

Small Angle Scattering *of neutrons and x-rays*

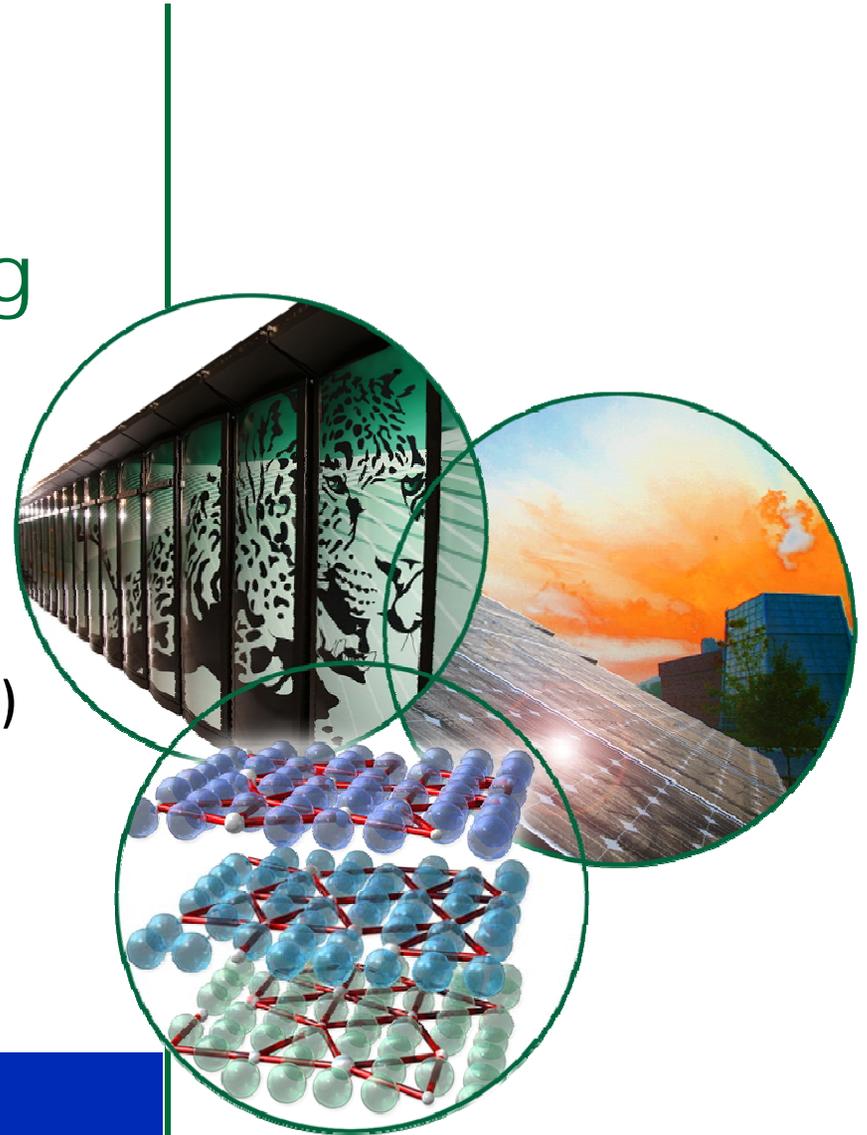
Volker Urban

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& Energy and the Environment Group

Biology and Soft Matter Division

Oak Ridge National Laboratory



National School on Neutron and X-ray Scattering

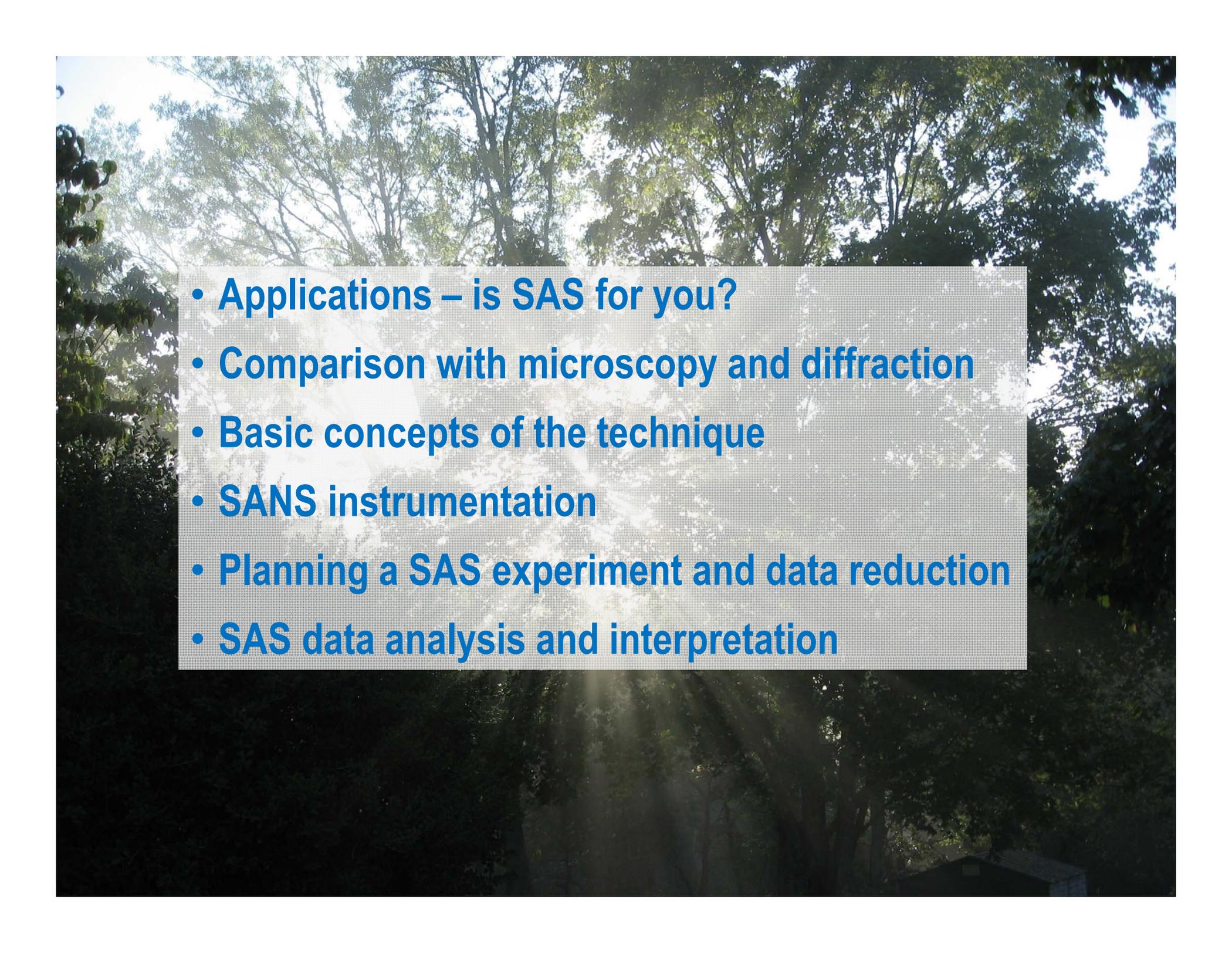


U.S. DEPARTMENT OF
ENERGY



OAK RIDGE NATIONAL LABORATORY

MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

- 
- **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-1 μ m**
- **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-1 μ m**



SAS applications A to Z

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

Oriental 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

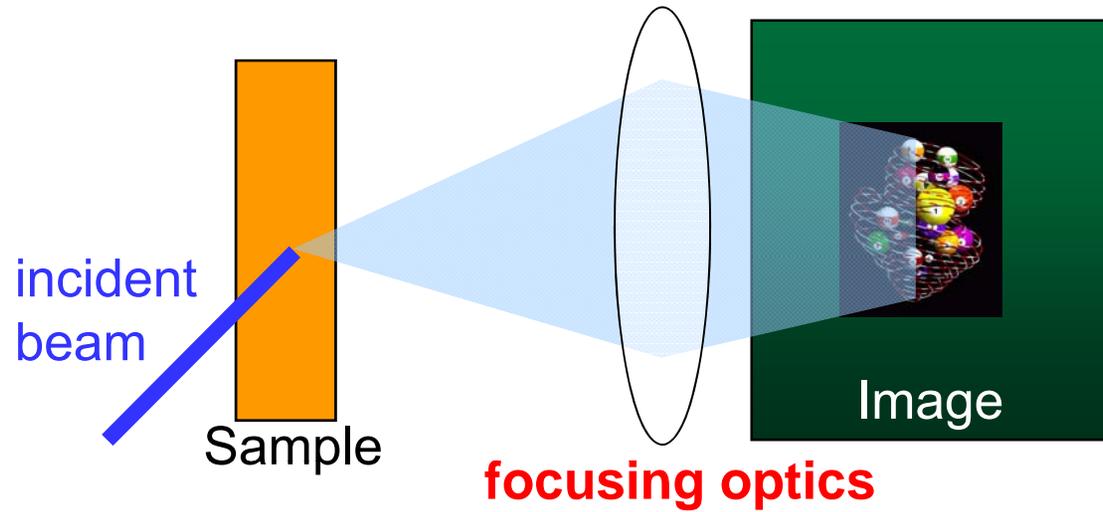
Yttrium-stabilized zirconia (YSZ)

Zeolites

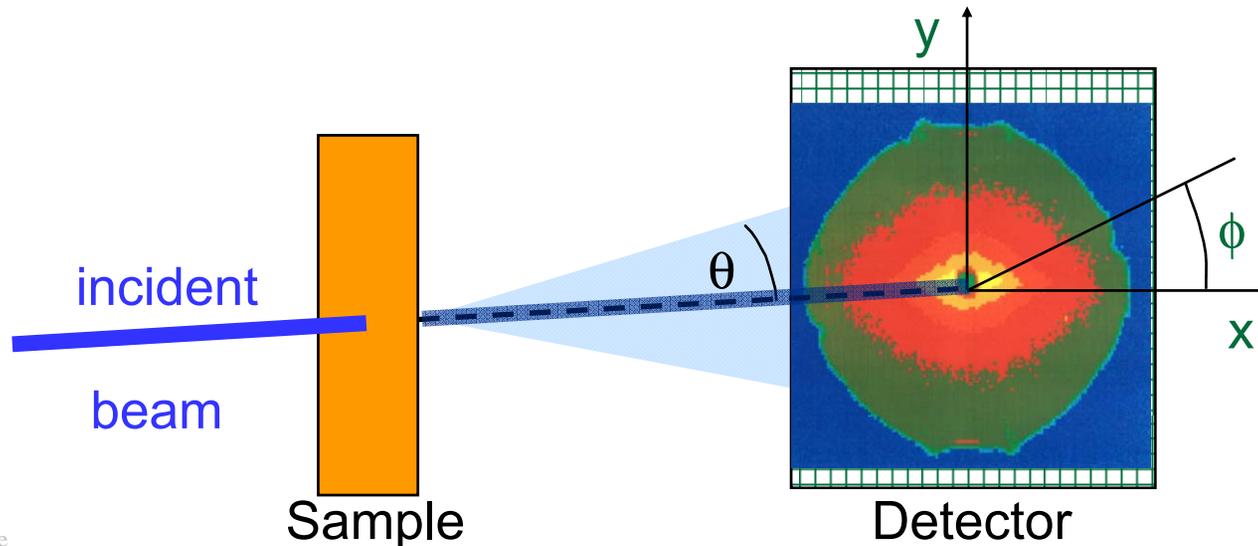


But what
about SEM,
TEM, AFM
...?

Microscopy : enlarged image



SAS : interference pattern

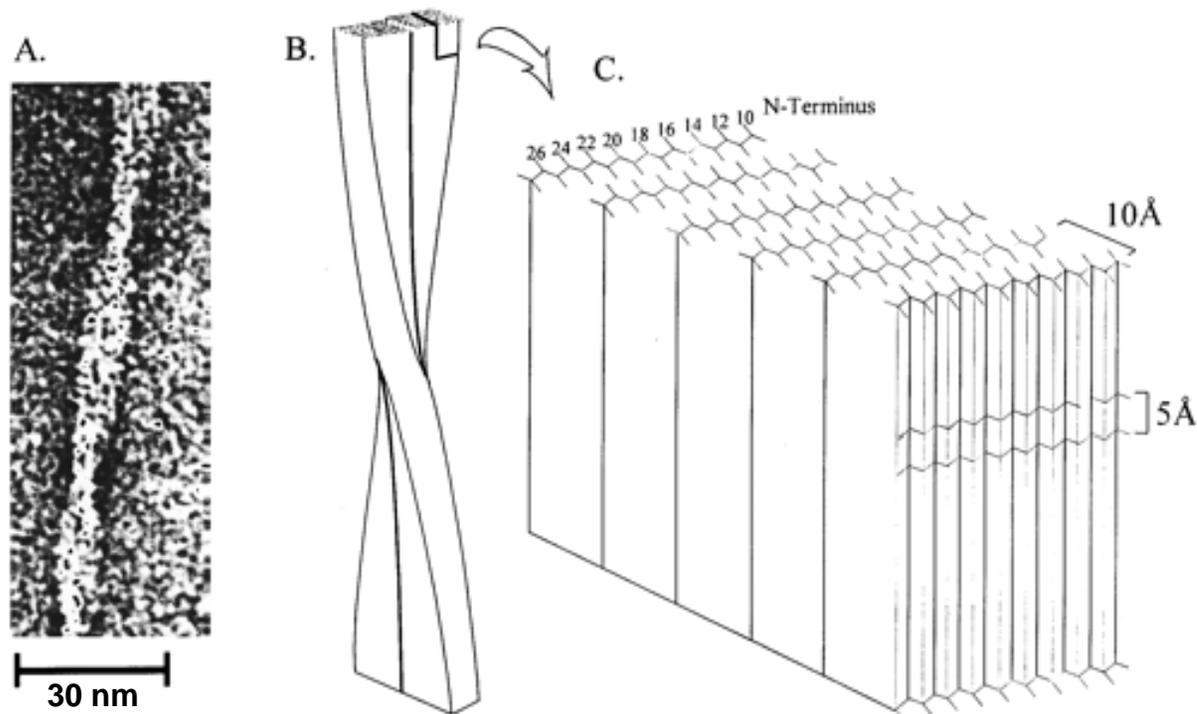


Neutron Scattering and Microscopy

- **Common features**
 - Size range 1nm-1 μ m
 - 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-1 μ m)
- 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**

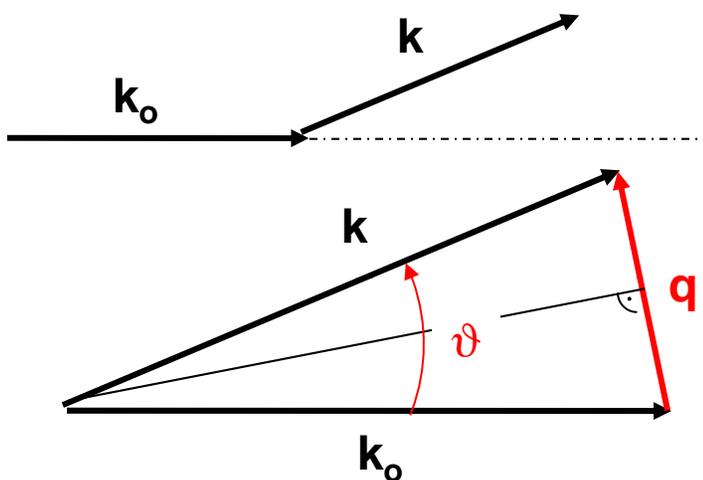
- ‘see’ light atoms: polymers, biology, soft condensed matter, hydrogen in metals
- **Isotope labeling**
- High penetration
 - bulky specimens, e.g. residual stress in motor block
 - complicated environments (P,T), e.g. ^4He cryostat
- Magnetic contrast
- No radiation damage

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:
 $\Delta\text{SLD} = \text{Contrast}$ \rightarrow contrast variation!

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

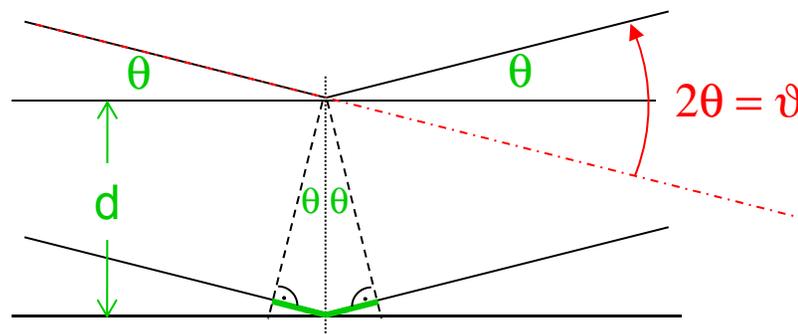
Wave vector \mathbf{k} : $|\mathbf{k}| = k = 2\pi/\lambda$



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

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

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



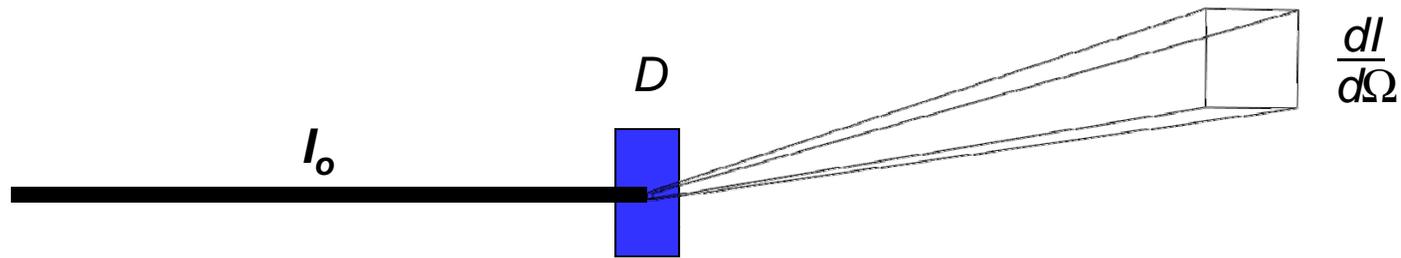
$$\Delta = 2d \sin(\theta)$$

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

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

q in nm^{-1} or \AA^{-1}

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



$$\frac{dI}{d\Omega} = TI_0 D \frac{d\Sigma}{d\Omega} \quad \longleftrightarrow \quad \frac{d\Sigma}{d\Omega} = \frac{1}{TI_0 D} \frac{dI}{d\Omega} \quad [\text{cm}^{-1}\text{sterad}^{-1}]$$

- $dI/d\Omega$ = Scattered intensity per solid angle
- I_0 = Primary beam intensity
- T = Transmission (x-ray absorption, incoherent neutron scattering)
- D = Thickness
- $d\Sigma/d\Omega$ = Scattering **cross section per unit volume** [$\text{cm}^{-1}\text{sterad}^{-1}$]

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).

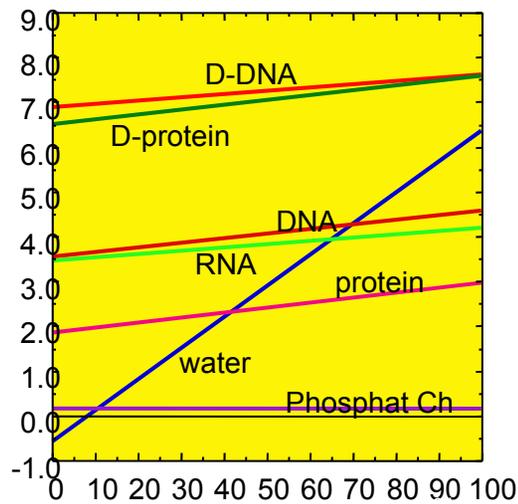
$$I(q) = \left| \int_V (\rho(\vec{r}) - \rho_s) e^{-i\vec{q} \cdot \vec{r}} d^3 r \right|^2$$

Contrast – Atomic Scattering Lengths

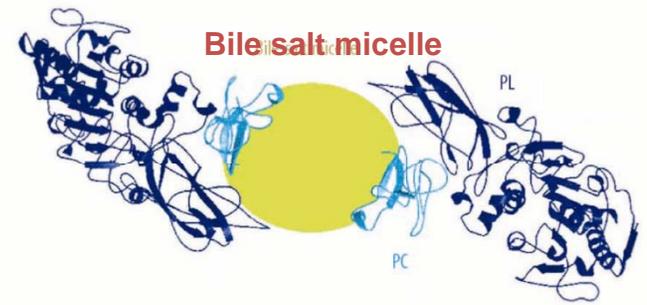
Element	Neutrons (10^{-12} cm)	X-rays (10^{-12} cm)	Electrons
^1H	-0.374	0.28	1 
^2H (D)	0.667	0.28	1 
C	0.665	1.67	6 
N	0.940	1.97	7 
O	0.580	2.25	8 
P	0.520	4.23	15 

For SAS: SL \rightarrow SLD \rightarrow Δ SLD

SANS – Contrast Variation

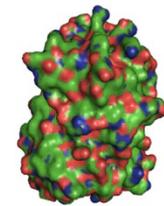
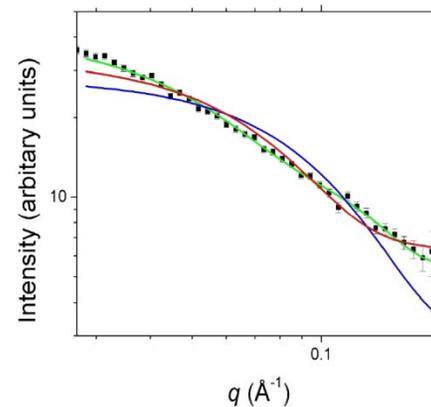
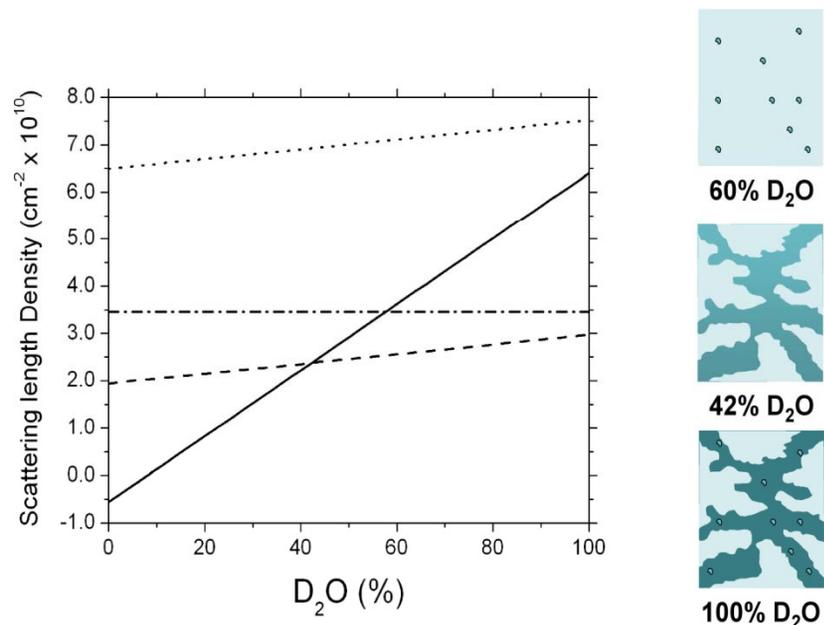


**D₂O/H₂O
contrast variation**

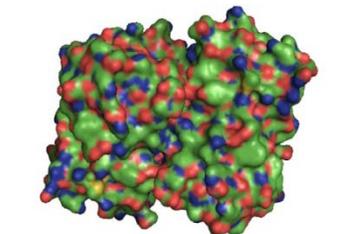
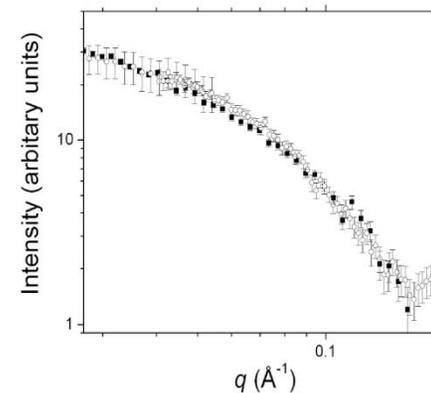


Visualizing Proteins in Inorganic Hydrogels

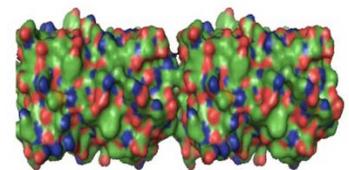
- Entrapment of bio-macromolecular assemblies: bio-composite, biomimetic, bio-inspired for catalysts, sensors, functional materials – for example light harvesting antenna complexes for solar energy
- SANS shows that green fluorescent protein, an enzyme with potential applications in energy transfer and 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**



monomer



parallel dimer

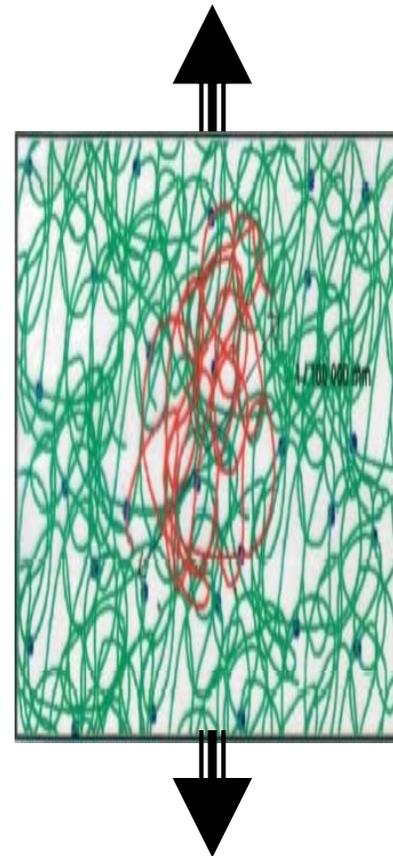
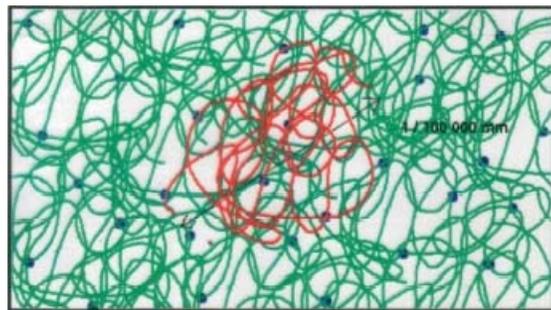


end-to-end dimer

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

Rubber (Polymer Network)

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

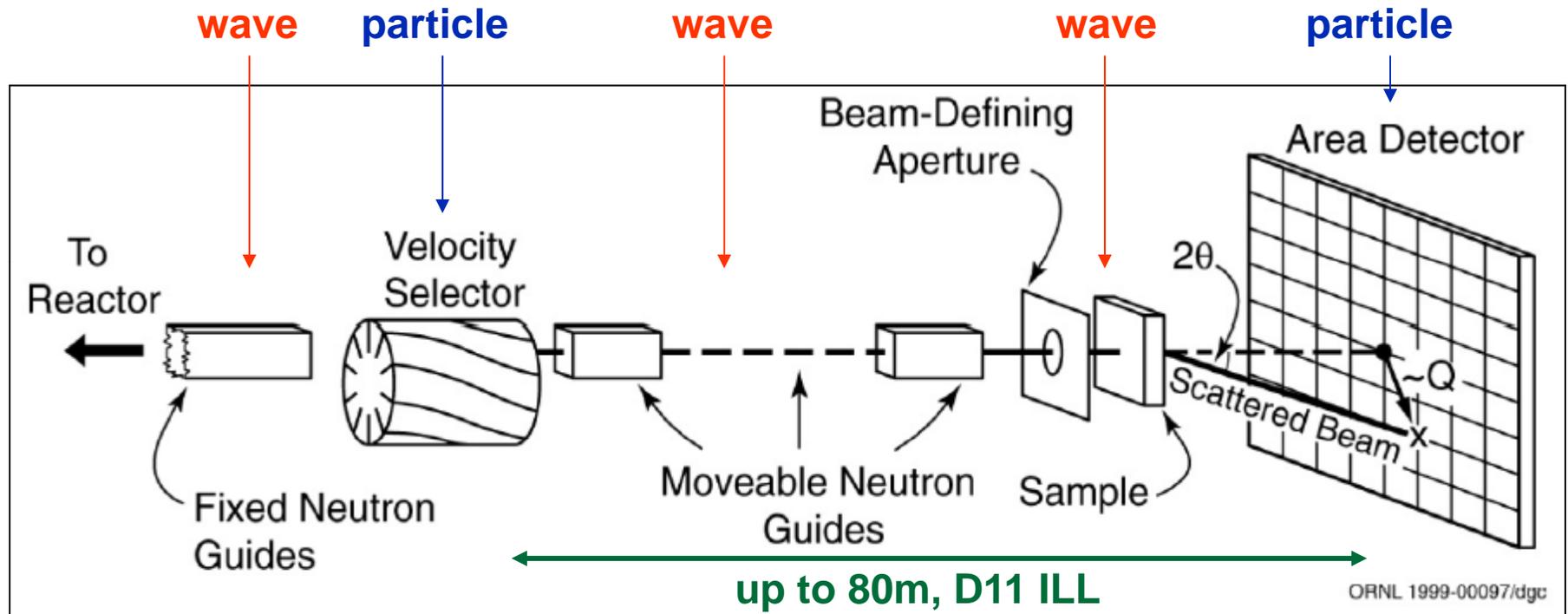


- Blend “normal” H- and some % D-polyisoprene
- Cross-link to form rubber network
- Stretch rubber sample in the SANS beam and collect data

SANS guide hall (HFIR)
a few years ago

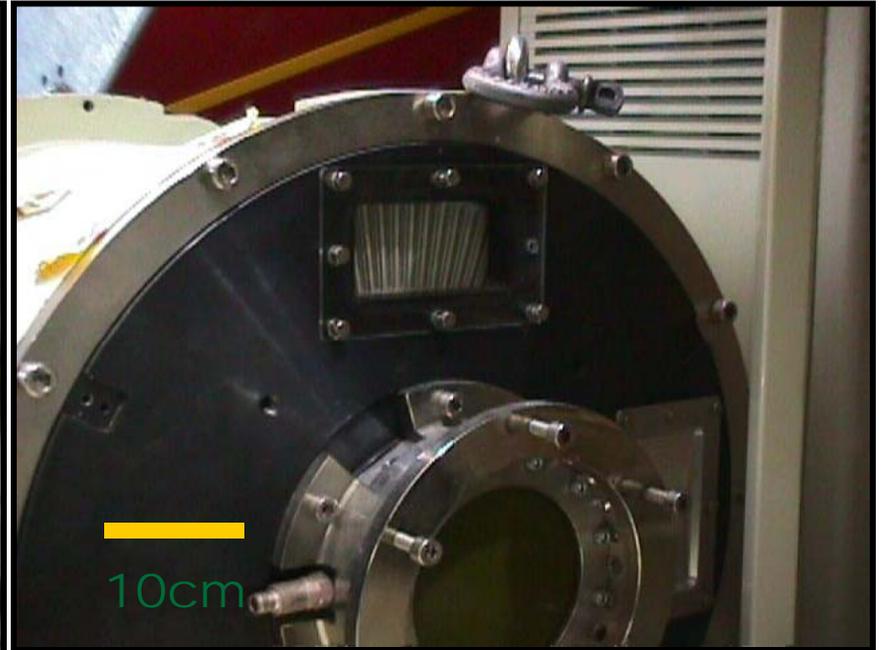


Layout of a SANS instrument



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

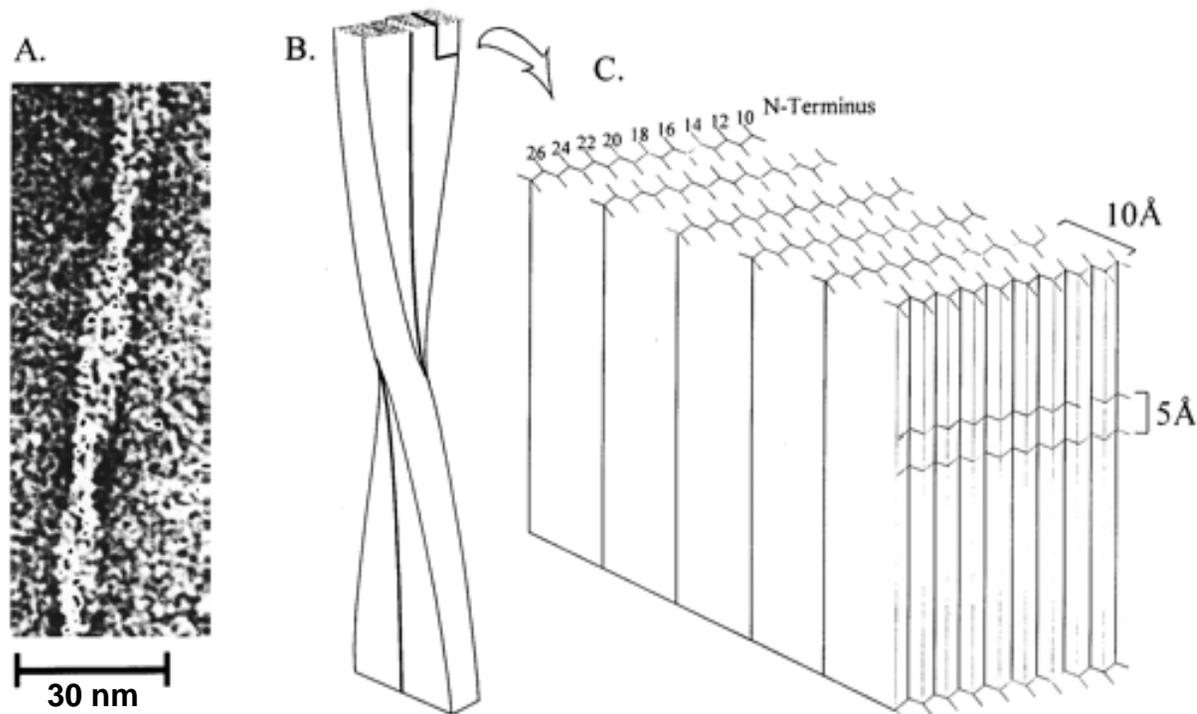
- **Plan your experiment well!**
- **What Q-range would I like, and what must I have?**
- **For how long should I measure my samples? – *counting statistics, sample size (~ 10 x 10 x 1 mm³)***
- **How will I correct for backgrounds?**
- **How can I optimize my sample quality?**
- **Less is often more: 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



- **NMR**
 - β -fold
- **SANS**
 - Fiber
 - Diameter
 - **6 sheet stack**
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 - Overall morphology
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T.S. Burkoth et al. *J. Am. Chem. Soc.* **2000**, 122, 7883-7889

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



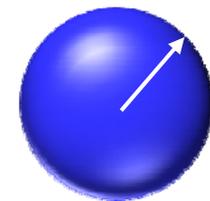
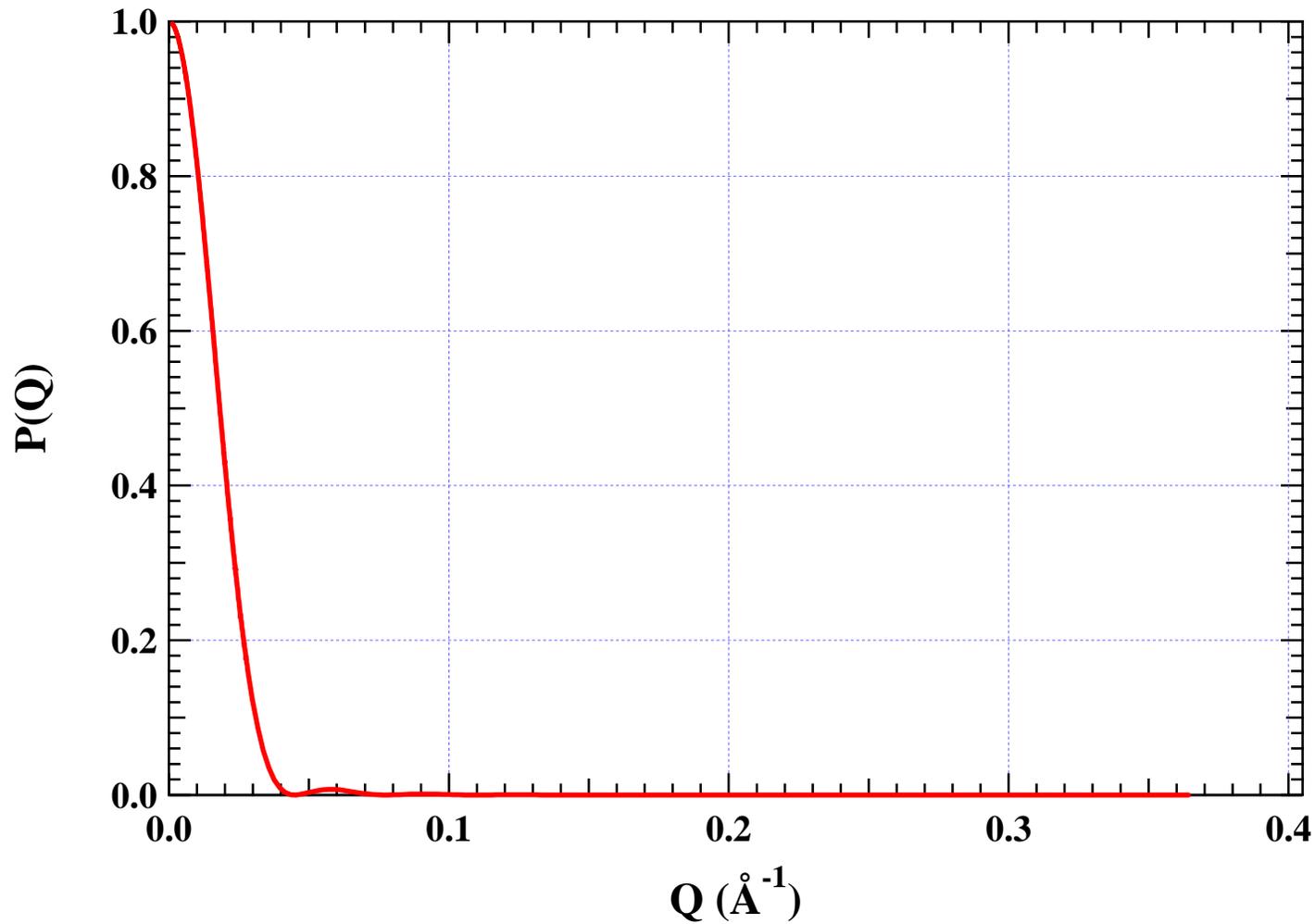
Bruce McCandless II took the first untethered space walk in February 1984. Here we see him from Challenger, floating above Earth.



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.

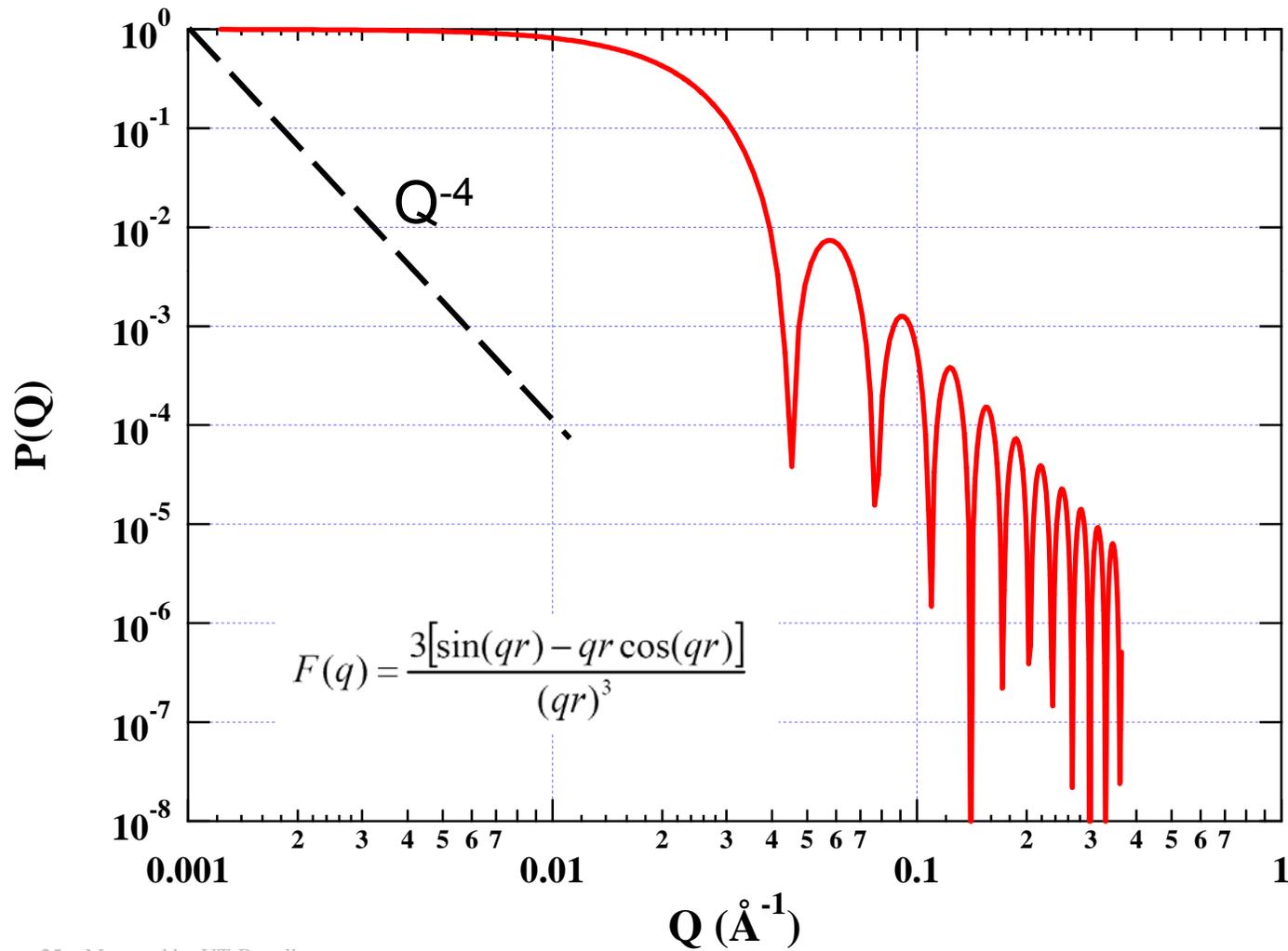
Sphere

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

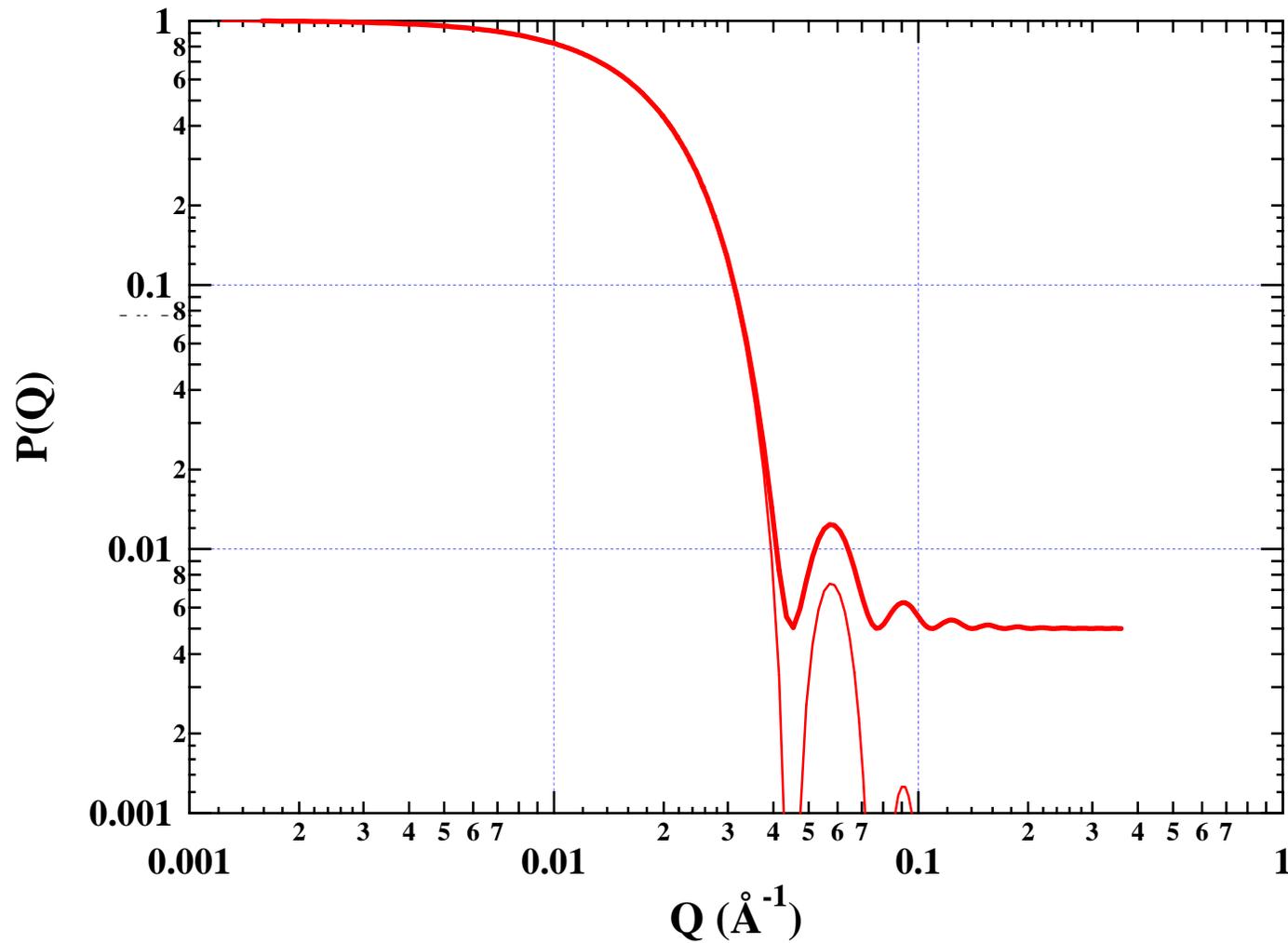


100 \AA
radius

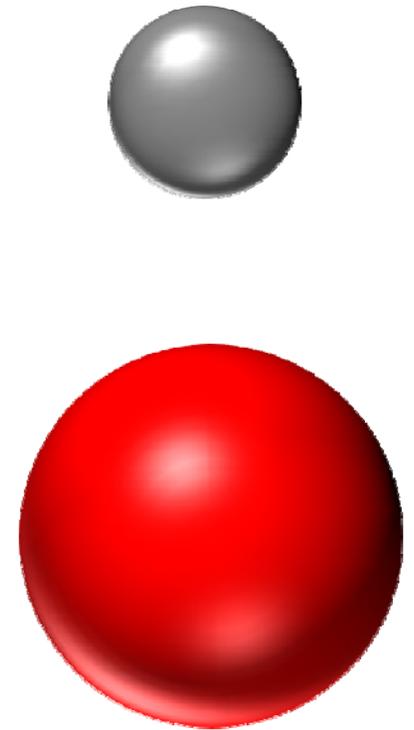
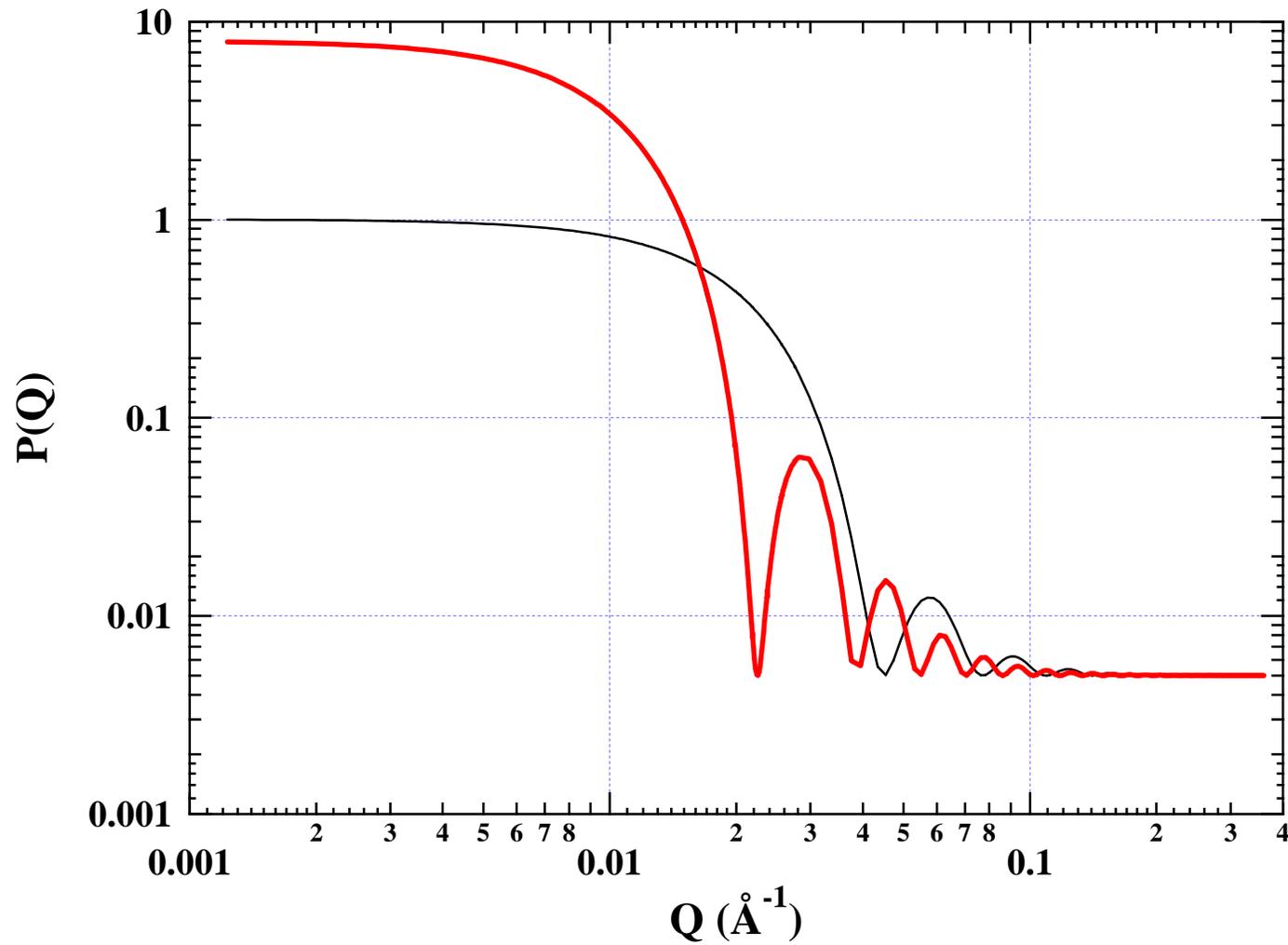
Sphere



In practice: sphere + constant background

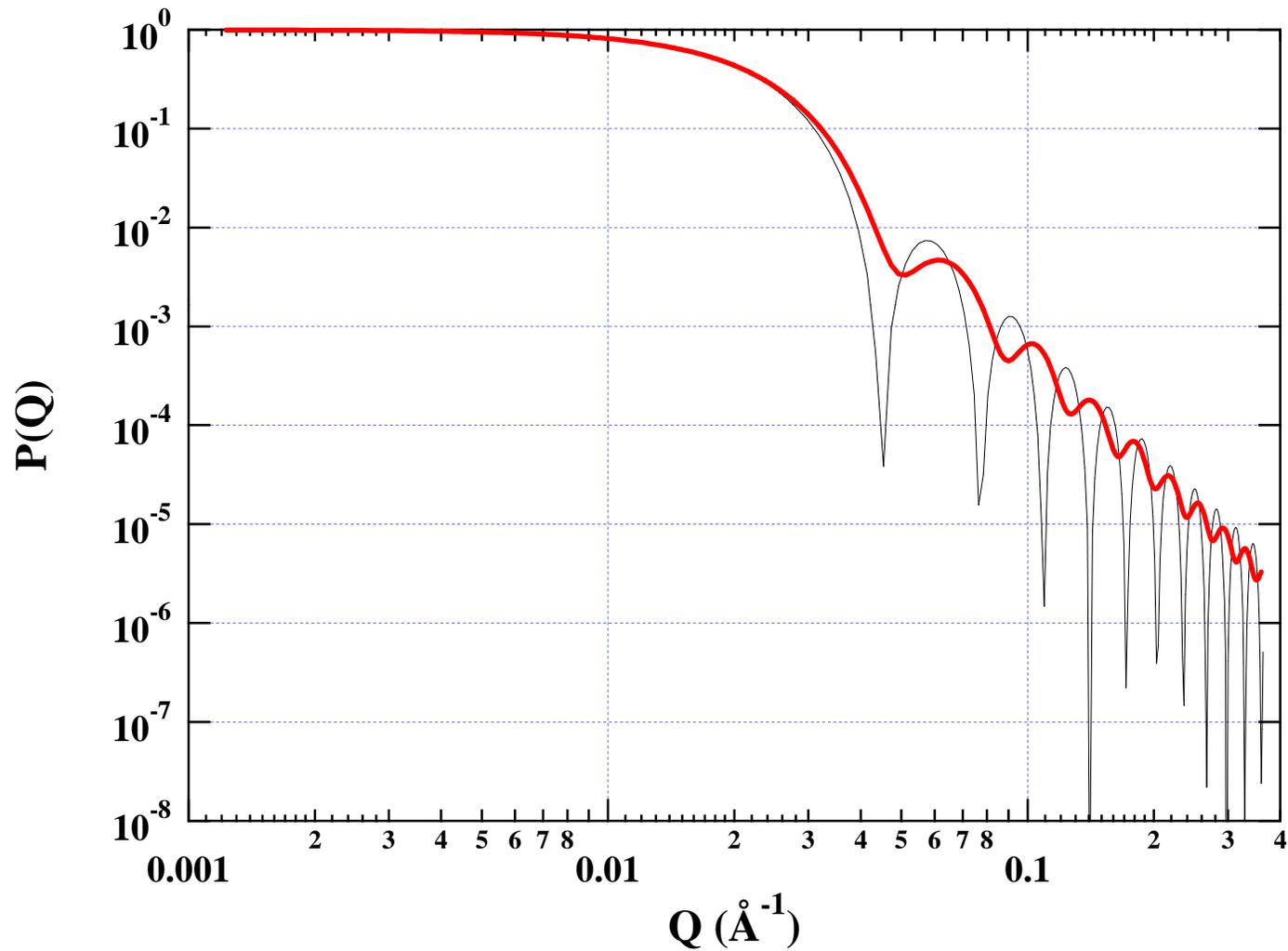


Spheres of different sizes

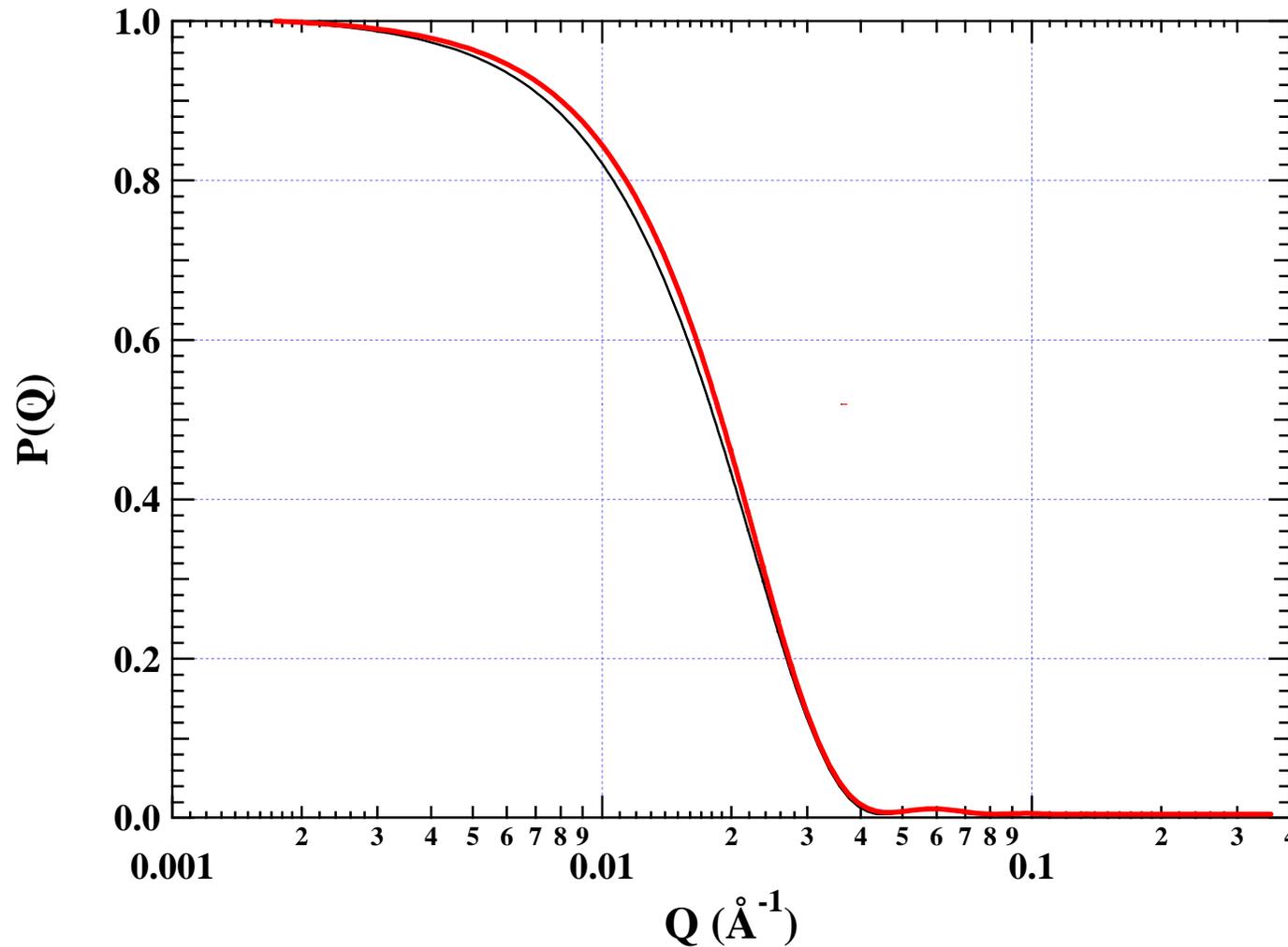


Ellipsoid

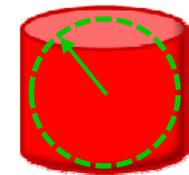
aspect ratio 1.5



Circular Cylinder - *with same R_g as the sphere*



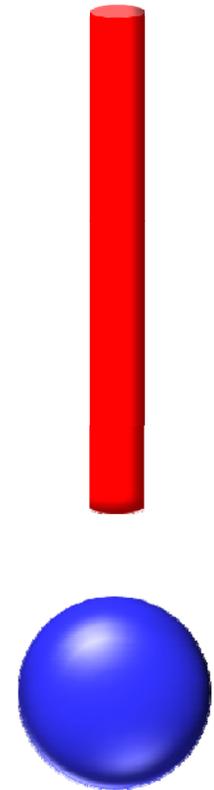
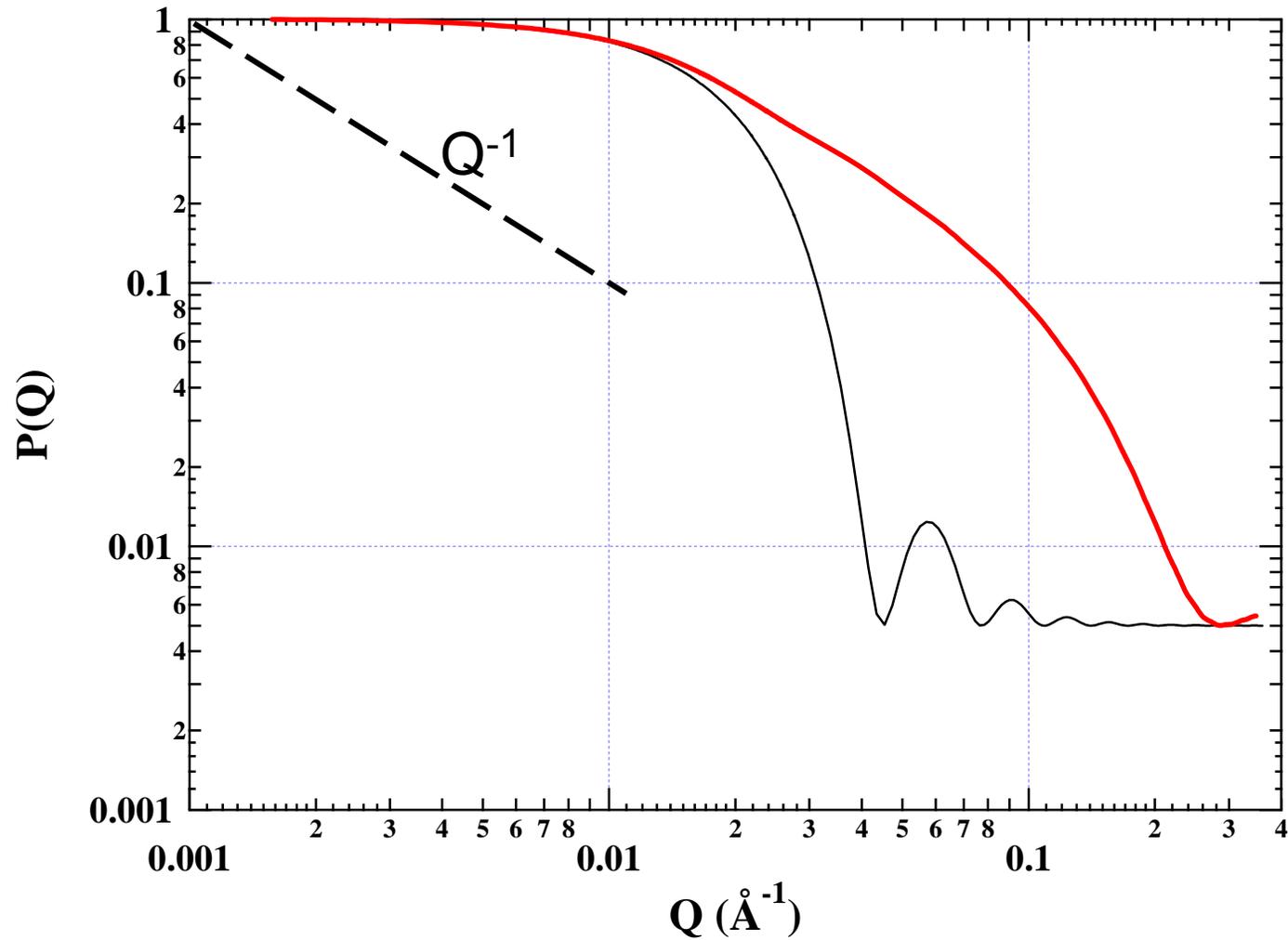
$\sim 77.46 \text{ \AA } R_g$



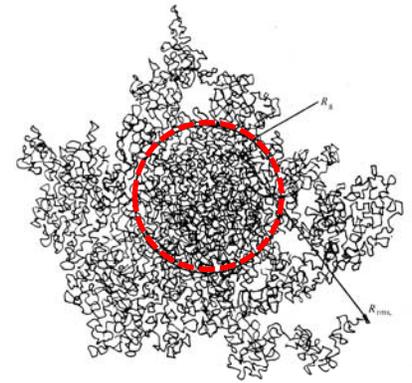
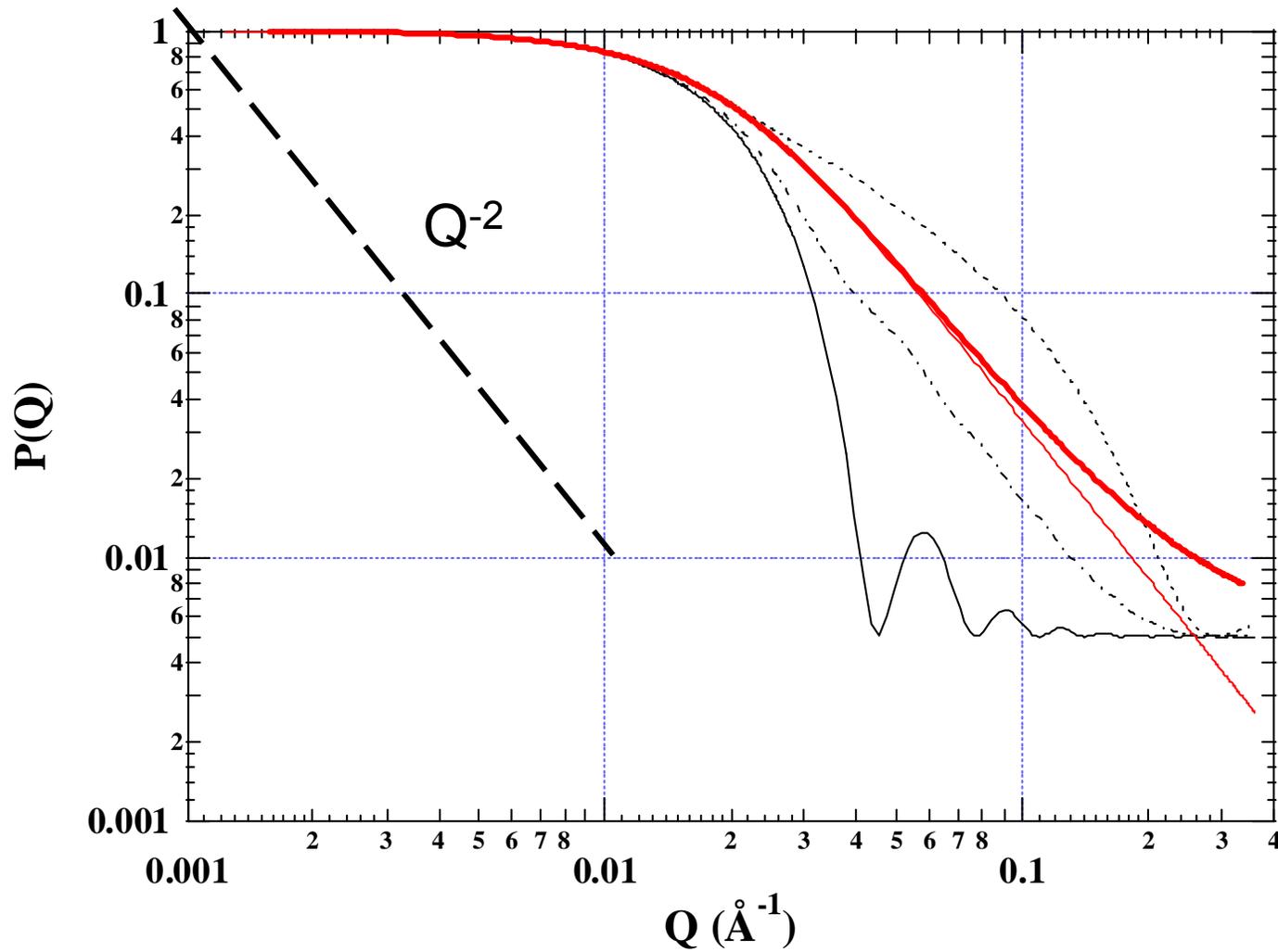
100 \AA radius

Radius of Gyration, R_g = rms average distance from center of scattering mass

“Long & thin” cylinder



Polymer coil



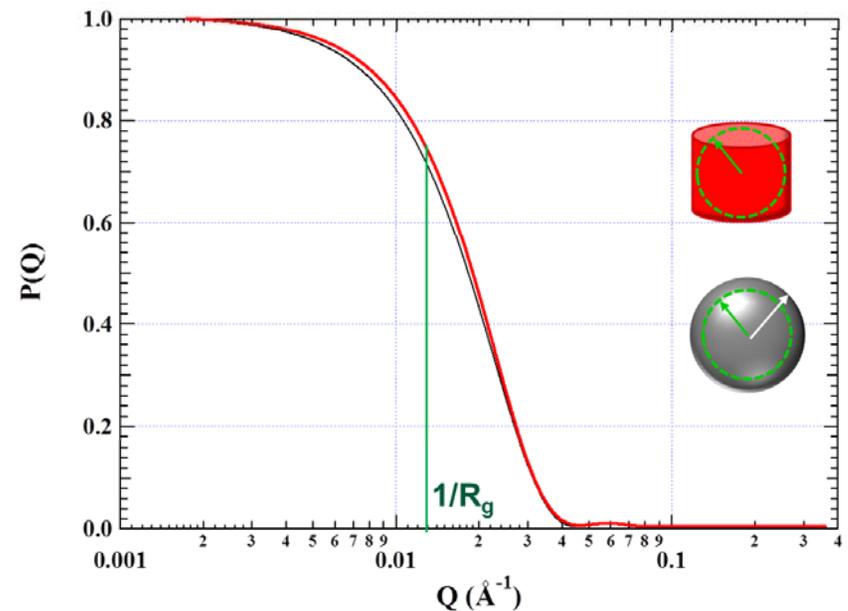
Guinier Analysis

size of any kind of object

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

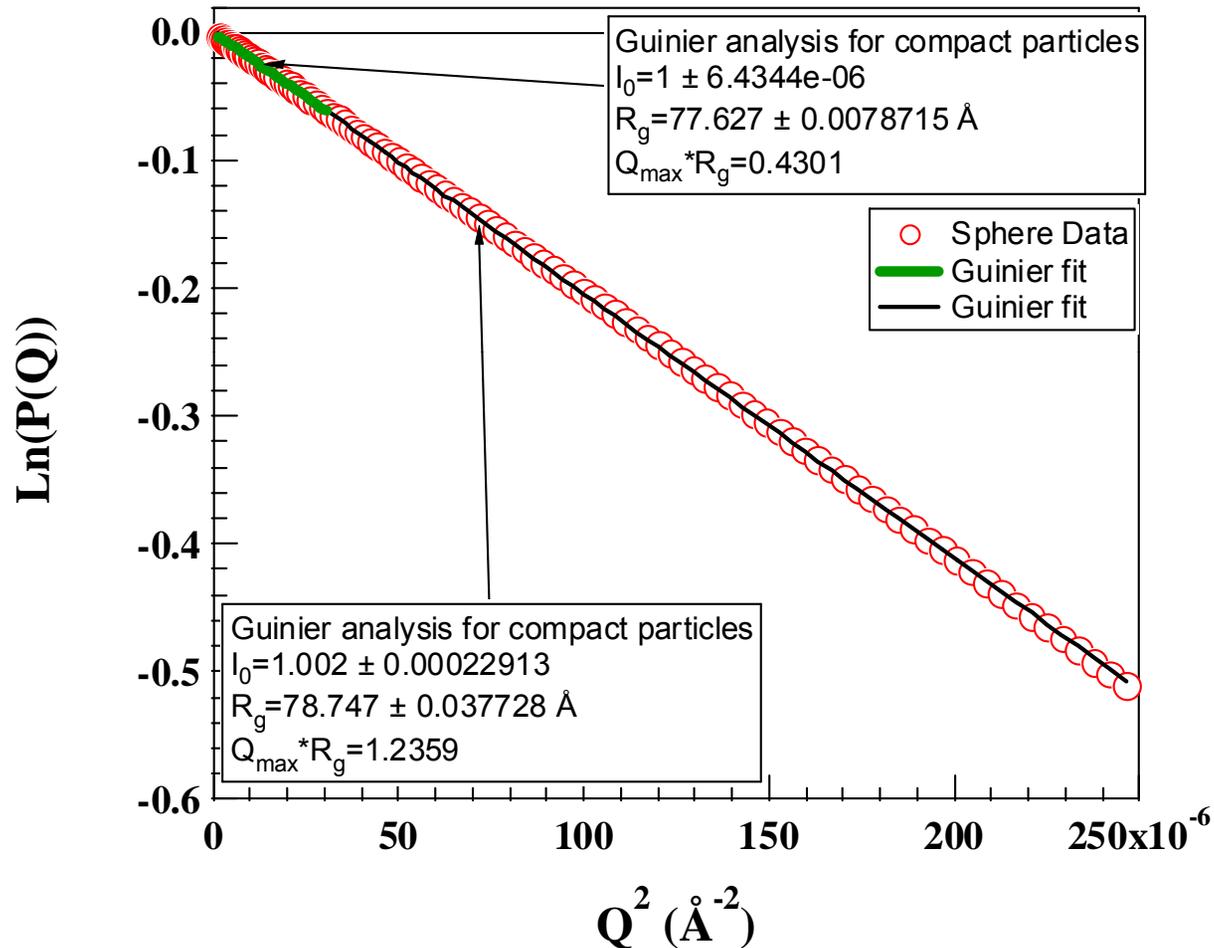
$$\ln[I(q)] \propto q^2 R_g^2 / 3 \quad qR_g < 1; \quad \text{sphere : } R = \sqrt{\frac{5}{3}} R_g$$

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



Guinier Analysis

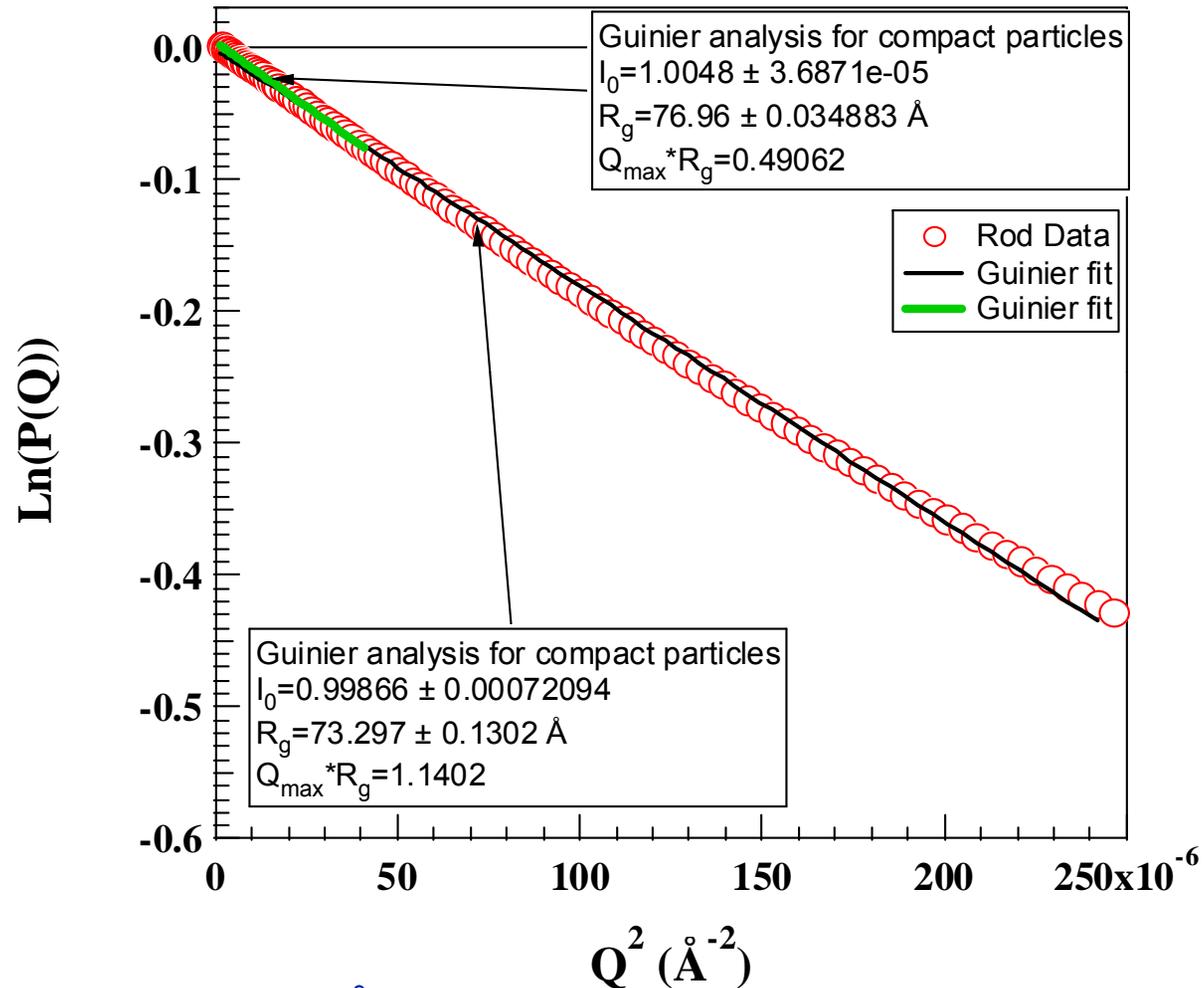
size of any kind of object



Precise R_g is 77.46 \AA

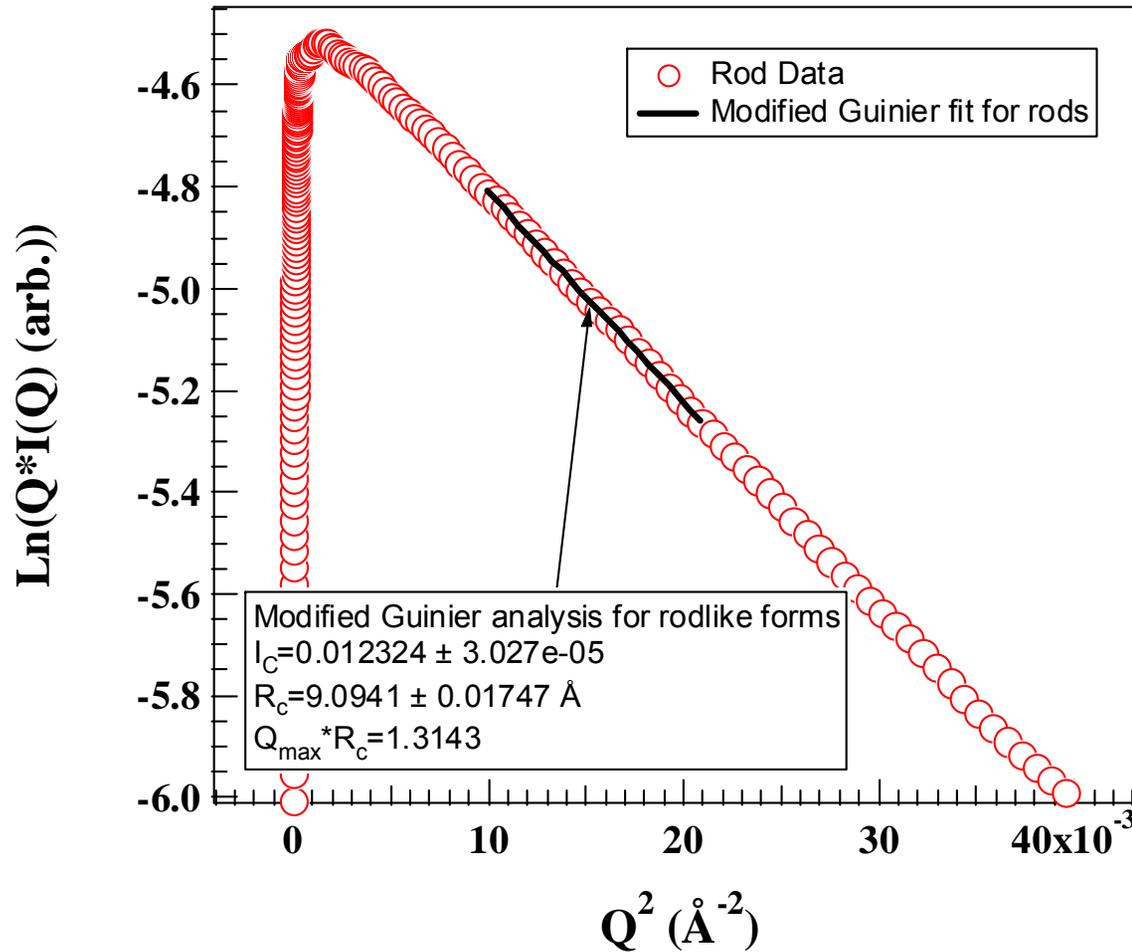
Guinier Analysis

size of any kind of object



Precise R_g is 77.46 \AA

Modified Guinier Analysis *for object extended in 1 dimension*

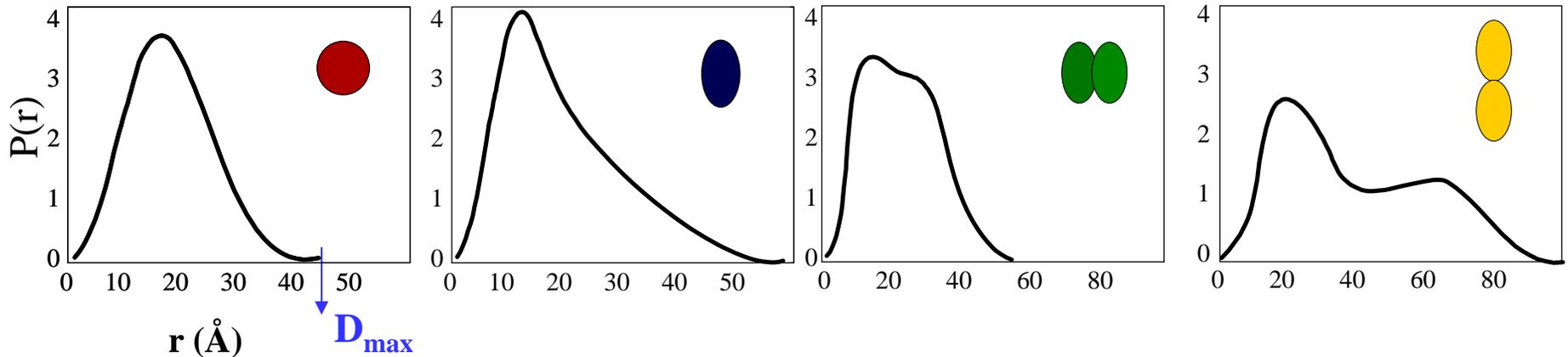
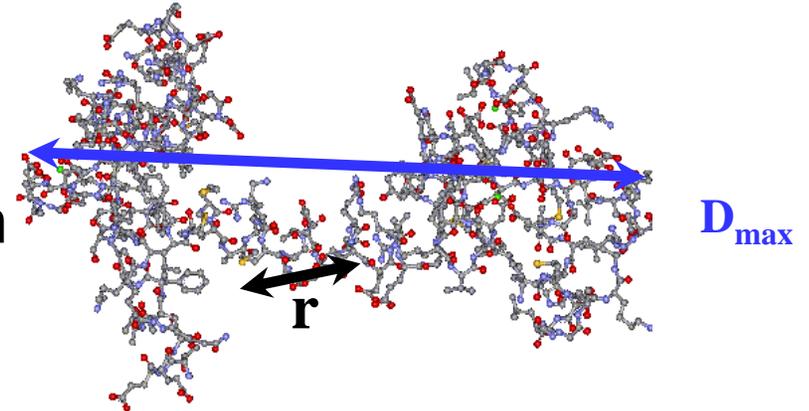


Rod radius = $\sqrt{2} * R_C = 12.9 \text{ \AA}$, exact radius = 13.3 \AA

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

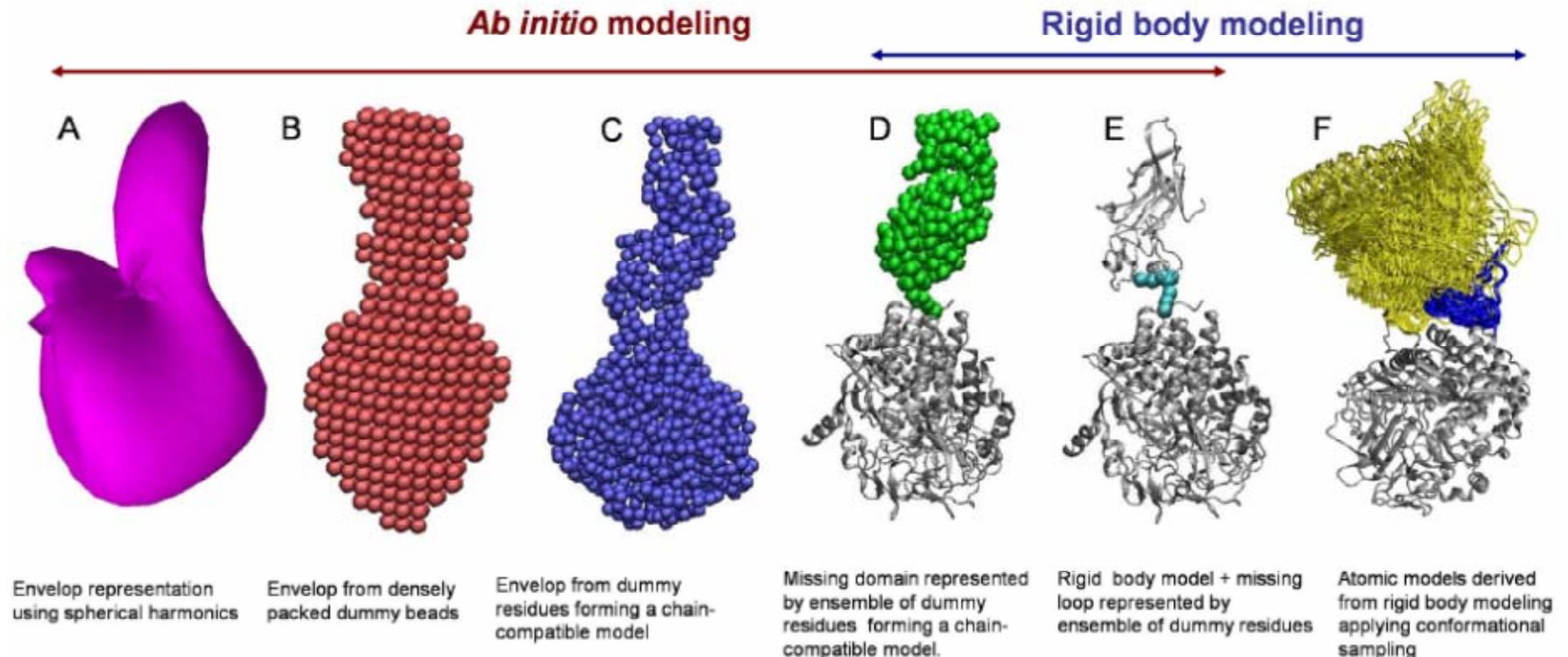
Pair correlation function and shape

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



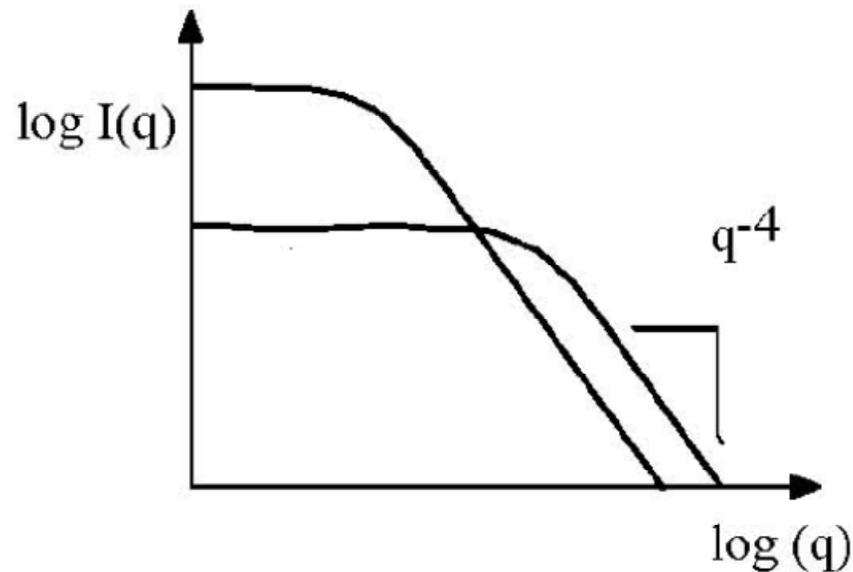
Shape : Modeled as a uniform density distribution that best fits the scattering data.

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

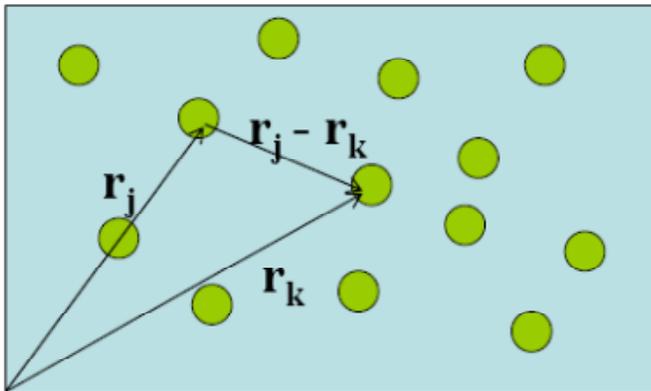
$$\lim_{q \rightarrow \infty} I(q) = 2\pi S_V |\Delta\rho|^2 q^{-4}$$

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

Interparticle Structure Factor $S(Q)$

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

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

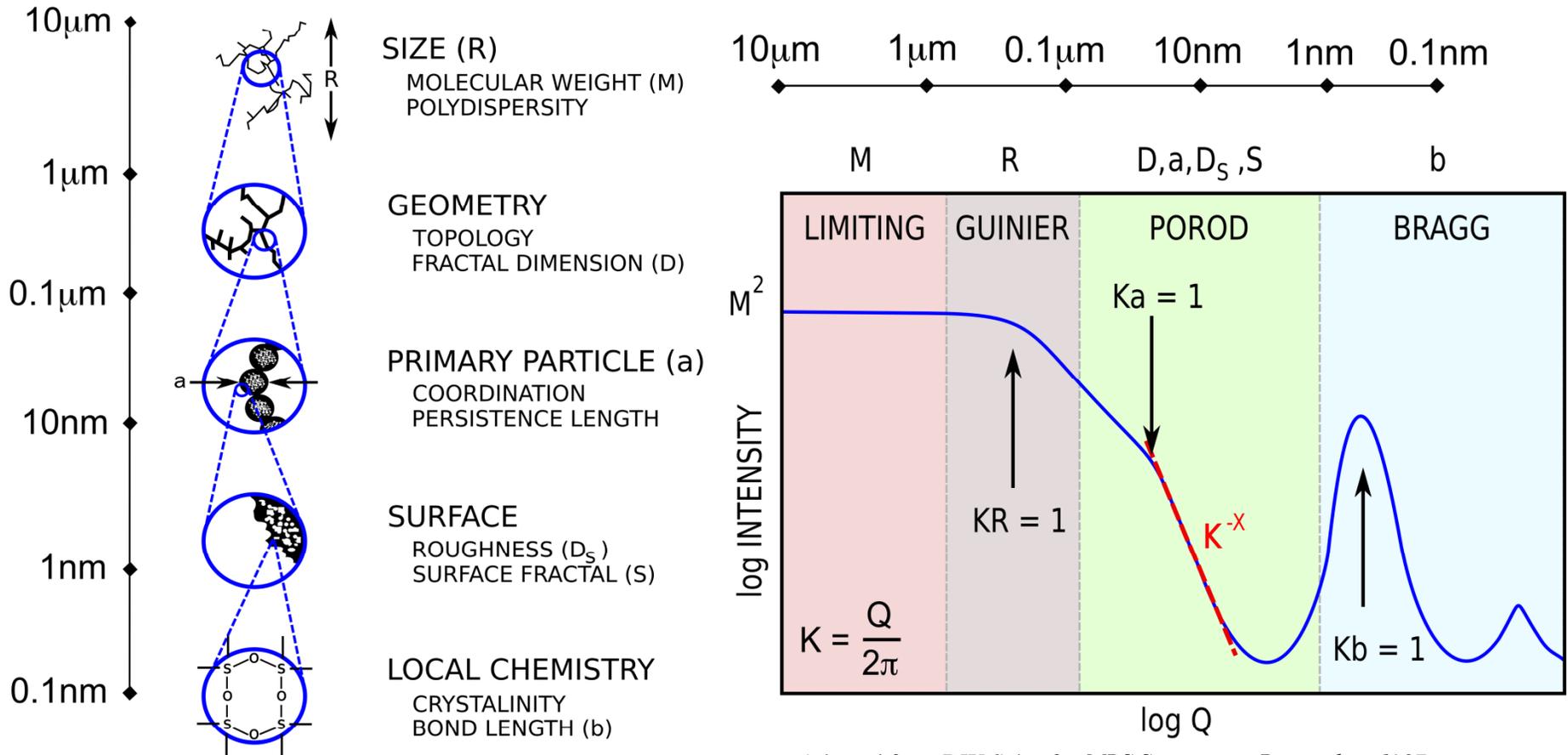


$I(q)$ is modulated by interference effects between radiation scattered by different scattering bodies.

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

$S(q) \cdot P(q)$ is not always valid and useful!

Structural Hierarchy (particulate)



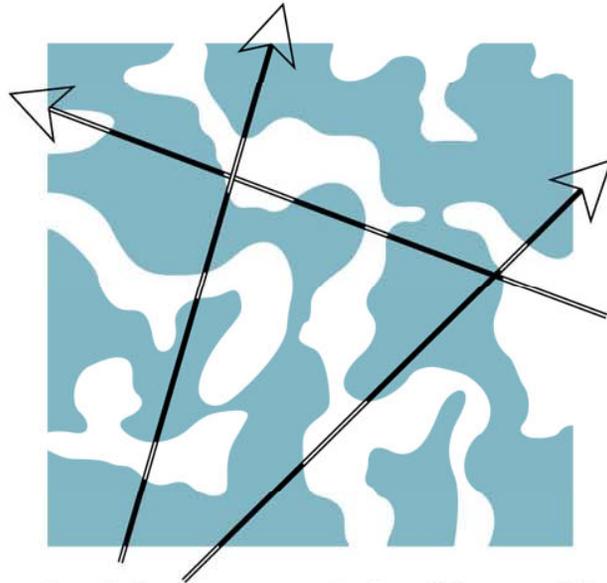
Adapted from DW Schaefer *MRS Symposium Proceeding 1987*

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: $\gamma(r) = e^{-r/a}$

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

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

SAS Summary

- **SAS applications are in the nm to mm 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.**

SAS Literature Suggestions

- Guinier, A., Fournet, G. 1955. Small-Angle Scattering of X-rays. John Wiley & Sons, New York.

The classical work on small-angle scattering. Even though focused on x-rays, much of the theory and data interpretation apply just as well to neutrons.

- Roe, R. J. 2000. Methods of X-Ray and Neutron Scattering in Polymer Science. Oxford University Press, New York and Oxford.

Even though focused on polymers, this book gives a very thorough account on the basic scientific principles of small-angle scattering in a fashion that is accessible to non-expert scatterers.

- Higgins, J. S., and Benoît, H. C. 1994. Neutron Scattering from Polymers. Clarendon Press, Oxford.

A comprehensive description on neutron scattering and in particular small angle neutron scattering. Even though focused on polymers, the book is very useful for anyone interested in small angle neutron scattering.

- Pedersen, J. S., 1997. Analysis of small-angle scattering data from colloids and polymer solutions: modeling and least-squares fitting. *Adv. Colloid Interface Sci.* 70:171-210.

Contains a comprehensive list of form factors and structure factors that are used for interpreting small-angle scattering data.