# An Introduction to Small-Angle Scattering

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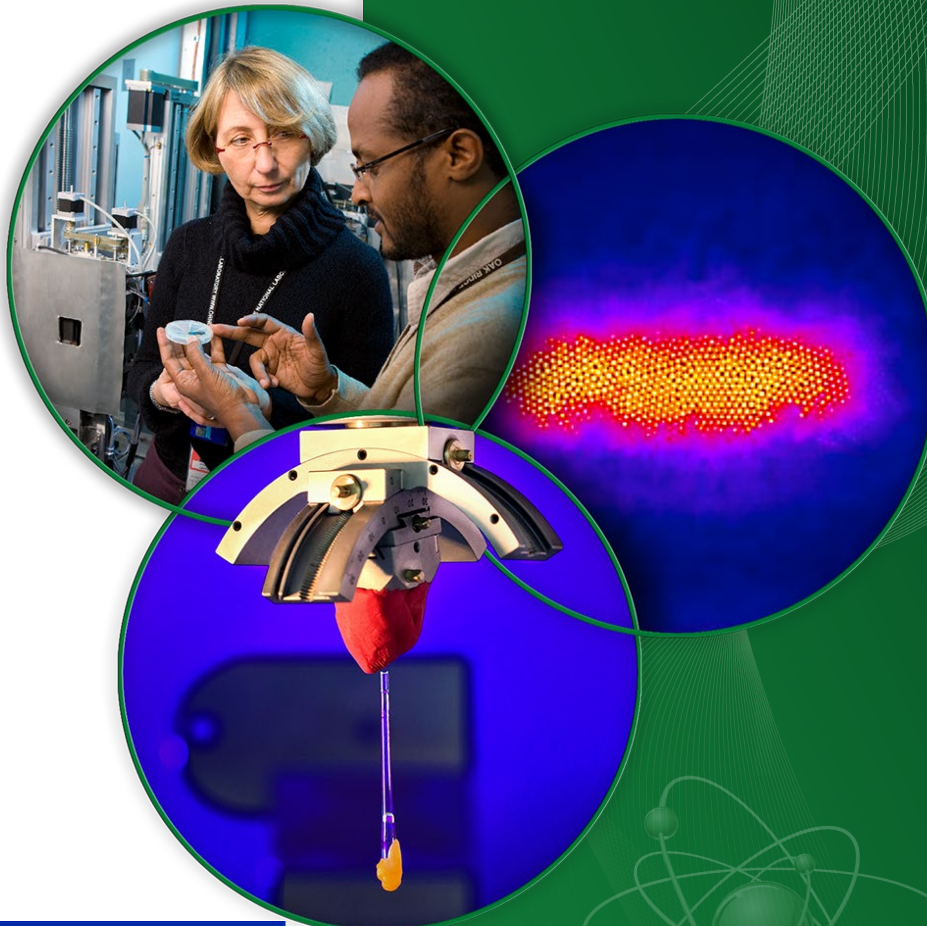

National School on Neutron and X-ray Scattering

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# Outline

- What is SAS and what can it do for you?
- Basic concepts of the technique
- SANS instrumentation
- Planning a SAS experiment and data reduction
- SAS data analysis and interpretation

# SAS

- SAS is a tool for structural characterization of materials
  - X-rays, neutrons and laser light can be used for SAS

- One of the most widely applicable structural characterization techniques
  - Solids, liquids, gasses
  - Amorphous, crystalline or anything in between
  - Pretty much any kind of material

# SAS applications A to Z

…anything? Pretty close!

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

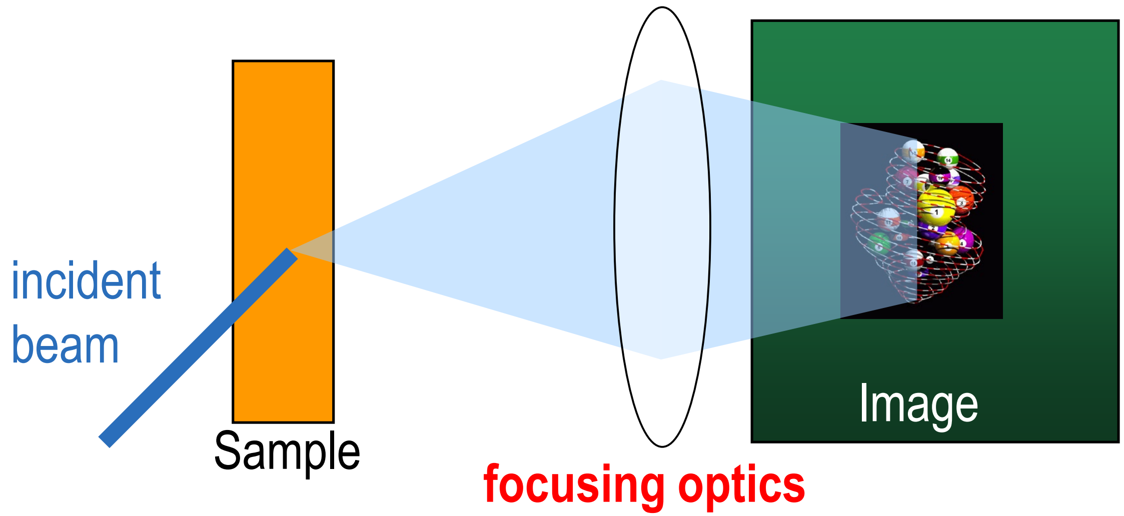
Xylose isomerase

Yttrium-stabilized zirconia (YSZ)

Zeolites

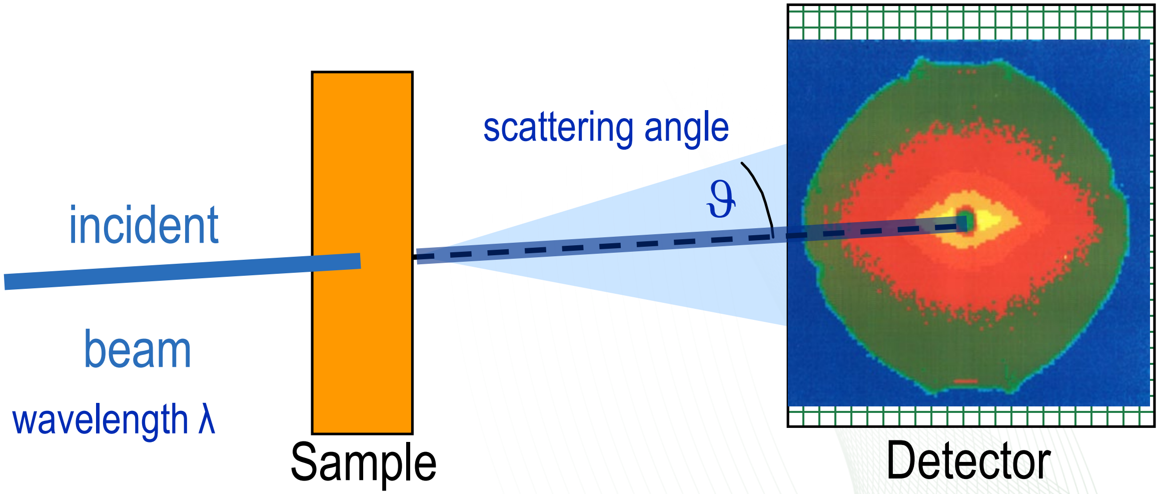
# Difference between SAS and Microscopy

**Microscopy** uses lenses to resolve a real-space image of the sample



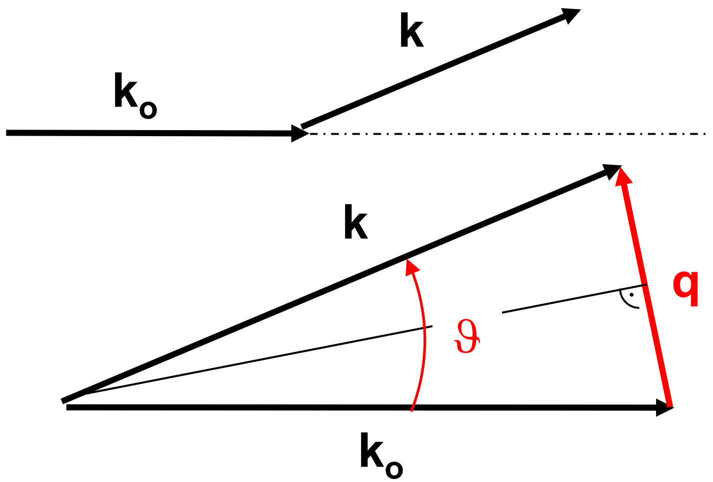

**SAS** measures the interference of waves

- Fourier space!
- Averaged over volume!



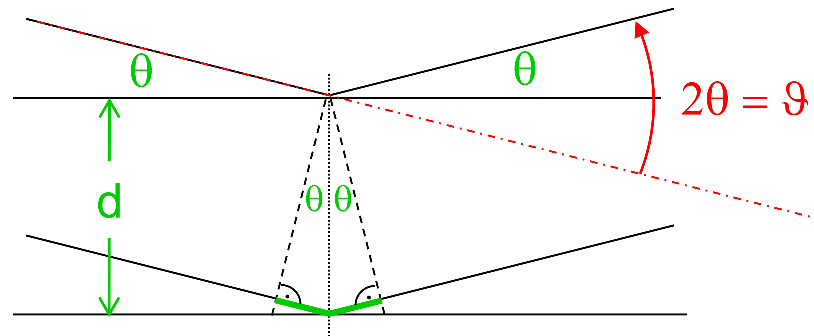
# SAS is related to diffraction

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




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

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




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

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

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

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

$q$ in $nm^{-1}$ or $Å^{-1}$

# SAS probes density differences

- Incoming waves scatter off the electron cloud (x-rays) or nuclei (neutrons)
- Interference of scattered wavelets from the material adds up to a "net scattering" amplitude
  - Fourier transform of the structure.
- Measured intensity is the magnitude square of the amplitude.

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

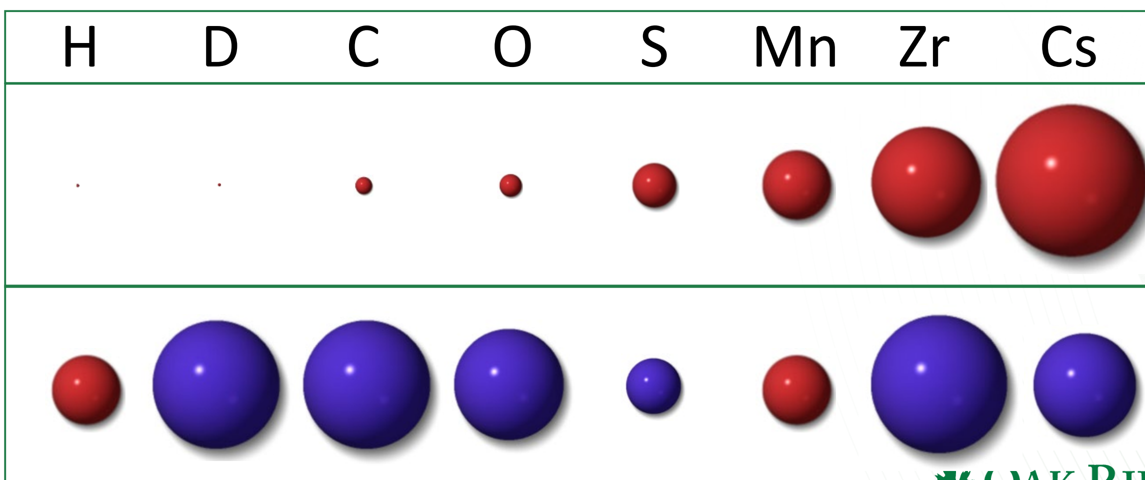
# SAS – SAXS and SANS

- The fundamental physics of x-ray and neutron scattering don't really differ, but their properties differ a great deal

**X-rays**
•No charge
•No mass
•Interacts with electrons

•Interaction varies with atomic number

**Neutrons**
•No charge
•Has mass
•Interacts with atomic nucleus
•Has spin
•Interaction is a property of the nucleus



# SAS – SAXS and SANS

- SAXS and SANS are very closely related and provide directly complementary information
- The choice between x-rays and neutrons is dictated by the problem

**X-rays**

- Readily available
  - Lab-based sources
  - Synchrotrons
- Massive fluxes possible
  - Time-resolved studies
  - Extremely precious material

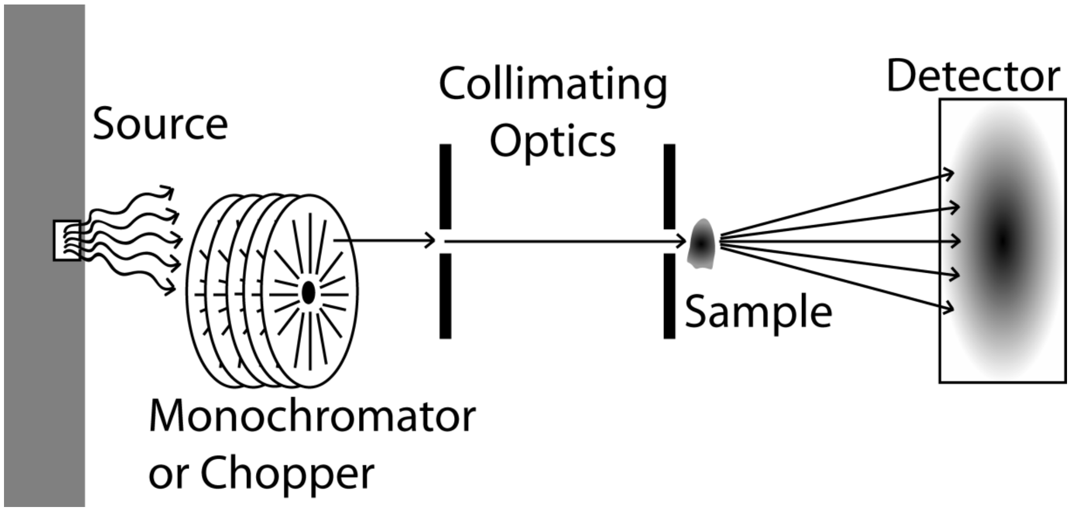
**Neutrons**

- Large user facilities only
  - Spallation sources
  - Reactors
- No radiation damage
- Contrast variation

**There are many experiments that really don't require the use of neutrons.**

# SAS Instrumentation

SAS instruments are conceptually simple




**Source:** x-ray generator, synchrotron, spallation source or reactor

**Monochromator/Chopper:** Defines wavelength(s)

**Collimating Optics:** Defines the angular divergence of the beam

Determines the maximum size probed

**Detector:** Collects the radiation scattered by the sample

Large detectors provide better angular coverage

# SAS Instrumentation

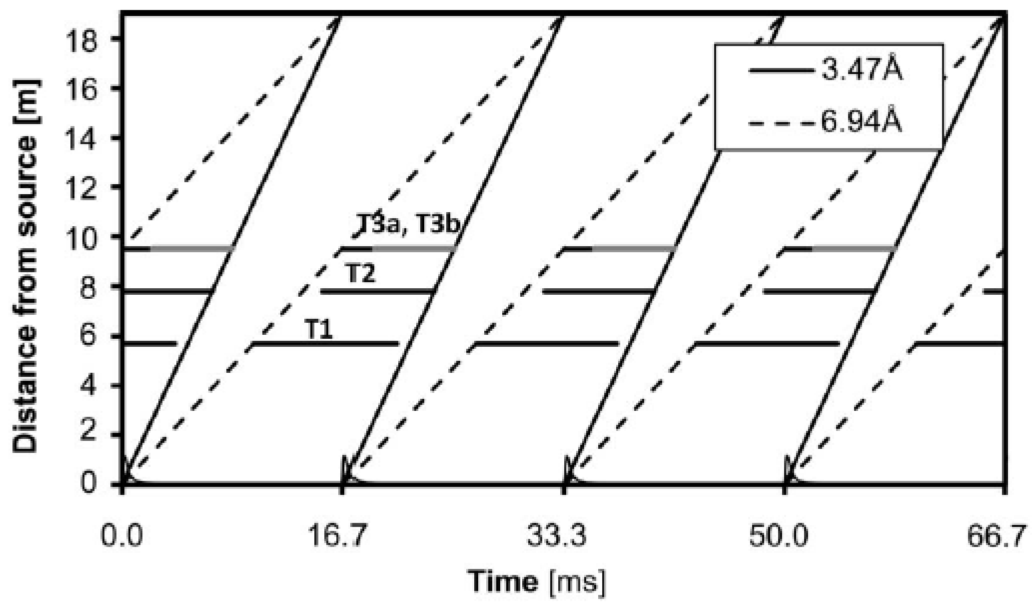
# SAS Instrumentation

- The neutron wavelength is related to its momentum

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

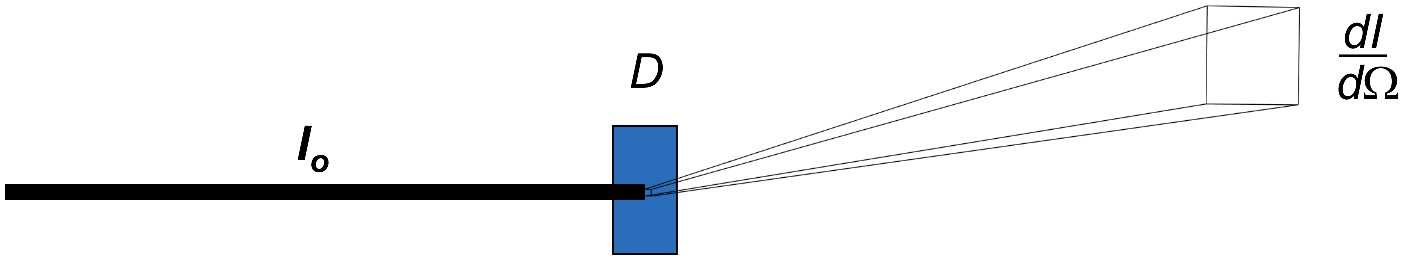
| | Cold | Thermal |
|---|---|---|
| T (K) | 20 | 300 |
| v (m/s) | 574 | 2224 |
| E (meV) | 1.7 | 25.9 |
| λ (Å) | 6.89 | 1.78 |

The wavelength-velocity relationship enables time-of-flight neutron scattering techniques



# SAS measurements

## A SAS measurement, once properly reduced, provides the scattering cross section per unit volume




$$\frac{dI}{d\Omega} = T I_o D \frac{d\Sigma}{d\Omega} \quad \longleftrightarrow \quad \frac{d\Sigma}{d\Omega} = \frac{1}{T I_o D} \frac{dI}{d\Omega}$$

[$cm^{-1}sterad^{-1}$]

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

# SAS measurements

## Plan your experiment well!

- What Q-range would I like, and what must I have?
- How large is each sample?
- How much material do I need?
- For how long should I measure my samples?
- How can I optimize my sample quality?
- What control measurements do I need to perform?
- How will I reduce my data?

- 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!**

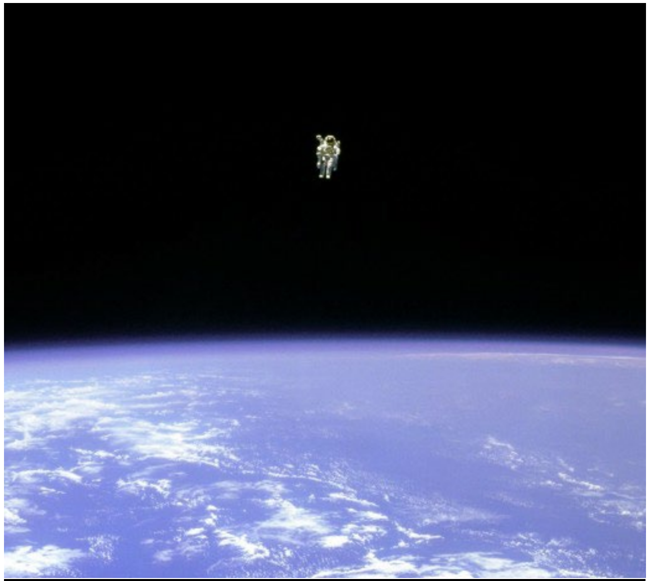
# SAS Measurements

- Normalization to monitor or time
- Background data sets
- Sample transmission
- Azimuthal averaging
- Absolute intensity scale ($cm^{-1}$)

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

# SAS Analysis

- **Analyzing SAS data is far harder than taking SAS data**
- **Model fitting is complicated by the sheer number of models available for fitting the data**
- **Be patient and be prepared to explore**



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

**If you feel like you are floating off in the middle of nowhere, you are neither the first, nor will you be the last, SAS practitioner to feel that way**

# Scattering from Particles

## Discreet particles are often the easiest to understand

$$I(q) = n\left|F(q)\right|^2 S(q)$$

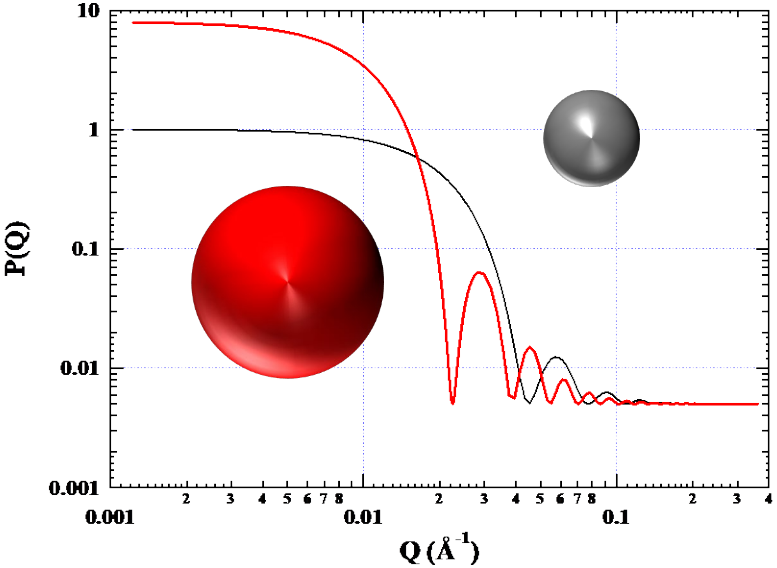
$n$ is the number density of particles

$F(q)$ is the form factor (particle shape)

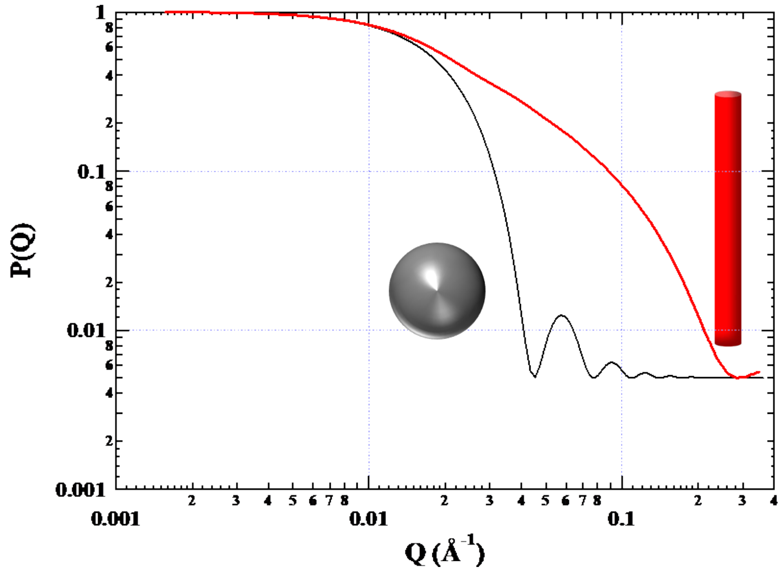
$S(q)$ is the structure factor (particle interactions)

# Form Factors

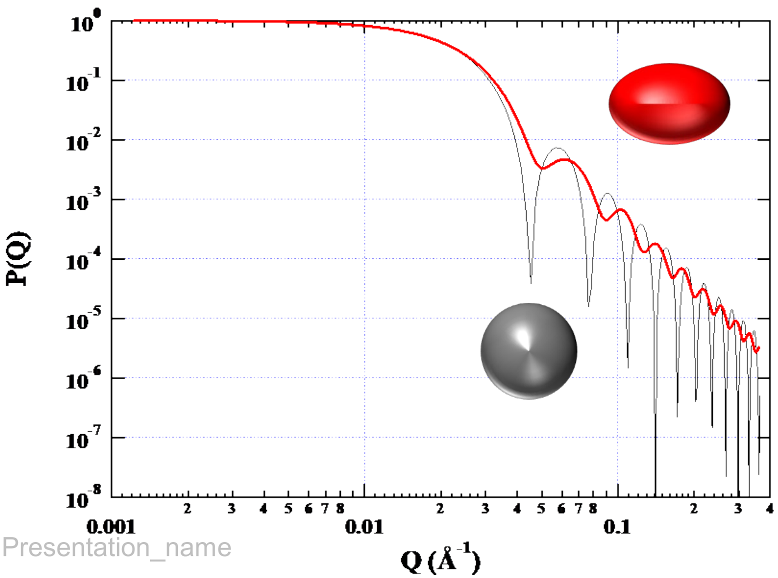
## Sphere



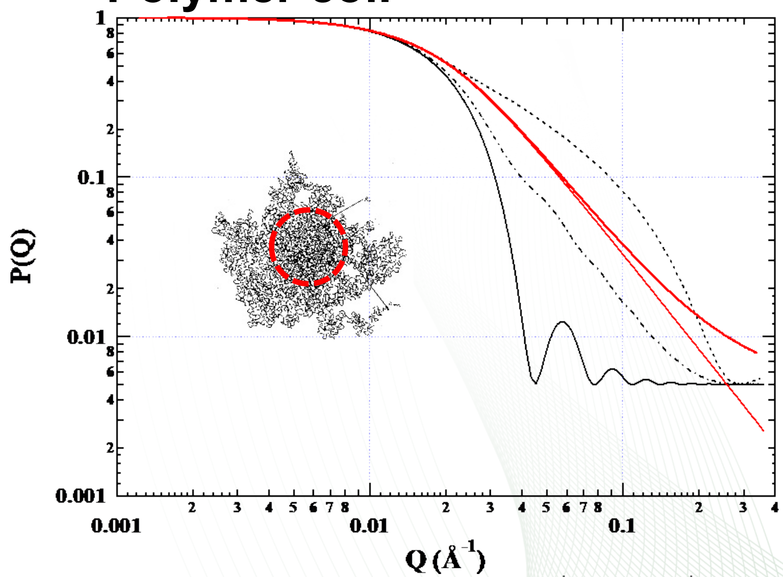

## Long & Thin cylinder




## Ellipsoid of Revolution




## Polymer coil



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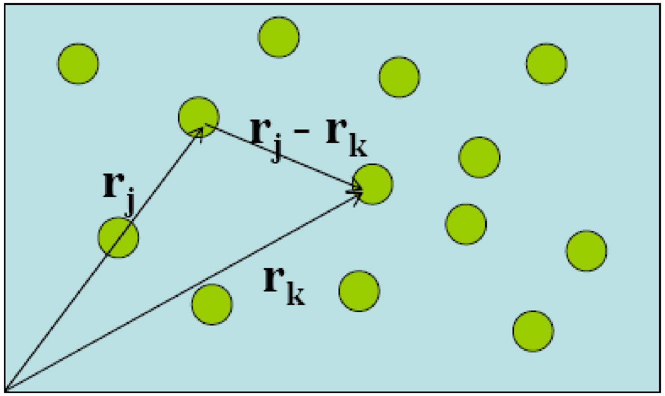
# Structure Factor

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

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




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

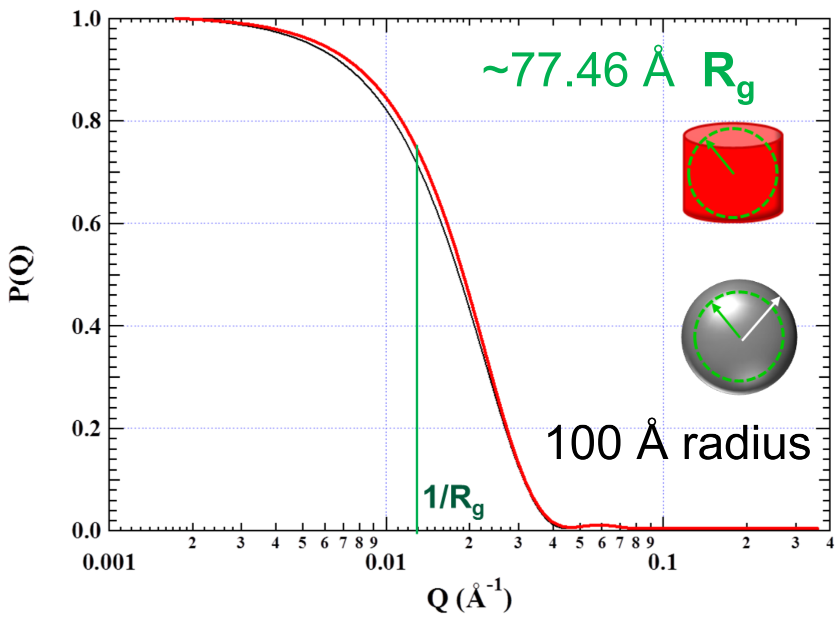
S(q) examples: hard sphere potential, sticky sphere, screened coulomb etc.

**S(q)·P(q) is not always valid and useful!**

# Guinier Analysis

**At small *q*, anything that could reasonably be considered a discrete object follows Guinier's approximation.**

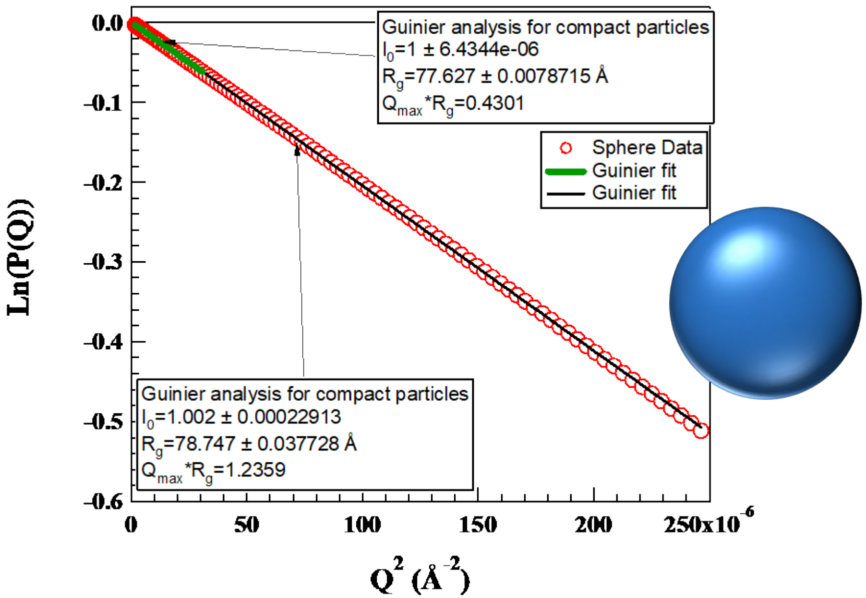
$$\ln[I(q)] \propto q^2 R_g^2 / 3 \quad qR_g < 1; \quad \text{sphere}: R = \sqrt{\tfrac{5}{3}} R_g$$

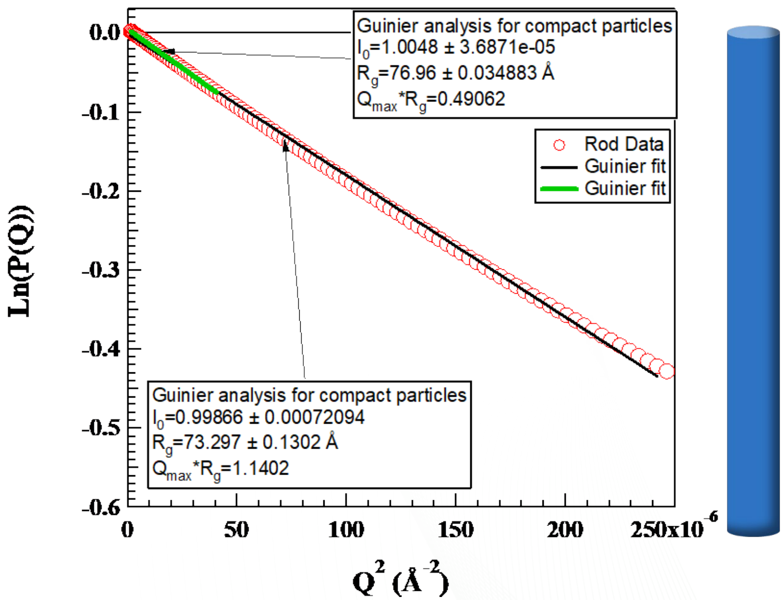



**Modified Guinier approximations exist to determine cross sectional radius of rods or thicknesses of sheets**

# Guinier Analysis

**Guinier fitting can be applied to scattering data from discreet particles regardless of the shape of the particle**

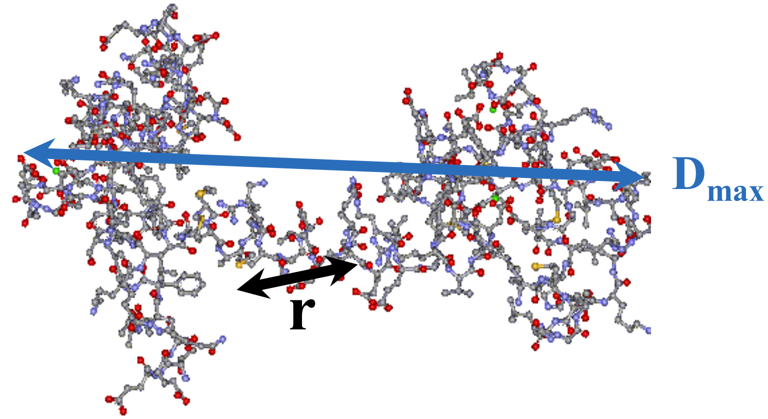


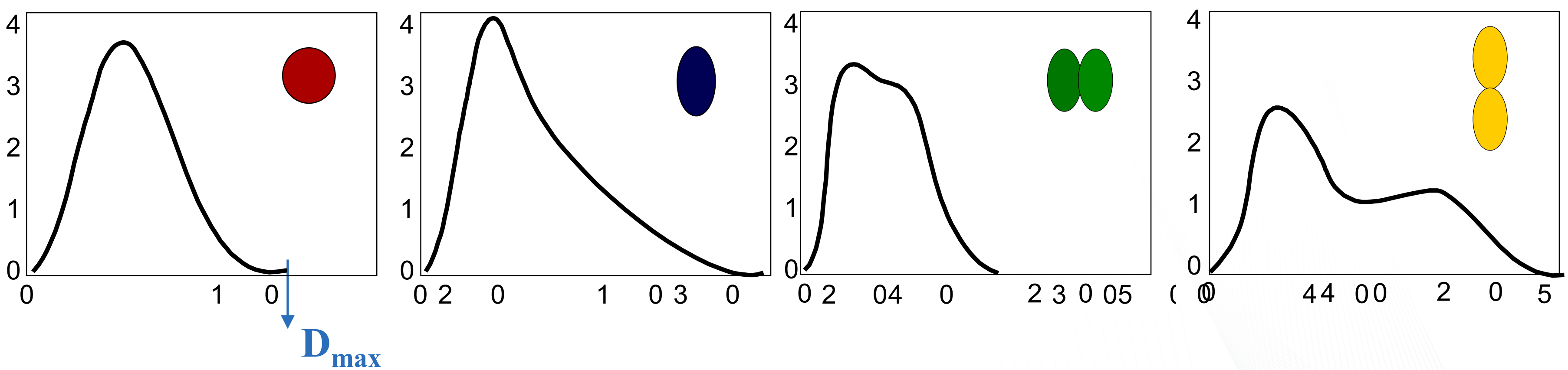




Precise $R_g$ is 77.46 Å

# Pair Correlation Function Analysis

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



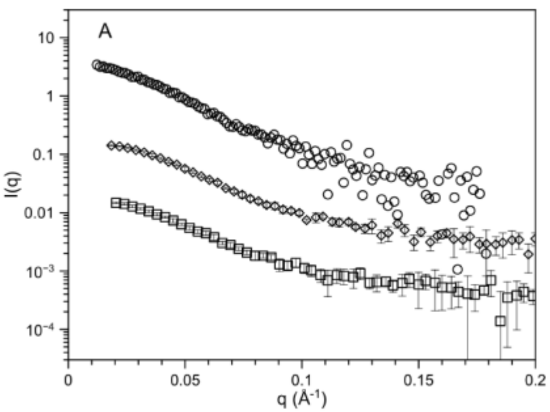



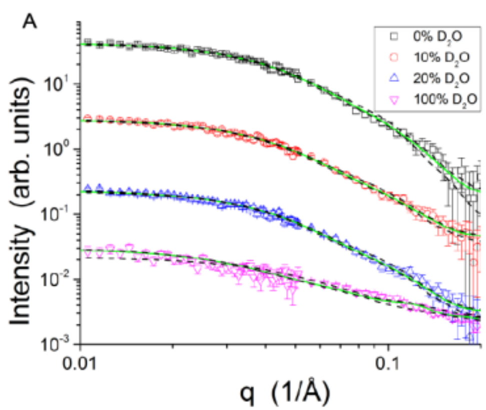

**P(r) provides some indication of particle shape**

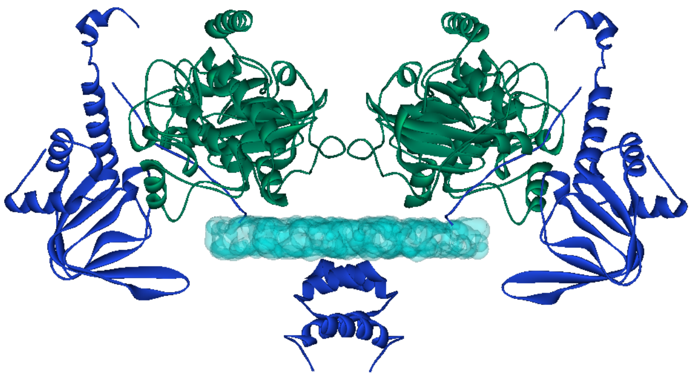
# Example:  A Protein Complex

•**Protein Kinase A is an important regulatory protein complex that phosphorylates proteins in response to a cellular signal**

• **SAXS and SANS with contrast variation, when combined with structural modeling, made it possible to construct a model that shows how the subunits in the complex assemble into the holoenzyme**



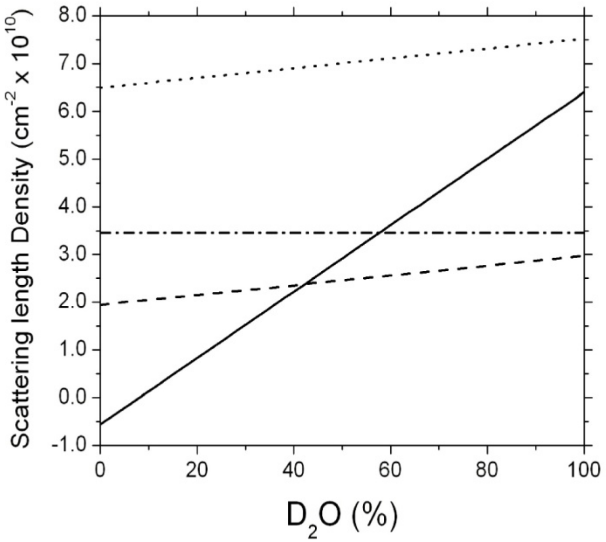



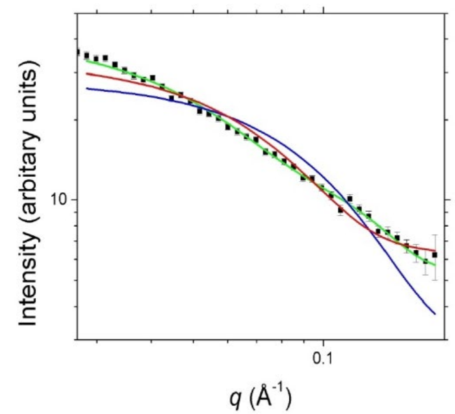
Blumenthal, et al., *J. Biol. Chem* **289**: 28505-28512 (2014).

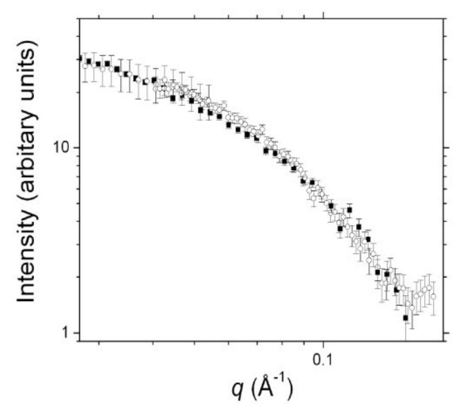
# Example: Proteins in a Porous Material

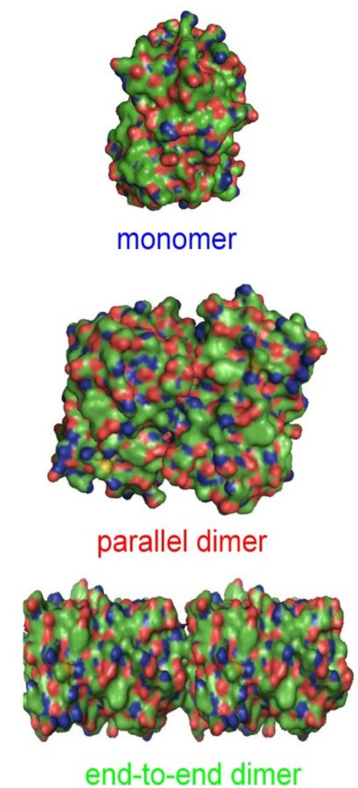
- Entrapment of bio-macromolecular assemblies: bio-composite, biomimetic, bio-inspired for catalysts, sensors, functional materials – for example light harvesting antenna complexes for solar energy
- SANS with contrast variation shows structure of proteins in a complex gel matrix





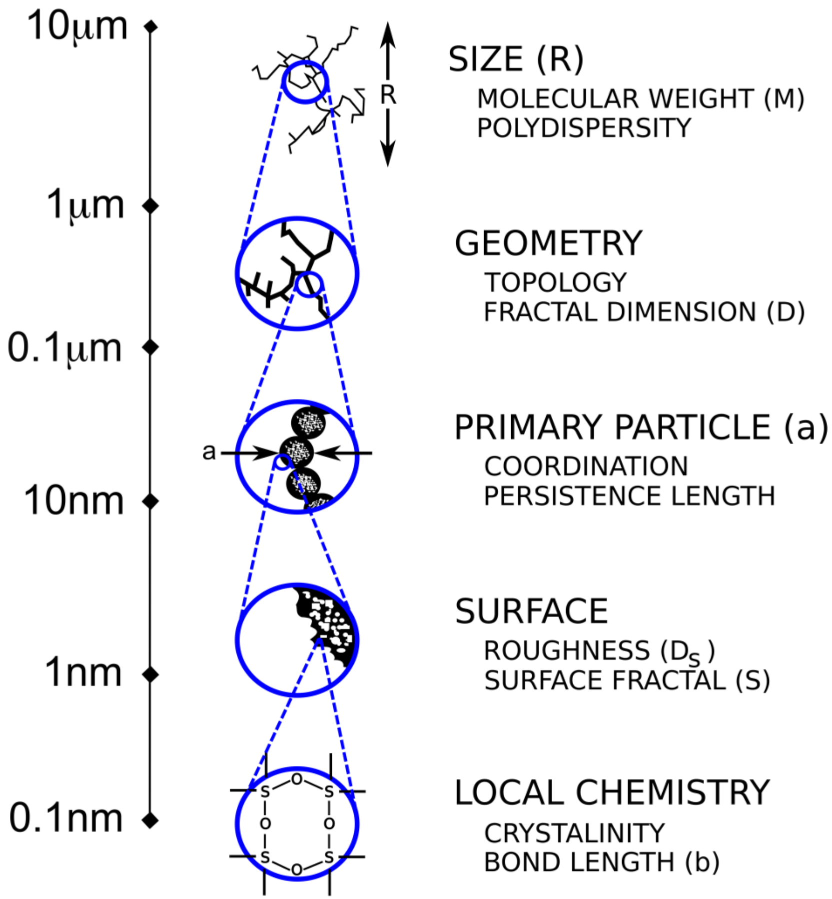


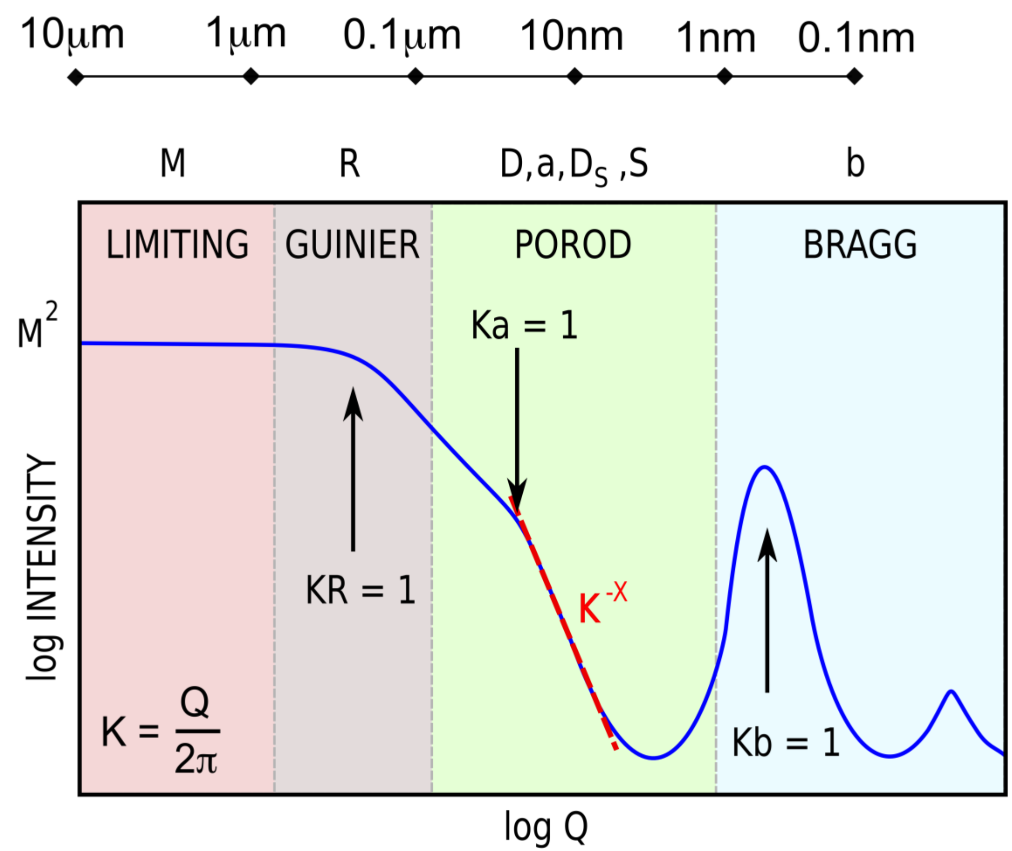




Luo, et al., *ACS Appl. Mater. Interfaces* **1**: 2262-2268 (2009).

# Hierarchical Structures



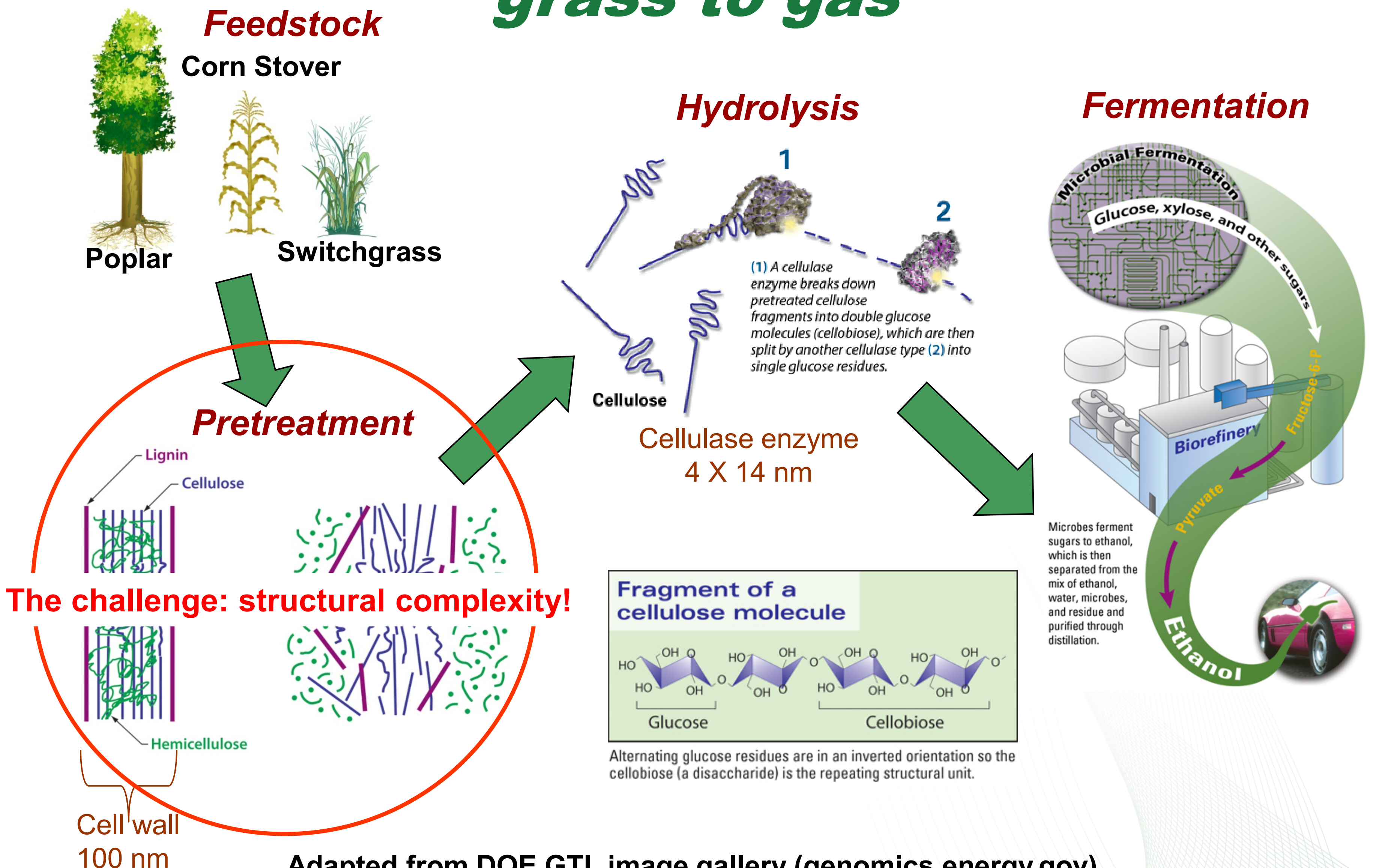




Adapted from DW Schaefer *MRS Symposium Proceeding* 1987

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*

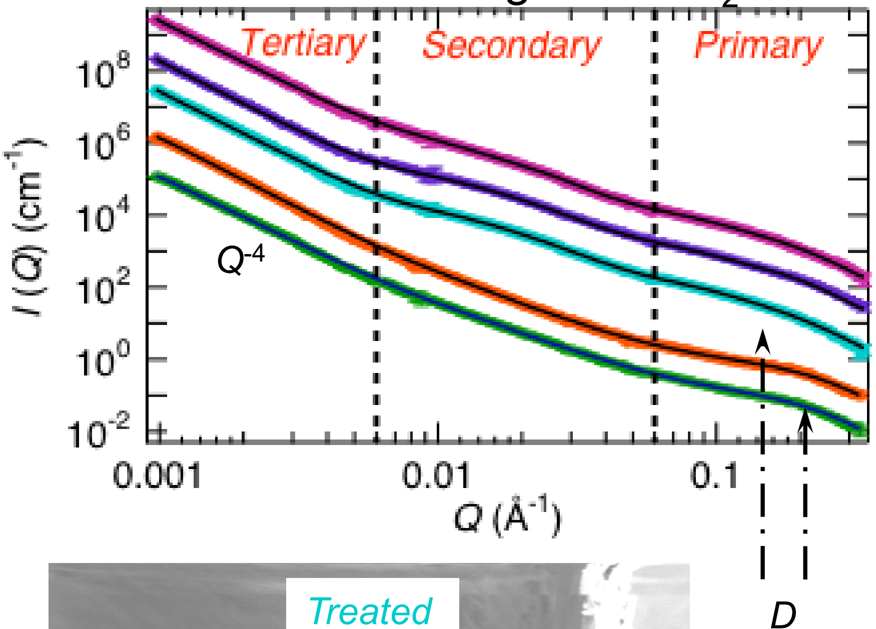
# Example: Biomass to Cellulosic Ethanol
## *"grass to gas"*

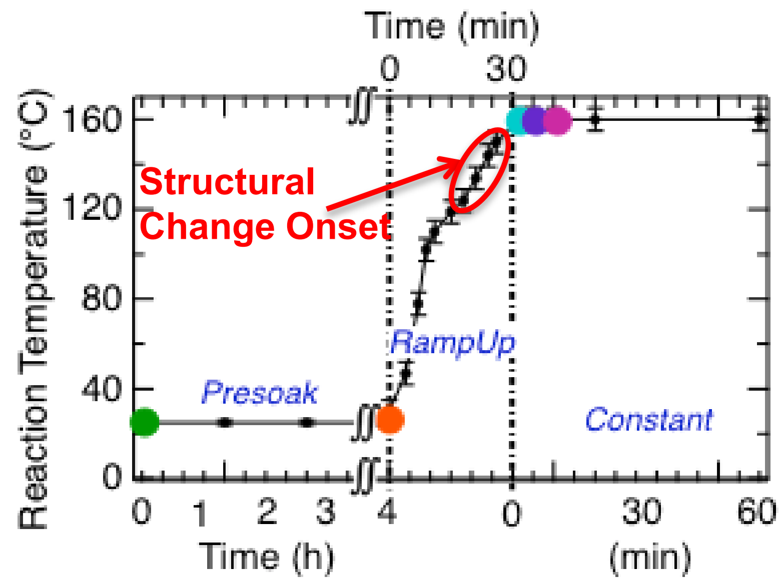


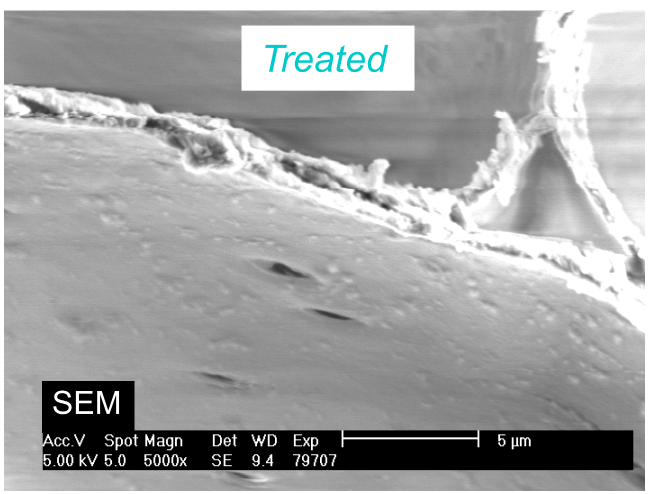

**Adapted from DOE GTL image gallery (genomics.energy.gov)**

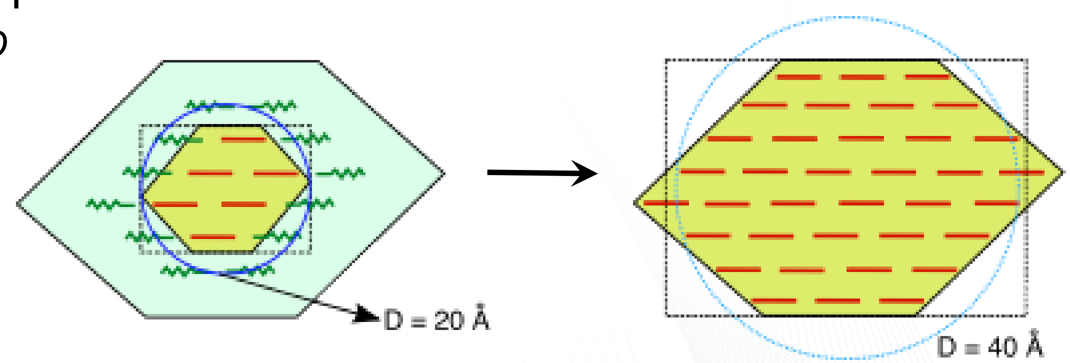
# Dilute Acid Pretreatment of Switchgrass

SANS of Switchgrass in $D_2O$



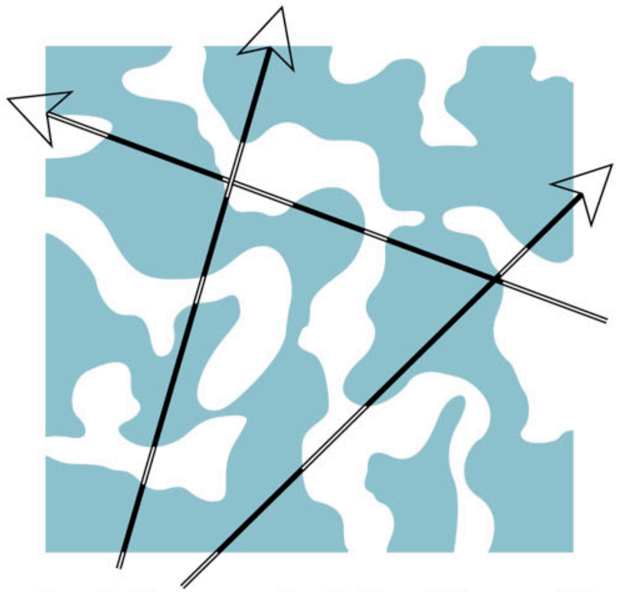




Elementary Cellulose Fibril
Cross-sectional View

Pingali, et al., Biomacromolecules **11**: 2329-2335 (2010).

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

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

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

ORNL-DWG 92M-9485

# SAS Summary

- SAS probes length scales from 1nm to 100nm
- SAS does not see atoms, but larger, interesting features over many length scales
- SAS is similar to diffraction but does not require crystals
- SAS applications are only limited by imagination
- SAS can be used alone, but often complementary to other methods, such as microscopy, NMR
- SAS data analysis is application dependent, using a diverse set of approximations, models and software

# Further Reading


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

  ***The classical work on SAS. The book focuses on x-rays, but the theory and data interpretation also applies to SANS.***

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

  ***This book covers the basic scientific principles of SAS thoroughly and is suitable for the non-expert.***

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

  ***A comprehensive description of neutron scattering, particularly SANS, that is focused on polymers. It is very useful for anyone interested in SANS.***

- **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 SAS data.***

- **Urban, V. S., 2012. Small-Angle Neutron Scattering. In: *Characterization of Materials*, edited by Elton N. Kaufmann. Copyright 2012 John Wiley & Sons, Inc.**

  ***A concise introduction to theory and practical considerations of SANS.***