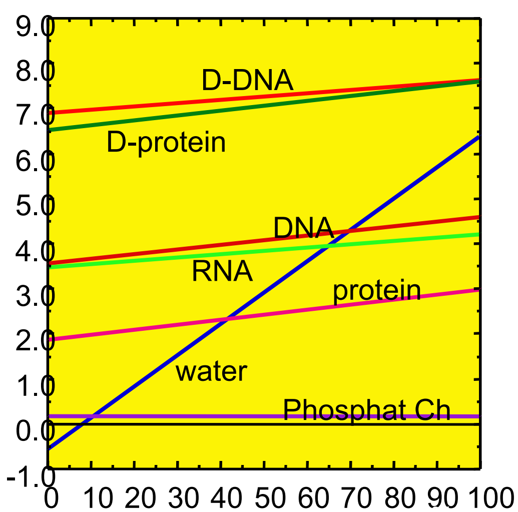
$$\frac{dI}{d\Omega} = TI_o D \frac{d\Sigma}{d\Omega} \longleftrightarrow \frac{d\Sigma}{d\Omega} = \frac{1}{TI_o D}\frac{dI}{d\Omega}$$ **[cm^{-1}sterad^{-1}]**

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

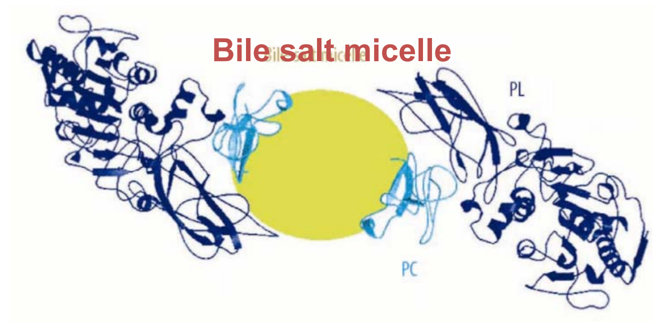
Contrast – Atomic Scattering Lengths

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**

SANS – Contrast Variation

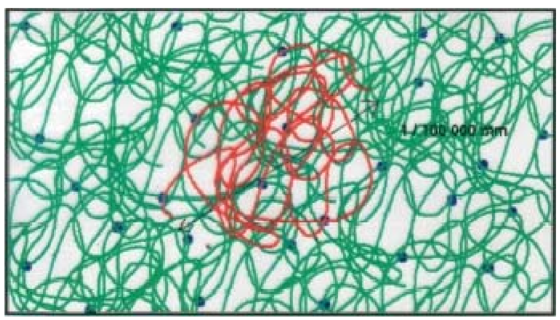


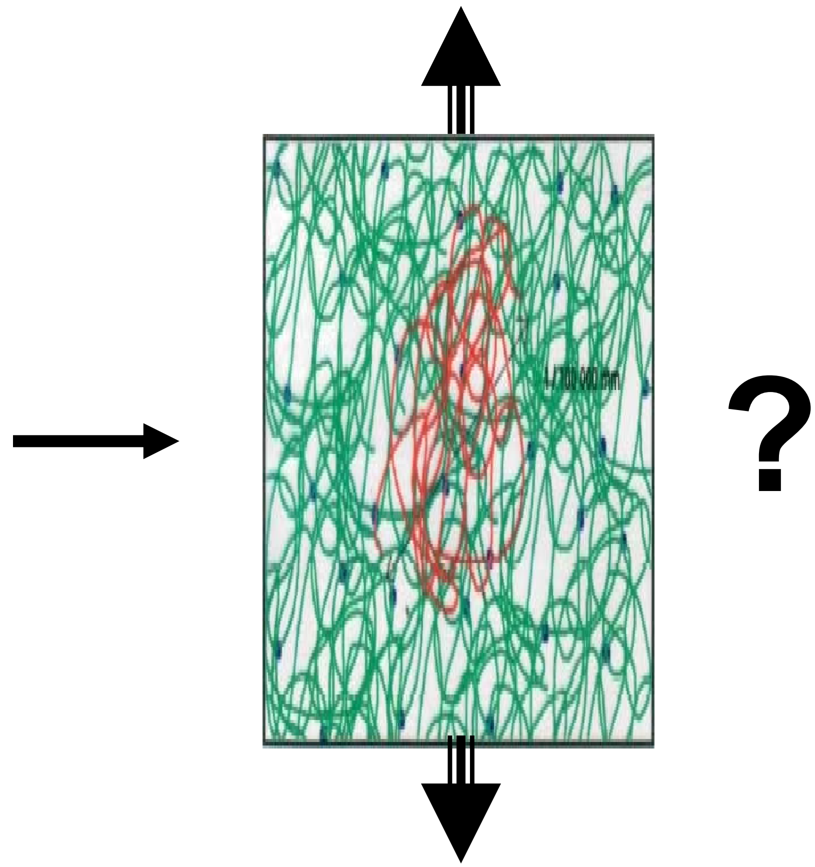
D_2O/H_2O contrast variation



Rubber (Polymer Network)

- Unique mechanical properties – “liquid” on local scale but long range structure memory
- Economic importance – Tires





- Blend “normal” H- and some

  % D-polyisoprene
- Cross-link to form rubber network
- Stretch rubber sample in the SANS beam and collect data

SANS of labeled stretched rubber

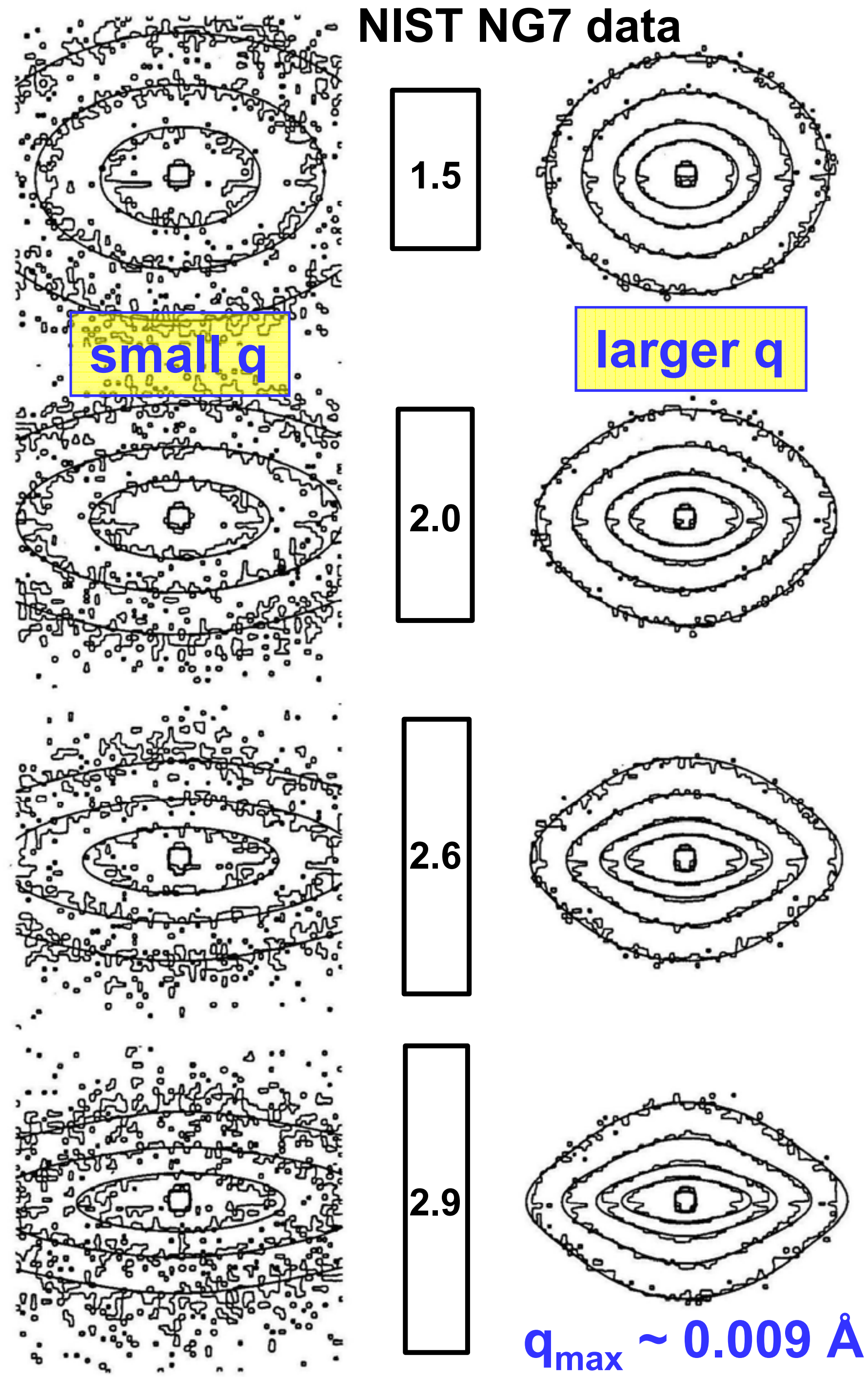
• Stronger anisotropy at smaller q (larger distances)
• Ellipse > diamond transition at large deformation
• Warner-Edwards tube approach:

affinely deformed Gauss chain

$$S(\vec{q},\lambda) = 2N\int_0^1 dx \int_0^x dx' \prod_\mu \exp\left\{ -(Q_\mu \lambda_\mu)^2 (x-x') - \right.$$

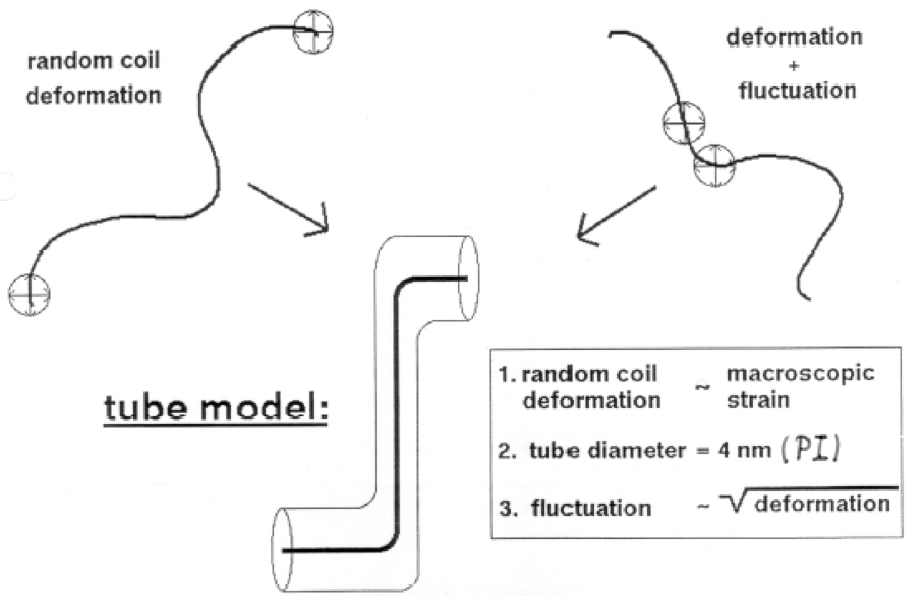
$$\left. Q_\mu^2 (1-\lambda_\mu^2) \frac{d_\mu^2}{2\sqrt{6}R_g^2} \left(1 - \exp\left[-\frac{(x-x')}{\frac{d_\mu^2}{2\sqrt{6}R_g^2}} \right] \right) \right\}$$

non-affine fluctuation contribution

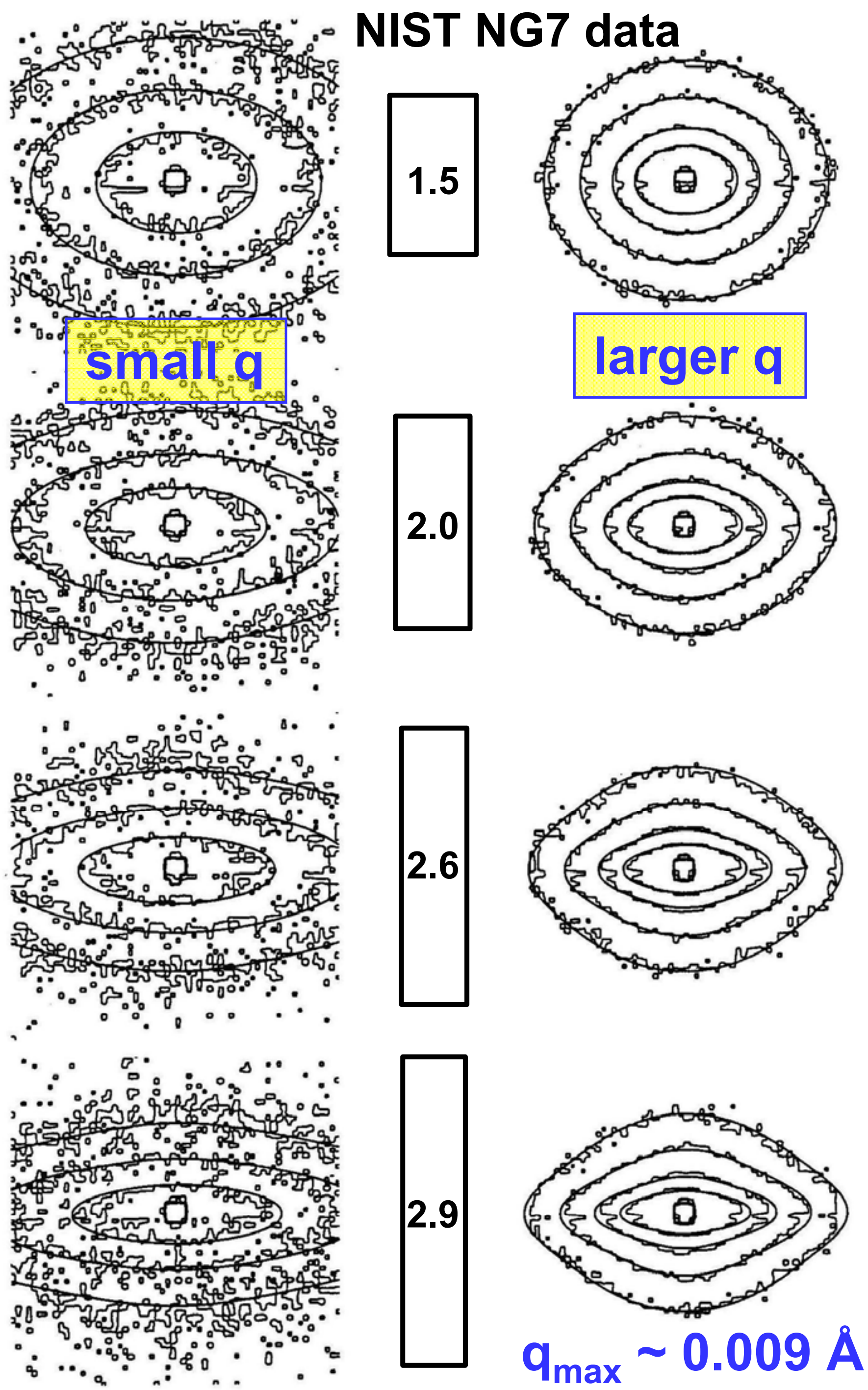


SANS at increasing deformation

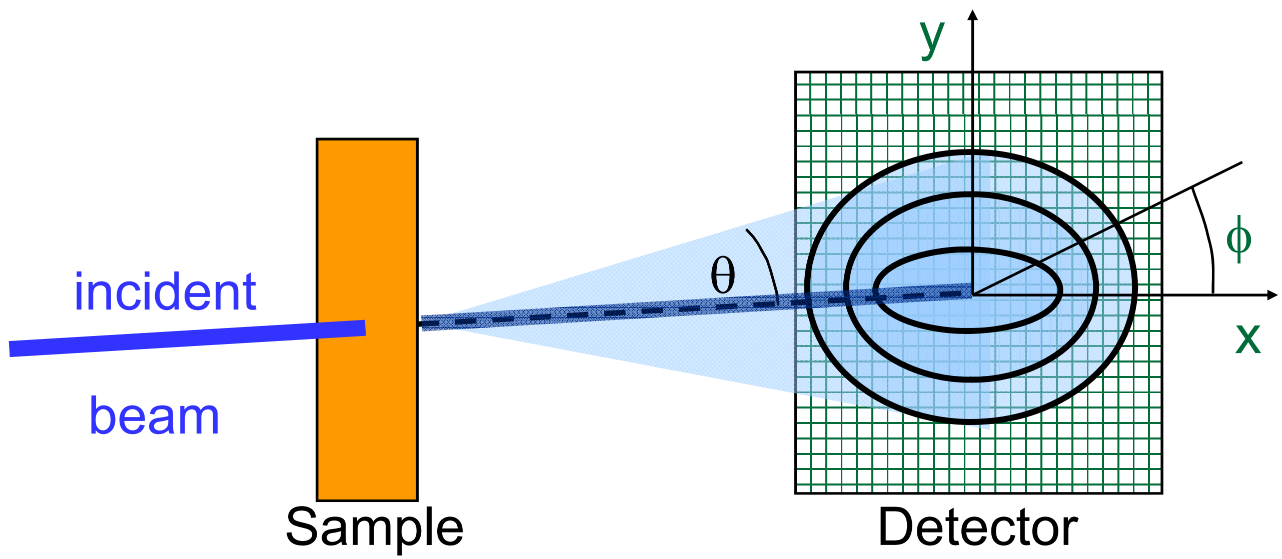
- Self-consistent tube model with deformation dependent tube width:



E. Straube et al., *Macromolecules* **27**, 7681 (1994)
E. Straube et al., *Physical Review Letters* **74**, 4464 (1995)



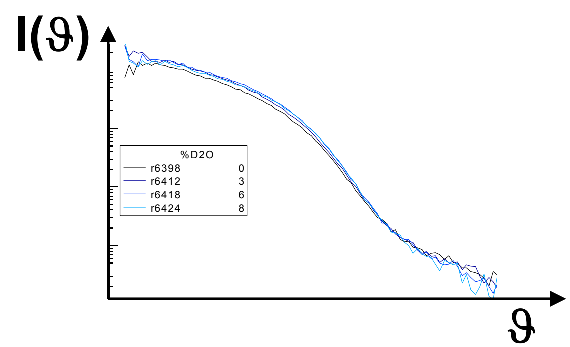
At the beamline



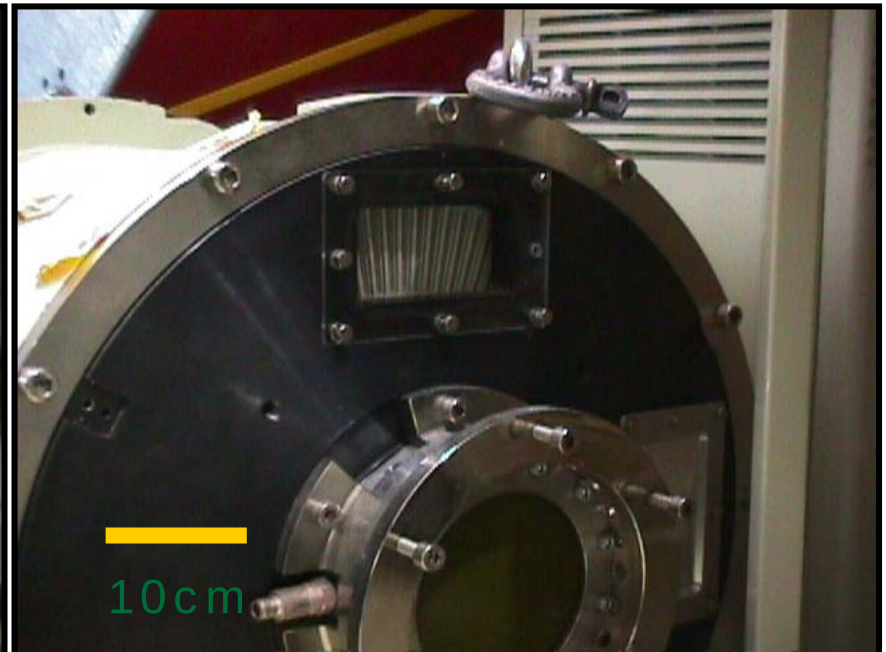
Monochromatic beam (Δλ/λ) Pinhole camera (Δθ/θ)

Area detector

If data isotropic:
azimuthal average I(ϑ)
(aka "radial average")



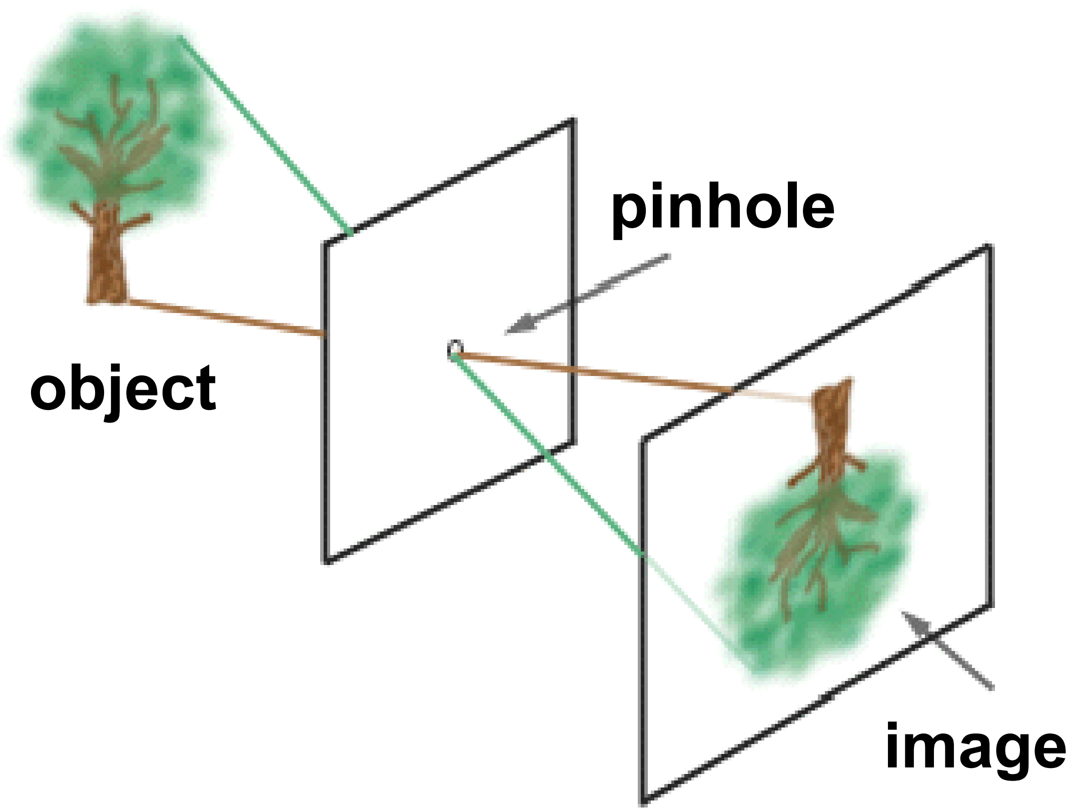
Monochromator – Velocity Selector



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

SANS Instrument – a pinhole camera?

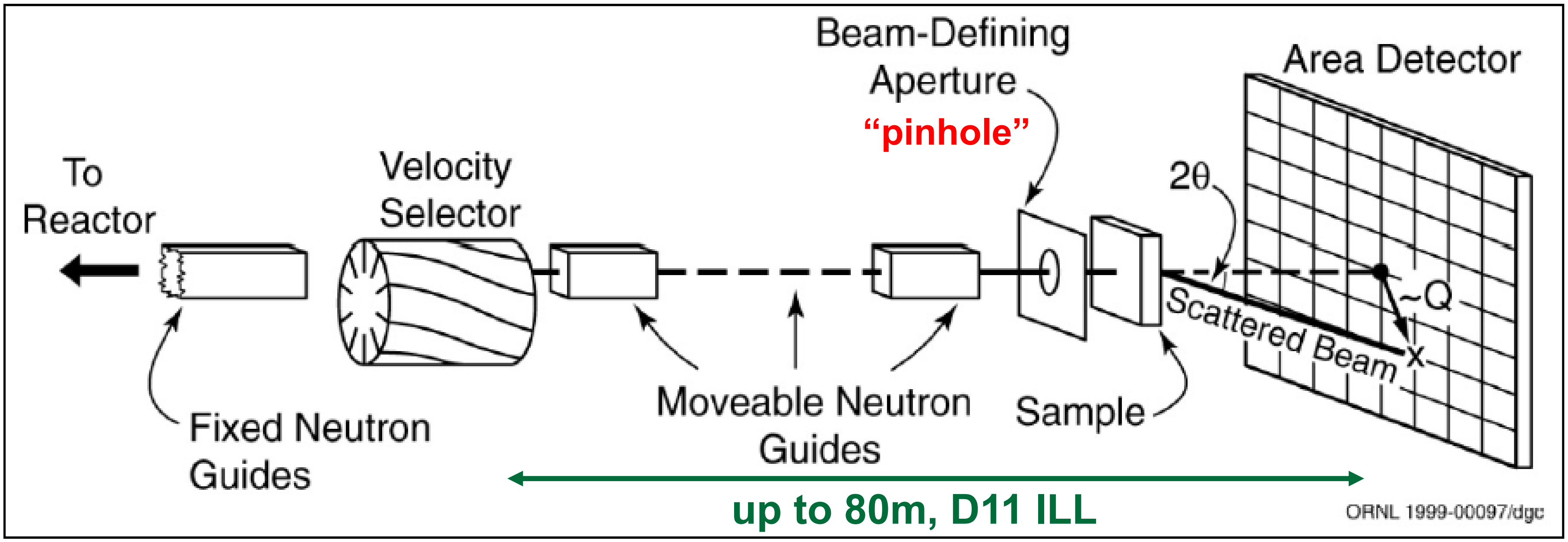


So it does take pictures?

Yes, but of what?

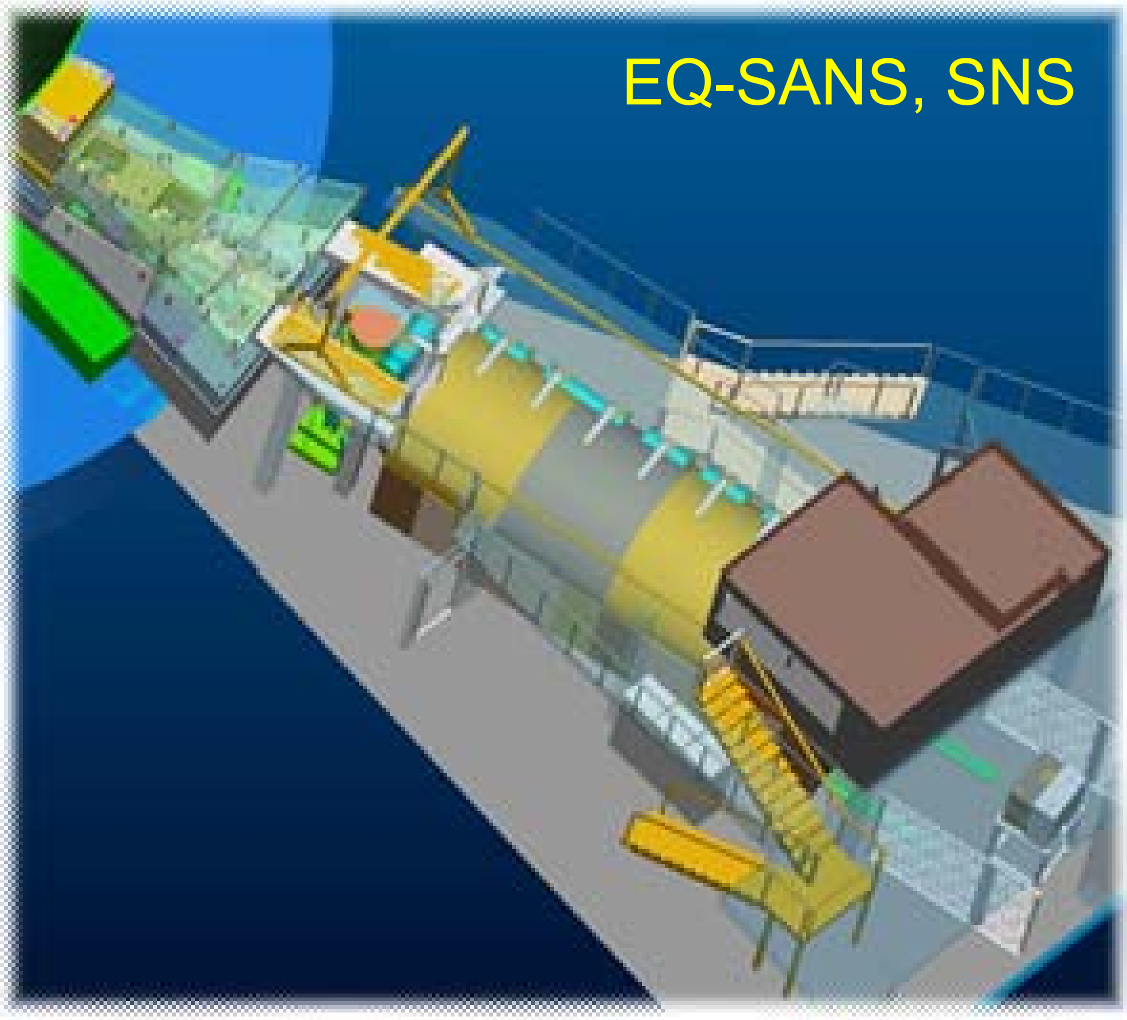
Of the source aperture, not of the sample!

Layout of a SANS instrument



Typical layout at a continuous (reactor) source

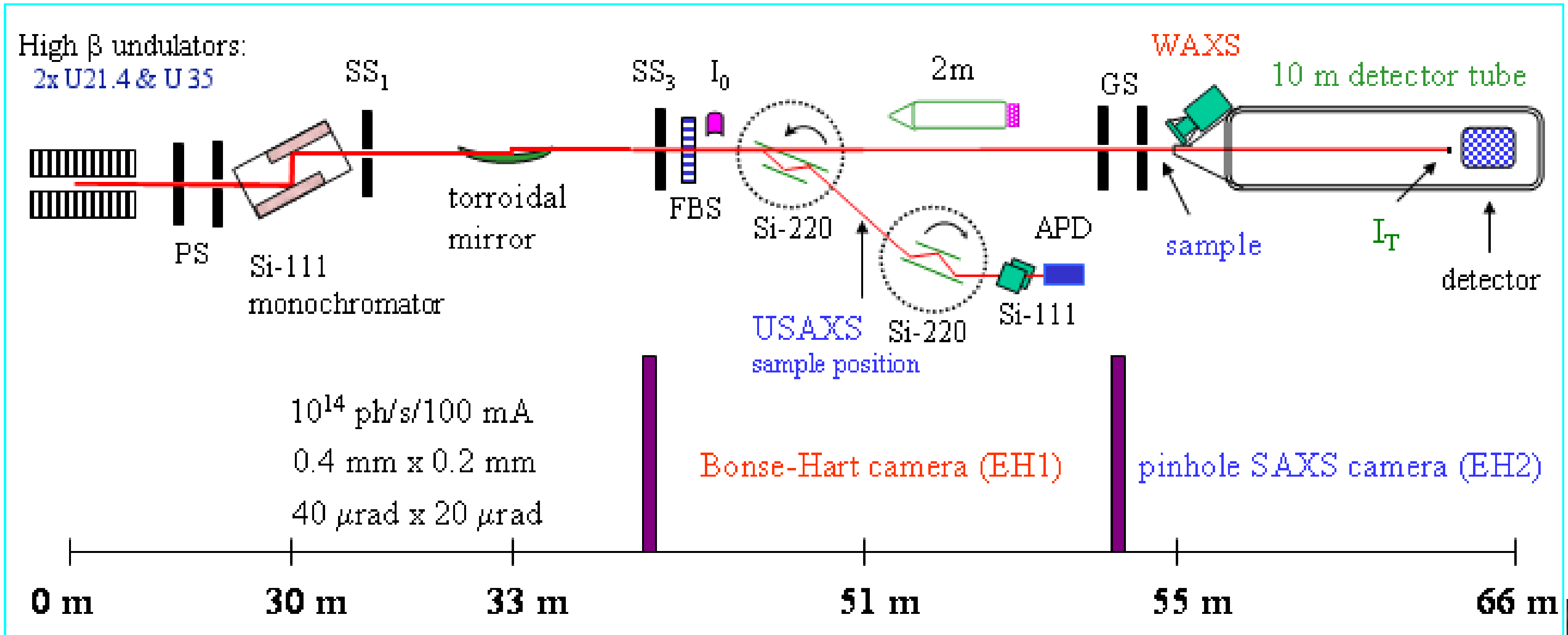
SANS at a pulsed source



SPECIFICATIONS

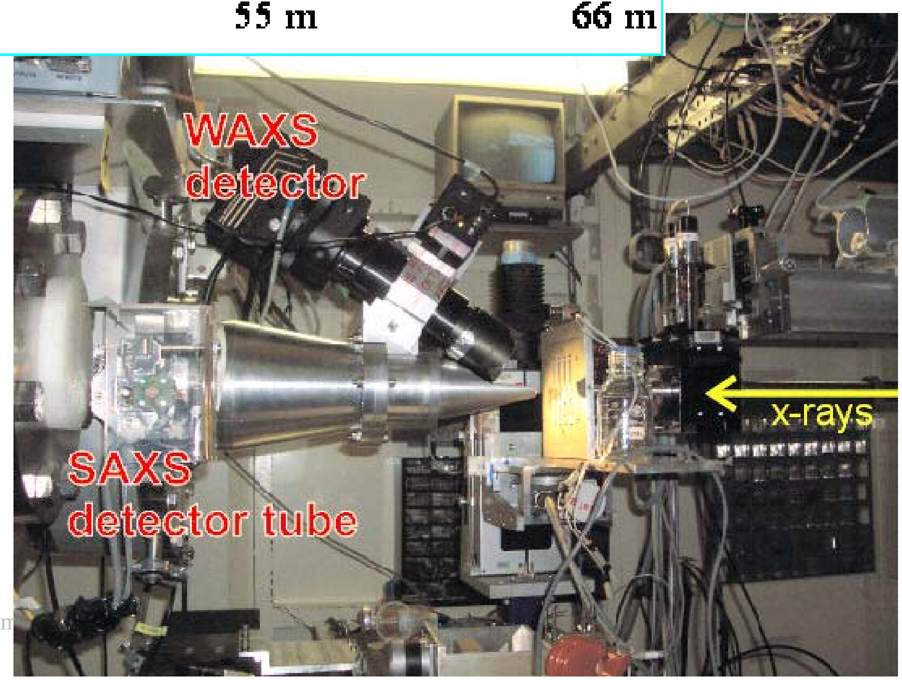
Source-to-sample distance	14 m
Bandwidth	3–4.3 Å
Moderator	Coupled supercritical hydrogen
Integrated flux on sample	~10^7–10^9 n/cm²/s
Q range	0.004 $Å^{-1}$ < Q < 10 $Å^{-1}$

SAXS at synchrotrons



ESRF ID-2 High Brilliance Beamline

SAXS, WAXS, USAXS, ASAXS



SANS guide hall (HFIR)

SANS guide hall (HFIR)


DeSHAZO
CRANE COMPANY
10-TON
SOUTH
BEAM
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BEAM
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4

Practical Considerations at SANS and SAXS User Facilities

- Thou shalt plan well thy experiment!
- What Q-range would I like, and what must I have?
- For how long should I measure my samples? – *counting statistics*
- 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})

Break

Analysis of SAS data

here typical particulate solution scattering

$$\frac{d\Sigma}{d\Omega}(q) = \Delta\rho^2\, n\, V^2\, P(q)\, S(q)$$

lim q,n → 0:

$$\frac{d\Sigma}{d\Omega}(q=0) = \Delta\rho^2\, n\, V^2$$

- n - Number density (concentration)
- V - Particle volume (molecular mass)

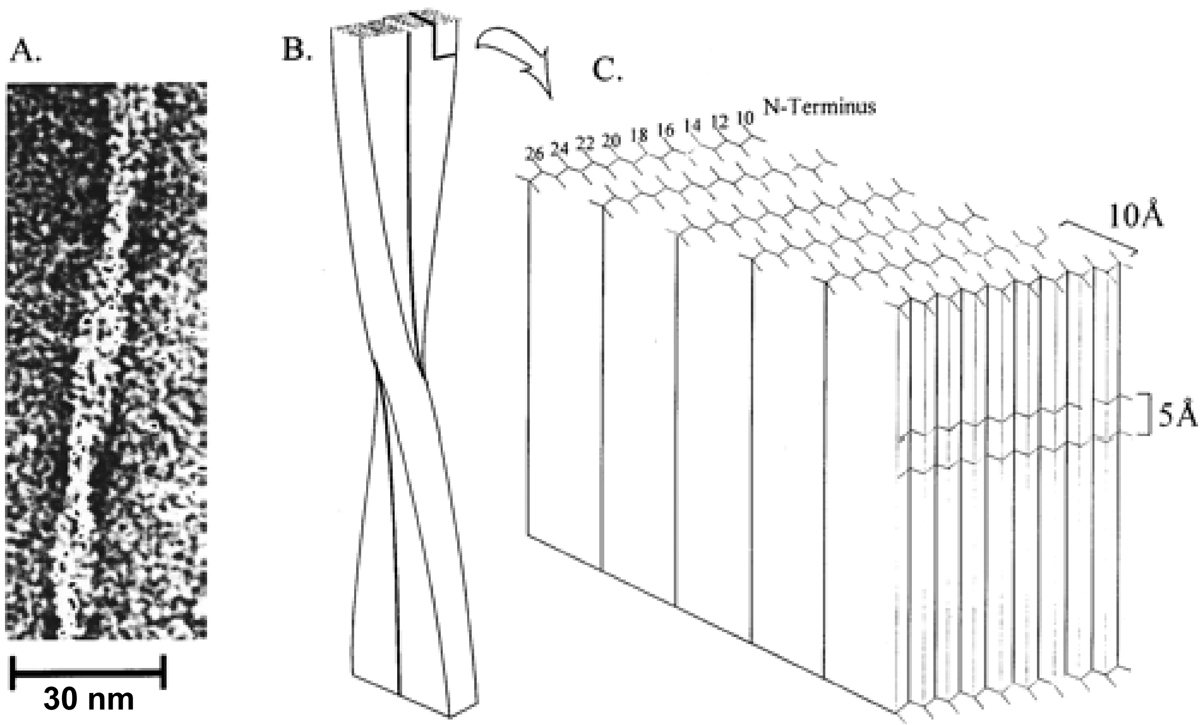
- $\Delta\rho^2$ - Contrast = square of scattering length density difference between particle and medium
  - x-rays: electron density
  - neutrons: isotope labeling, particularly H > D
- P(q) - Size & shape
- S(q) - Interaction

Measure and subtract background very carefully!

Do the absolute calibration – it's worth the 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



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

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

Analysis of SAS data

S(q) * P(q) is not always a useful approach!

- *P*(*q*)
  - Guinier approximation → radius of gyration: R_g

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

    (modified Guinier for rods and sheets)
  - Form factor fit / modeling

    sphere, ellipsoid, rod, protein structure, fractal etc.
- *S*(*q*)
  - hard sphere potential, sticky sphere etc.

SAS Analysis –
A spacewalk of sorts
Fourier, Q, reciprocal space

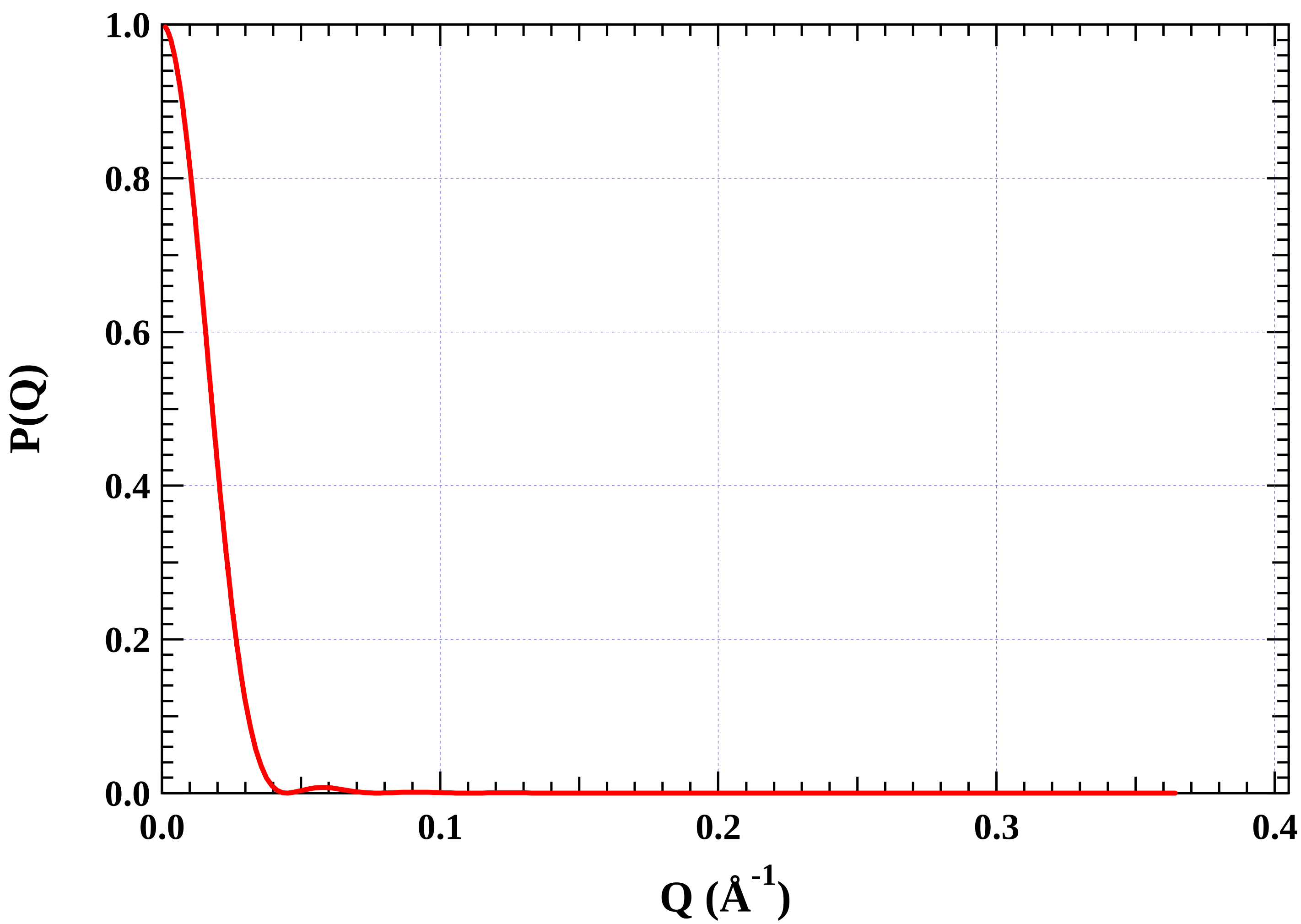
Carl Meade and Mark Lee rehearse spacewalk contingency plans in 1994

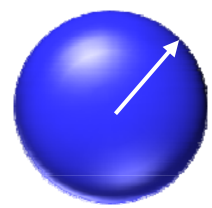
Bruce McCandless II took the first untethered space walk in February 1984. Here we see him from Challenger, floating above Earth.

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

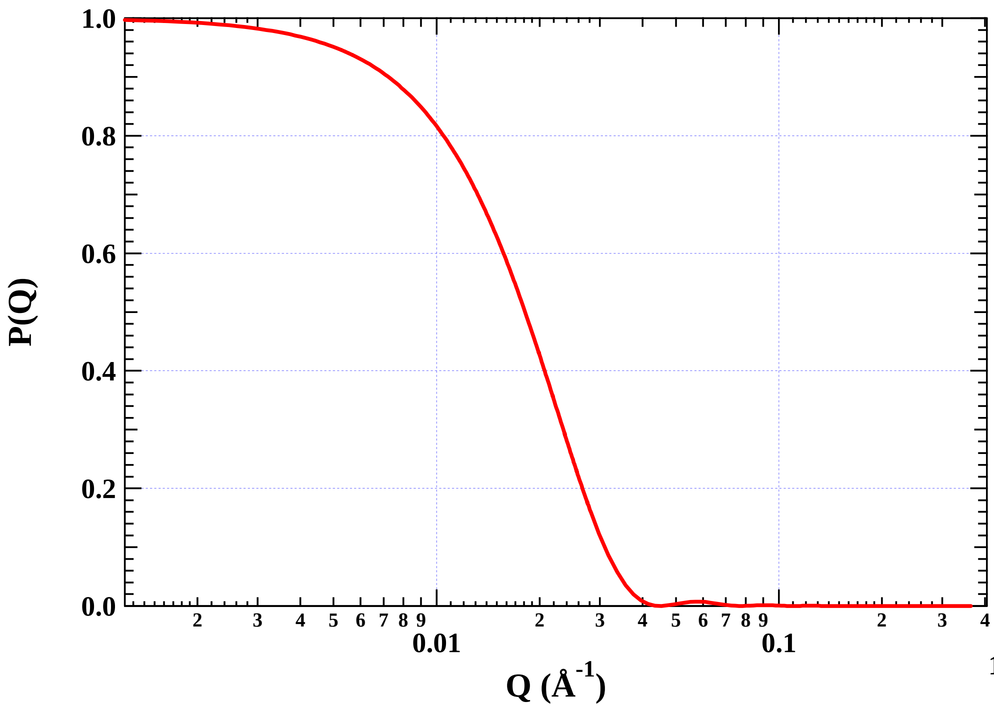
precisely: monodisperse sphere of uniform density with sharp and smooth surface

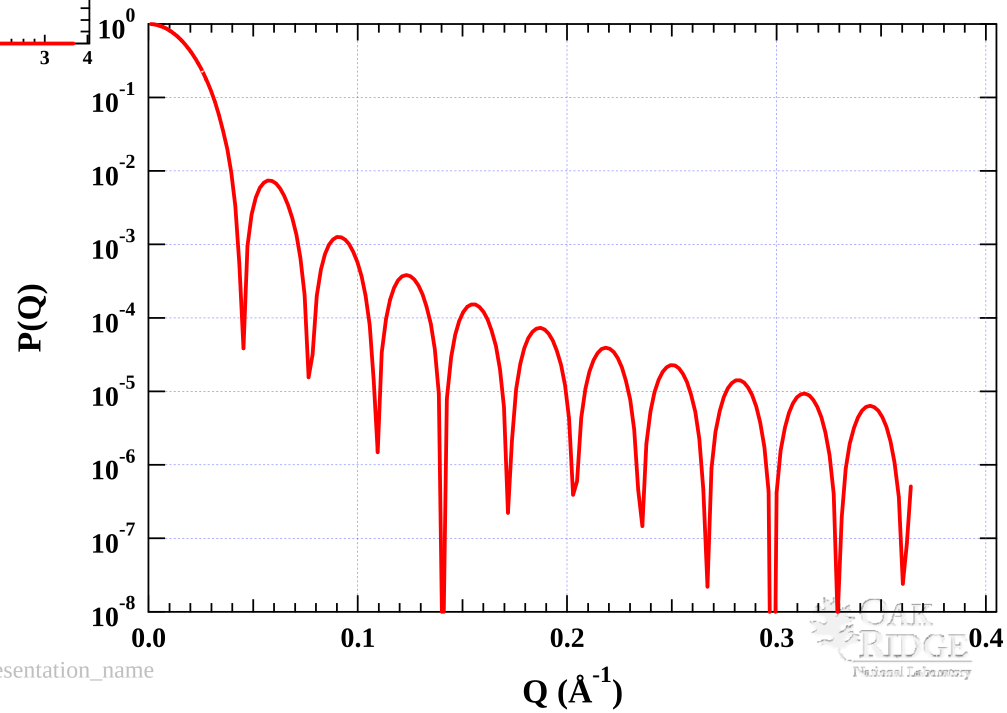


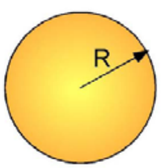


100 Å
radius

Sphere





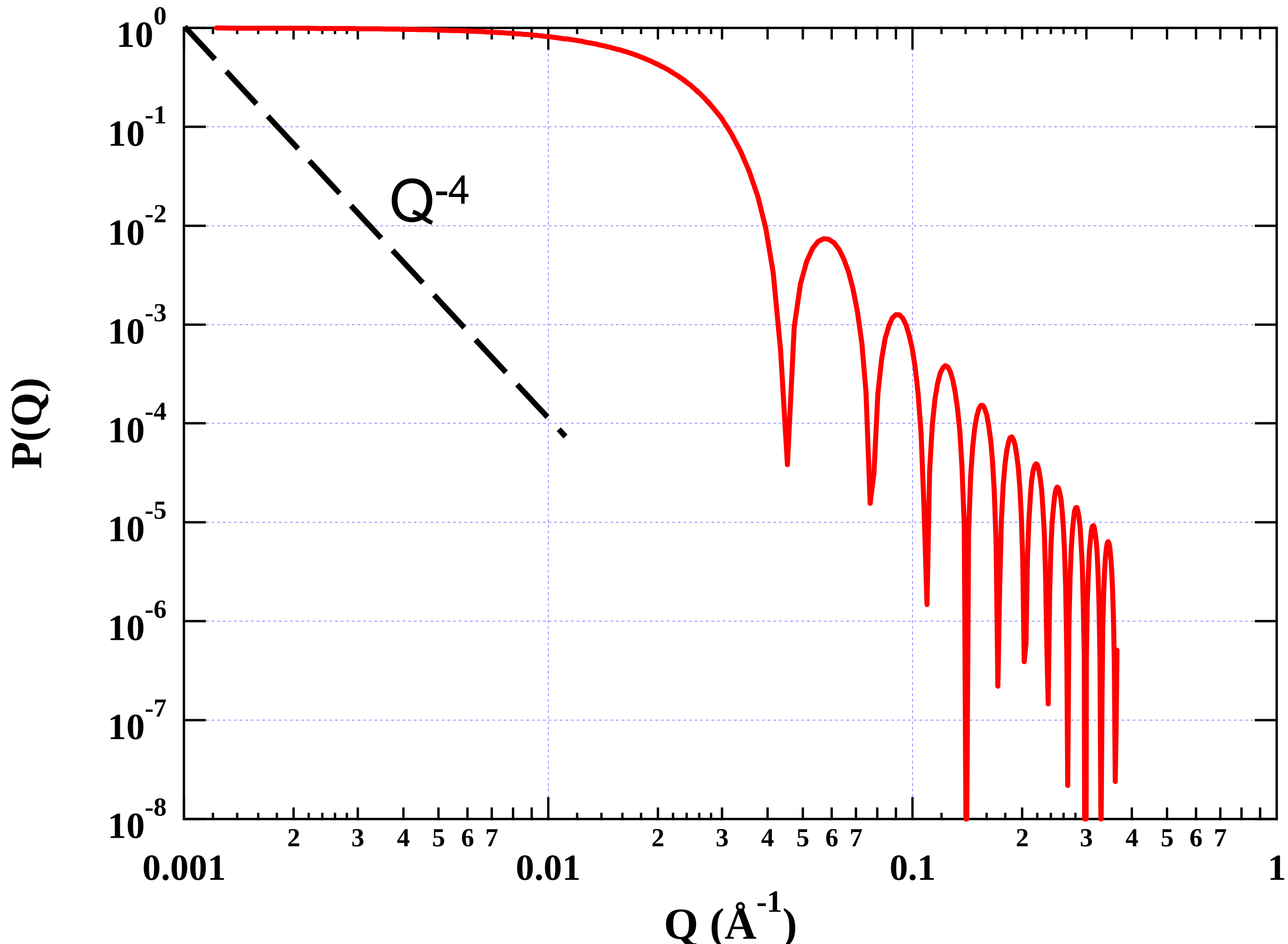


Sphere

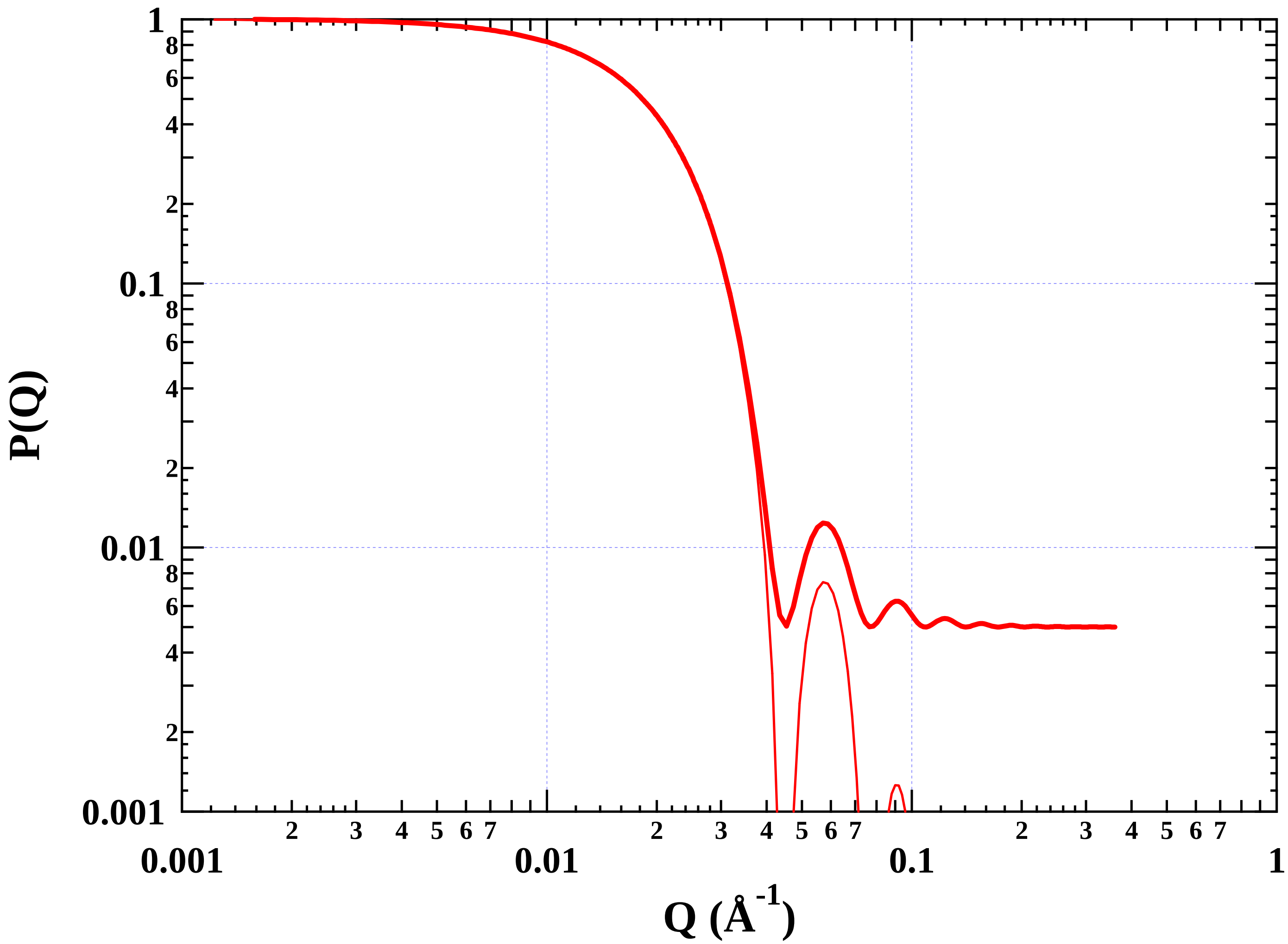
$$F(q) = \frac{3[\sin(qr) - qr\cos(qr)]}{(qr)^3}$$

Sphere

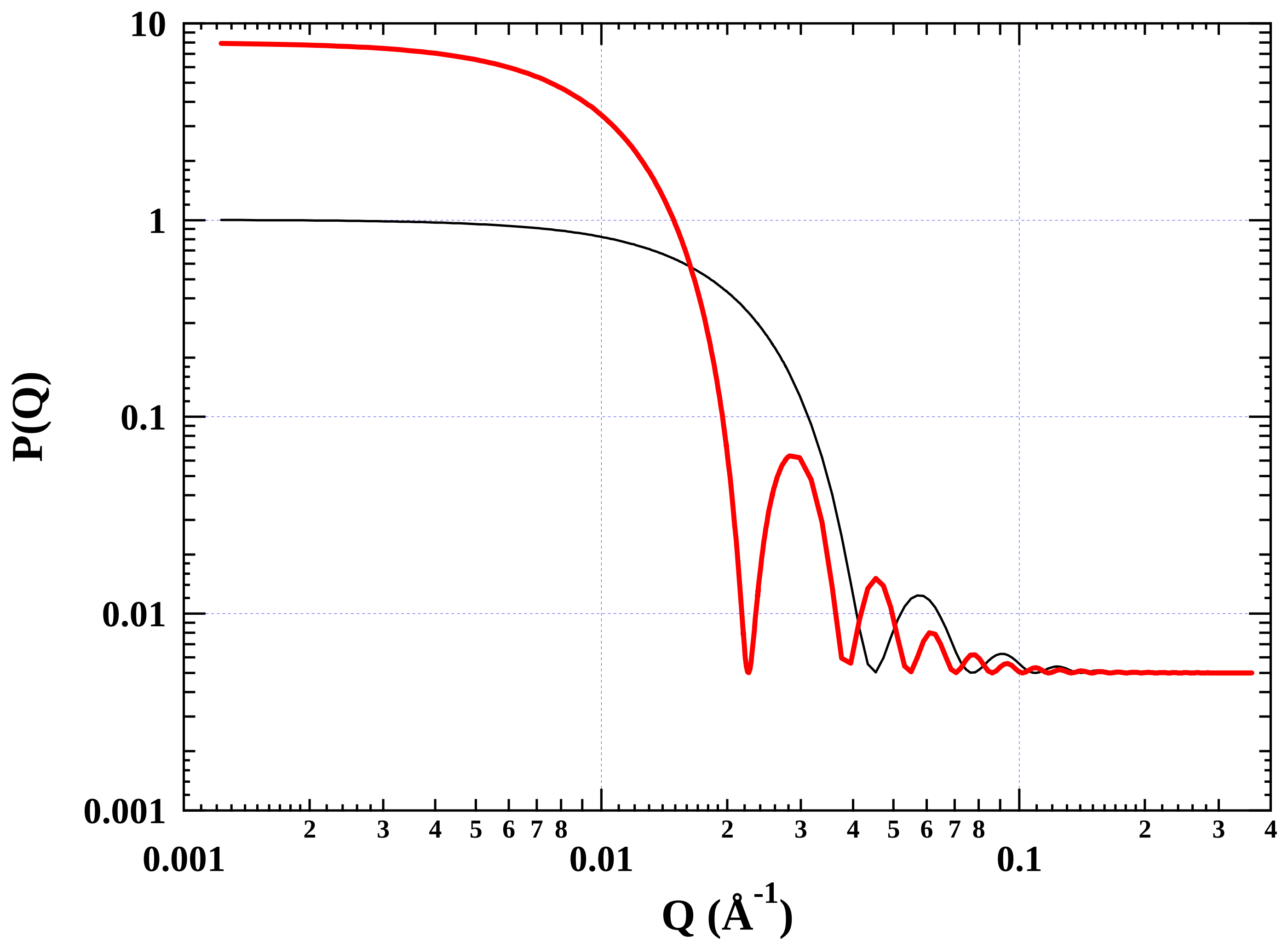
precisely: monodisperse sphere of uniform density with sharp and smooth surface

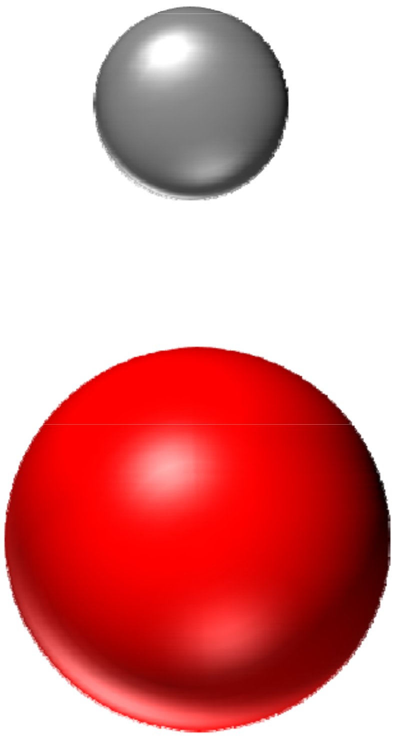


Sphere + constant background

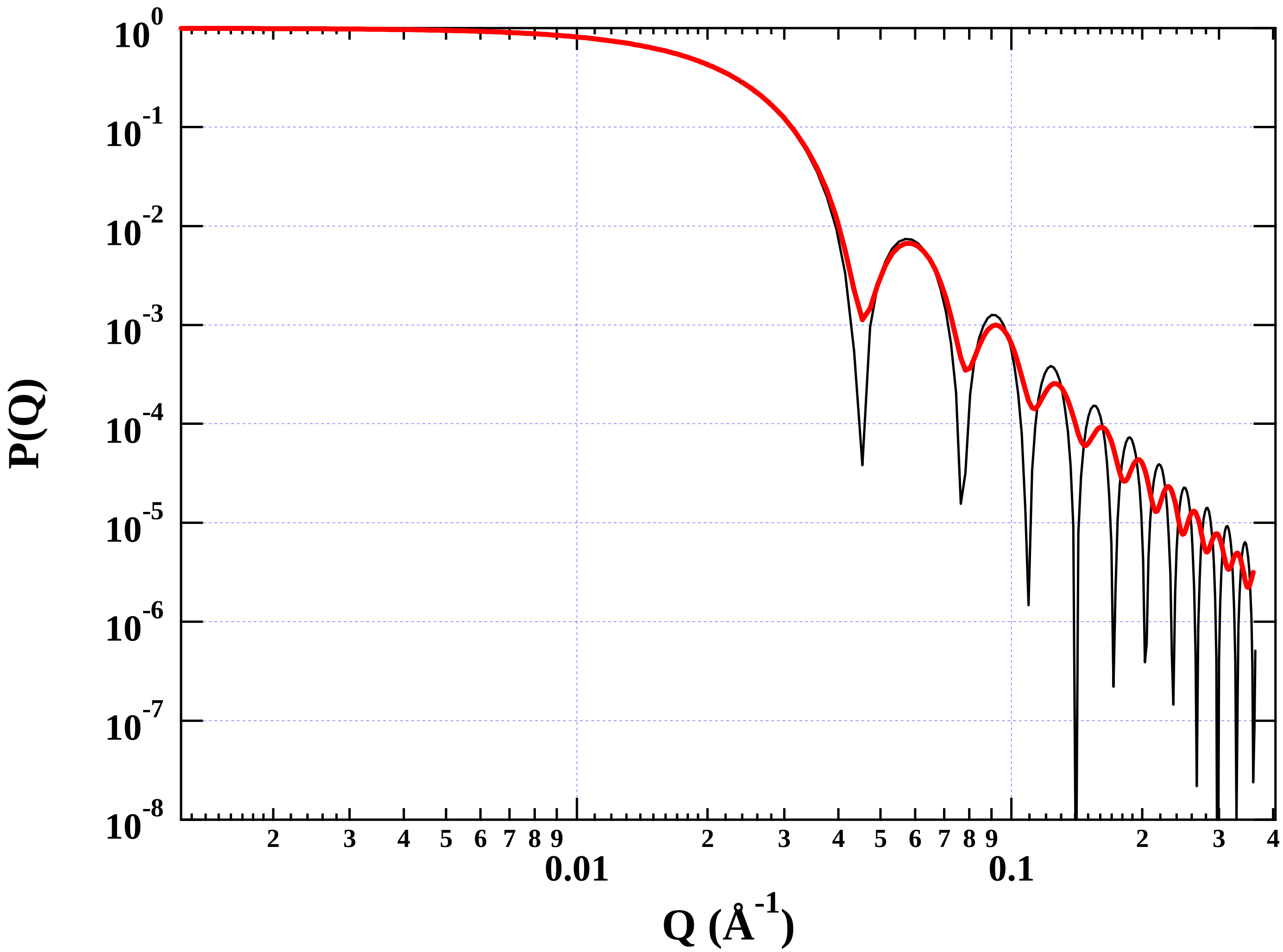


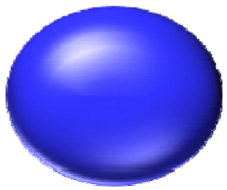
Spheres of different sizes





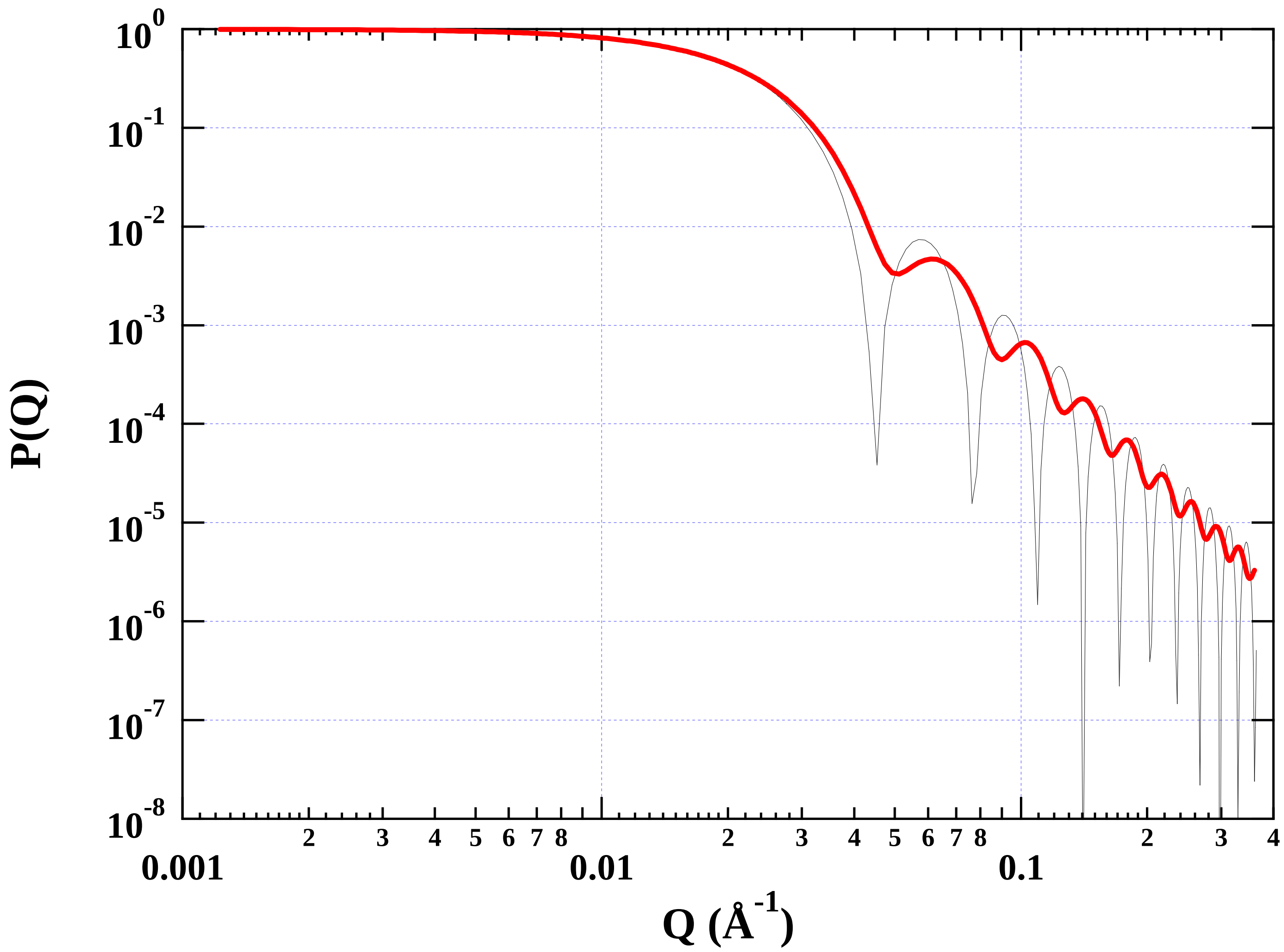
Ellipsoid
aspect ratio 1.2

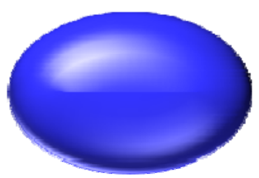




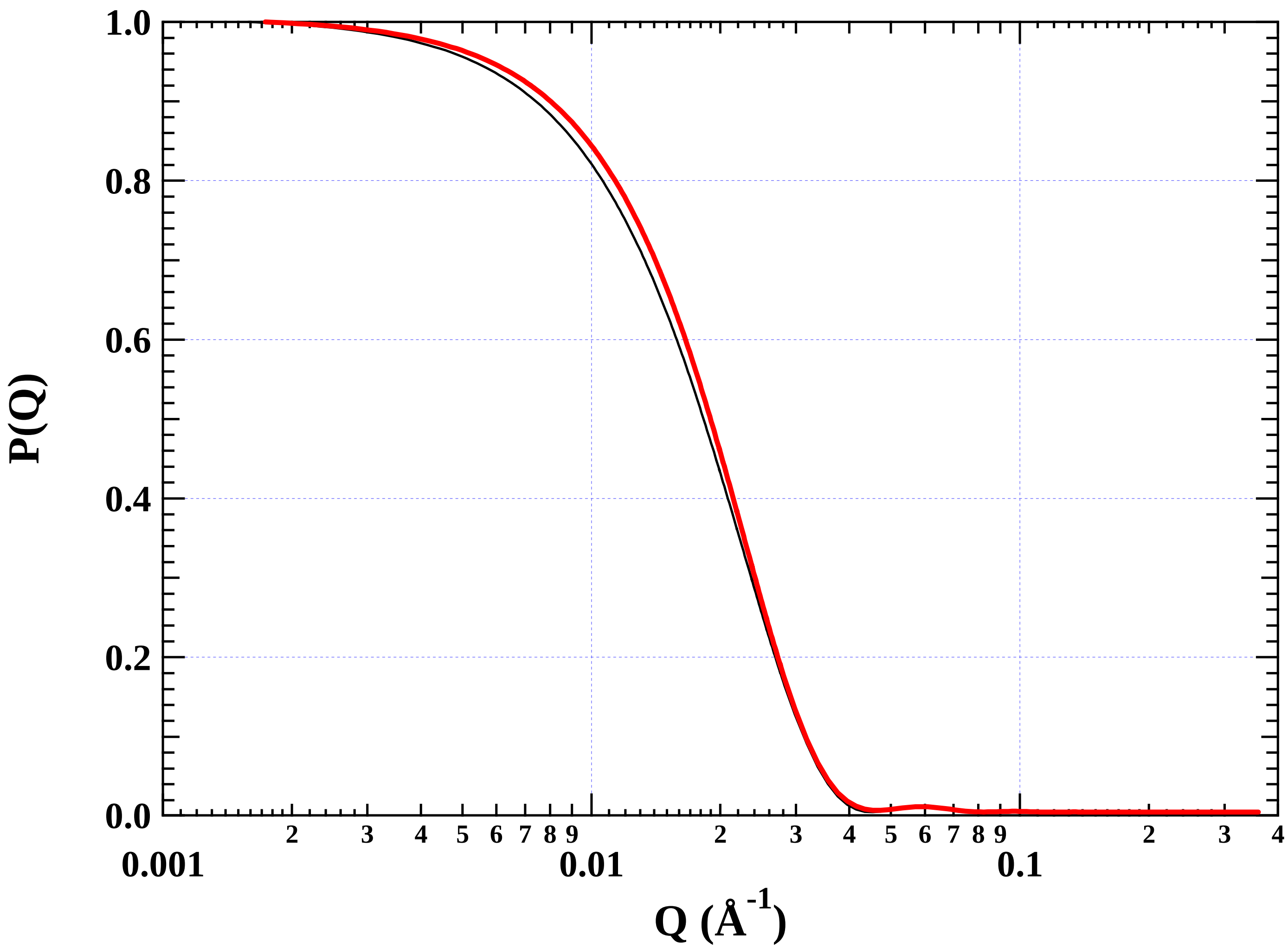
R_g same as sphere for following objects

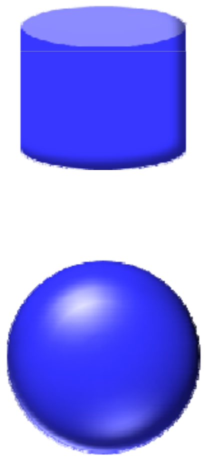
Ellipsoid
aspect ratio 1.5



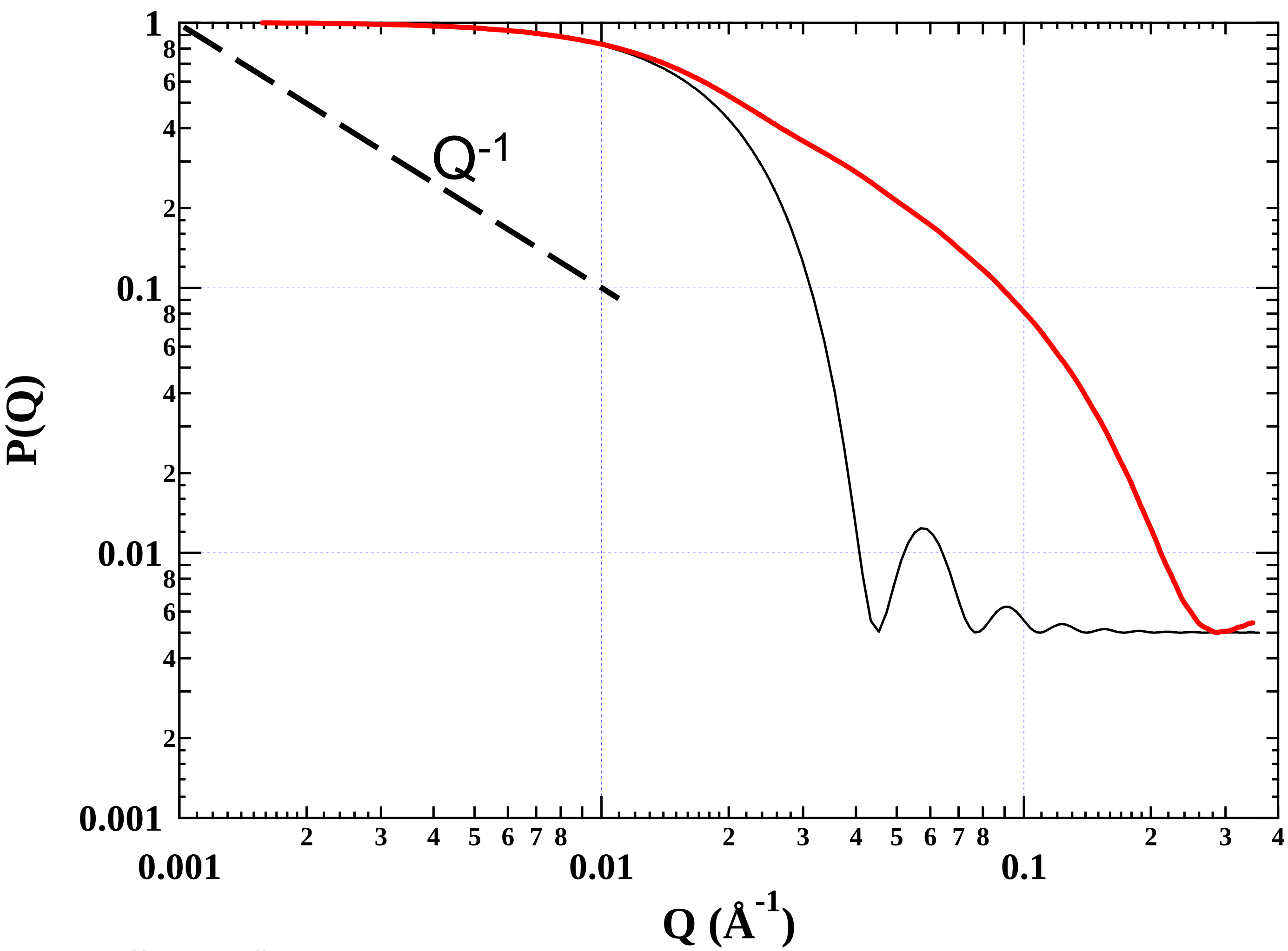


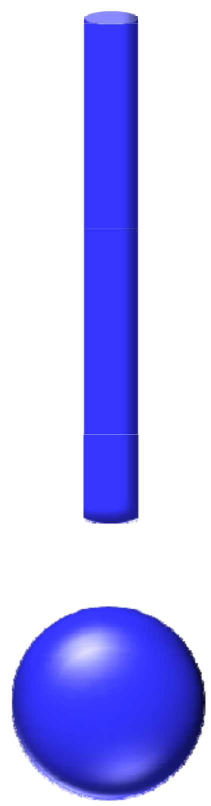
Circular Cylinder
with same Rg as the sphere



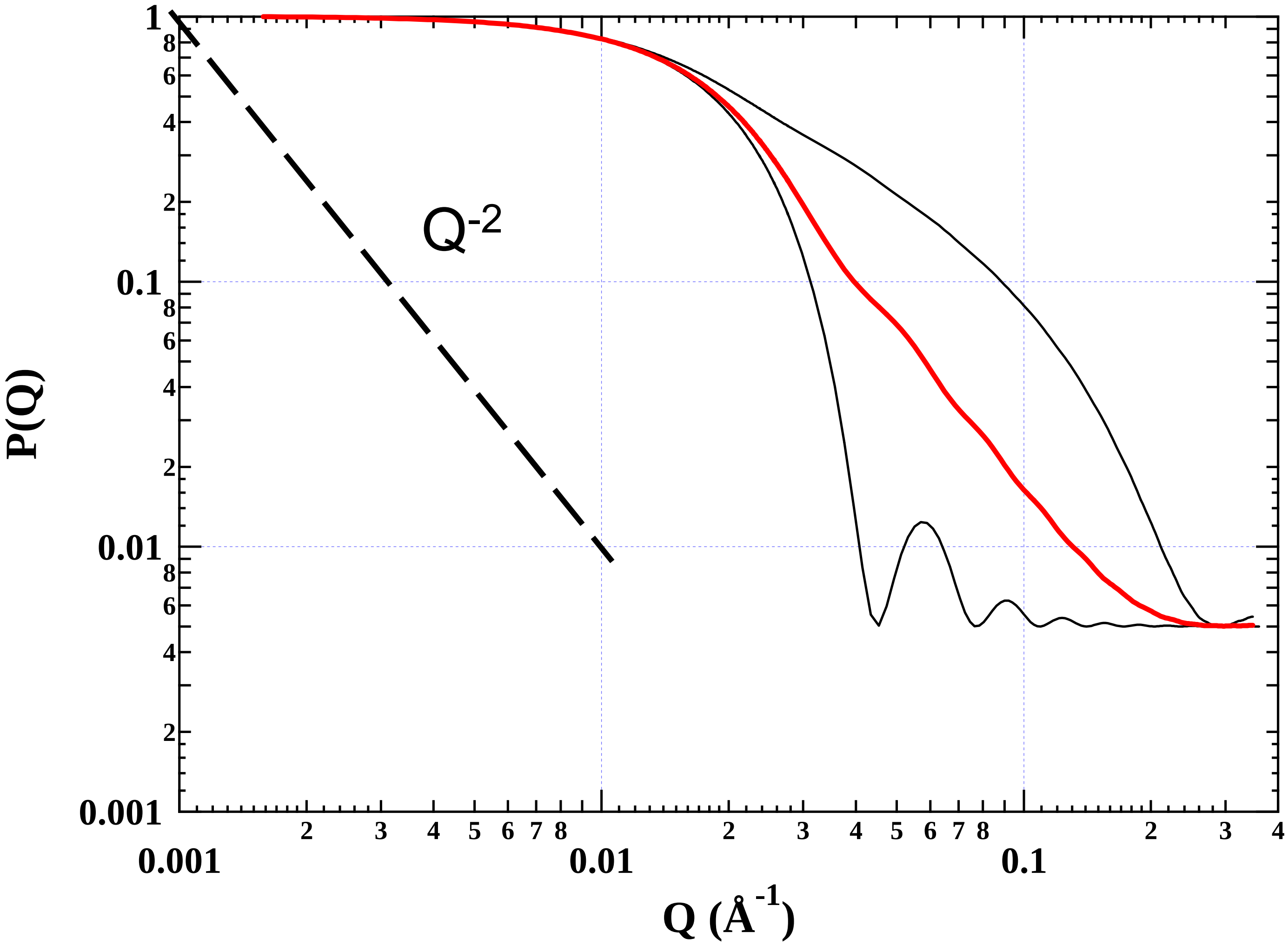


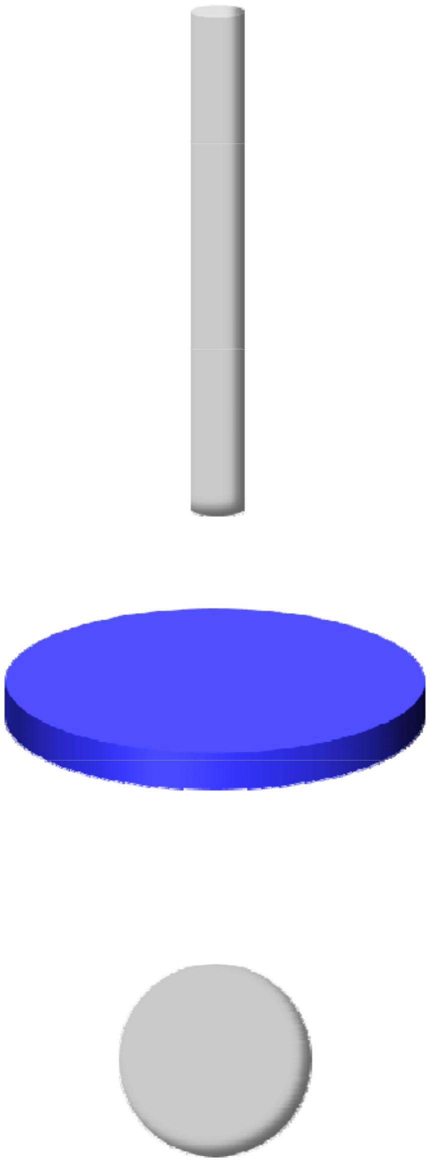
“Long & thin” cylinder



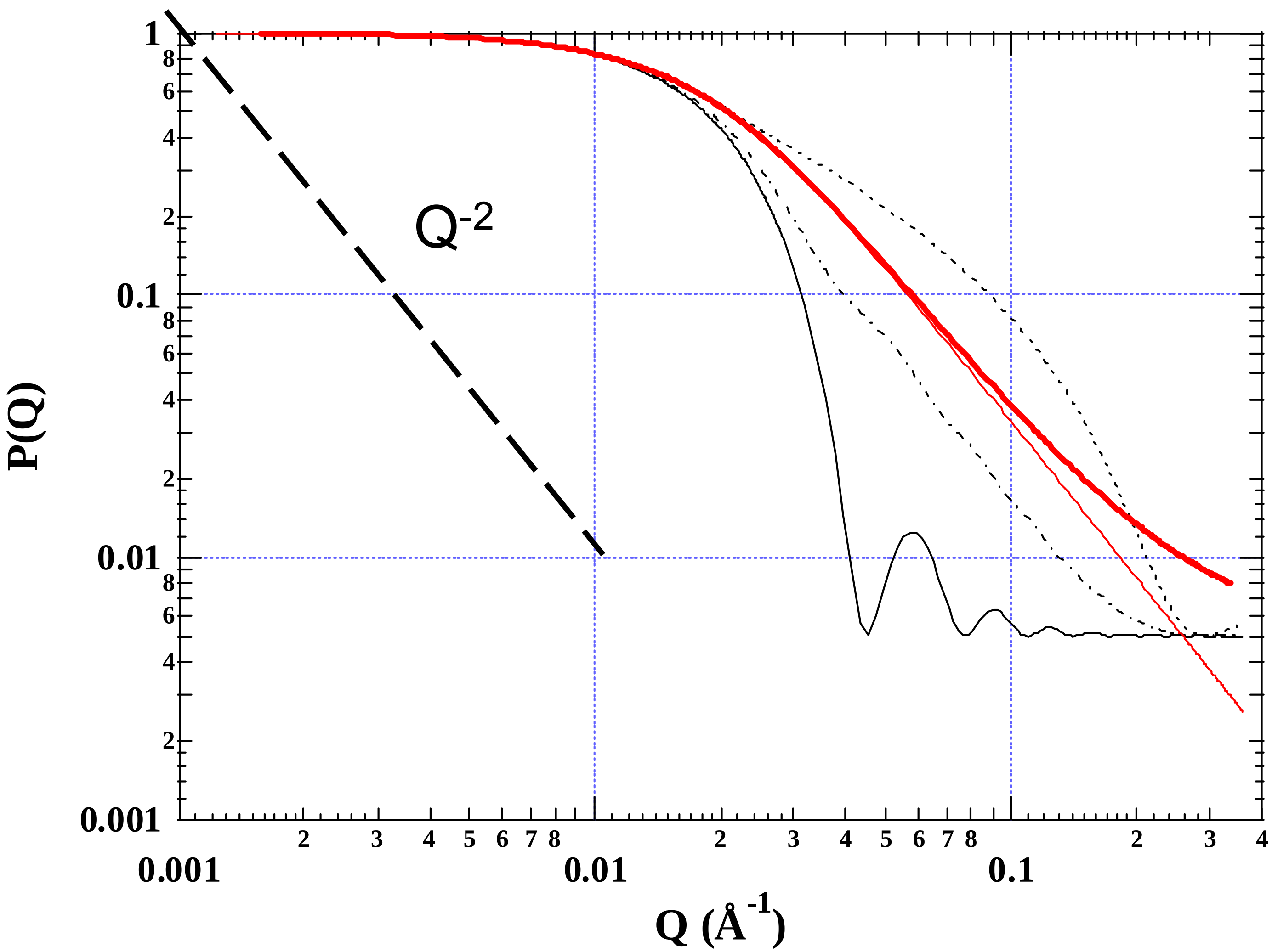


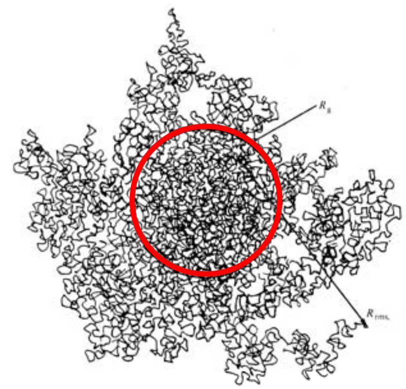
Disk





Polymer coil





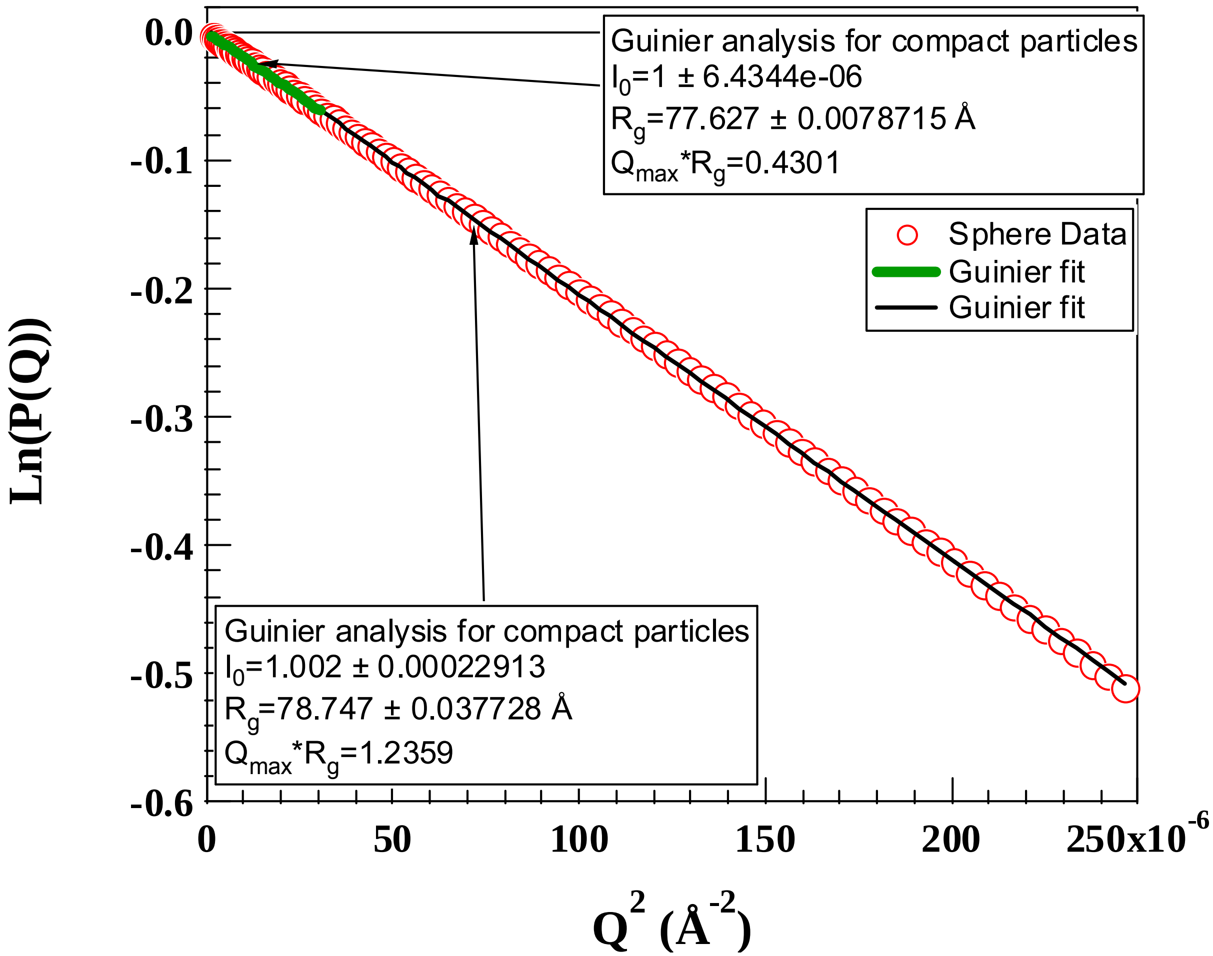
Guinier Analysis
size of any kind of object

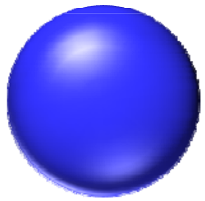
- At small Q anything that could reasonably be considered an object follows Guinier approximation.

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

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

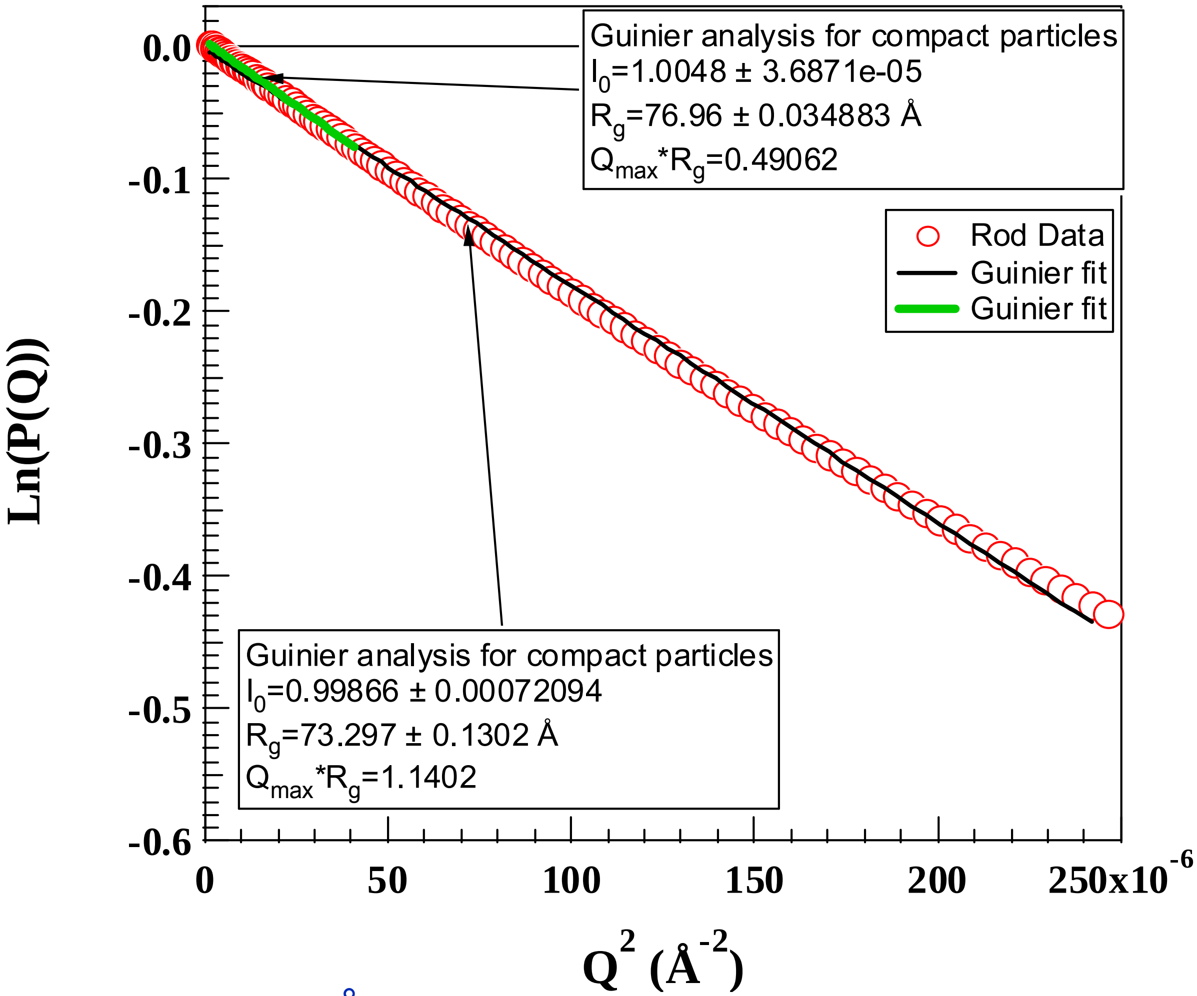
Guinier Analysis
size of any kind of object

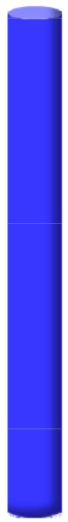




Precise R_g is 77.46 Å

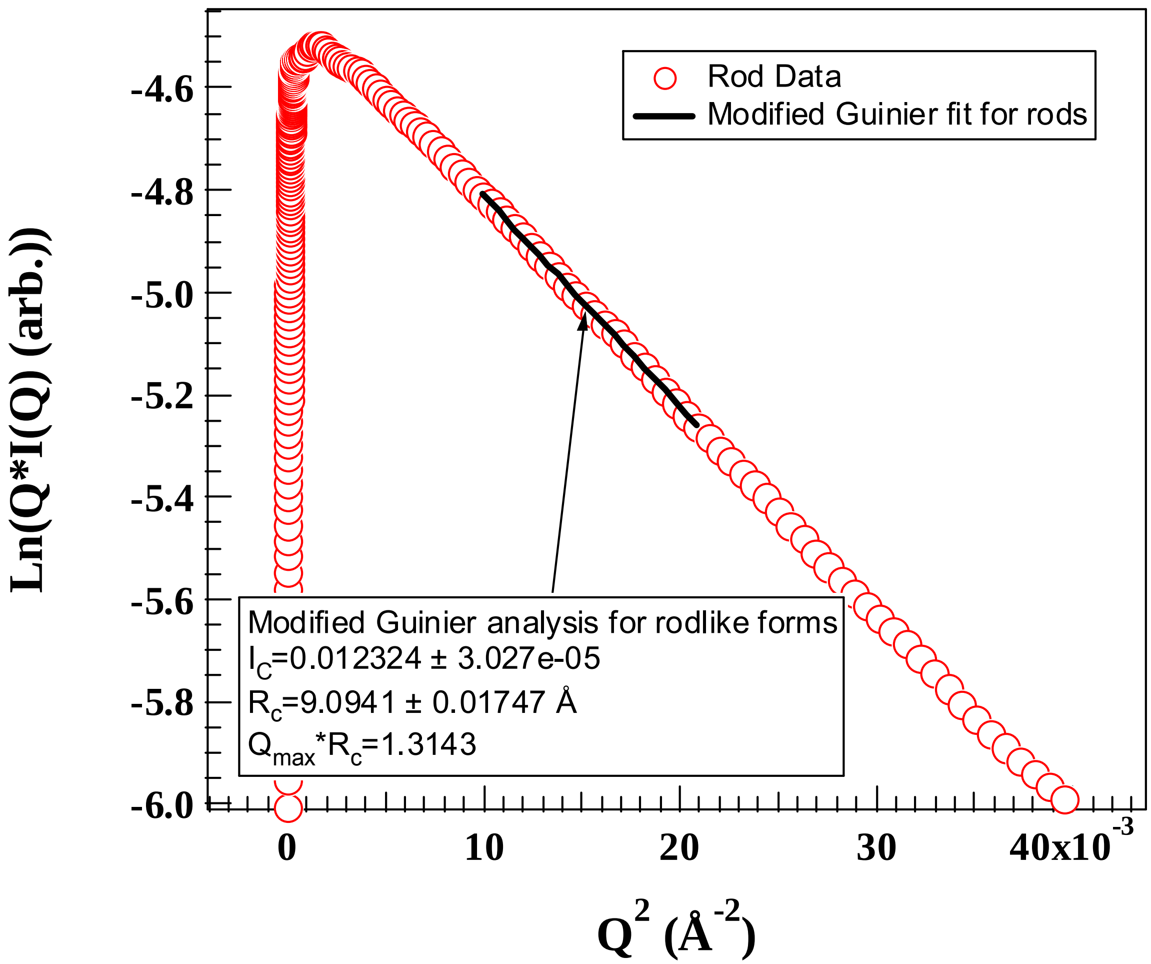
Guinier Analysis
size of any kind of object

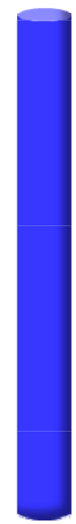




Precise R_g is 77.46 Å

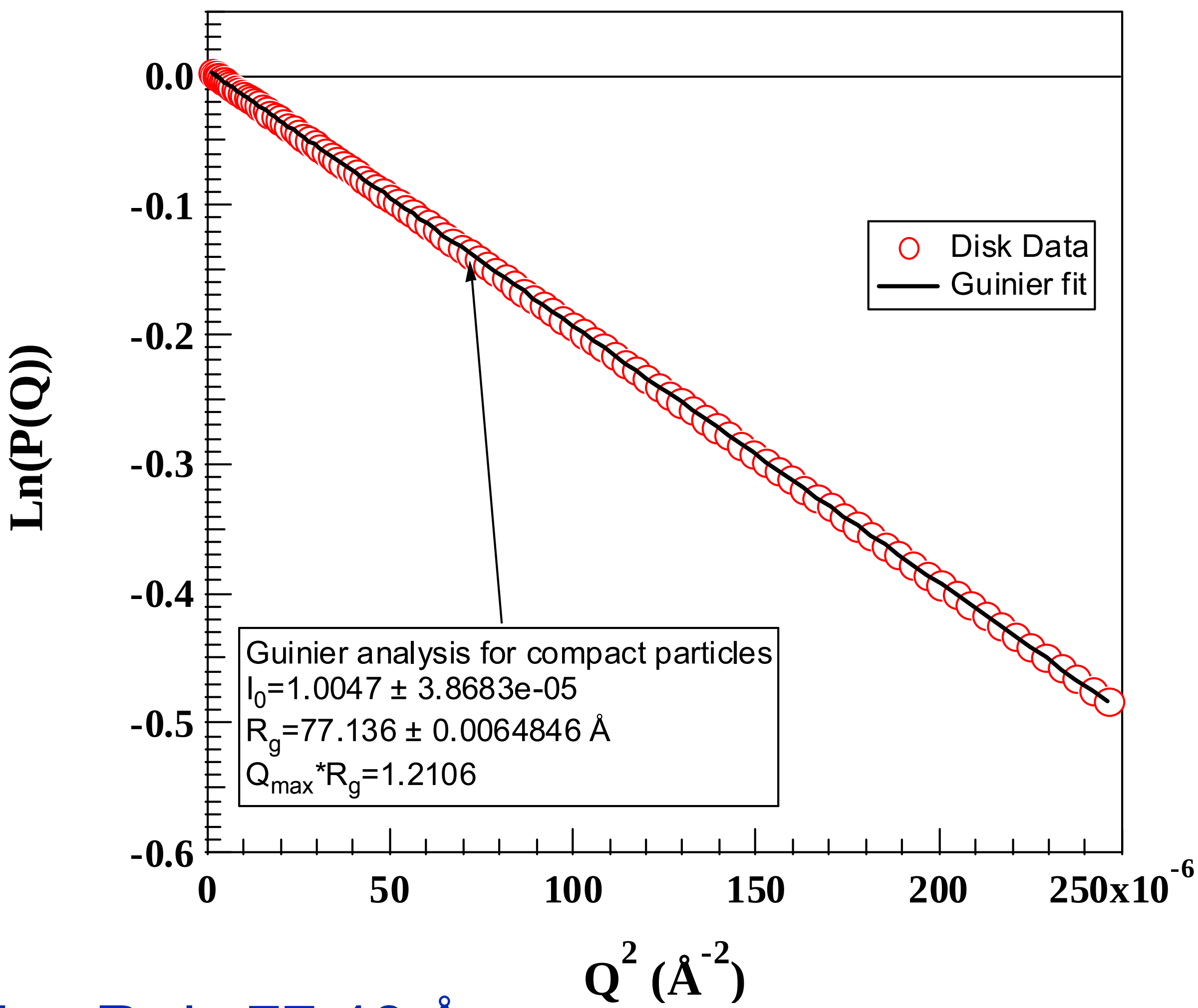
Modified Guinier Analysis
for object extended in 1 dimension





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

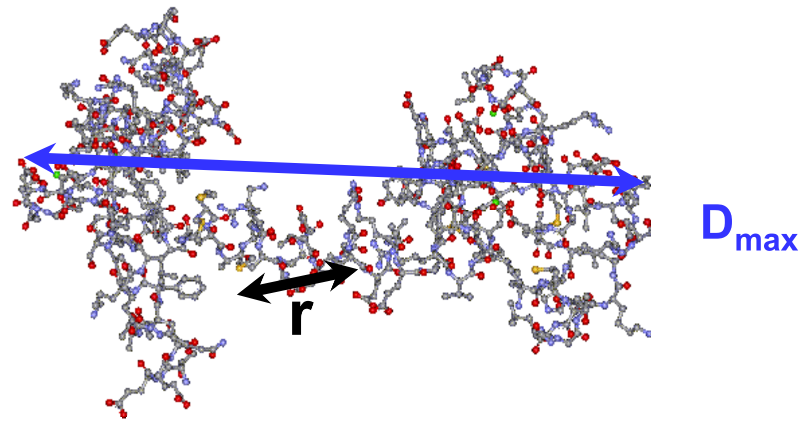
Guinier Analysis
size of any kind of object

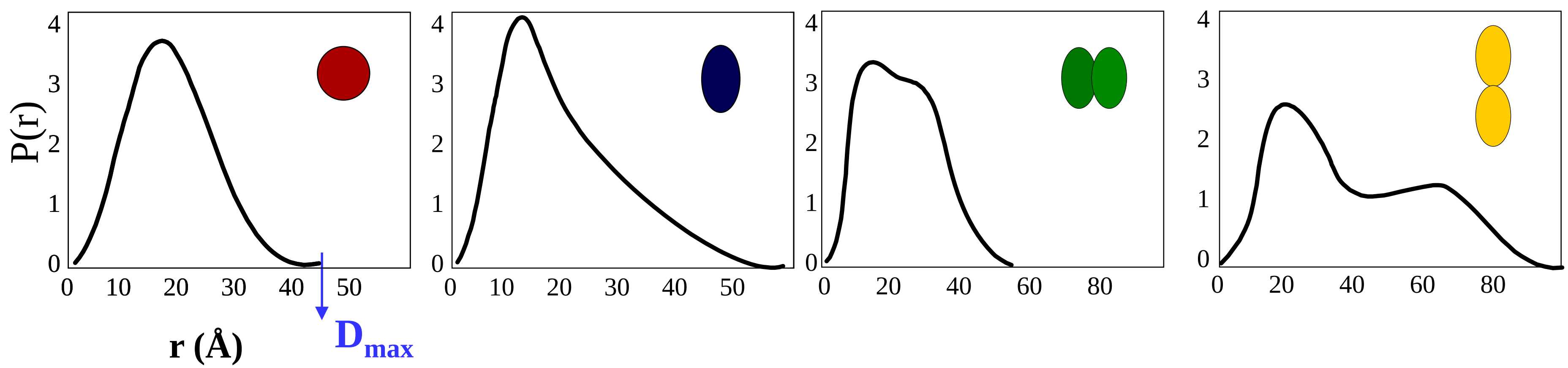


Precise R_g is 77.46 Å

Pair correlation function and shape

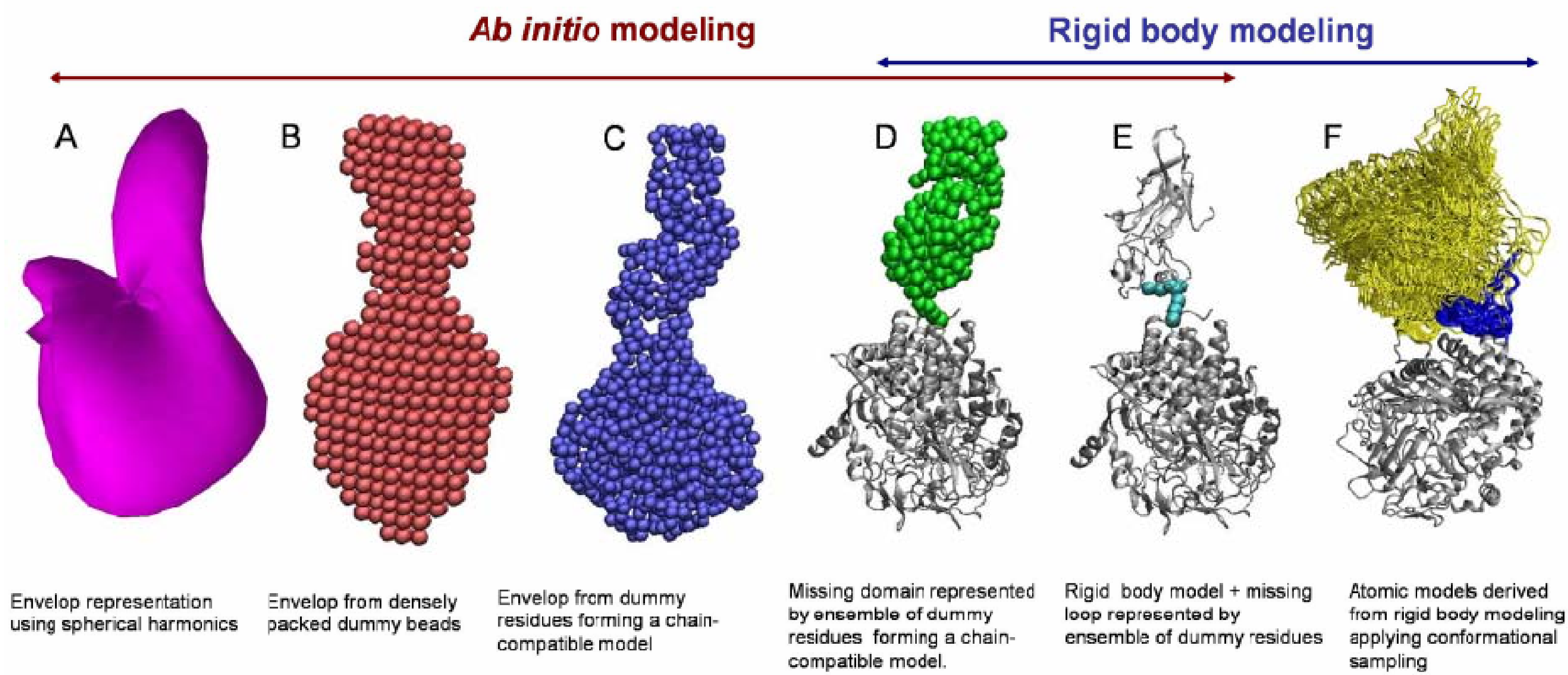
P(r) : inverse Fourier transform of scattering function : Probability of finding a vector of length r between scattering centers within the scattering particle.





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

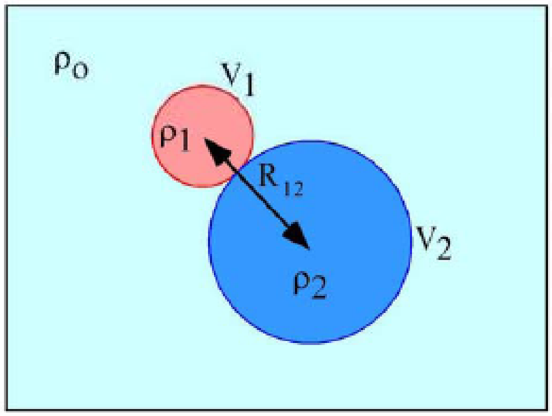
SAS Form Factor Modeling
of great use in biology



SAS Form Factor Modeling
of great use in biology

- Spherical Harmonics
  - Svergun, Stuhrmann, Grossman, etc.
- Aggregates of Spheres
  - Svergun, Doniach, Chacón, Heller, etc.
- Sets of High-resolution Structures
  - Svergun, Heller, Grishaev, Gabel, etc.
- Simple Shapes and Custom Approaches for Specific Problems
  - Henderson, Zhao, Gregurick, Heller, etc.

Two-component Systems / Compound Objects

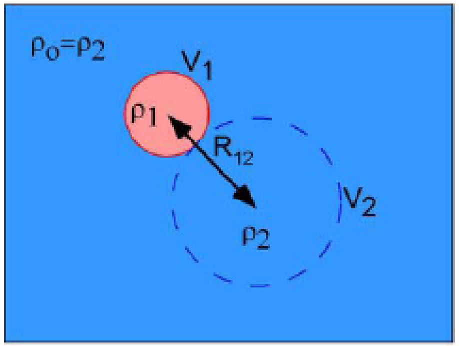


Model as an assembly of uniform particle subunits.

$$I(q) \propto \left\langle \left| (\Delta\rho)_1 \int_{V_1} e^{i\vec{q}\cdot\vec{r}} d\,\vec{r}_1 + (\Delta\rho)_2 \int_{V_2} e^{i\vec{q}\cdot\vec{r}} d\,\vec{r}_2 \right|^2 \right\rangle =$$

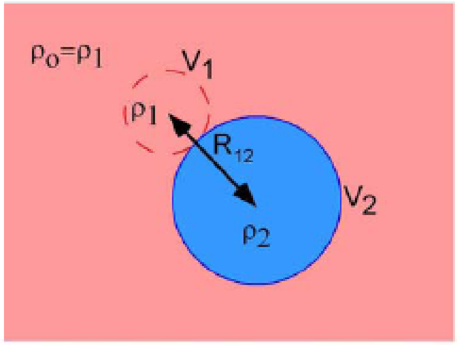
$$(\Delta\rho)_1^2 \left\langle \left| F_1(q) \right|^2 \right\rangle + (\Delta\rho)_2^2 \left\langle \left| F_2(q) \right|^2 \right\rangle + (\Delta\rho)_1 (\Delta\rho)_2 \left| F_1 \right| \left| F_2 \right| \frac{\sin(qr_{12})}{qr_{12}}$$

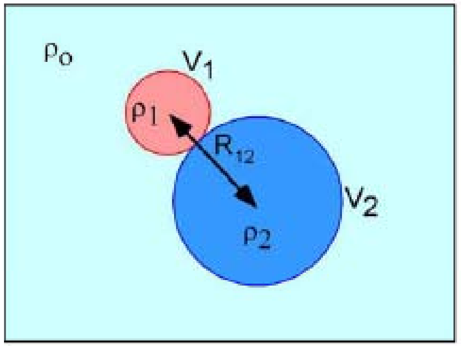
Two-Component Systems



$$I_1(q) = (\Delta\rho)_1^2 F_1^2$$

$$I_2(q) = (\Delta\rho)_2^2 F_2^2$$





$$I_{12}(q) = 2(\Delta\rho)_1(\Delta\rho)_2 F_1 F_2 \frac{\sin(qr_{12})}{qr_{12}}$$

Separate scattering from subunits using **contrast variation**.

Two-Component Systems
R_g as function of contrast

Stuhrmann Analysis

$$R_g^2 = R_o^2 + \frac{\alpha}{\Delta\rho} + \frac{\beta}{(\Delta\rho)^2}$$

β ≠ 0 ⇒ centers of mass of the two components are not concentric

R_g of an equivalent homogeneous complex

Ibel, K. and Stuhrmann, H. B. (1975). *J. Mol. Biol.* **93**, 255–265

Parallel Axis Theorem

$$R_g^2 = \frac{\Delta\rho_1 V_1}{\Delta\rho V} R_1^2 + \frac{\Delta\rho_2 V_2}{\Delta\rho V} R_2^2 + \frac{\Delta\rho_1 V_1 \, \Delta\rho_2 V_2}{(\Delta\rho V)^2} D^2$$

Component 1 Component 2 Cross-term

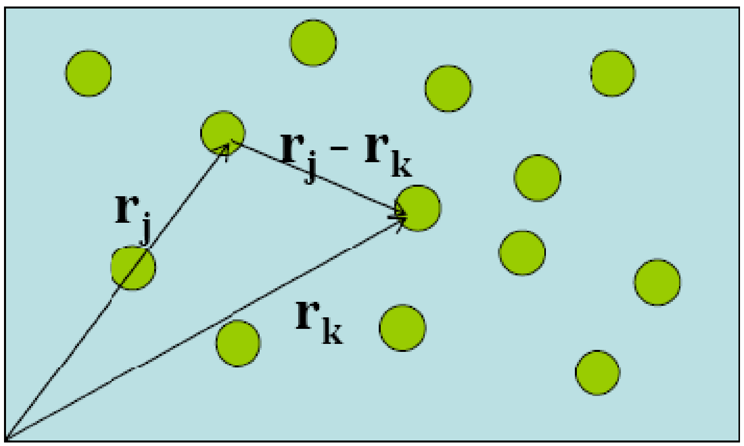
Distance between centers of mass

Moore, P. B. (1982). *Methods Exp. Phys.* **20**, 337–390

Interparticle Structure Factor S(Q)

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

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

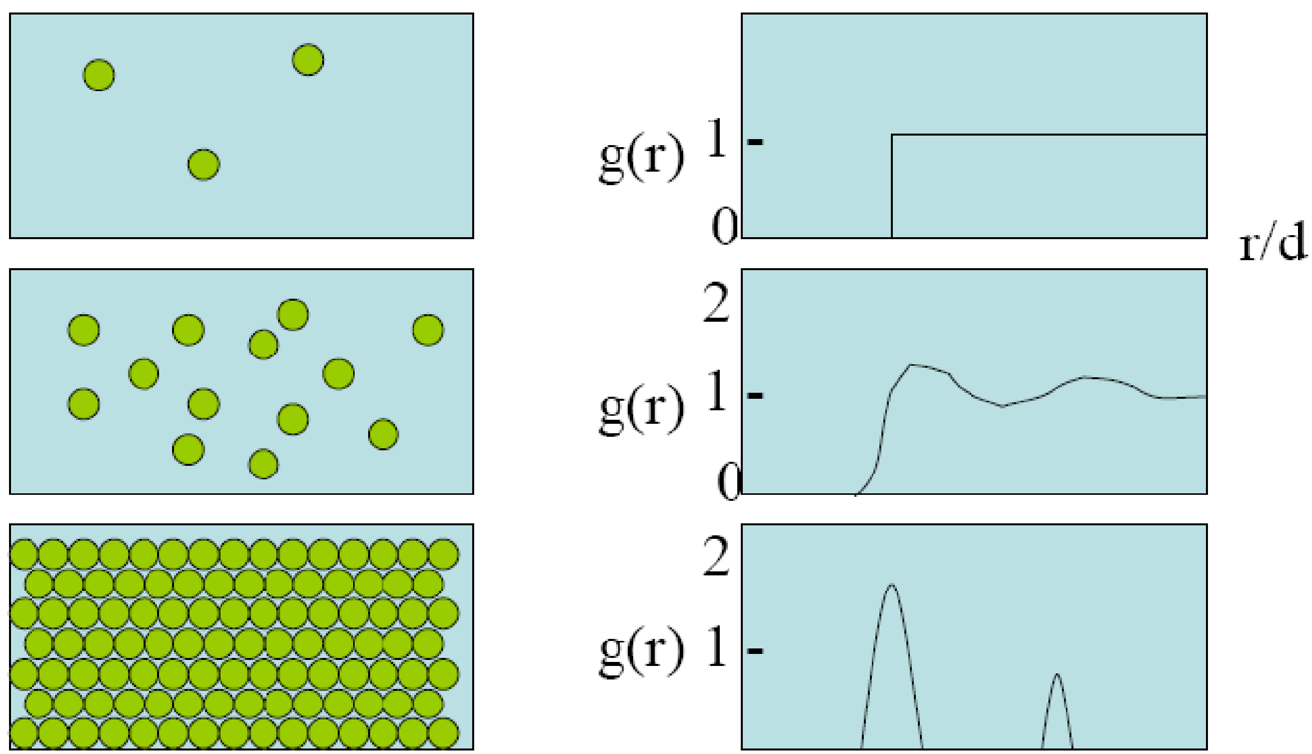


I(q) is modulated by interference effects between radiation scattered by different scattering bodies.

S(Q) and Pair Correlation Function

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

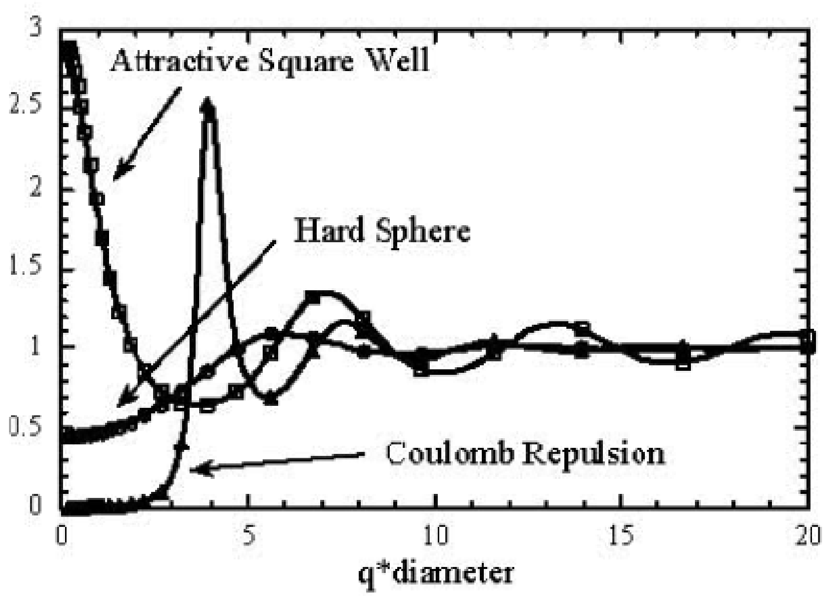
Pair correlation function



S(Q) and Statistical Thermodynamics

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

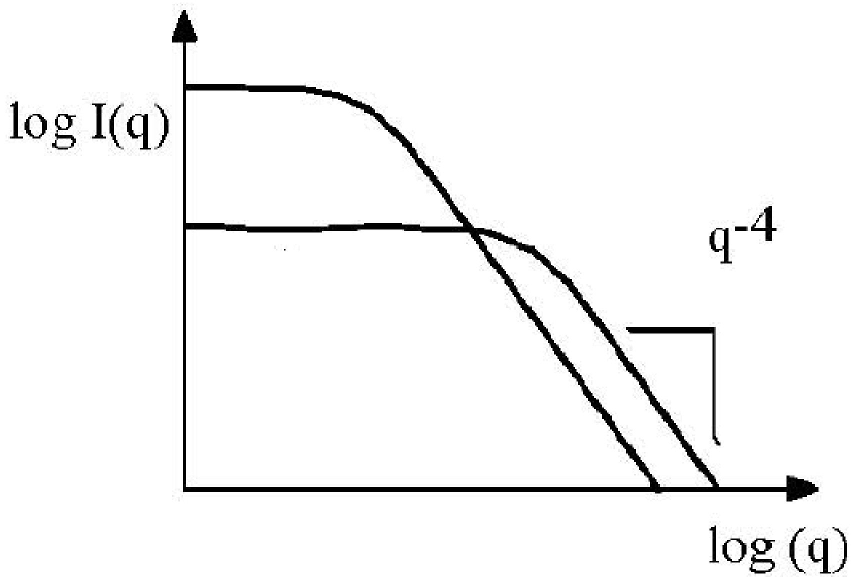
Osmotic Compressibility



Attractive $\Rightarrow$ More compressible

Repulsive $\Rightarrow$ Less compressible

Surface Scattering - *Porod*



At large q:

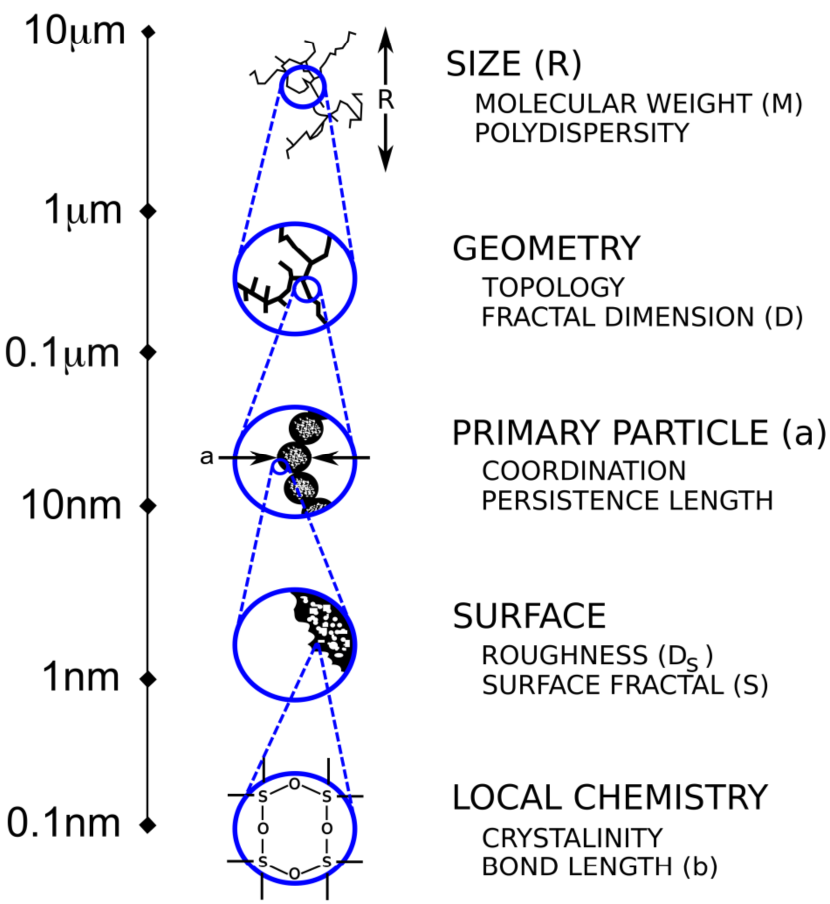
$$I(q) \propto q^{-4}$$

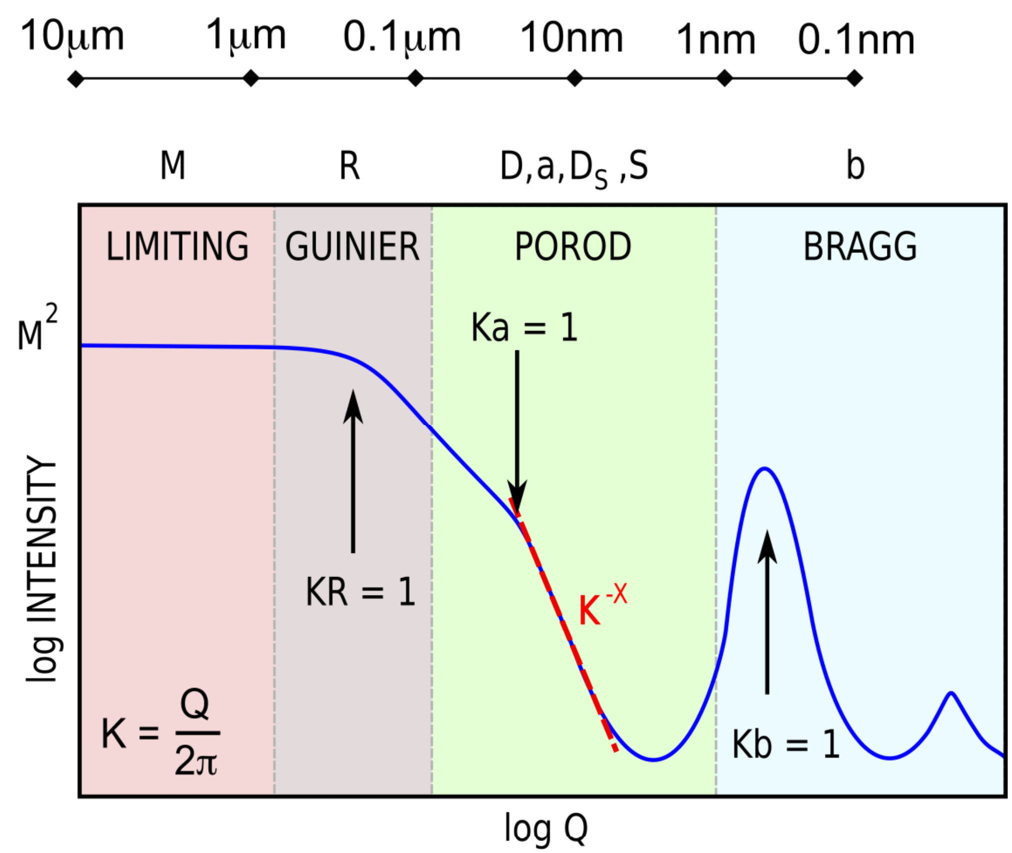
Specific Surface Area, S_V

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

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

Structural Hierarchy (particulate)





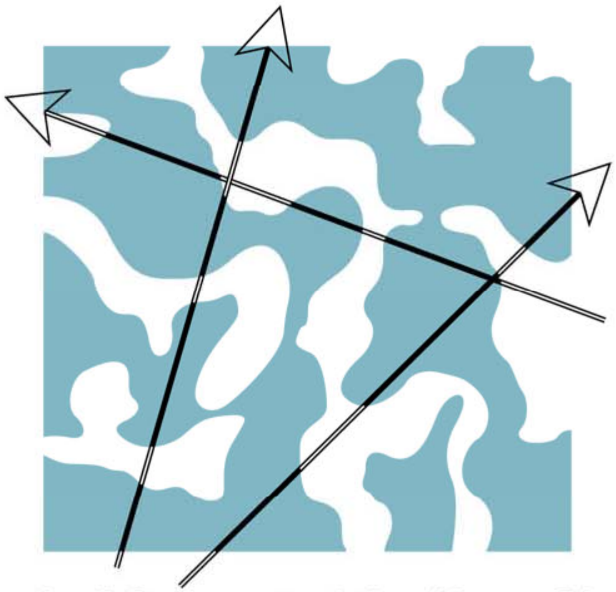
Adapted from DW Schaefer *MRS Symposium Proceeding* 1987

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 $\gamma(r) <\eta^2>_{AV} = <\eta_A\eta_B>_{AV}$. For random two phase system: $\gamma(r) = e^{-r/a}$

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

J. Appl.Cryst., 28, 679 (1957)

ORNL-DWG 92M-9485

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.