Small-angle Scattering in Materials Science

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- SAXS (SANS, LS) use
- SAXS Instrumentation
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  - USAXS (Bonse-Hart), Kratky cameras, capabilities, examples
- Theory and basic methods
  - Basic theory
  - Unified fit approach
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- Software
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  - Analysis
- Applications examples

What is "Materials Science"?

- Materials science is the interface between :
  - "Basic" Science (physics, chemistry, ….)
  - Engineering applications (how do make this into the product)
    - ***Develops & studies complex, multiscale, engineering materials***
- Typically done in academia, national labs, government institutes, and less in industry (US state of affairs)
- Typically relatively shorter cycles (at most few years, not decades) but much longer than industry cycles (weeks/months)
- Suitable for application of synchrotrons (access time is months)
- Develops relations models (even "Edisonian way" = aka: trial and error) which can be applied in engineering
- Builds on "basic" science results
- Synergetic and complex – crosses boundaries among all fields, interdisciplinary, usually is justification : "WHY DO YOU DO IT?" & "WHAT IS THIS GOOD FOR?"
- Seems to get funding reasonably well in the US (DOE< NSF). Easier to justify, more financially efficient (in our lifetime), often more satisfying.
- Primary purpose of National Laboratory System (ANL, LLNL, ORNL,…) in the US.

Why small-angle scattering?

Premier method for size characterization of nano- to micro-scale density inhomogeneities

- Applicable to wide variety of technologically important materials
- Easy experiment, harder analysis
- Sample in transmission, $t=1/\mu$
- Monochromatic radiation ($\Delta\lambda/\lambda$ up to 25% is acceptable, common in SANS)

Why use small-angle x-ray scattering?

- Complement microscopy, diffraction, NMR, spectroscopy techniques.
- Statistical description of structure is needed, mean particle size, size distribution (polydispersity), etc.
- Quantitative (if done correctly) measure of volume of scatterers, surface areas…
- Statistically representative (quantification) of structural features
- In situ measurements are needed. Especially for biological and chemical systems, stop-flow or flow through experiments, processing studies, deformation studies etc.
- Pump-probe experiments at big synchrotrons can get down to ~100 fs time resolutions.
- Disordered structures and transitions between disorder and order, i.e. folding processes, aggregation, polymer chain structure.
- Measure thermodynamics, interaction parameter, critical phenomena.
- Quantify nanoscale orientation.

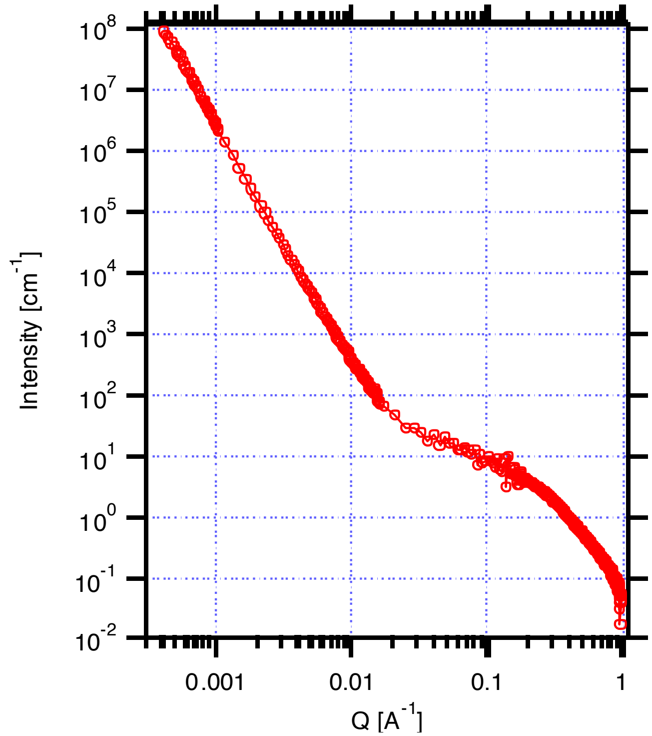
Few warnings for future small-angle scatterers

- Know your material
  - SAS will not uniquely solve microstructure – *SAS should complement other methods*
  - It is nearly impossible to get really useful data without microstructure model
  - Indirect measure of size, amount, or shape
- Know what to expect
  - Scattering signal strength
  - Size range of interest
  - Appropriate technique needed (is it anisotropic?)
  - Sample transmission $t = 1/\mu$ ***(Easy to calculate!)***
- Select appropriate "probe"
  - X-rays (tube-based or synchrotron-based)
    - *know energy needed (~7keV – 100 keV available)*
  - Neutrons (Monochromatic radiation - $\Delta\lambda/\lambda$ up to 25% is acceptable)
  - Light
- Easy experiment, harder analysis

The more you know the more you can learn.

What can be learned from a Small-Angle Scattering Experiment?

- Size of scatterer
- Amount of scatterers
- Polydispersity
- Distribution of scatterers
- Shape of scatterers
- Morphology of scatterers
- Composition of scatterers



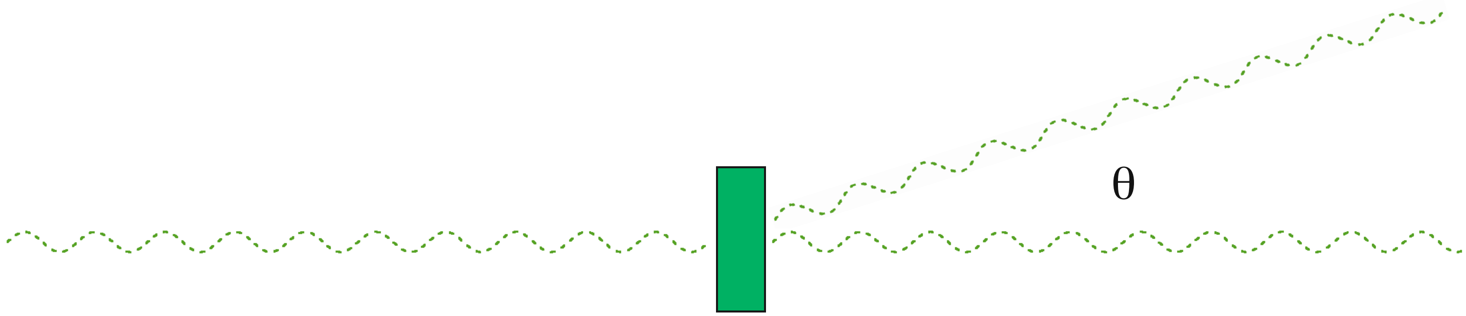
•There is *strong* dependence between some of these terms.
•SAS experiments, *complemented by other measurements*, can yield rich information about the microstructure.

Need for complementary methods

The richness of an integrated approach to materials characterization is dependent on the availability of complementary methods.

The more you know
the more you can learn.

Nanostructure from Small Angle X-ray Scattering

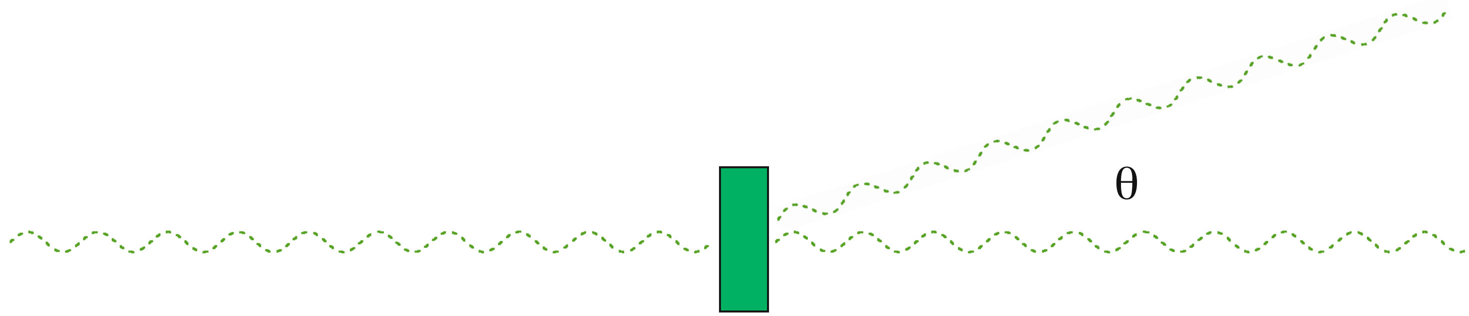


3-Techinques are similar
SALS/LS, SANS, SAXS

λ = 0.5 μm	λ = 0.01 – 2 nm
For light	For x-ray/neutron

Contrast: index of refraction, electron density, neutron cross section

Time Resolution (at APS/ESRF)



Time Resolution using detector speed : 10 ms (Synchrotron Facility, X-ray flux not limit, may be pink beam)

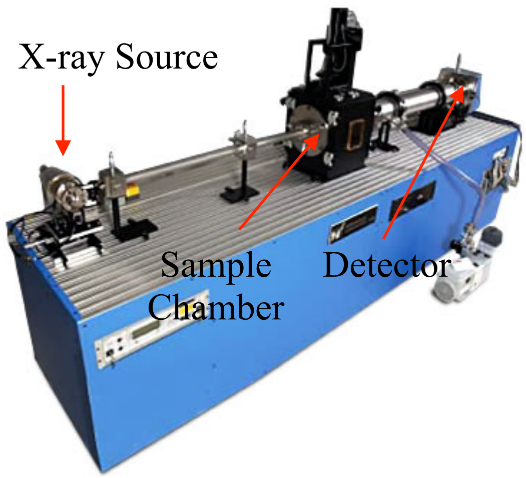
For Flow Through Experiment (Flame/Liquid/Gas Flow) can be 10 μs (using flow reaction cell)

Using bunch pattern with pump-probe (laser) method: ~100 ps time resolution, better with current/future development

Size Resolution 1 Å to 1 μm

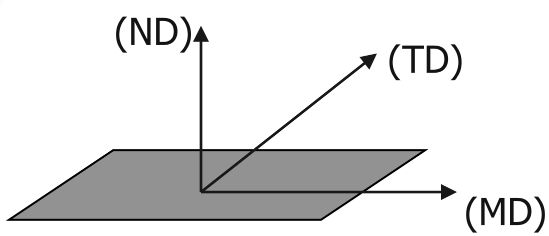
Instrumentation

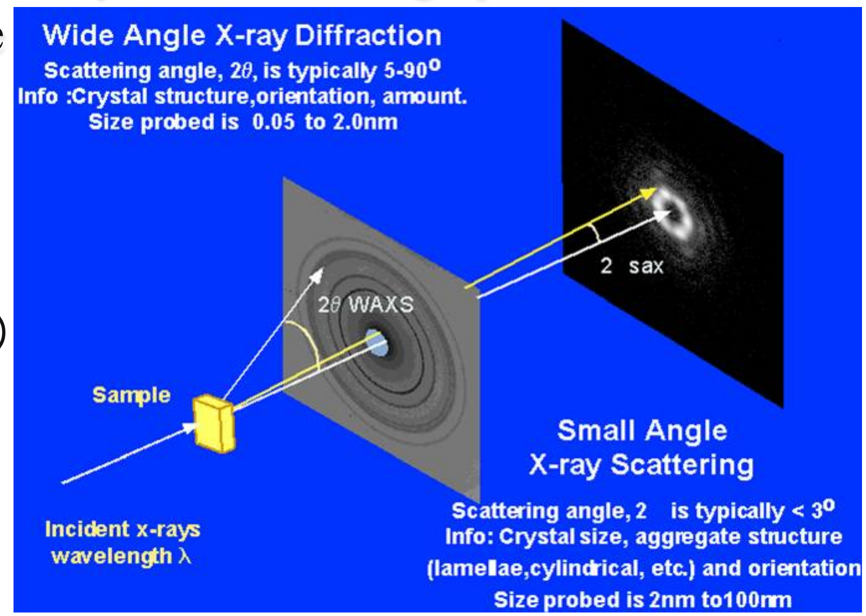
Small- and Wide-Angle X-ray Scattering Measurements



<u>SAXS</u> : pinhole camera : 2-d detector at 1m from the sample

<u>WAXS</u> : pinhole geometry camera : image plate detector at 5cm from the sample

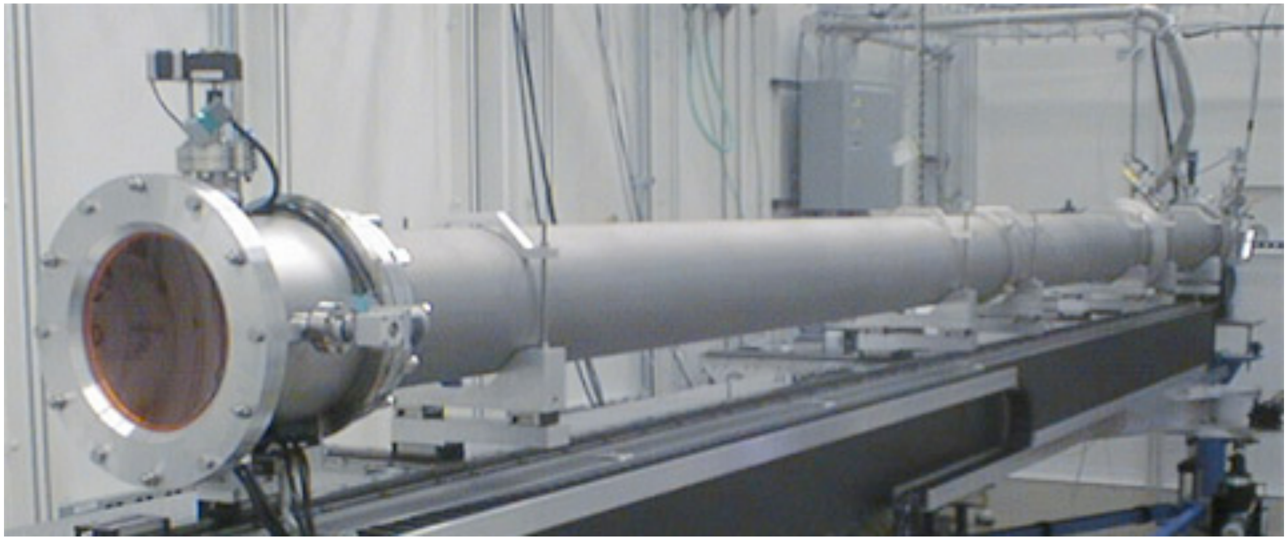


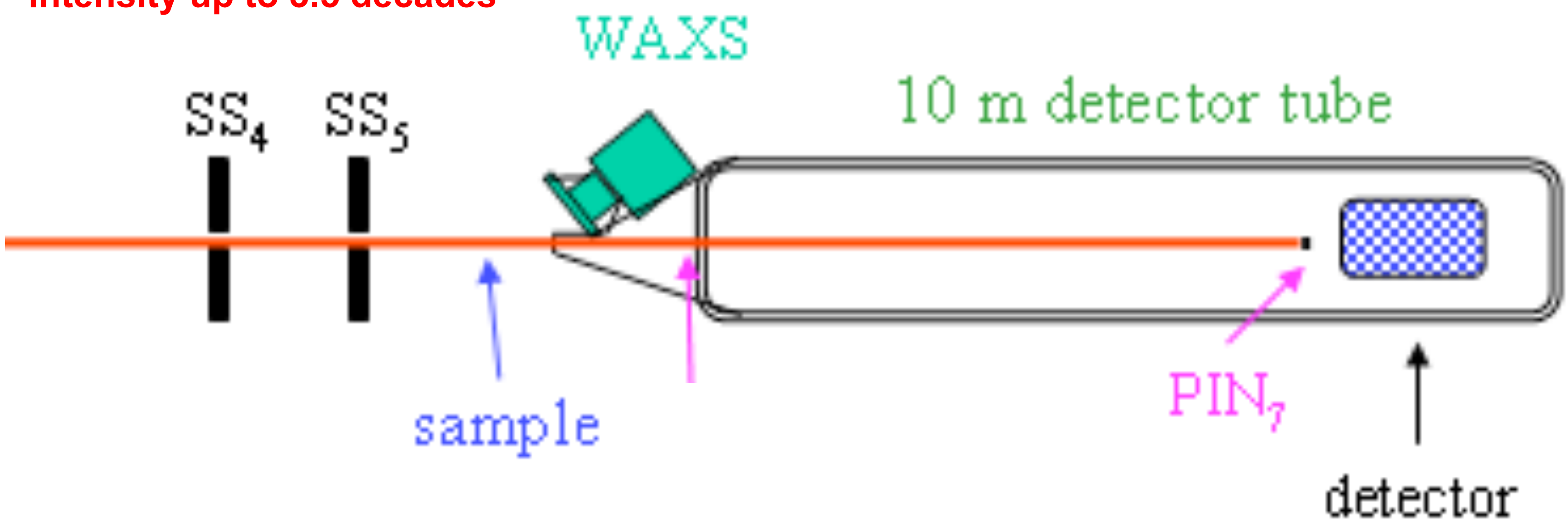


- 2D measurements are useful in determining both size and relative orientation of various structural components

Typical(?) synchrotron SAXS instrument = pinhole camera

- Typically 10 – 35 keV
- High flux, small beam (200 micron x 200 micron)
- Fast data collection (<1sec standard, 30Hz common, 100 Hz possible?)
- High sensitivity (very dilute systems)
- **Q range coverage up to 2 decades**
- **Intensity up to 3.5 decades**



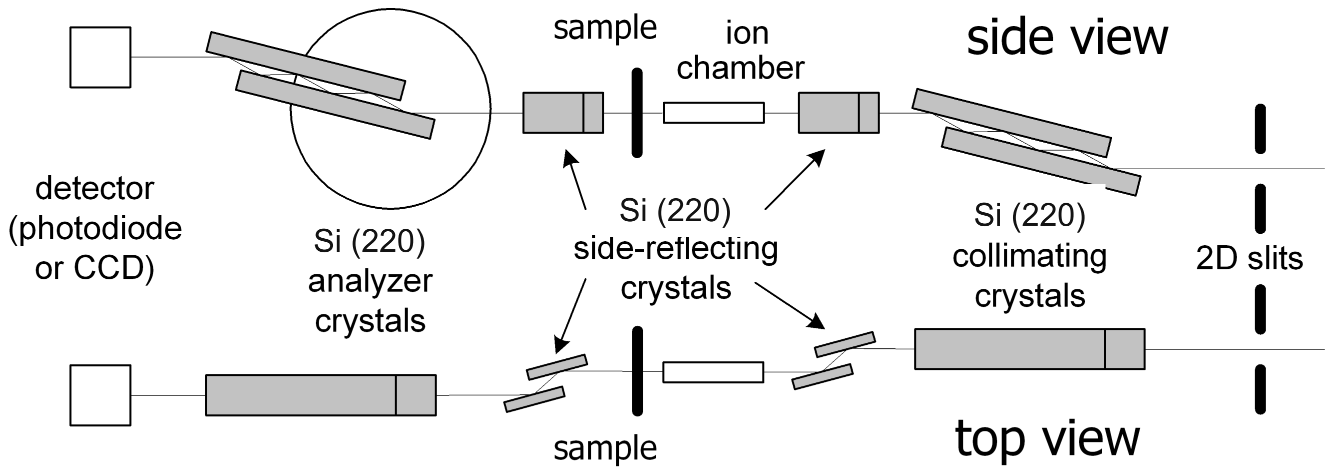


Alternative Geometries Offer Improvement in Flux or Improvement in Angular Resolution with Smearing of Scattering Pattern

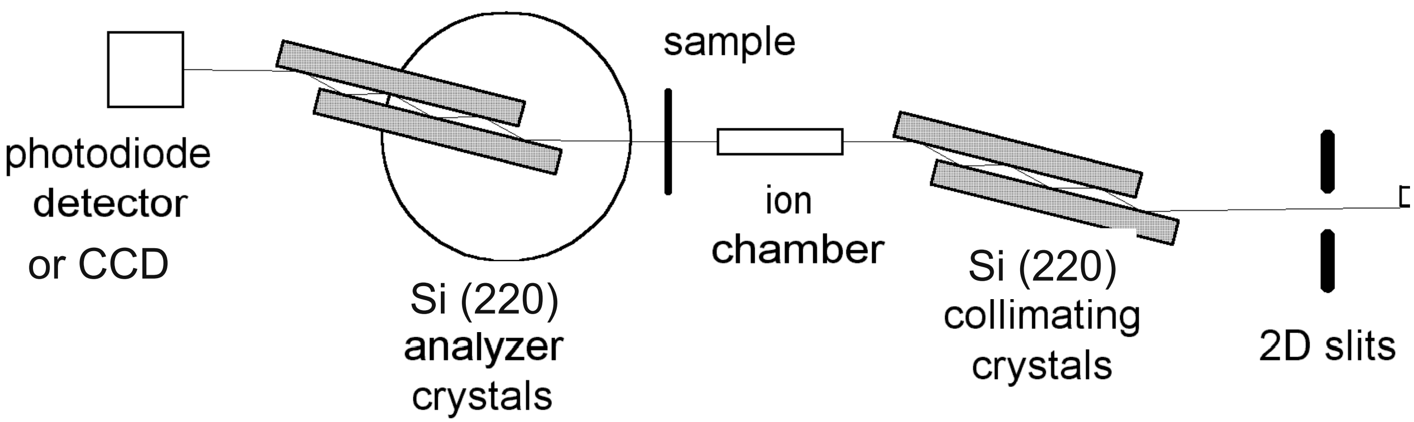
USAXS instrument (Bonse-Hart camera)

- Unique instruments (two available – APS & ESRF).
- My is APS 15ID beamline
- Currently unique intensity and Q range:
  - Up to 9 decades of intensity range
  - 0.00015 A^{-1} to 1 A^{-1} Q range (0.5 nm ----> >1 micron)
  - Both 1-D (slit smeared) and 2-D collimated (“2D-USAXS”) geometries available
  - 10 min/scan (shortest scans down to 3 minutes)
  - Flexible beam size (1 x 2 mm ---> 0.02 x 0.2 mm)
- Measurement methods:
  - At fixed sample orientation – Intensity vs Q (1D and 2D collimated)
  - At fixed Q vector – Intensity vs sample orientation (2D collimated)
  - USAXS-XPCS for slow materials dynamics
  - USAXS-Imaging (imaging materials at various q vectors)

2-D collimated Bonse-Hart Camera



1-D collimated Bonse-Hart Camera (slit smeared)

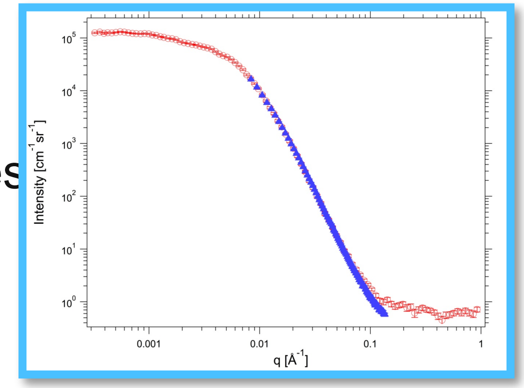


Ultra-Small Angle X-ray Scattering (USAXS)

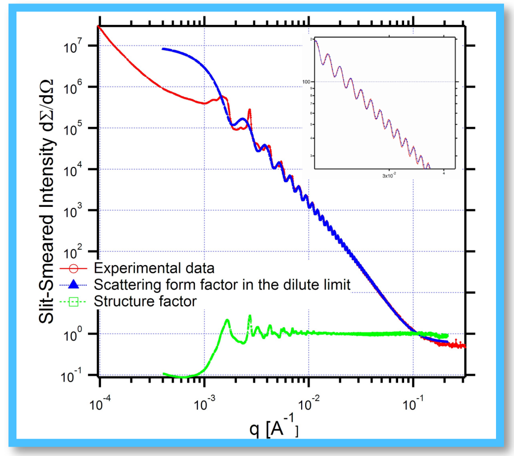
Compared with pinhole SAXS, USAXS offers:

- Wider range of scattering vectors (≈ 1 ×10^{-4} $Å^{-1}$ to ≈ 1 $Å^{-1}$)
- Better angular resolution (≈ 1 ×10^{-4} $Å^{-1}$). Scattering features are better resolved.
- Absolute calibration of scattering intensity: scattering volume is readily quantified.
- Measurements of equilibrium and non-equilibrum dynamics with recently-developed USAXS X-ray Photon Correlation Spectroscopy.
- Some degree of measurement for anisotropic scattering samples.
- A worse time-resolution. Not suitable for study of fast kinetics.
- Radiation damage can be avoided for most soft materials when operating with care.

Wider Q Range

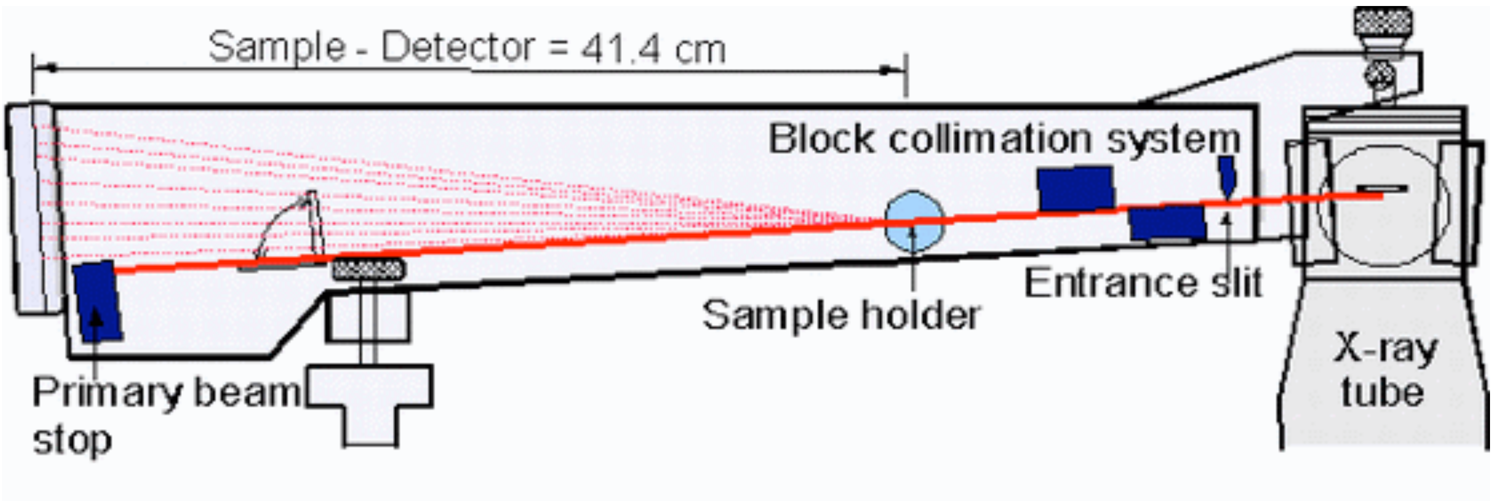


High Q Resolution



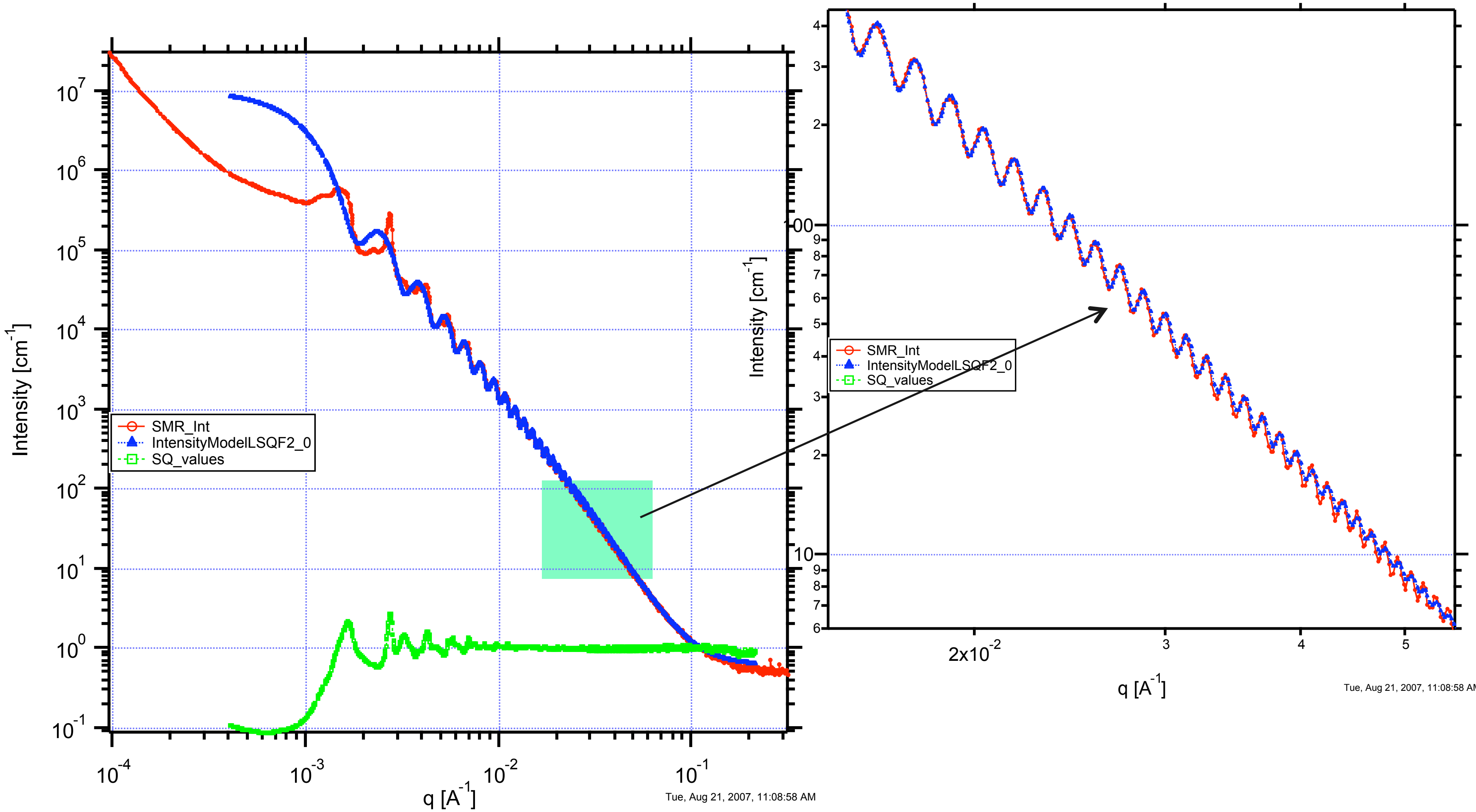
Kratky camera

Commercially available, e.g. http://www.hecus.at/

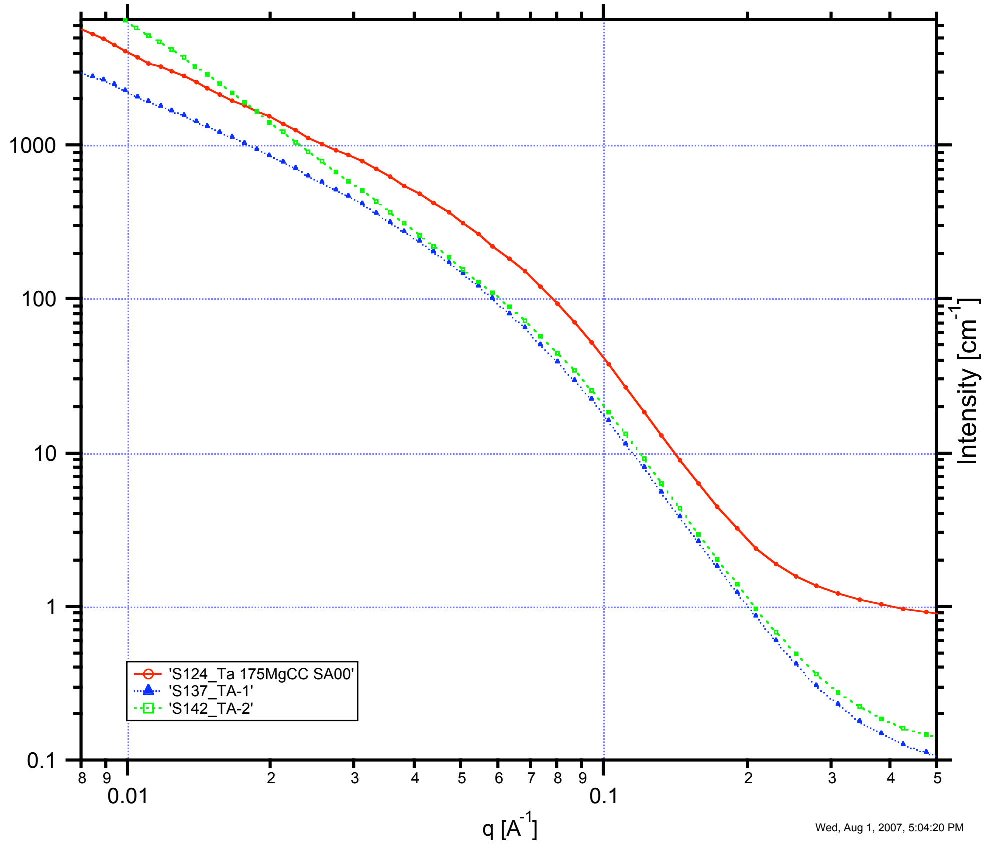


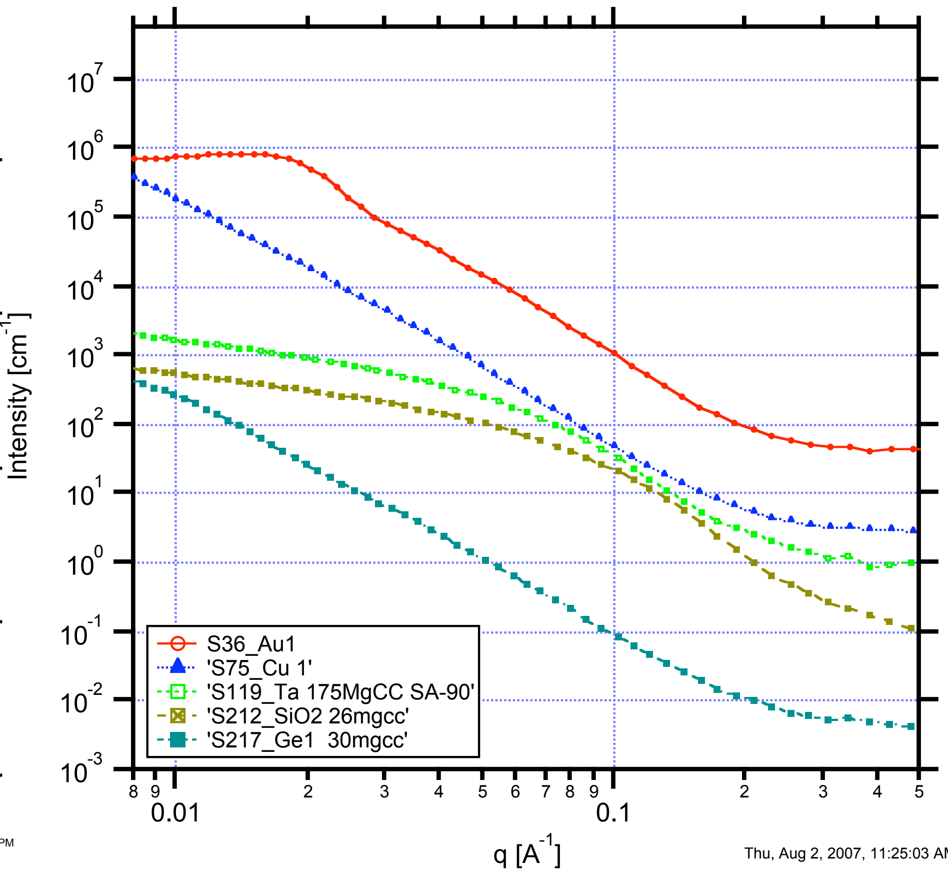
www.chemie.uni-bayreuth.de/pci/de/forschung/22427/saxs1.gif

Real World materials – mono sized distribution of spheres, powder



Instrument q range selection:
Aerogels - this is what pinhole camera is likely going to look like:





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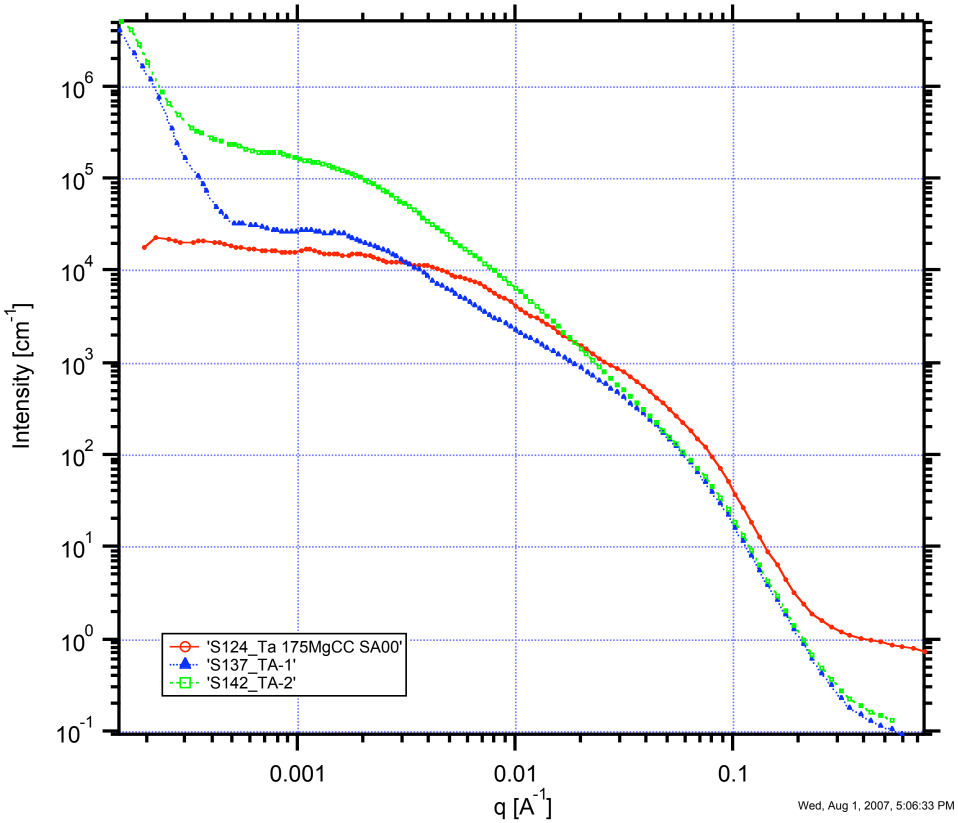
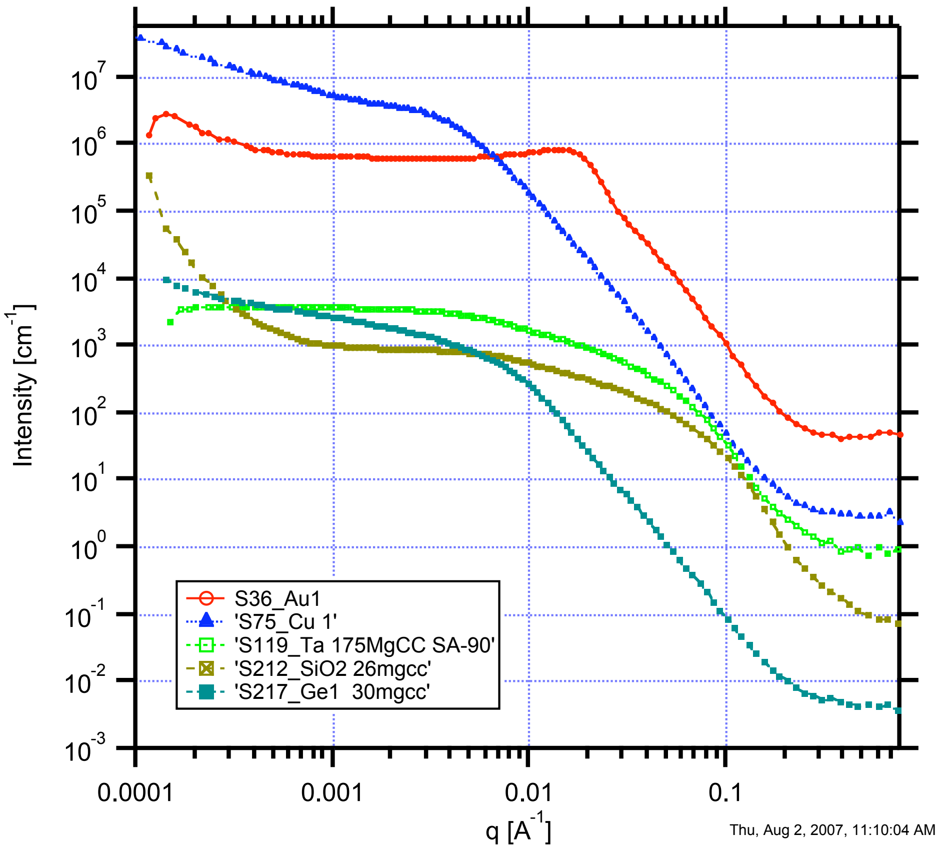
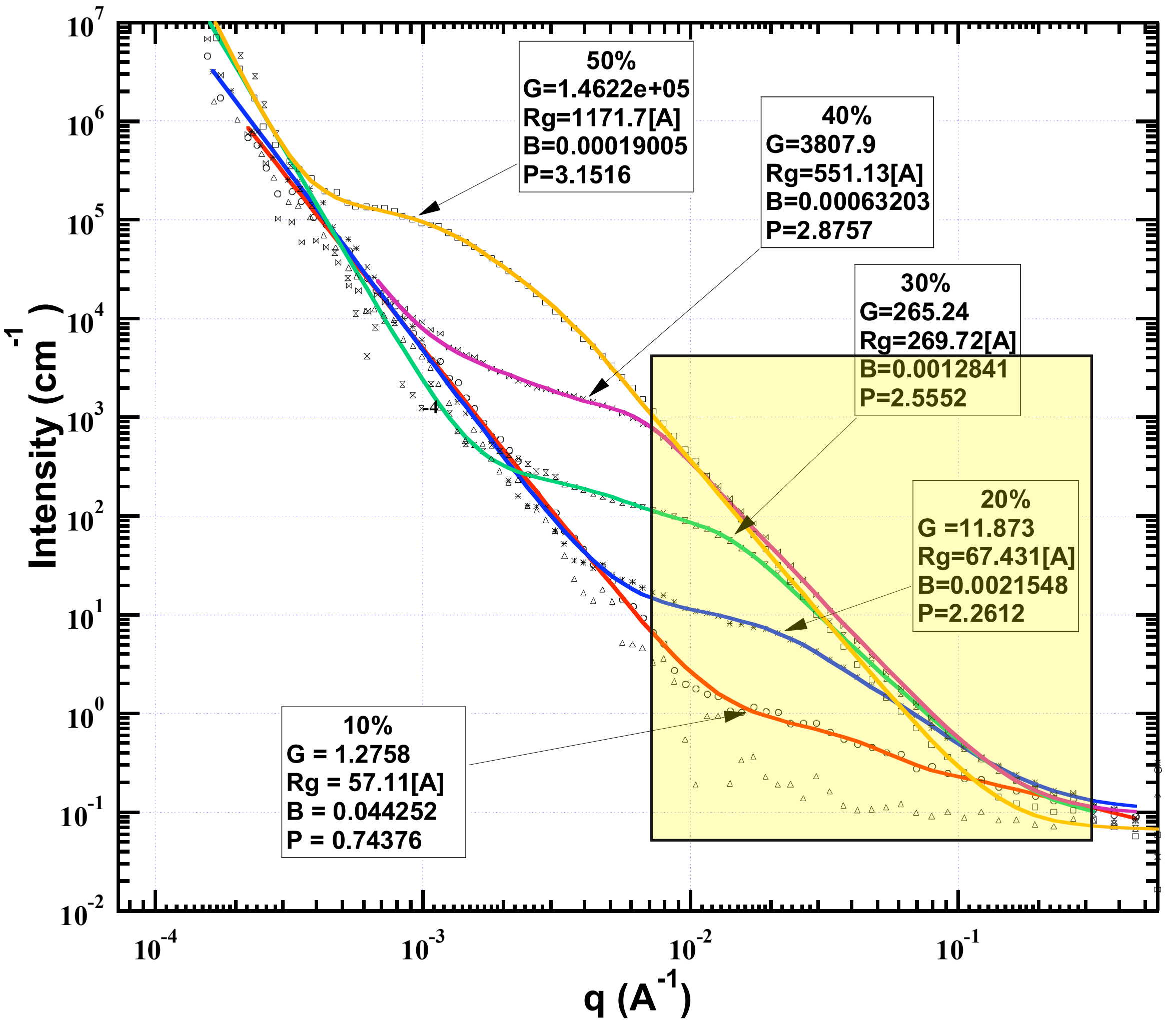
Aerogels - this is how USAXS data look like:





Example of small angle scattering from Ta aerogels. Slit smeared data left graph, same data desmeared right graph. Aerogels are unique materials with very low density which are considered for many applications in aerospace industry. Graphs from work by Ted Baumann, Joe Satcher, Trevor Willey, and Tony Van Buuren, LLNL.

Liquid crystals dispersed in polymers



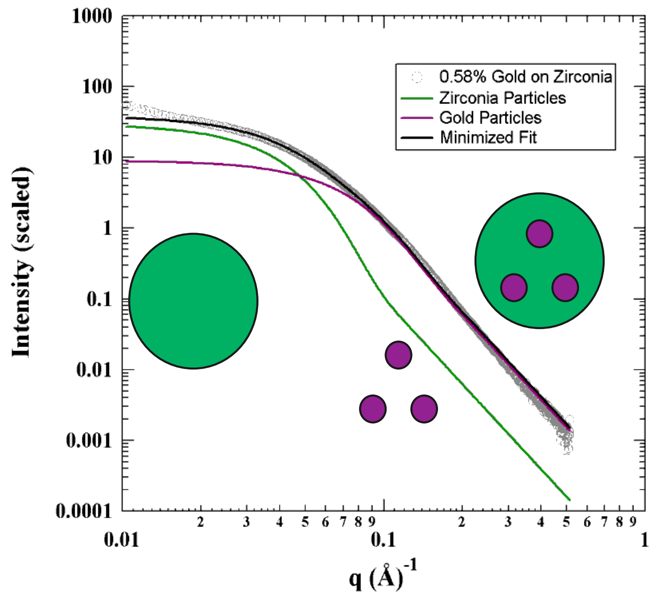
USAXS data from Polymer-dispersed liquid crystals. The loading of liquid crystals in polymer changes the structure over wide size range accessible only by USAXS. Polymer-dispersed liquid crystals (PDLCs) are of technological importance for electro-optic applications such as privacy windows, electro-optic shutters, and large area flat-panel displays. Graph from current work by Ryan S. Justice, Dale Schaefer, Richard Vaia, David Tomlin, and Timothy Bunning, "*Interface morphology and phase separationin polymer-dispersed liquid crystal composites*", accepted to *Polymer*. Authors are from University of Cincinnati, Air Force research Lab, and UES Incorporated.

Yellow box is estimate of pinhole camera range

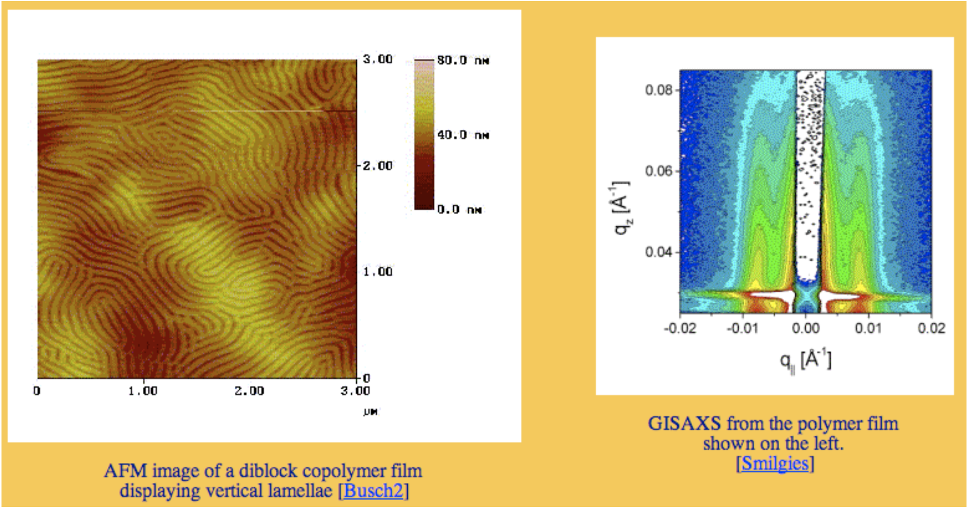
2-Closely related Techniques:

ASAXS- Anomalous x-ray scattering, vary wavelength leads to change in contrast due to the complex absorption spectra, requires synchrotron source.

GISAXS- Promise of high resolution spectra for surface structures but there are technical issues with data interpretation.



Chopra S, Beaucage G, in preparation



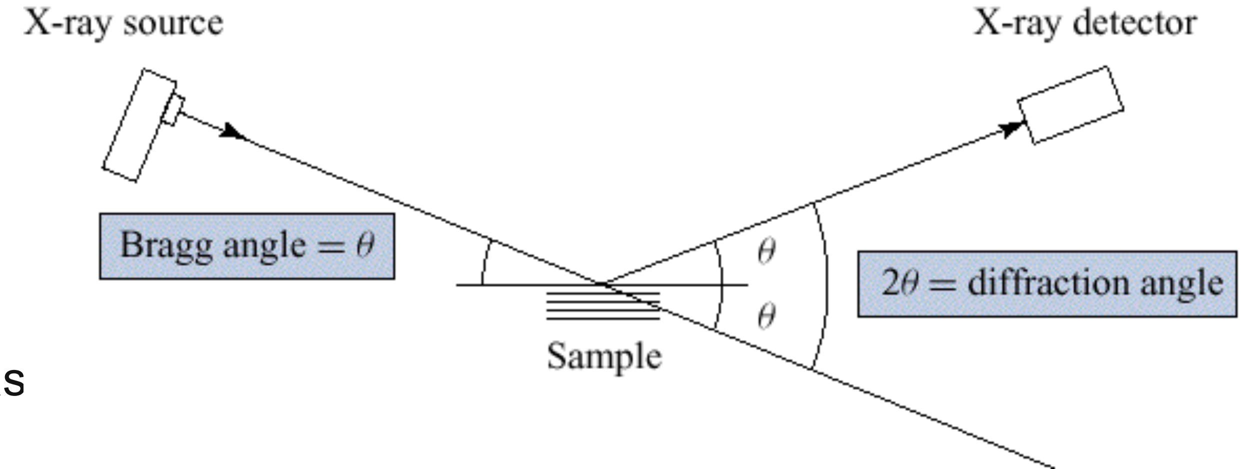
AFM image of a diblock copolymer film displaying vertical lamellae [Busch2]

http://staff.chess.cornell.edu/~smilgies/gisaxs/GISAXS.php

Theory & Analysis

Instruments / theory

- SANS instruments
- Pinhole SAXS cameras
- USAXS
- Other geometries (Kratky…)



$$q = 4\pi \frac{\sin(\theta)}{\lambda}$$

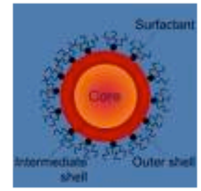
$$d = \frac{2\pi}{q}$$

Q [A^{-1}]	D [nm]
1	0.6
0.1	6
0.01	60
0.001	600
0.0002	3000 (3 um)

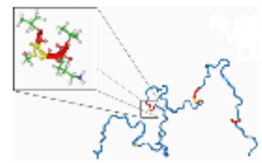
Detector dynamic range is important – Intensity ~ q^4

Four Methods of SAXS Modeling

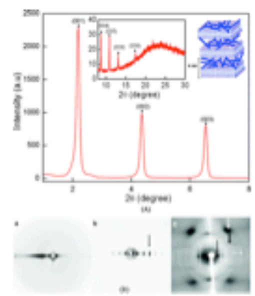
1) Calculate the amplitude for specific structures.
Viable for simple structures, spheres, rods, core/shell models
Intensity for some cases Gaussian coil.



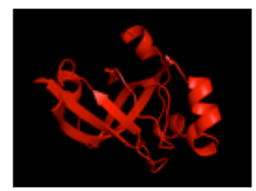
2) Develop general laws for scattering.
Viable for all structures, analysis depends on specific models. Most useful for systems with low degrees of structural regularity (unfolded states or aggregates).



3) Calculate the pair distance distribution function PDDF from the scattered intensity. Analyze the PDDF using models and general rules.
Viable when a wide range of scattering vector, q, is available or valid extrapolations can be made to high and low q. A direct link between calculated structural features and the observed features in the data is lost.



4) Calculate the PDDF using structural models (spheres).
Use an inverse Fourier transform to calculate the scattered intensity and a least-squares or other method to iterate the model parameters for a best fit.
Most useful for systems with a high degree of structural regularity (native state).



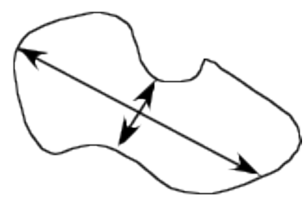
Debye Function

$$I(q) = \langle F^2(q) \rangle = V\rho_e^2 \int_0^\infty \gamma_0(r) \frac{\sin qr}{qr} 4\pi r^2 dr$$

Assumptions:

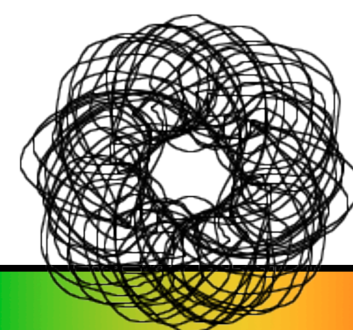
1) Centro-symmetric Particle

$$e^{-i\bar{q}\bullet OM_k} = \cos(\bar{q} \bullet OM_k)$$



2) Random Orientation (translational & rotational symmetry)

$$\langle \cos(\bar{q} \bullet \bar{r}) \rangle = \frac{\sin qr}{qr}$$



Debye Function

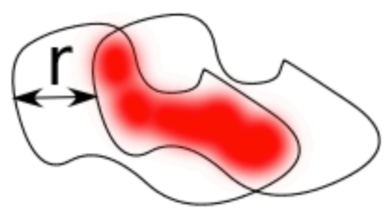
$$I(q) = \langle F^2(q) \rangle = V\rho_e^2 \int_0^\infty \gamma_0(r) \frac{\sin qr}{qr} 4\pi r^2 dr$$

ρ_e Electron Density

$\gamma_0(r)$ Characteristic Function, Correlation Function

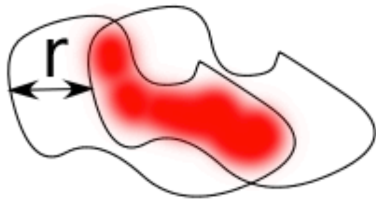
Probability that at a distance "r" from a point in a particle another particle can be found

$$\gamma_0(r) = \frac{\langle V(r) \rangle}{V}$$



Average for translation and rotation

Debye Function



$$I(q) = \langle F^2(q) \rangle = V\rho_e^2 \int_0^\infty \gamma_0(r) \frac{\sin qr}{qr} 4\pi r^2 dr$$

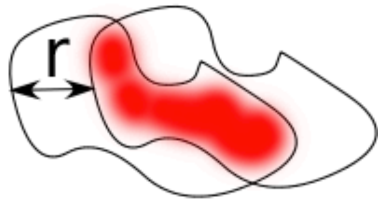
$\gamma_0(r)$ Characteristic Function, Correlation Function

For simple objects such as a sphere we can calculate the characteristic function

$$\overline{V}(r) = \frac{\pi}{12}(2R - r)^2(4R + r)$$

$$\gamma_0(r) = \frac{\overline{V}(r)}{V} = 1 - \frac{3r}{4R} + \frac{1}{16}\left(\frac{r}{R}\right)^3$$

Debye Function



$$I(q) = \langle F^2(q) \rangle = V\rho_e^2 \int_0^\infty \gamma_0(r) \frac{\sin qr}{qr} 4\pi r^2 dr$$

$\gamma_0(r)$ Characteristic Function, Correlation Function

For simple objects such as a sphere we can calculate the characteristic function

$$\gamma_0(r) = \frac{\bar{V}(r)}{V} = 1 - \frac{3r}{4R} + \frac{1}{16}\left(\frac{r}{R}\right)^3$$

$$I(q) = Nn_e^2 \left(3\frac{\sin qR - qR\cos qR}{(qR)^3} \right)^2$$

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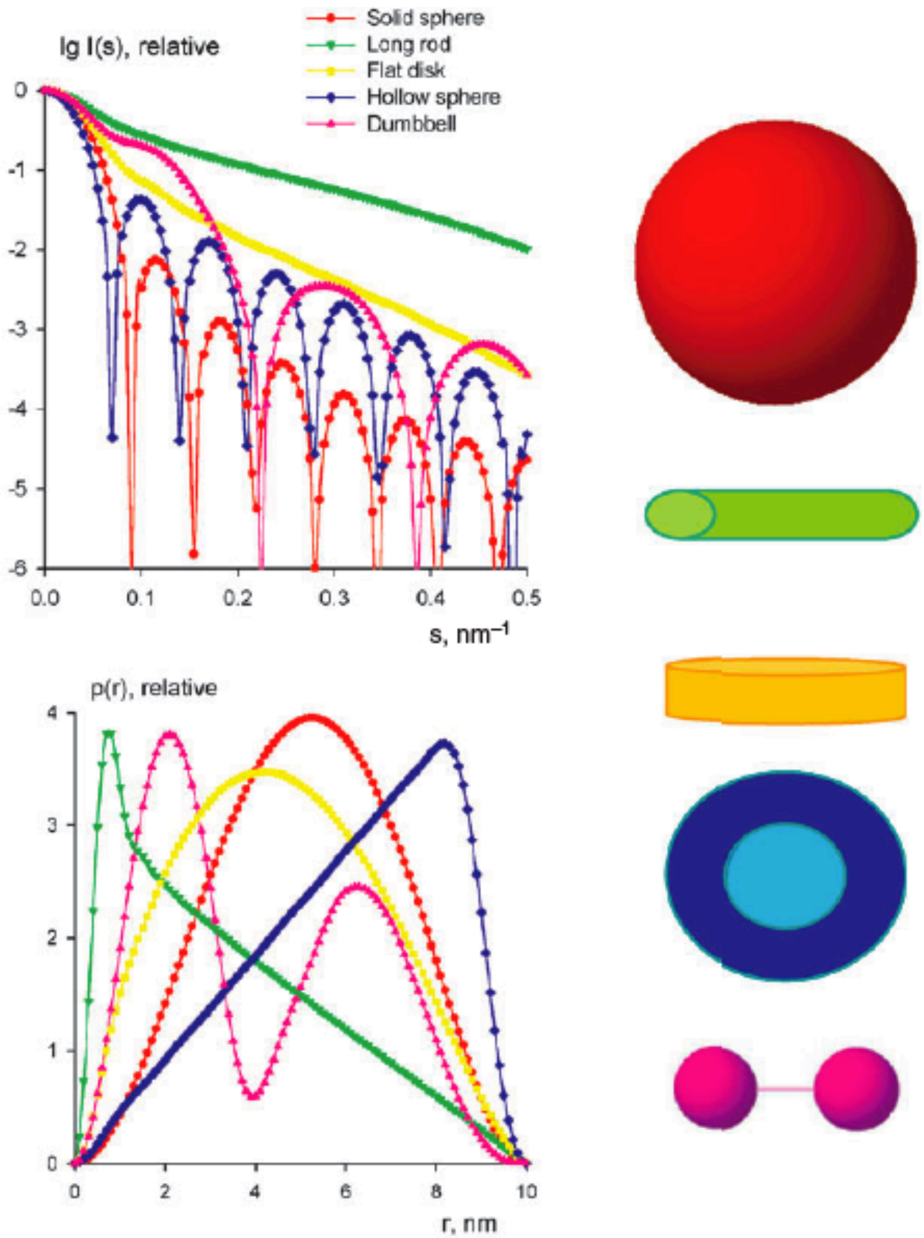


Figure 5. Scattering intensities and distance distribution functions of geometrical bodies.

Svergun DI, Koch MHJ *Rep. Prog. Phys.* **66** 1735-1782 (2003)

Other direct calculations are possible for simple objects $I(q) = Nn_e^2 F^2(q) S(q)$

Sphere

$$F_{sphere}(q) = 3\frac{\sin qR - qR\cos qR}{(qR)^3}$$

Rod

$$F^2(q) = 2\frac{Si(qL)}{qL} - 4\frac{\sin^2(qL/2)}{(qL)^2}$$

Disk

$$F^2(q) = \frac{2}{q^2R^2}\left[1 - \frac{J_1(2qR)}{qR}\right]$$

Core and Shell Sphere

$$F_{Core\&Shell}(q) = \frac{\left(V_{Shell}(\rho_{Shell} - \rho_{Solvent})F_{Sphere}(R_{Shell}) - V_{Core}(\rho_{Shell} - \rho_{Core})F_{Sphere}(R_{Core})\right)}{(V_{Core} - V_{Shell})}$$

Gaussian Polymer Chain

$$F^2(q) = 2\frac{\exp\left(-q^2R_g^2\right) + q^2R_g^2 - 1}{\left(q^2R_g^2\right)^2}$$

Core and Shell with Gaussian Chain Attached

...

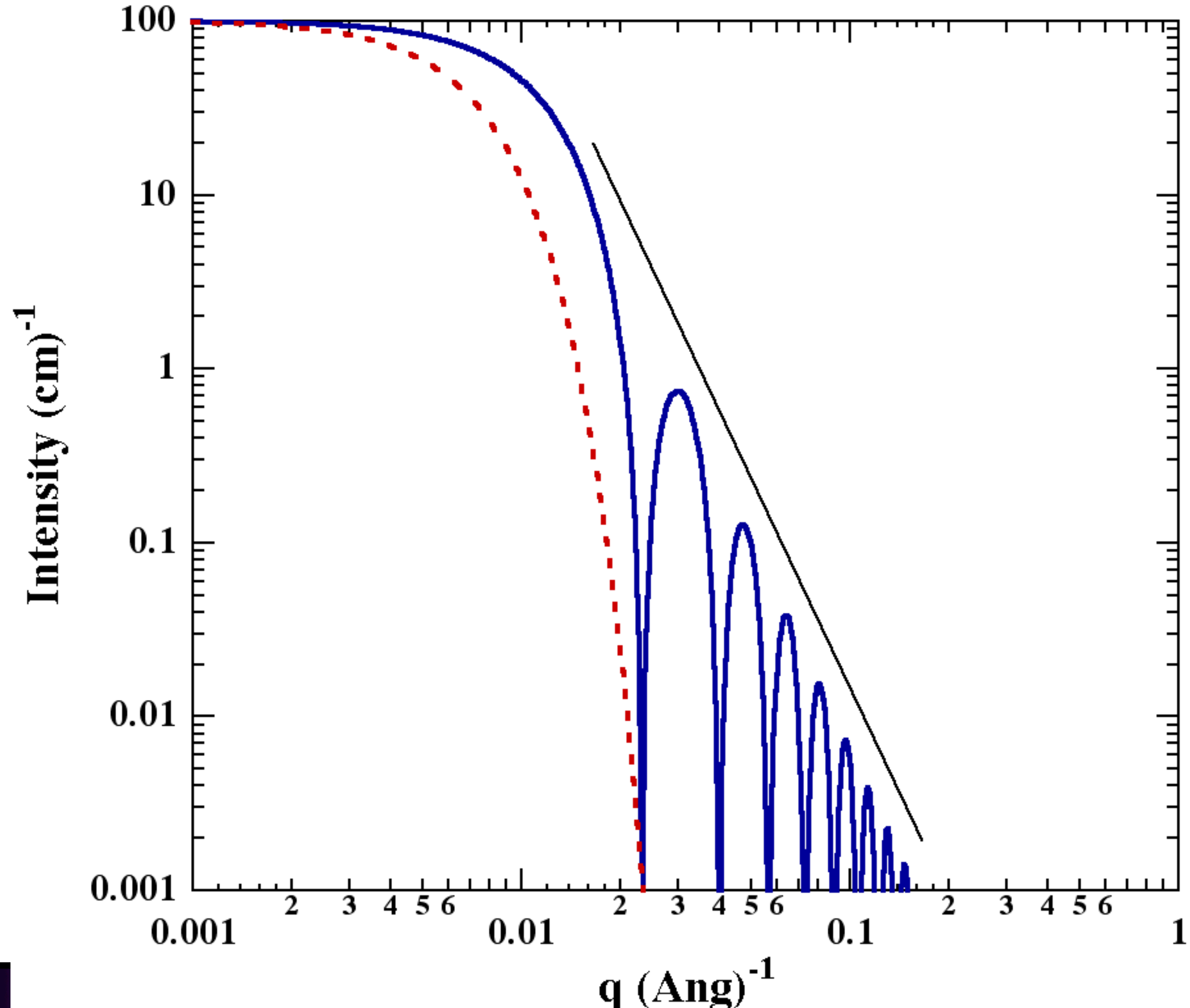
Pedersen JS, *Chapter 16 in Neutrons, X-rays and Light: Scattering Methods Applied to Soft Condensed Matter,* Linder P, Zemb Th editors North Holland Press (2002).

Scattering Function for Monodisperse Spheres

Rayleigh, 1914

$$I(q) = 9G\left[\frac{\sin qR - qR\cos qR}{(qR)^3}\right]^2$$

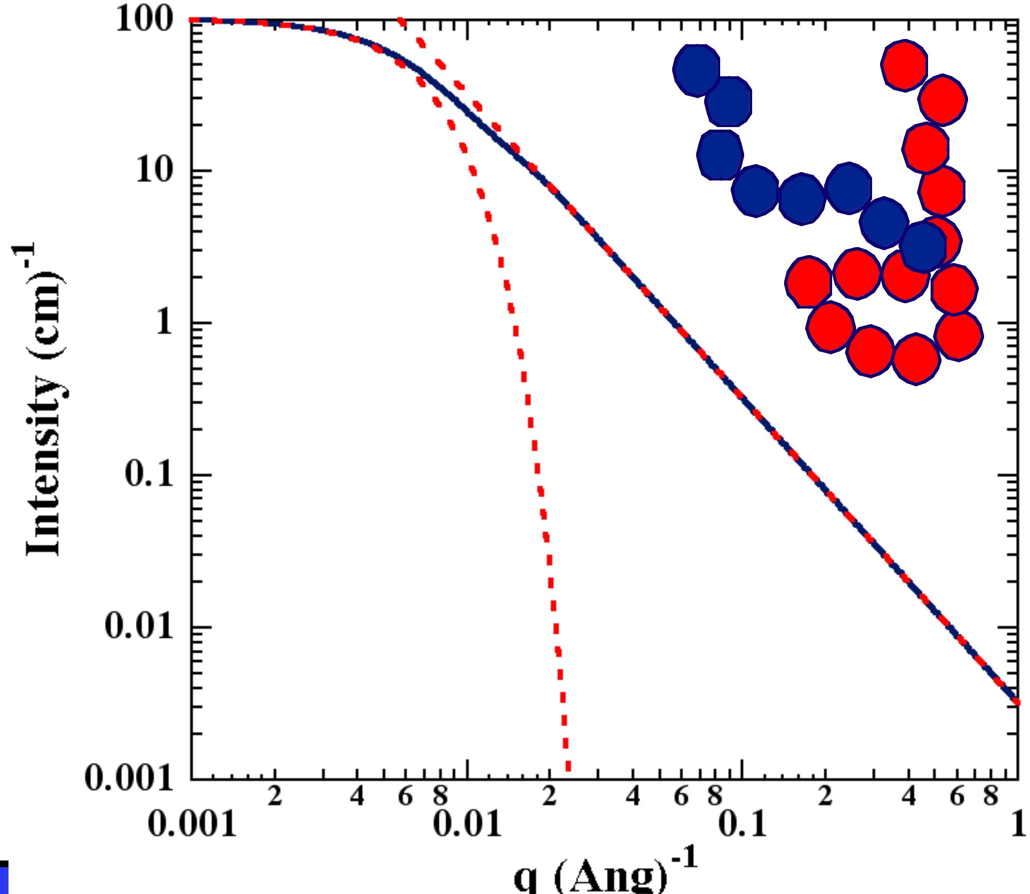
$G = Nn_e^2$



The Debye (1947) Scattering Function for a Polymer Coil

$$I(Q) = \frac{2}{Q^2}\left(Q - 1 + \exp(-Q)\right)$$

$$Q = q^2 R_g^2$$



Basic measures from a Small-Angle Scattering experiment

Guinier law $$\lim_{Q \to 0} I(Q) = I(0) \exp\left(-\frac{1}{3} R_G^2 Q^2\right)$$

$$Q_{\max} R_G < 1.2$$

Porod law $$\lim_{Q \to \infty} I(Q) = 2\pi S_V \left|\Delta\rho\right|^2 Q^{-4}$$

$$Q_{\min} D > 3$$

invariant $$2\pi^2 V_V \left(1 - V_V\right) \left|\Delta\rho\right|^2 = \int_0^\infty Q^2 I(Q)\, dQ$$

Advantages of Quantitative SAS

- Sampling volume large compared to features investigated: *Statistically Significant Sampling*
  - *Sample volume typically 10^{-12} - 10^{-10} m^3*
  - *Scatterer size typically 10^{-9} - 10^{-6} m*
  - *10^3 - 10^{13} scatterers in a single sample volume*
- SAS probes through bulk material, not limited to surface or open porosity
- X-ray or neutron radiation sources can probe optically opaque substances
- Can separate different components in multi-component system (in some cases)
- SAS can often address anisotropy
- Local SAS can address inhomogeneites

Information Obtained from Quantitative Small-Angle Scattering

volume fraction

$$V_V = \sum_i f_i(D)\Delta D_i$$

number density

$$N_V = \sum_i \frac{f_i(D)\Delta D_i}{\left(\pi/6\right)D_i^3}$$

Radius of gyration

$$R_G = \sqrt{\langle r^8\rangle / \langle r^6\rangle}$$

specific surface

$$S_V = 6\sum_i f_i(D)\frac{\Delta D_i}{D_i}$$

mean spacing

$$\Lambda = \left(N_V\right)^{-1/3}$$

	volume-weighted	number-weighted
mean diameter	$\bar{D}_V = V_V^{-1}\left[\sum_i D_i f_i(D)\Delta D_i\right]$	$\bar{D}_N = N_V^{-1}\left[\sum_i D_i \frac{f_i(D)\Delta D_i}{\left(\pi/6\right)D_i^3}\right]$
standard deviation	$\sigma(\bar{D}_V) = \sqrt{V_V^{-1}\left[\sum_i D_i^2 f_i(D)\Delta D_i\right] - \left(\bar{D}_V\right)^2}$	$\sigma(\bar{D}_N) = \sqrt{N_V^{-1}\left[\sum_i D_i^2 \frac{f_i(D)\Delta D_i}{\left(\pi/6\right)D_i^3}\right] - \left(\bar{D}_N\right)^2}$

General Laws for Scattering

Unified Function

$$I(q) = G \exp(-q^2 R_g^2/3) + B\{[\mathrm{erf}(qR_g/6^{1/2})]^3/q\}^P$$

One Structural Level

$$\begin{aligned} I(q) \simeq\ & G \exp(-q^2 R_g^2/3) \\ & + B \exp(-q^2 R_{\mathrm{sub}}^2/3)\{[\mathrm{erf}(qR_g/6^{1/2})]^3/q\}^P \\ & + G_s \exp(-q^2 R_s^2/3) + B_s\{[\mathrm{erf}(qR_g/6^{1/2})]^3/q\}^{P_s} \end{aligned}$$

Two Structural Levels

$$\begin{aligned} I(q) \simeq \sum_{i=1}^{n} \Big(& G_i \exp(-q^2 R_{g_i}^2/3) + B_i \exp(-q^2 R_{g_{(i+1)}}^2/3) \\ & \times \{[\mathrm{erf}(qkR_{g_i}/6^{1/2})]^3/q\}^{P_i} \Big). \end{aligned}$$

"n" Structural Levels

Beaucage G *J. Appl. Cryst.* **28** 717-728 (1995).

General Laws for Scattering

Unified Function

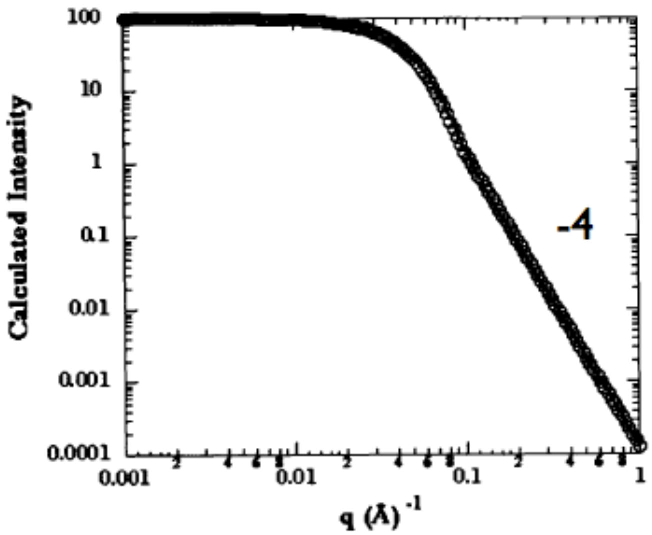


Fig. 11. Calculated scattering (○) from polydisperse spheres with Porod surfaces (power law −4). The solid line follows equation (24) with $R_g = 39.495$ Å as calculated and $P = 4$, $G = 100$ cm^{-1} (fixed in the sphere calculation) and $B = 0.000\,127\,52$ from Porod's law.

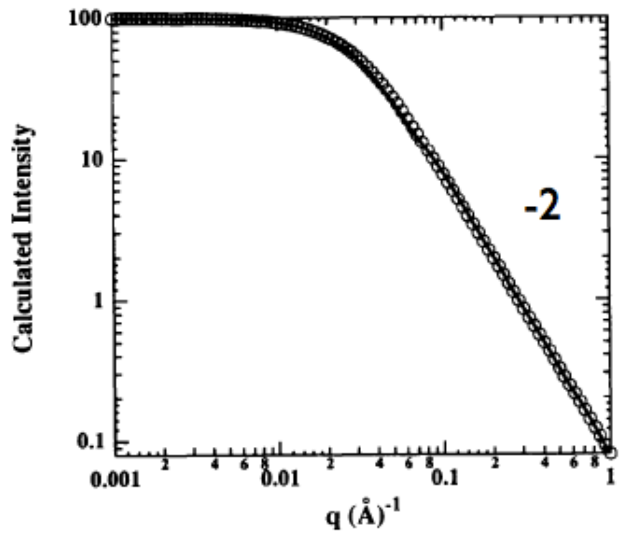


Fig. 10. Log–log plot of Debye equation (○) and equation (24) (solid line). For the Debye equation, $R_g = 50$ Å and $A = 100$ cm^{-1}. For the unified equation, (24), all parameters are fixed. $R_g = 50$ Å, $G = 100$ cm^{-1}, $P = 2$ (the Debye equation represents a mass fractal with $d_f = 2$) and $B = 0.08 = 2G/R_g^2$ from equation (30).

Beaucage G *J. Appl. Cryst.* **28** 717-728 (1995).

General Laws for Scattering

Unified Function

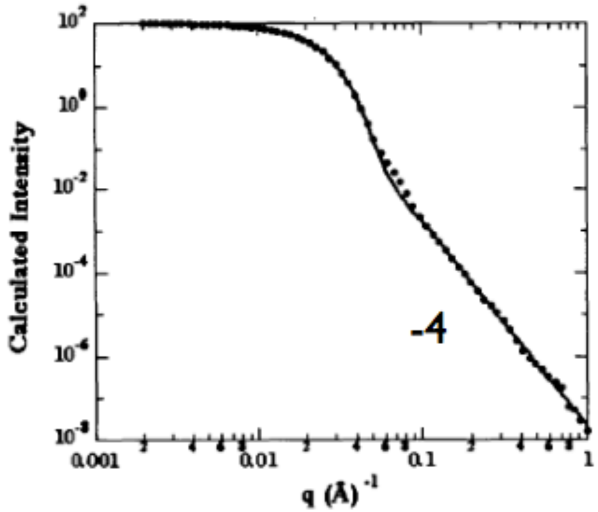


Fig. 12. Calculated scattering curve for an ellipsoid of revolution with a spherical shell of lower electron density, 0.36 of core, with major:minor axis ratio of 4:1 and minor axis of $R = 50$ Å and 60 Å for the core and shell, respectively. Equation (24) is calculated using $R_g = 87.9$, $G = 100$ cm^{-1}, $P = 4.91$ and $B = 1.99 \times 10^{-8}$. The mismatch at $q = 0.07$ Å^{-1} is due to a residual Fourier peak that has not been averaged out and that would normally not appear in experimental data for a diffuse interface.

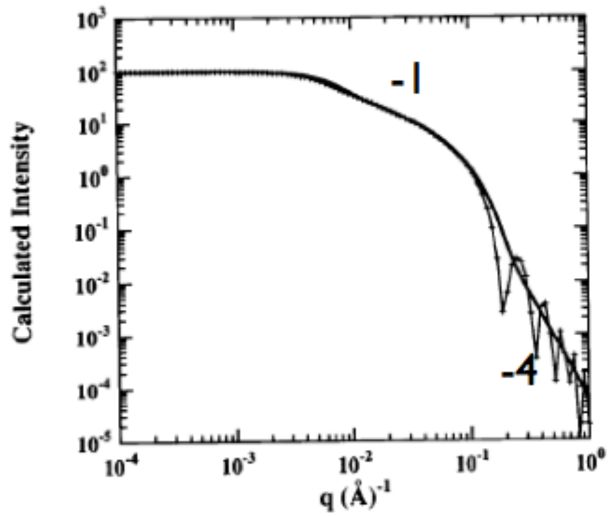


Fig. 13. Calculated scattering curve [Guinier & Fournet, 1955, p. 19, equation (33)] from randomly oriented rods of diameter 40 Å and length 800 Å (+). $I(0)$ is fixed at 100. The calculated scattering curve using equation (28) is shown by the bold line, and $G = 100$, $R_g = 231.4$ Å, $P = 1$, $B = 0.393$, $R_{sub} = R_s = 17.3$ Å, $G_s = 0.111$, $B_s = 6.25 \times 10^{-5}$ and $P_s = 4$ as discussed in the text. High-q oscillations in the + curve are due to poor averaging in the calculation.

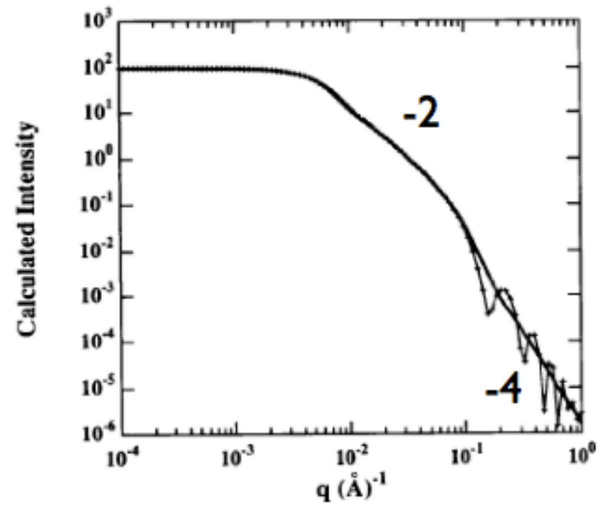
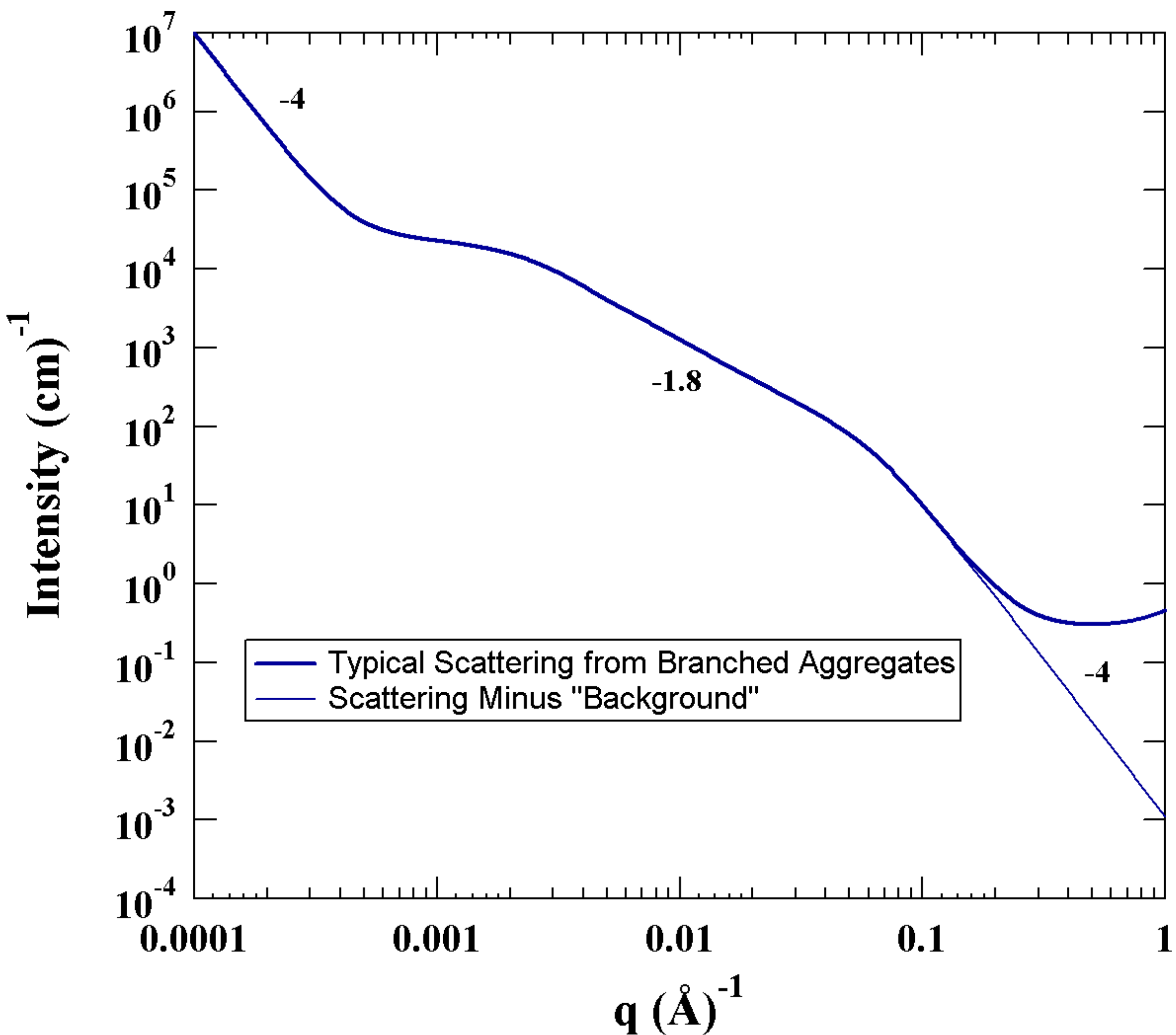


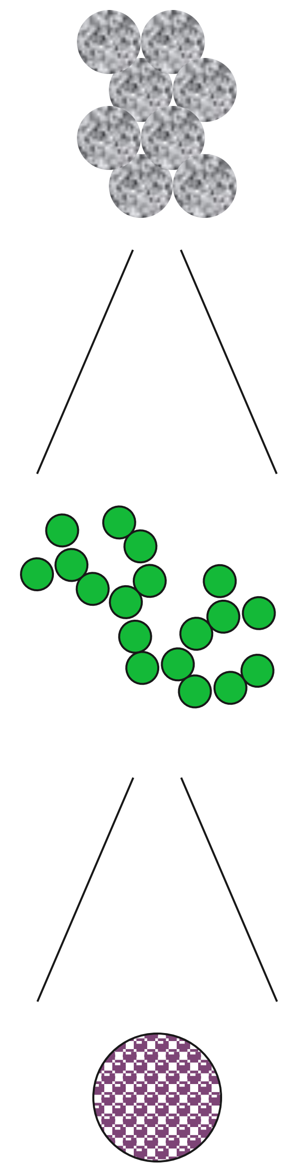
Fig. 14. Calculated scattering curve [Guinier & Fournet, 1955, p. 19, equation (33)] from randomly oriented disc-like lamellae of thickness 40 Å and diameter 800 Å (+). $I(0)$ is fixed at 100. The calculated scattering curve using equation (28) is shown by the bold line, and $G = 100$, $R_g = 283.1$ Å, $P = 2$, $B = 1.25 \times 10^{-3}$, $R_{sub} = R_s = 20$ Å, $G_s = 2.78 \times 10^{-4}$, $B_s = 1.56 \times 10^{-6}$ and $P_s = 4$ as discussed in the text. High-q oscillations in the + curve are due to poor averaging in the calculation.

Beaucage G *J. Appl. Cryst.* **28** 717-728 (1995).

Construction of a somehow complicated scattering curve (hierarchical system)

Complex Scattering Pattern (Unified Calculation)





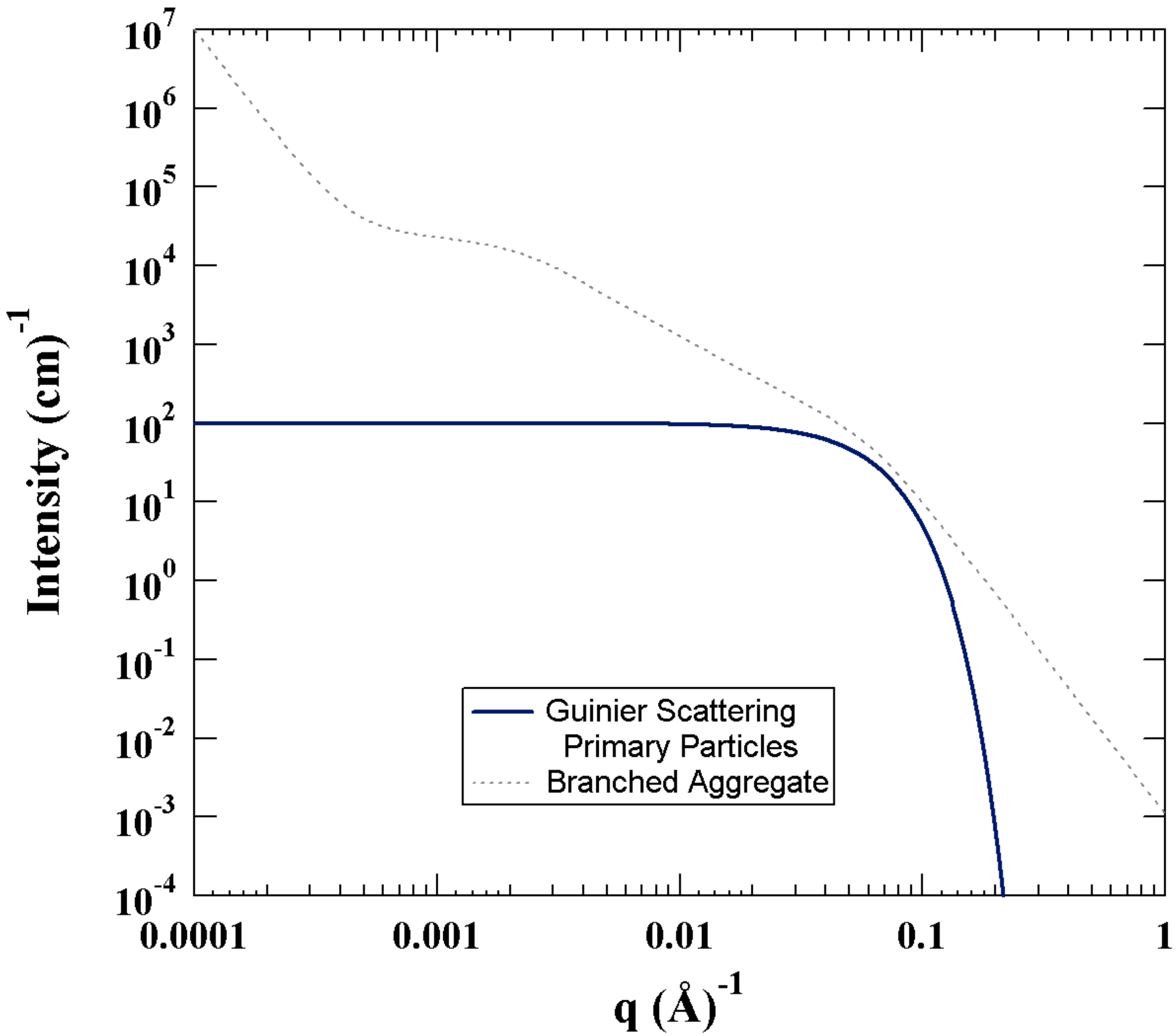
$$q = \frac{2\pi}{d}$$

$$I(q) = N(d)\,n_e^2(d)$$

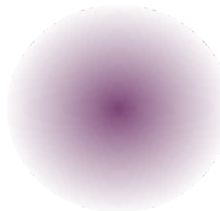
N = Number Density at Size “d”

n_e = Number of Electrons in “d” Particles

Guinier's Law



Particle with No Interface



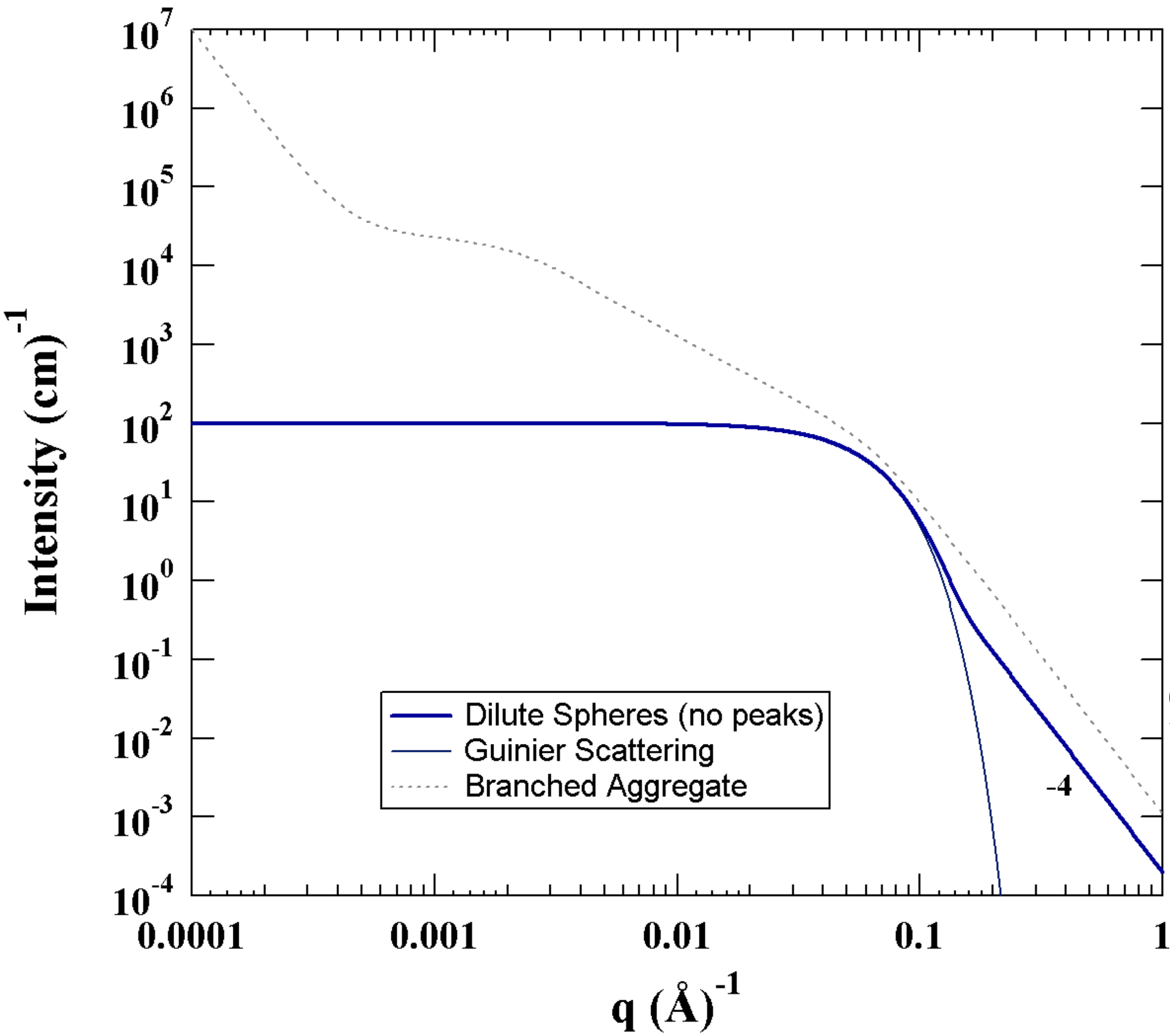
$$I(q) = N(d)n_e^2(d)$$

$$I(q) = G_1 \exp\left(\frac{-q^2\langle R_{g,1}^2\rangle}{3}\right)$$

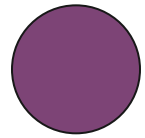
$$G = N\rho_e^2\langle V^2\rangle \sim \langle \mathrm{R}^6\rangle$$

$$\langle R_g^2\rangle \sim \frac{\langle \mathrm{R}^8\rangle}{\langle \mathrm{R}^6\rangle}$$

Guinier and Porod Scattering



Spherical Particle
With Interface (Porod)



$$I(q) = B_P q^{-4}$$

$$B_P = 2\pi N \rho_e^2 \langle S \rangle$$

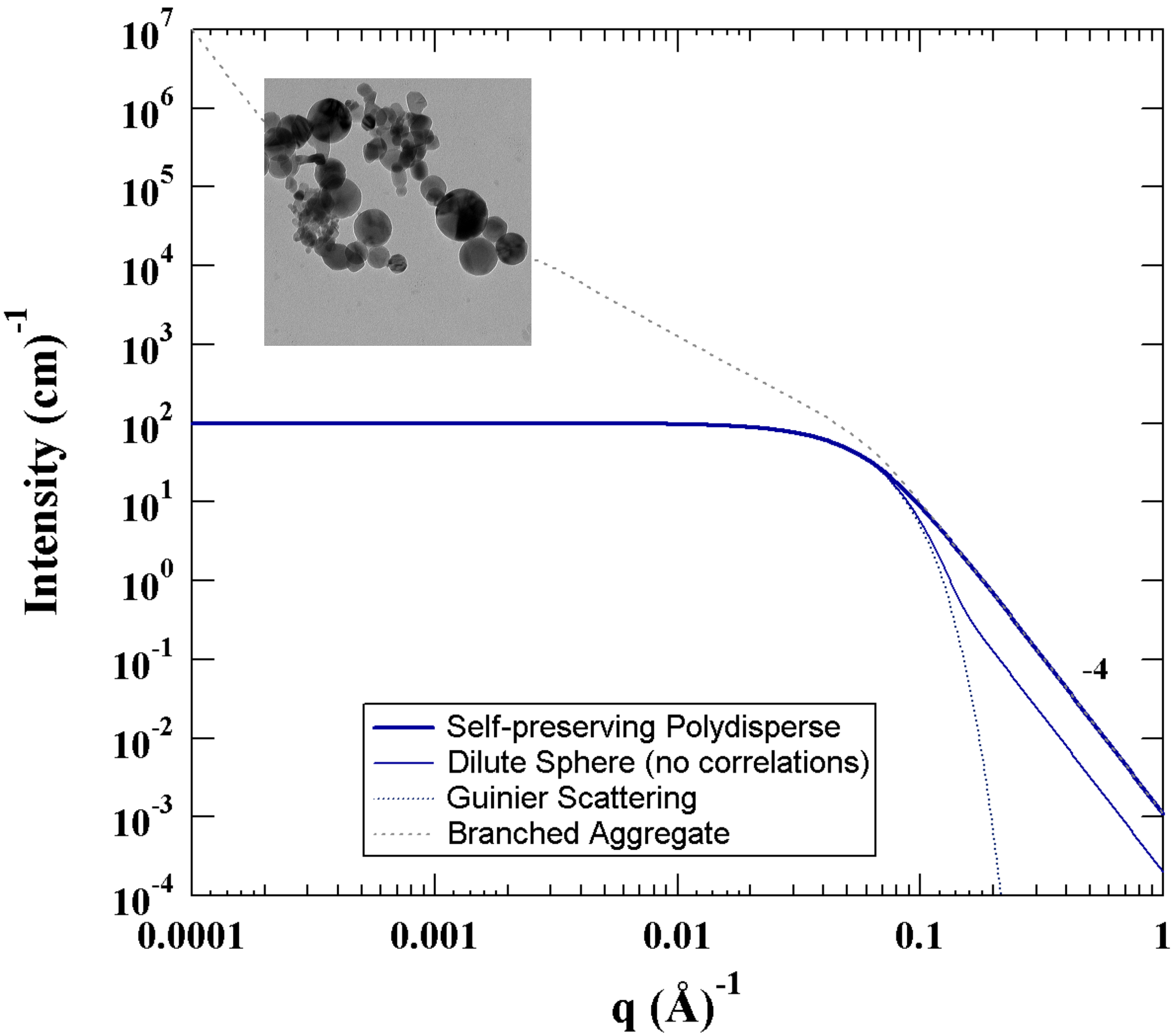
$$\langle S \rangle \sim \langle R^2 \rangle$$

$$Q = \int q^2 I(q) dq = N \rho_e^2 \langle R^3 \rangle$$

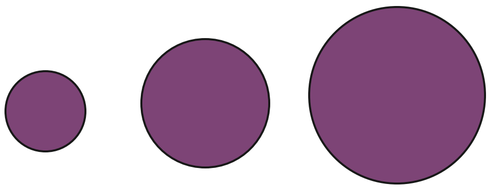
$$d_p = \frac{Q}{2\pi B_P} = \frac{\langle R^3 \rangle}{\langle R^2 \rangle}$$

Structure of Flame Made Silica Nanoparticles By Ultra-Small-Angle X-ray Scattering Kammler/Beaucage Langmuir 2004 20 1915-1921

Polydispersity Index, PDI



Polydisperse Particles



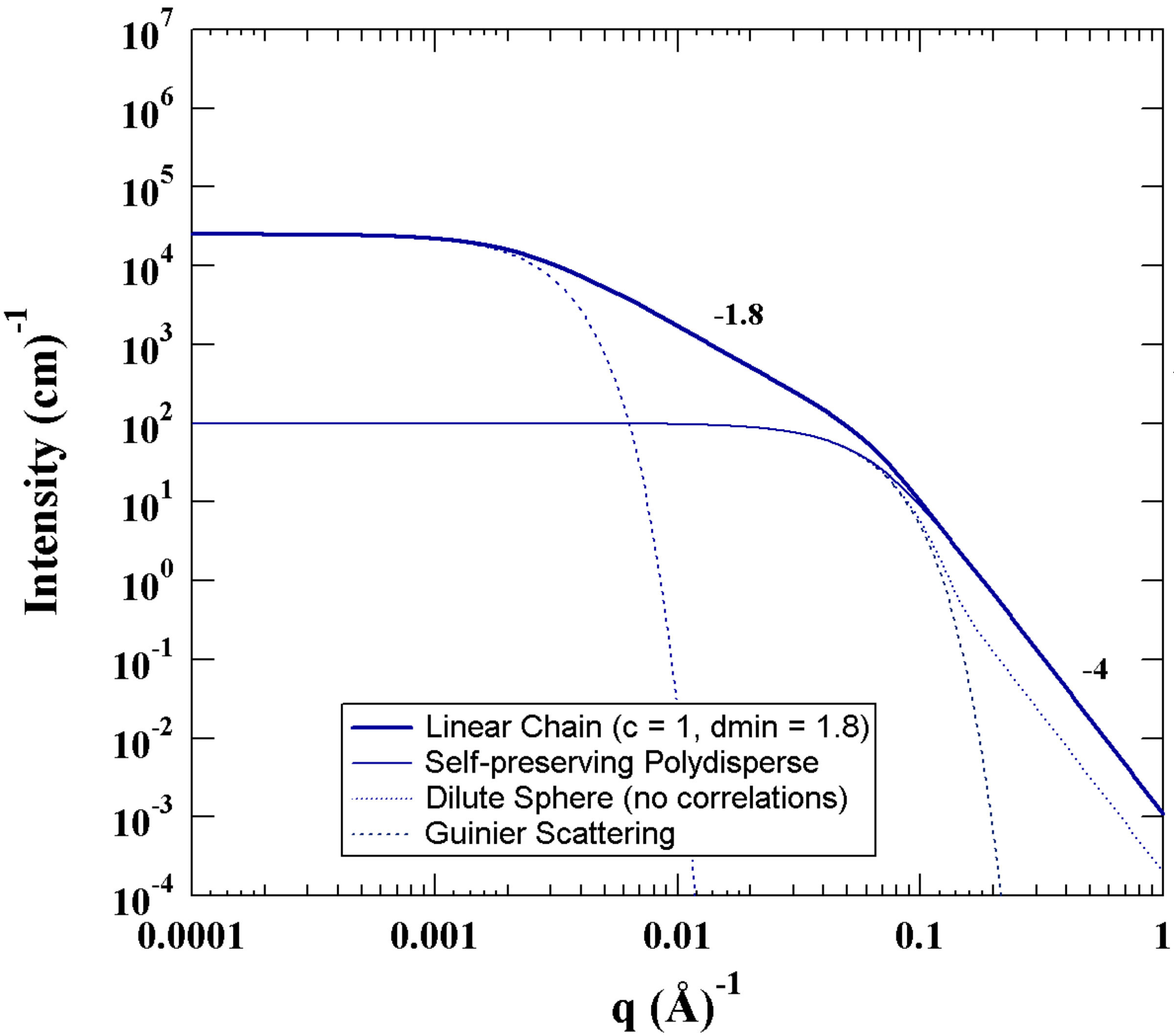
$$PDI = \frac{B_P R_g^4}{1.62G}$$

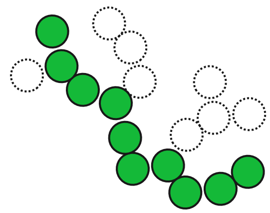
$$\sigma = \ln(\sigma_g) = \left[\frac{\ln(PDI)}{12}\right]^{1/2}$$

$$m = \left[\frac{5R_g^2}{3e^{14\sigma^2}}\right]^{1/2}$$

Particle size distributions from small-angle scattering using global scattering functions, Beaucage, Kammler, Pratsinis J. Appl. Cryst. 37 523-535 (2004).

Linear Aggregates





$$I(q) = G_2 \exp\left(\frac{-q^2 \left\langle R_{g,2}^2 \right\rangle}{3}\right)$$

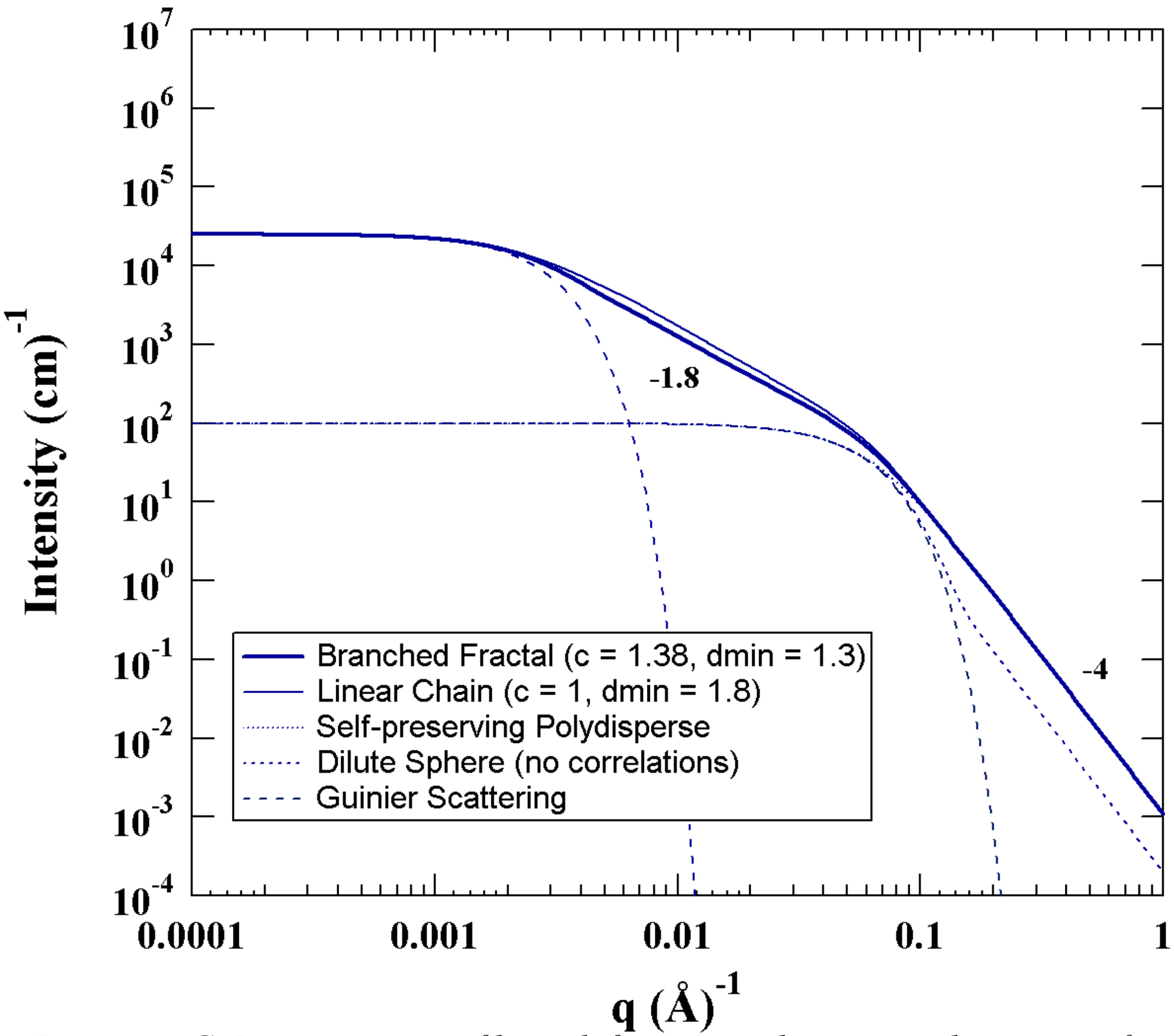
$$z = \frac{G_2}{G_1} = \left(\frac{R_2}{R_1}\right)^{d_f}$$

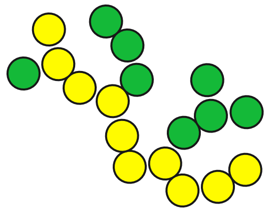
$$I(q) = B_f q^{-d_f}$$

$$B_f = \frac{G_2 d_f}{R_{g,2}^{d_f}} \Gamma(d_f/2)$$

Beaucage G, Small-angle Scattering from Polymeric Mass Fractals of Arbitrary Mass-Fractal Dimension, J. Appl. Cryst. 29 134-146 (1996).

Branched Aggregates





$$p = \left(\frac{R_2}{R_1}\right)^{d_{\min}} = z^{1/c}$$

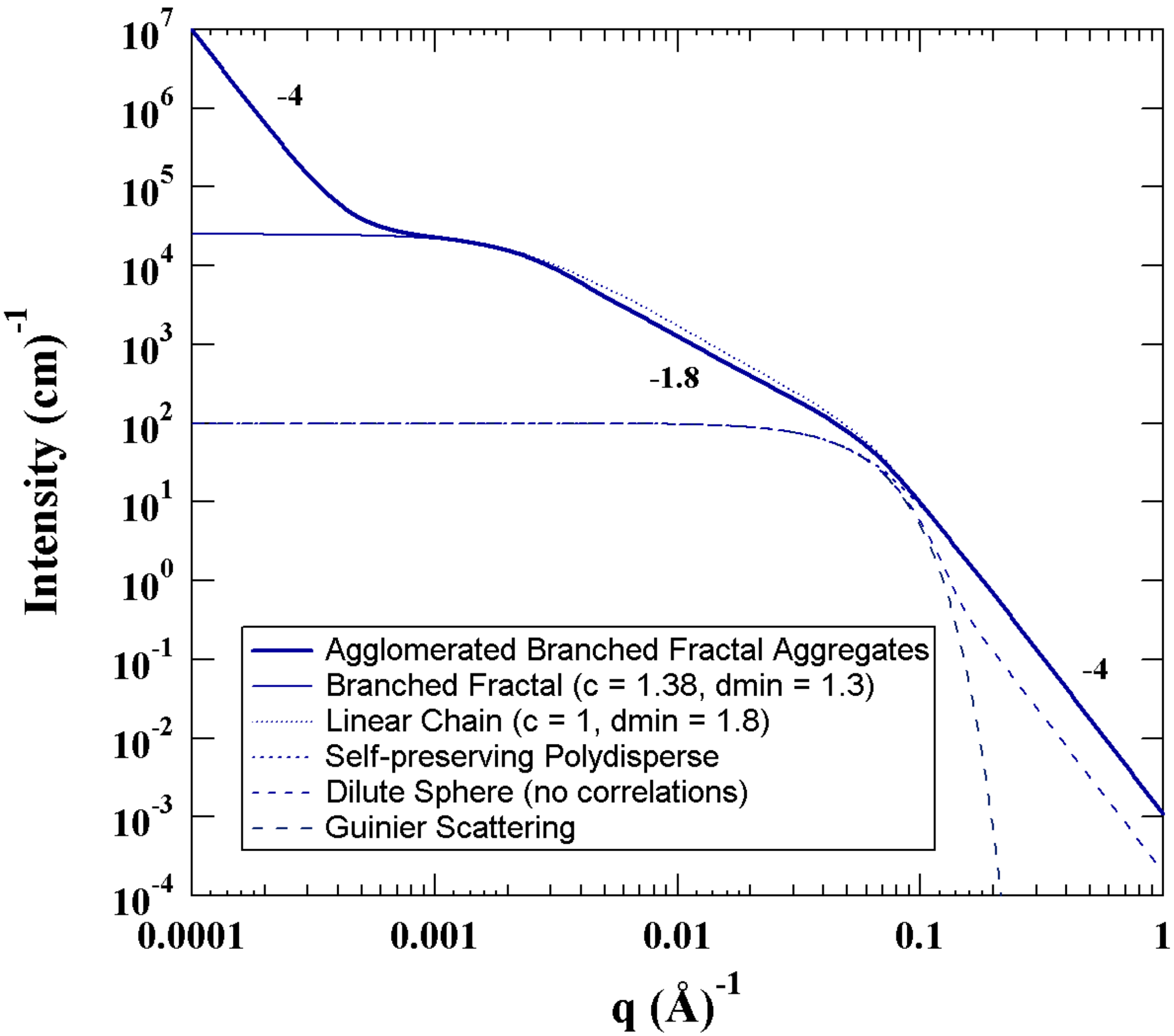
$$c = \frac{d_f}{d_{\min}}$$

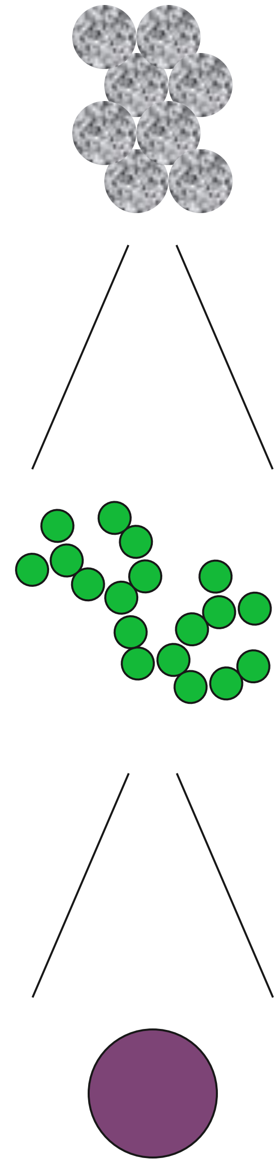
$$\phi_{Br} = 1 - \left(\frac{R_2}{R_1}\right)^{d_{\min} - d_f}$$

$$B_f = \frac{G_2 d_{\min}}{R_{g,2}^{d_f}} \Gamma\left(d_f/2\right)$$

Beaucage G, Determination of branch fraction and minimum dimension of fractal aggregates Phys. Rev. E 70 031401 (2004).

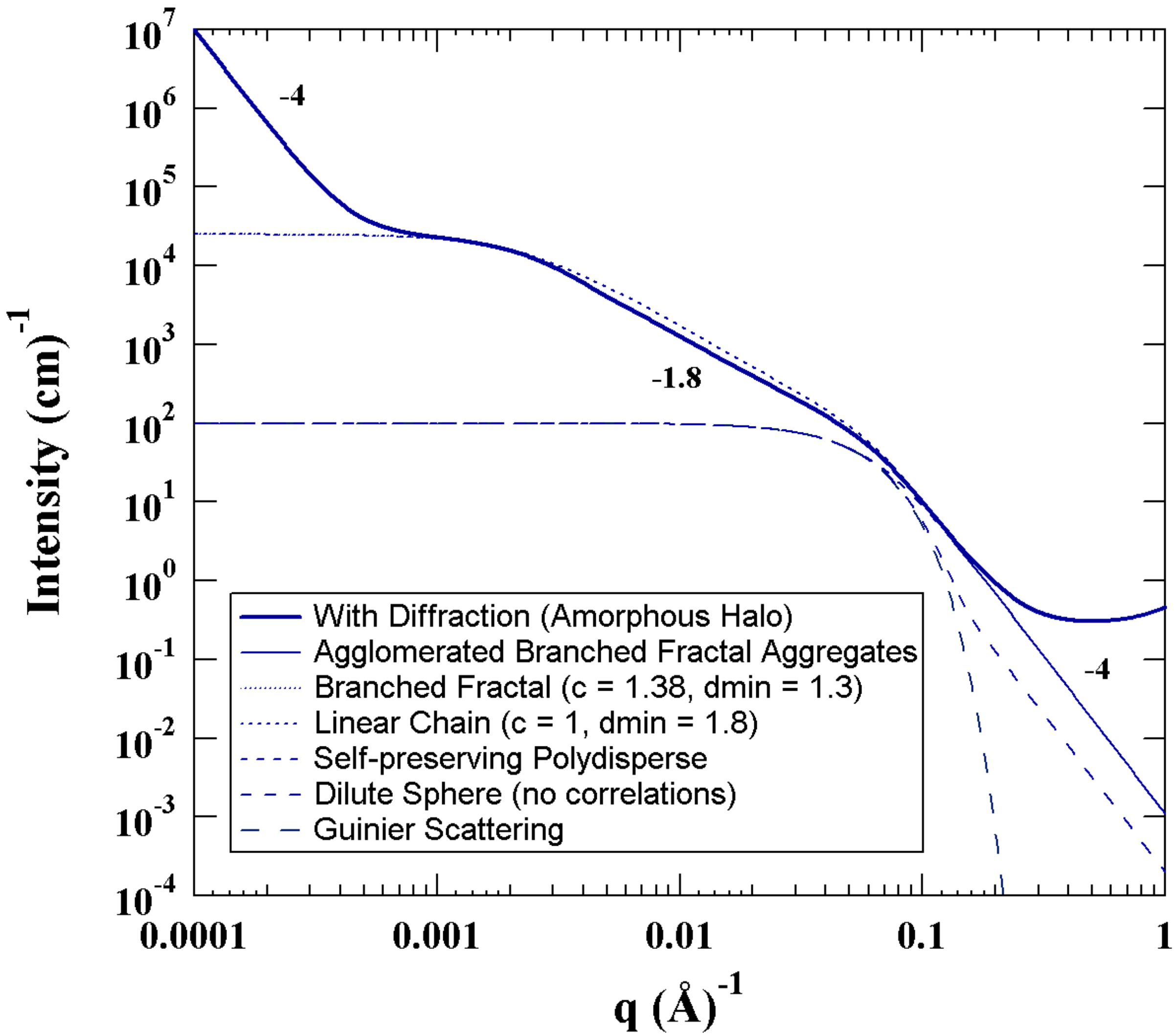
Large Scale (low-q) Agglomerates

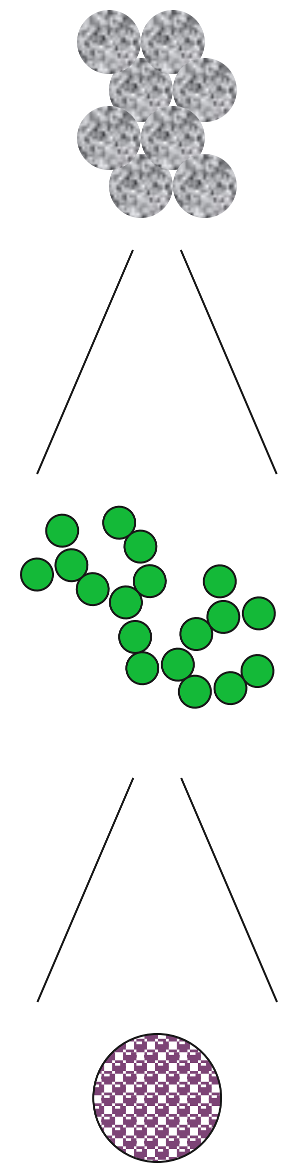


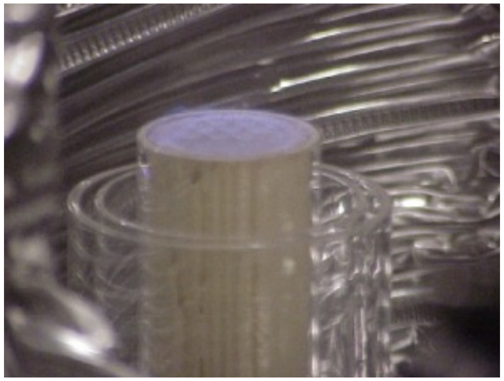


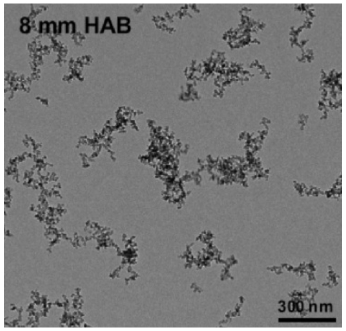
$$I(q) = B_P q^{-4}$$

Small-scale Crystallographic Structure









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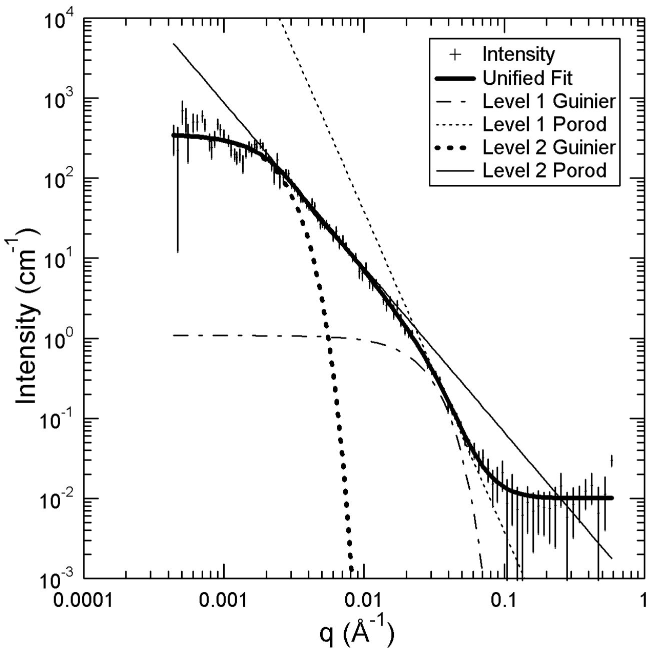
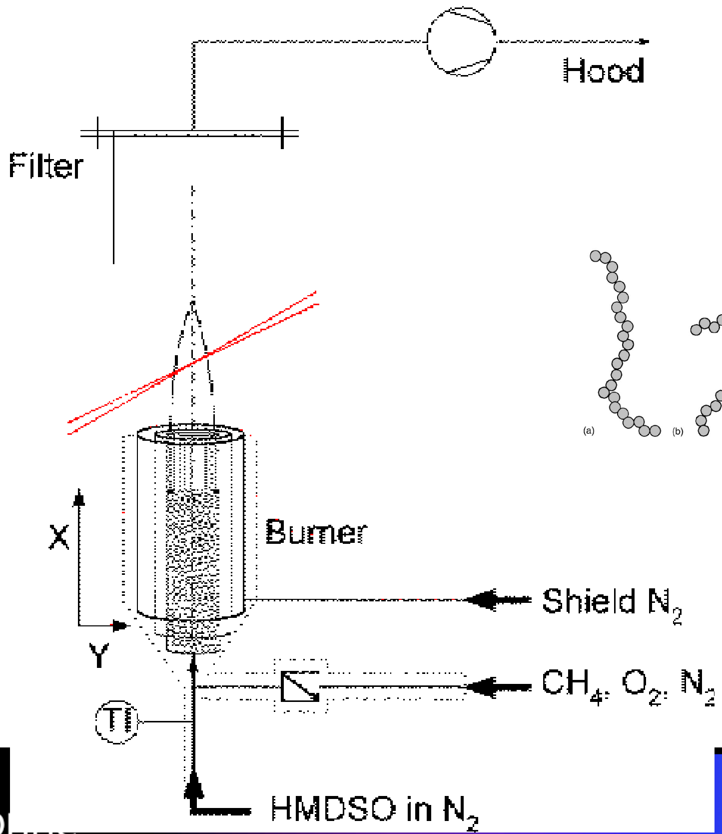
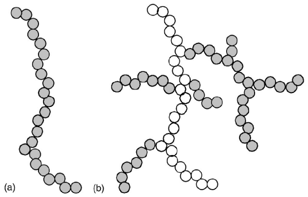
Silica Premixed Flames
J. Appl. Phys *97* *054309*
Feb 2005

Branched Aggregates







5mm LAT 16mm HAB
Typical Branched Aggregate
$d_p = 5.7$ nm
$z = 350$
$c = 1.5$, $d_{min} = 1.4$, $d_f = 2.1$
$\phi_{br} = 0.8$

Beaucage G, *Determination of branch fraction and minimum dimension of fractal aggregates* Phys. Rev. E 70 031401 (2004).

For Particles with Correlations (Concentrated non-fractal)

$$I(q) = I_{dilute}(q)S(q) = I_{dilute}(q)\frac{1}{1+pA(q,\xi)}$$

$$p = packing\ factor,\ \mathrm{A}(\mathrm{q},\xi) = \frac{3(\sin q\xi - q\xi\cos q\xi)}{(q\xi)^3}$$

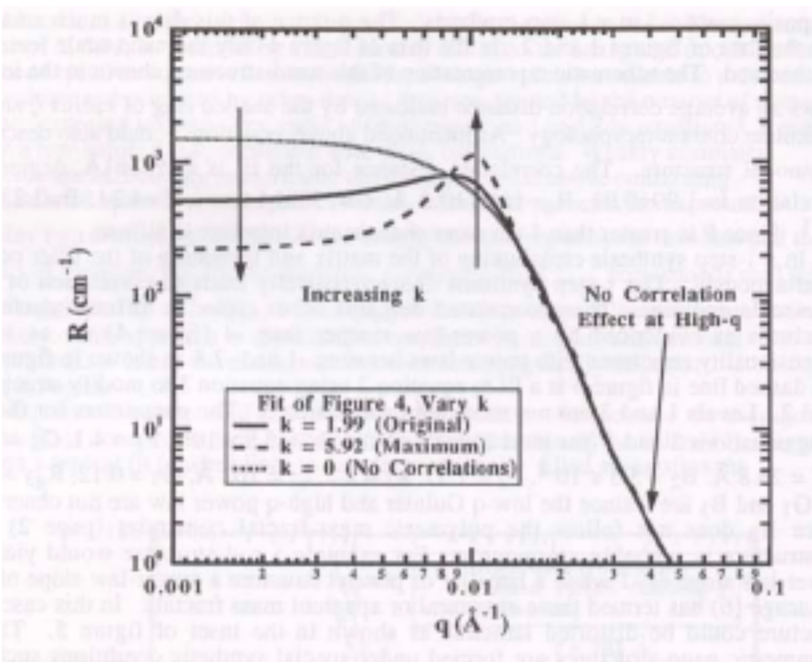
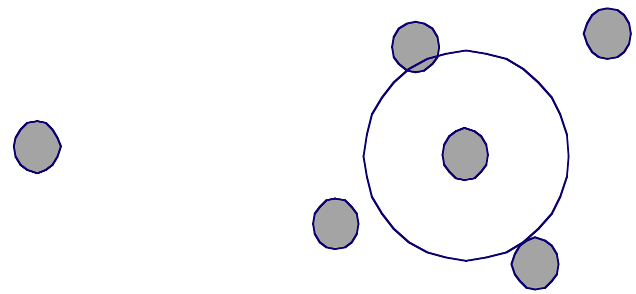
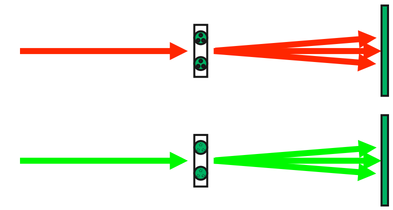


Figure 6. Demonstration of the effect of varying the packing factor "k" on the scattering pattern for the data of figure 4. Packing of the domains does not affect the power-law scaling regime at high-q.



Size distribution?

Particle Size Distribution Curves From SAXS



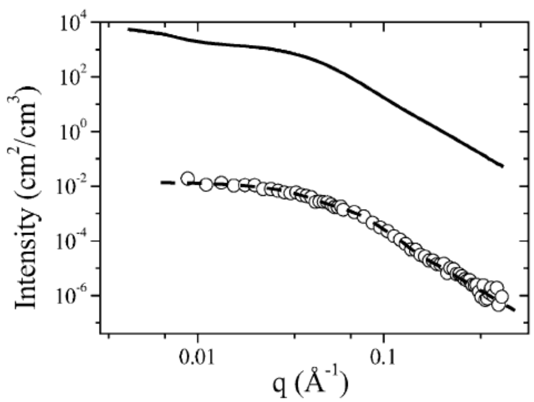


Fig. 7. ASAXS scattering curve measured at 8308 eV on the fresh catalyst (full line). The circles represent the separated scattering curve ($KI(q)$) obtained by subtracting the normalized scattering curves measured at 8308 and 8326 eV. The dashed line represent the best fit to the data using the approach described in the text.

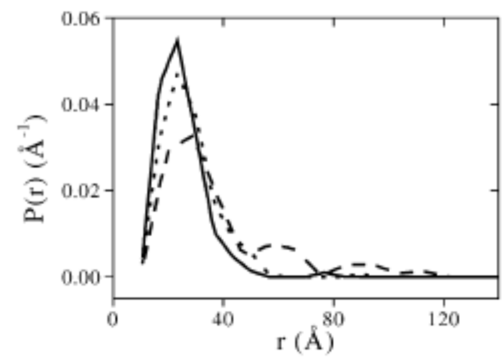


Fig. 8. Normalized nickel number particle size distributions of catalysts sintered at 650 °C obtained by ASAXS as described in the text. The nickel particles are assumed to be spherical with radius r, but otherwise no assumption on the shape of the distribution is made. The full line is the distribution of the fresh catalyst. The short dash (long dash) is the distribution after sintering for 5 h (100 h).

Assumption Method

i) Assume a distribution function.

ii) Assume a scattering function (sphere)

iii) Minimize calculation

$$I(q) = 9G\left[\frac{\sin qR - qR\cos qR}{(qR)^3}\right]^2$$

Particle Size Distribution Curves From SAXS

Maximum Entropy Method

i) Assume sphere or other scattering function
ii) Assume most random solution
iii) Use algorithm to guess/compare/calculate
iv) Iterate till maximum "entropy"

Advantages
- No assumption concerning distribution function
- No assumption for number of modes
- Matches detail PSD's well

Related Alternatives
- Regularization

Particle size distributions from small-angle scattering using global scattering functions, Beaucage, Kammler, Pratsinis J. Appl. Cryst. 37 523-535 (2004).

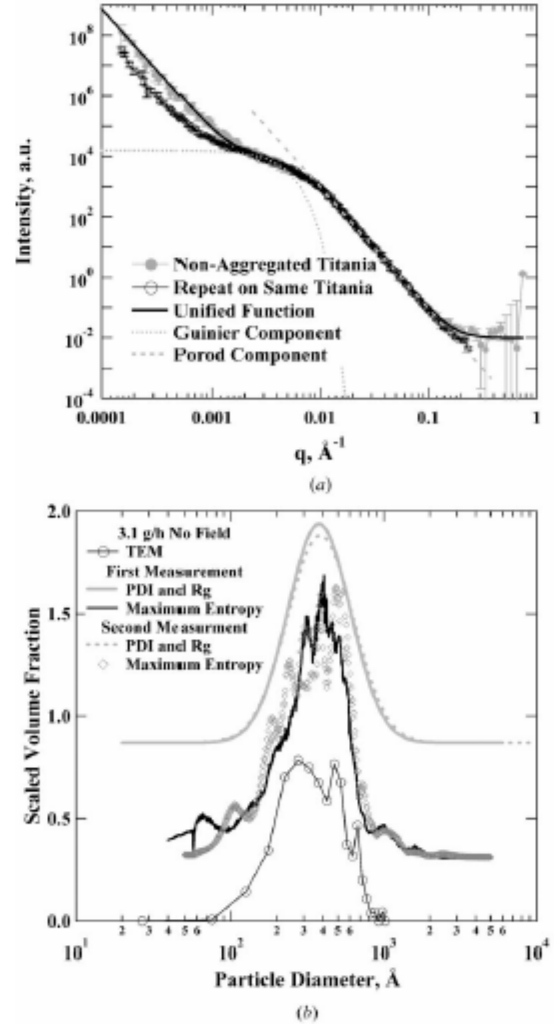


Figure 5
3.1 g h^{-1} titania. (*a*) Repeat USAXS runs on a non-aggregated titania powder (Fig. 1). (*b*) Particle size distributions from TEM (circles; Kammler *et al.*, 2003), equations (1), (2), (17) and (18) using PDI and R_g, and using the maximum-entropy program of Jemian (Jemian *et al.*, 1991). Distribution curves are shifted vertically for clarity. d_{VIS} = 34.9 nm, PDI = 14.4 (σ_g = 1.60), R_g = 44.2 nm.

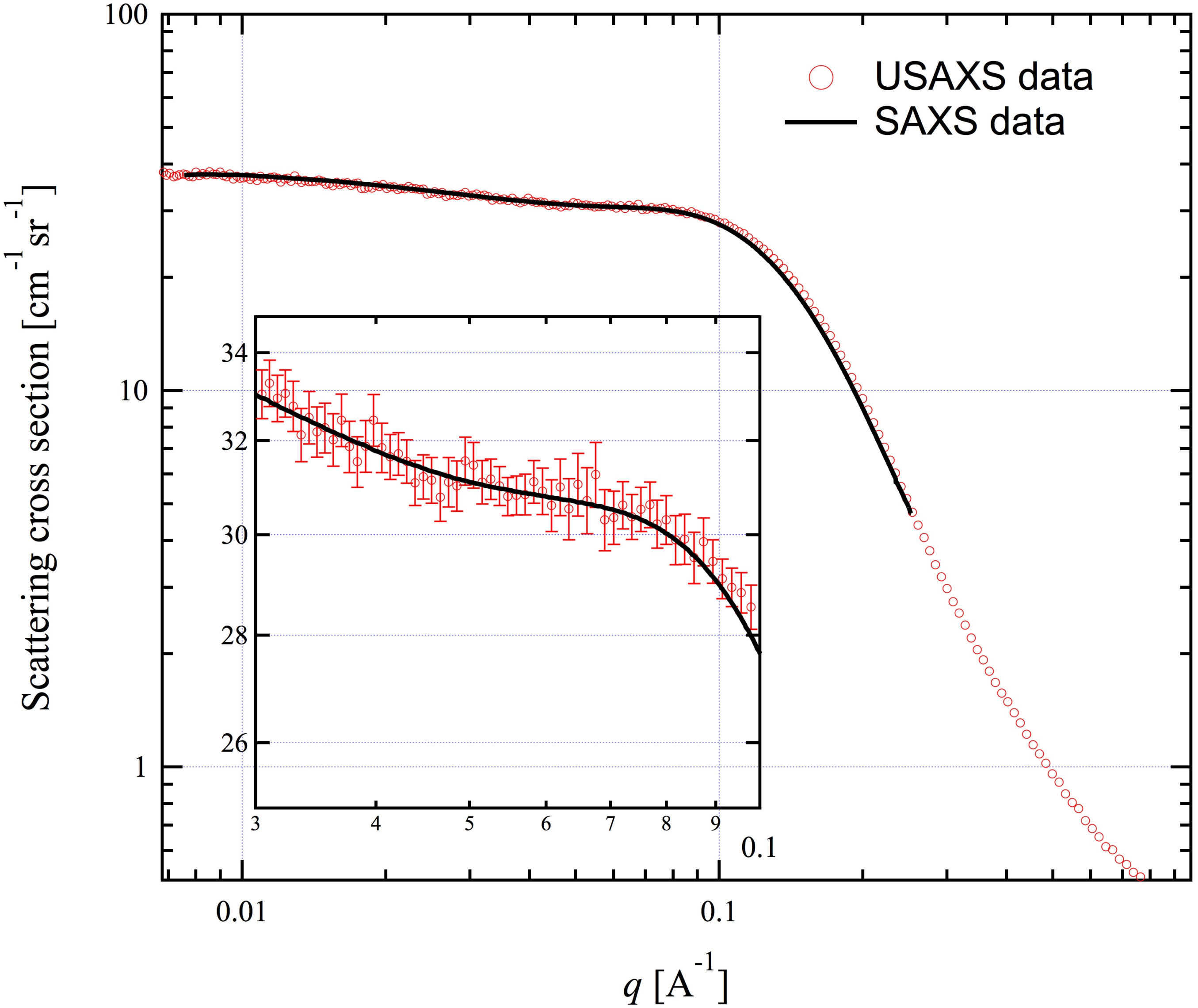
Absolute Intensity calibration

- Need to put intensity on absolute scale
  - Absolute volume of scatterers [cm3/cm3]
  - Specific surface areas [cm2/cm3]
  - Contrast, density analysis
  - …

Glassy Carbon as Absolute Intensity Standard

- Glassy carbon samples were considered previously :
  - G.D. Wignall & F.S. Bates, J. Appl. Cryst., 1987, vol. 20, pp. 28 – 40.
  - R. Perret & W. Ruland, J. Appl. Cryst., 1972, vol. 5, pp. 116 –19.
  - And probably few others…
- Porous structure can be customized to match the needs (W.S. Rothwell: J. Appl. Phys., 1968, vol. 39, pp. 1840–45, G.D. Wignall and C.J. Ping: Carbon, 1974, vol. 12, pp. 51–55).
- We use USAXS instrument with primary absolute intensity calibration (J. Ilavsky, P.R. Jemian, A.J. Allen, F. Zhang, L.E. Levine, and G.G. Long: J. Appl. Cryst., 2009, vol. 42, pp. 469–79) to characterize commercial product (Alpha Aesar Stock #38021) – 1mm thick Glassy carbon plate, "type 2".
- Provided free of charge to SAS users on request (send e-mail to : ilavsky@aps.anl.gov or just ask me here).
- At least 65 samples shipped in last ~ 4 years.

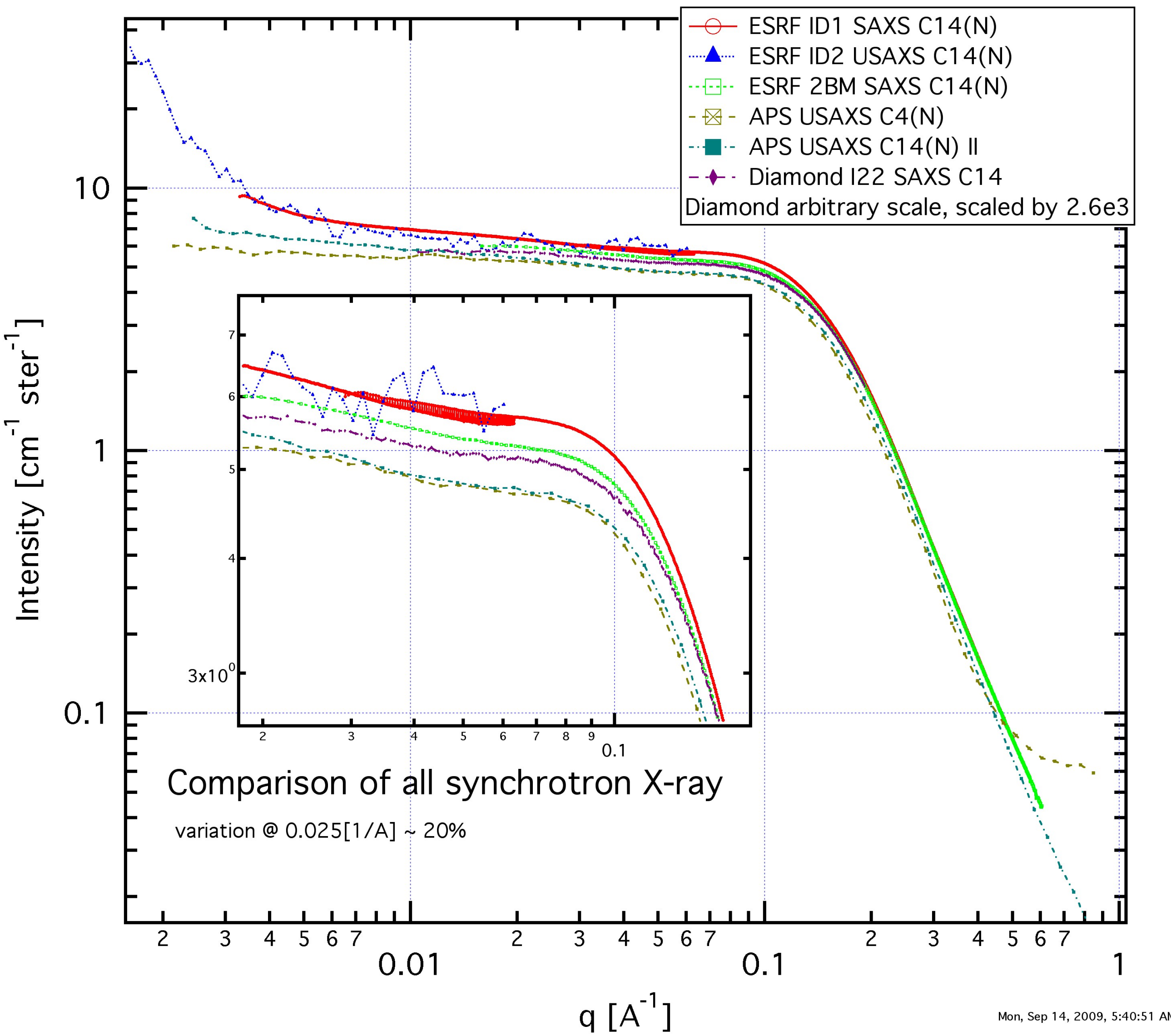
USAXS/SAXS data comparison



SAXS scaled to USAXS using “area under the curve” in overlapping Q range

Round Robin… Comparison of SAXS facilities

- Note: scaled to neutron contrast…
- Worth noting:
- 20% difference between min & max
- ESRF USAXS in 2D collimated mode
- APS USAXS in slit smeared mode
- ESRF ID1 & 2BM ???
- Seems agreement within facility…
- … why the differences?



SANS (reactor based)

- Calibration ~ wavelength (ILL D22, NIST)

Interestingly:

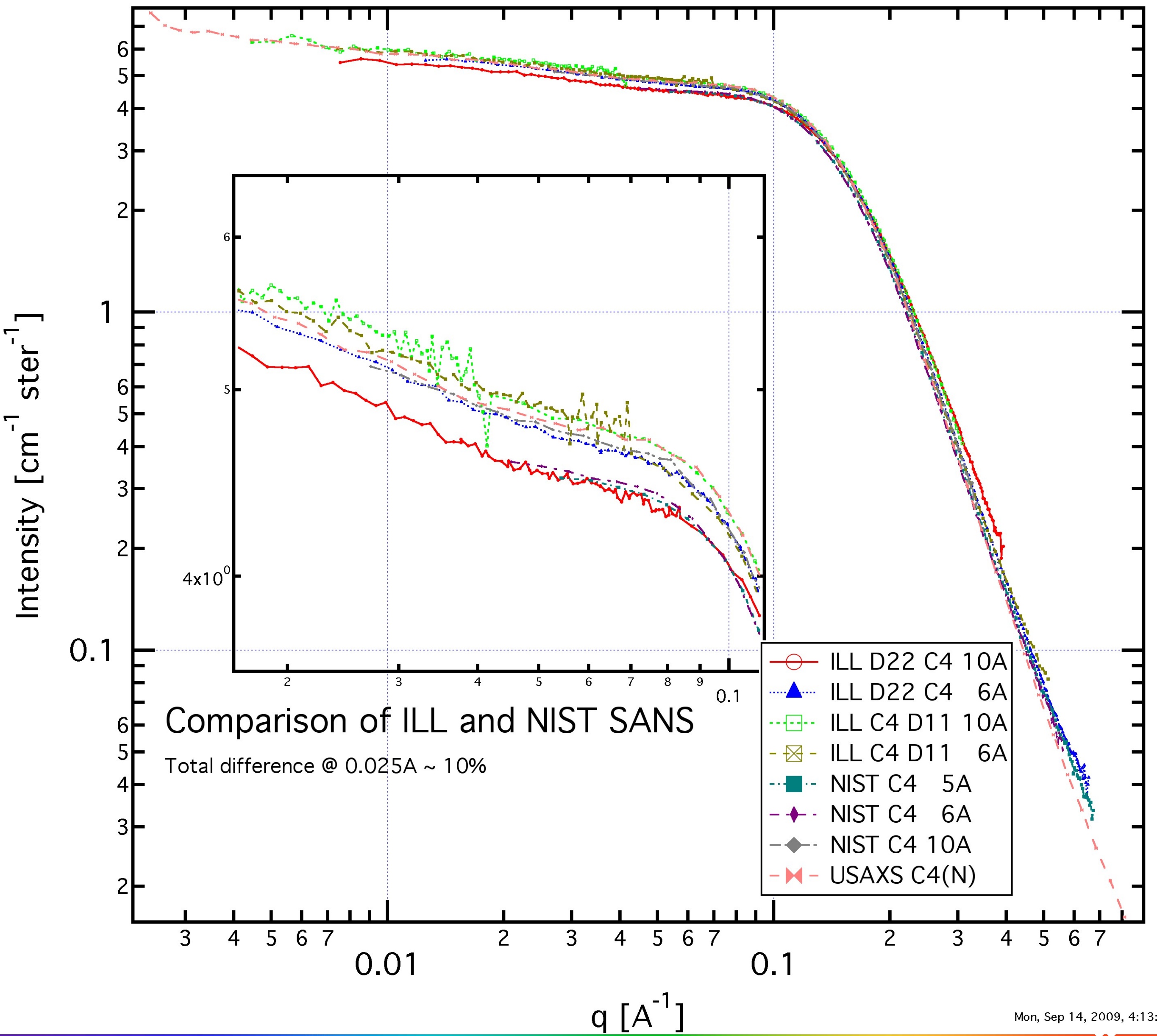
NIST increases with wavelength

ILL D22 decreases

D11 is wavelength independent

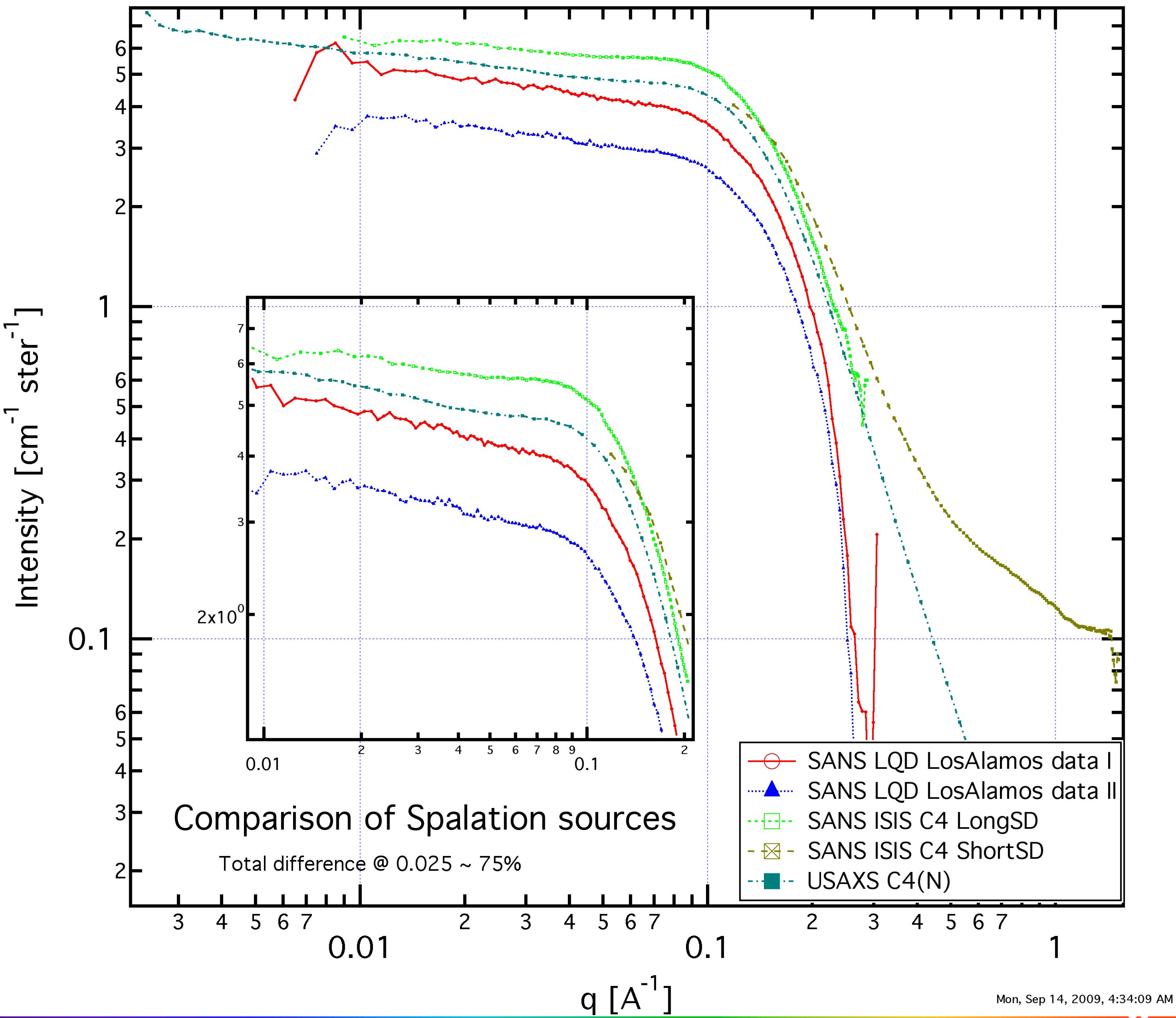
- Difference ~ 10%
- Good agreements:

ILL D11, NIST 10A, & D22 6A (with APS USAXS)



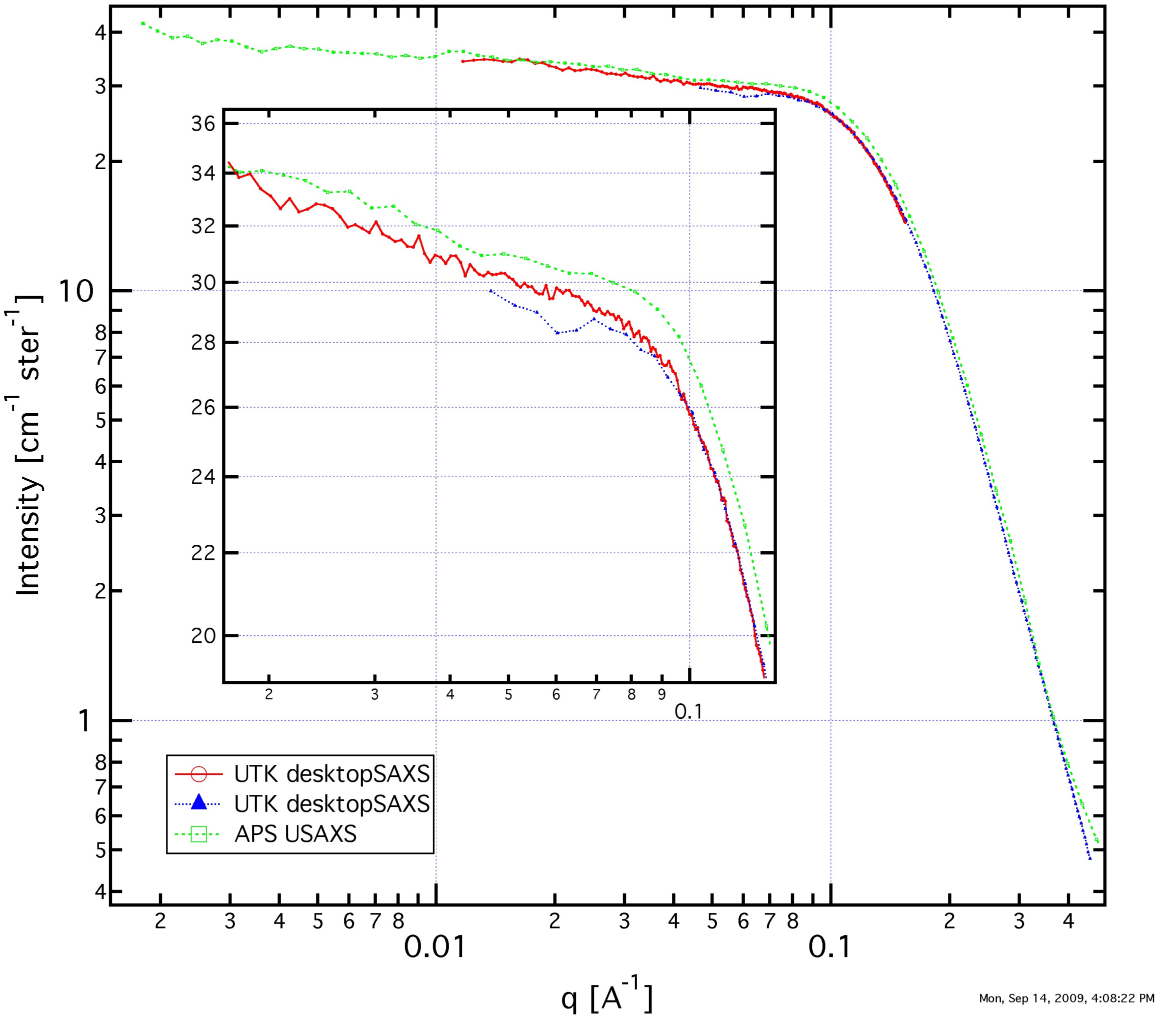
And spallation sources…

- Least agreement…
- Clearly issues
- Even background subtraction
- Total variation ~ 75%



Comparison with one desktop user…

- Prof. Joseph E. Spruiell, Materials Science and Engineering dept., University of Tennessee
- Uses secondary polyethylene standard (Lupolen sample S2907)
- pinhole SAXS system was developed by Molecular Metrology (Rigaku) with two sample-detector distances

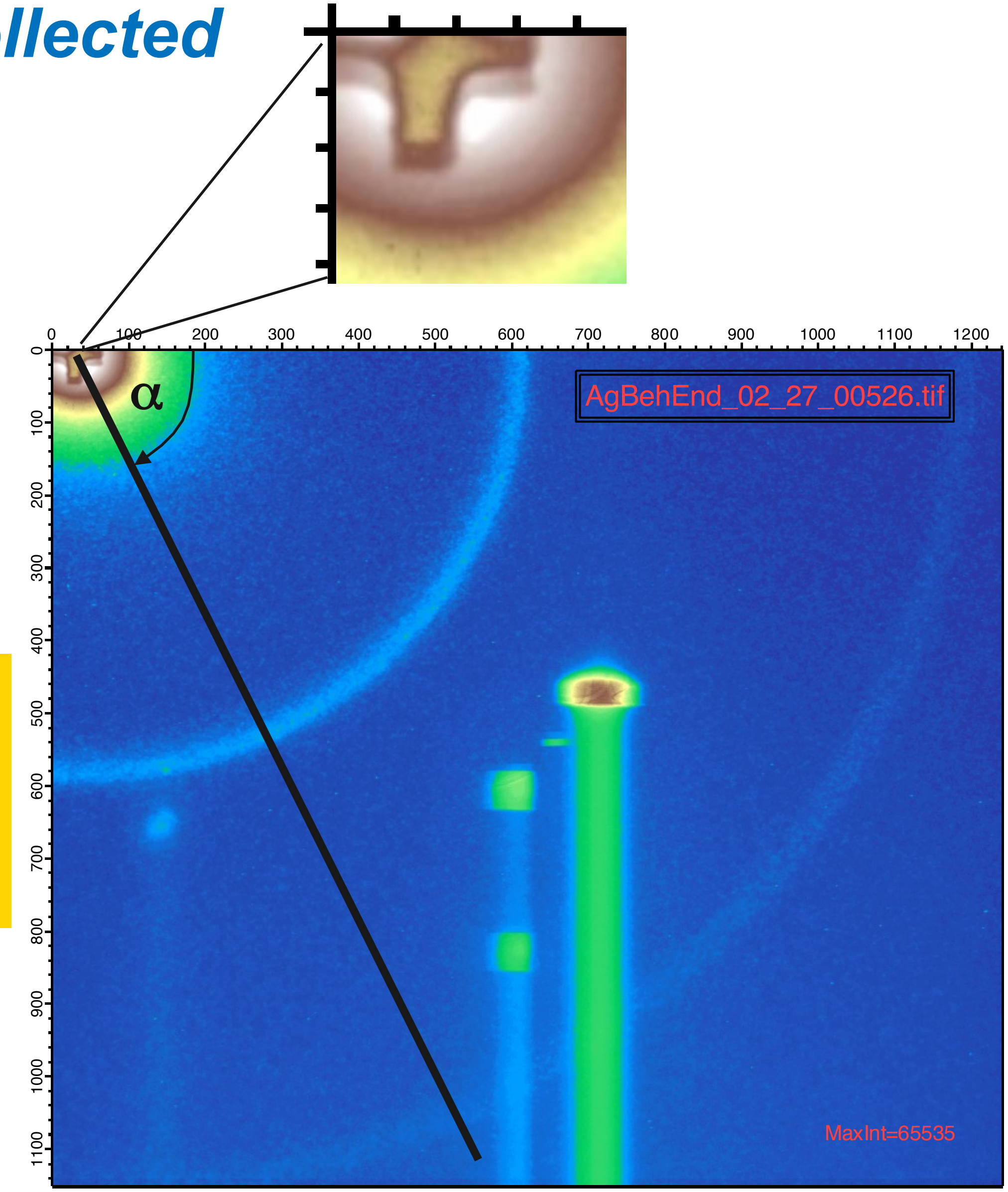


Clearly does a very good job…

SAXS Data reduction… What is that funny 2D image good for?

Basic SAS data types collected

- 2-D data – area detectors, most common currently
- 1-D data – step scans
  - Narrow lineout
  - Slit smeared



Wanted (usually):

I(*Q*) – for isotropic samples

I(*Q*,α) – for anisotropic samples

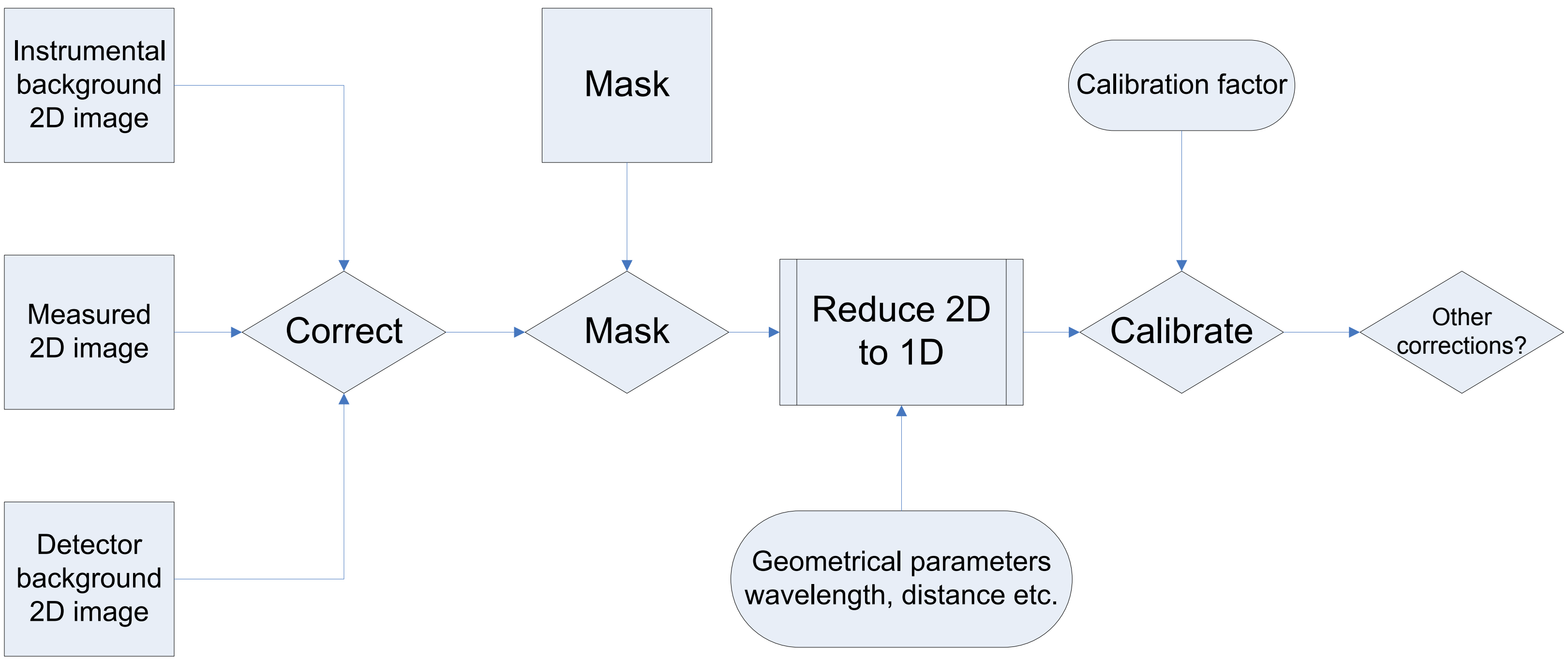
$$Q = \frac{4\pi}{\lambda}\sin\theta$$

2-D (area) detectors

- Most common for both desktop & synchrotron based instruments
- Many different types available
  - Image plate
  - CCD
  - Wire detectors…
- Each different dynamic range, dark current, offset, readout speed, pixel size, pixel bleeding, ….
- Require:
  - Corrections
    - *Flat-fielding (pixel sensitivity)*
    - *Dark field subtraction (readout offset and dark noise)*
    - *Unwarping (pixel positions)*
    - *….*
  - Masking (beam stop, bad detector areas, shadows of instrumental parts…)
- Needed corrections vary detector from detector (e.g., MarCCD has dark field subtraction and unwarping built in the data collection software)

Data reduction and calibration schematics

- Number of different approaches, often specific to the used area detector & instrument design



Data2D = (Sa2D – Dark2D) – C * (Bckg2D – Dark2D)

C ~ sample transmission, measurement times, incoming intensity etc.

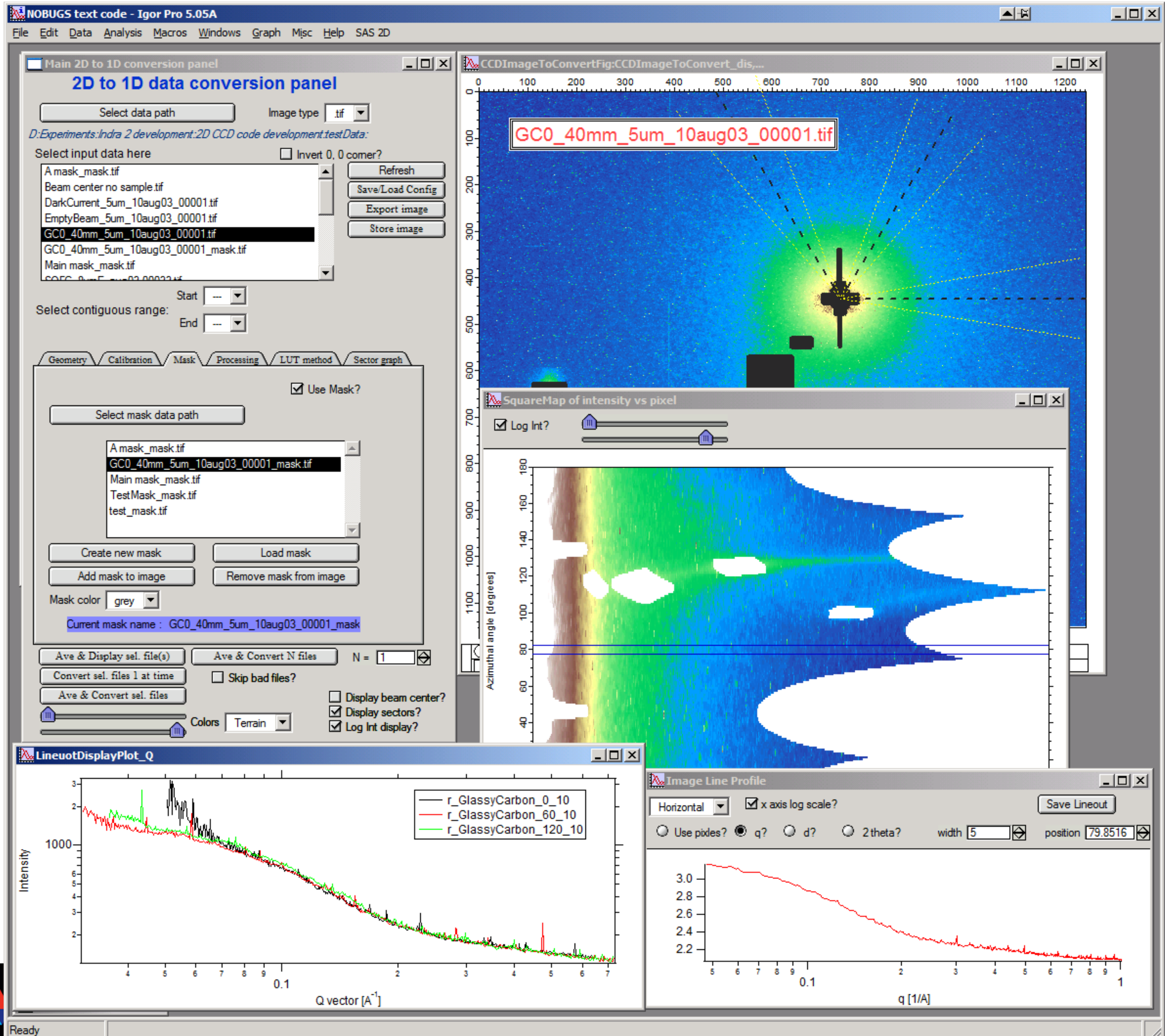
Tools to convert 2D data to 1D data

- Ideally – tools should be provided with instrument
  - Like ESRF (software is mostly specific for their data)
    - *http://www.sztucki.de/SAXSutilities/ (Michael Sztucki, processing of SAXS data)*
    - *http://www.esrf.eu/computing/scientific/SAXS/ (Peter Boesecke, manipulation of 2D data)*
- **Fit2D** - http://www.esrf.fr/computing/scientific/FIT2D/ free, in use for very long time (= debugged), large user base, _very_ capable
  - However, not very user friendly and cumbersome for data analysis of large number of data sets – need to learn how to write scripts.
  - Ideal for processing large sets of samples (scripting).
  - Available for many platforms
- **Datasqueeze** - http://www.datasqueezesoftware.com/, $100/$50 for user license, Windows/Linux/MacOS.
- **Nika** – Igor Pro (6.0, Mac & Windows) based package (http://usaxs.xor.aps.anl.gov/) – free but need Igor Pro license (http://www.wavemetrics.com/), $550/$395 for user license.
  - Igor Pro scripts are open source and can be modified by anyone. – Open source

Data reduction package "Nika" – for SAXS, WAXS, GISAXS/ GIWAXS

- Tools for following tasks:
  - Display & average 2D image(s)
    - *Circular average (SAXS/WAXS)*
    - *Sector average (SAXS/WAXS)*
    - *Arbitrary line/circle/ellipse average (SAXS/WAXS, GISAXS/GIWAXS)*
  - Design mask, Create flood field
  - Load & average 2D image(s) and convert them to "lineouts"
    - *Use dark field/empty field*
    - *Calibrate, correct for thickness*
    - *Correct with various combinations of parameters*
      - Transmission
      - I0, exposure time
    - *Lookup these parameters using user designed Igor function*
  - Graph & export resulting line-outs (ASCII data)
  - Easily integrates with Irena package

Nika example



Have 1D data…

Can you tell me how to get (Rg, Size distribution,…) from them?

Data analysis tools….

Know what are you doing!

Small-angle scattering (~F(*q*))
(dilute limit)

Small-angle diffraction (~S(*q*))

(NIST, Irena)

Same size & shape

GNOM, NIST

Size &/or shape variations

Same type particles

Irena, Gnom, NIST…

Multiple types of particles

Irena,…

Available tools

- Some of the common packages :
  - ATSAS 2.1 - Gnom, Crysol & Cryson,… Dimitri Svergun et. al.
  - SmolX (solution scattering)
  - NIST SAS routines
  - Irena package
  - SASFit

- See: http://small-angle.aps.anl.gov/software/

ATSAS 2.1 - Gnom, Crysol, Cryson, …

- Dmitri Svergun, http://www.embl-hamburg.de/ExternalInfo/Research/Sax/
- Suite of program for analysis of SAS from biological macromolecules
- Contains programs for Data reduction, computation of solution scattering from atomic models, Modeling, Ab initio structure analysis etc…
- Well established package
- Available for free for wide range of platforms (Windows/Linux/OSX,)
- Example : Gnom, currently works as command line program with GUI for graphing capabilities (on Windows).

SmolX- A coordinate-based computer simulation program for Solution molecular X-ray Scattering

- **Authors and Contact:**
  - X. Zuo, A. Goshe, R. Zhang, and D. M. Tiede
  - Chemistry Division, Argonne National Laboratory; Email: tiede@anl.gov
- **Goals:**
  - Wide applications: synthetic supramolecules and biomolecules
  - Synchrotron based wide-angle X-ray scattering technique
    - *High spatial resolution scattering*
    - *New X-ray techniques, e.g., anomalous scattering*
- **Major Functions and Features:**
  - Solution X-ray scattering/Diffraction Pattern (WAXS / SAXS)
  - Pair Distance Distribution Function (PDDF) with "Infinity Spatial Resolution"
    - *to validate experimental PDDF via direct / indirect Fourier transform*
    - *to identify required experimental resolution*
  - Anomalous Solution X-ray Scattering & PDDF
    - *to help new experimental design and data analysis*
  - Easy User Controls on Molecular Type, X-ray Parameters, and etc

Graphic User Interface & Functions of SmolX

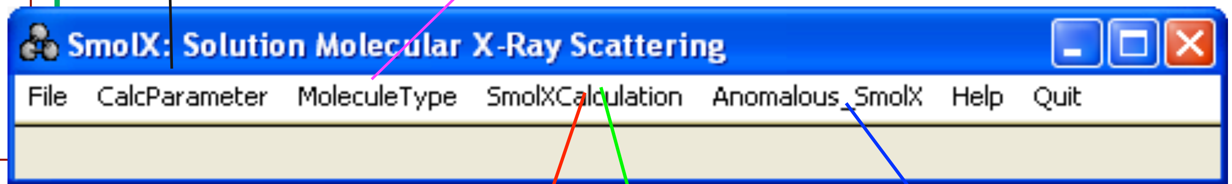
Input

SmolX parameter files:
- •Molecule & atom types
- •Atomic volumes
- •X-ray form factors
- •Anomalous X-ray data

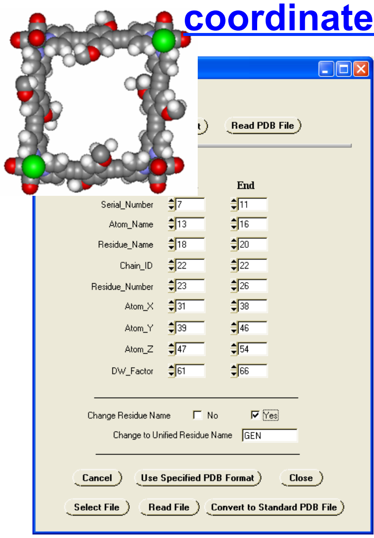
Easy to add & modify

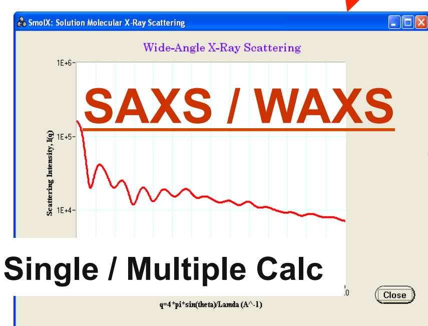
•q range, WAXS/SAXS
•Solvent, etc

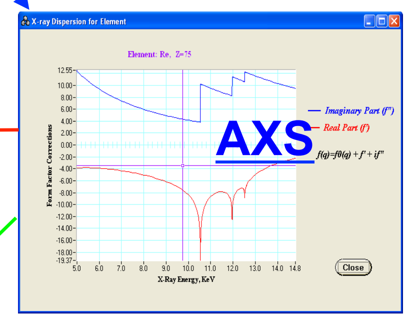
Molecule types: proteins, nucleic acids, generic type, user-defined molecules (e.g., supramolecules); recognize mixed-complex, e.g., protein-DNA-porphyrin adducts



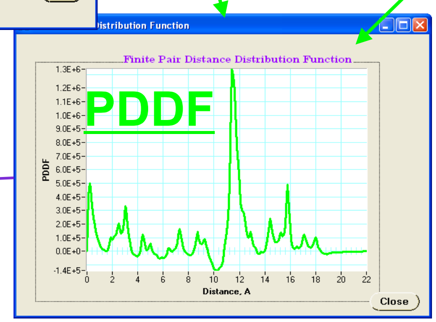
molecular pdb coordinate file







Calc Statistics:
- Composition
- Parameters
- Rg, etc

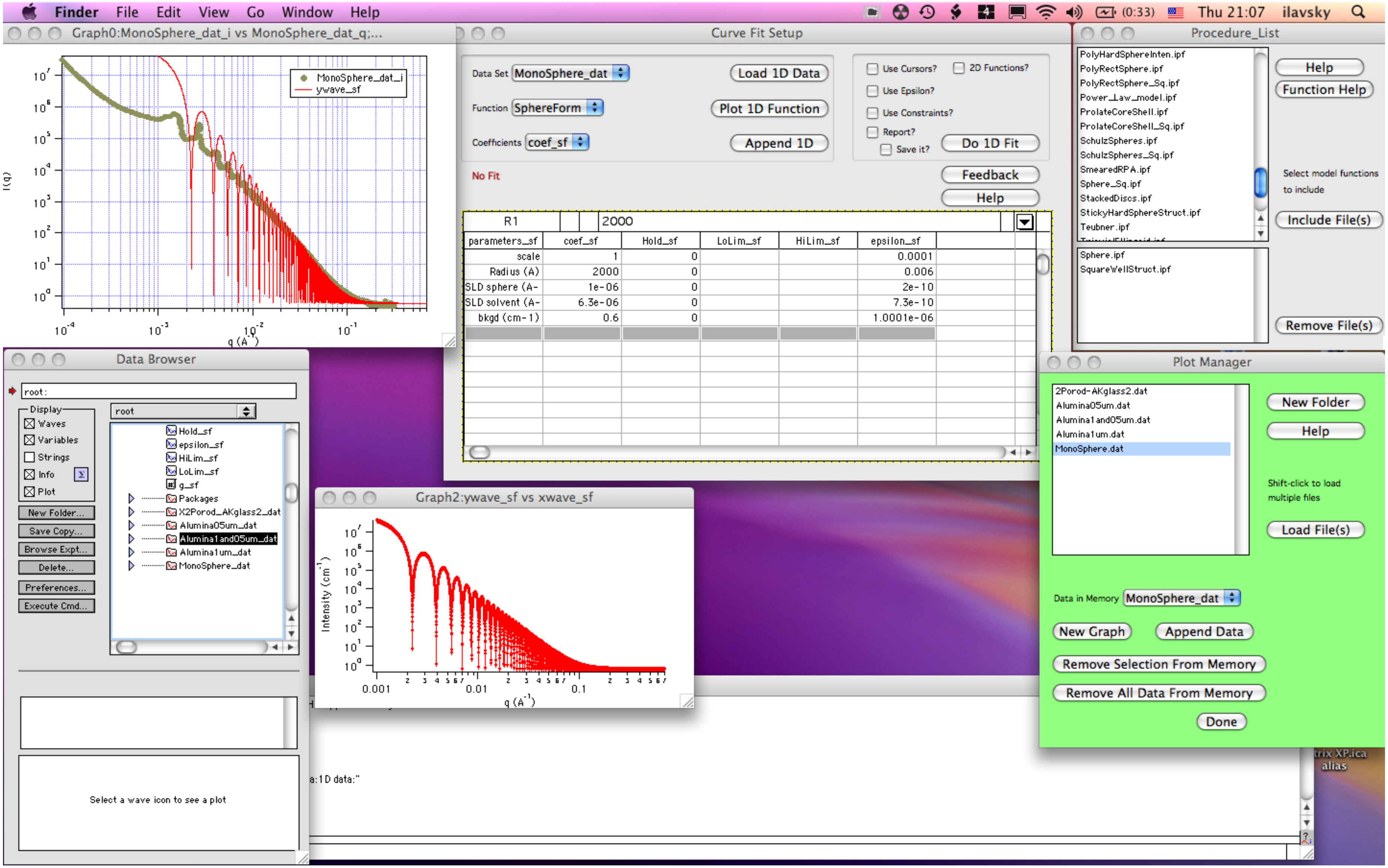


Output

NIST SANS data evaluation package

- Igor Pro (Wavemetrics Inc., www.wavemetrics.com) based package
- "Reduction and Analysis of SANS and USANS Data using Igor Pro", Kline, S. R. *J Appl. Cryst.* **39**(6), 895 (2006)
- http://www.ncnr.nist.gov/programs/sans/data/data_anal.html
- Very good package containing number of :
  - Form factors
  - Structure factors
  - And some other tools for SAS data analysis.
- Useful for "simpler" systems than Irena package (to be discussed later)
- Requires some Igor proficiency.
- Well suited for SANS and USANS calculations as can handle smearing by pixel size (less important for SAXS)
- Well established, tested and reliable.
- Supported and backed by NIST SANS group.
- Good manual & even "How to use" movies (Quicktime).

NIST package structure

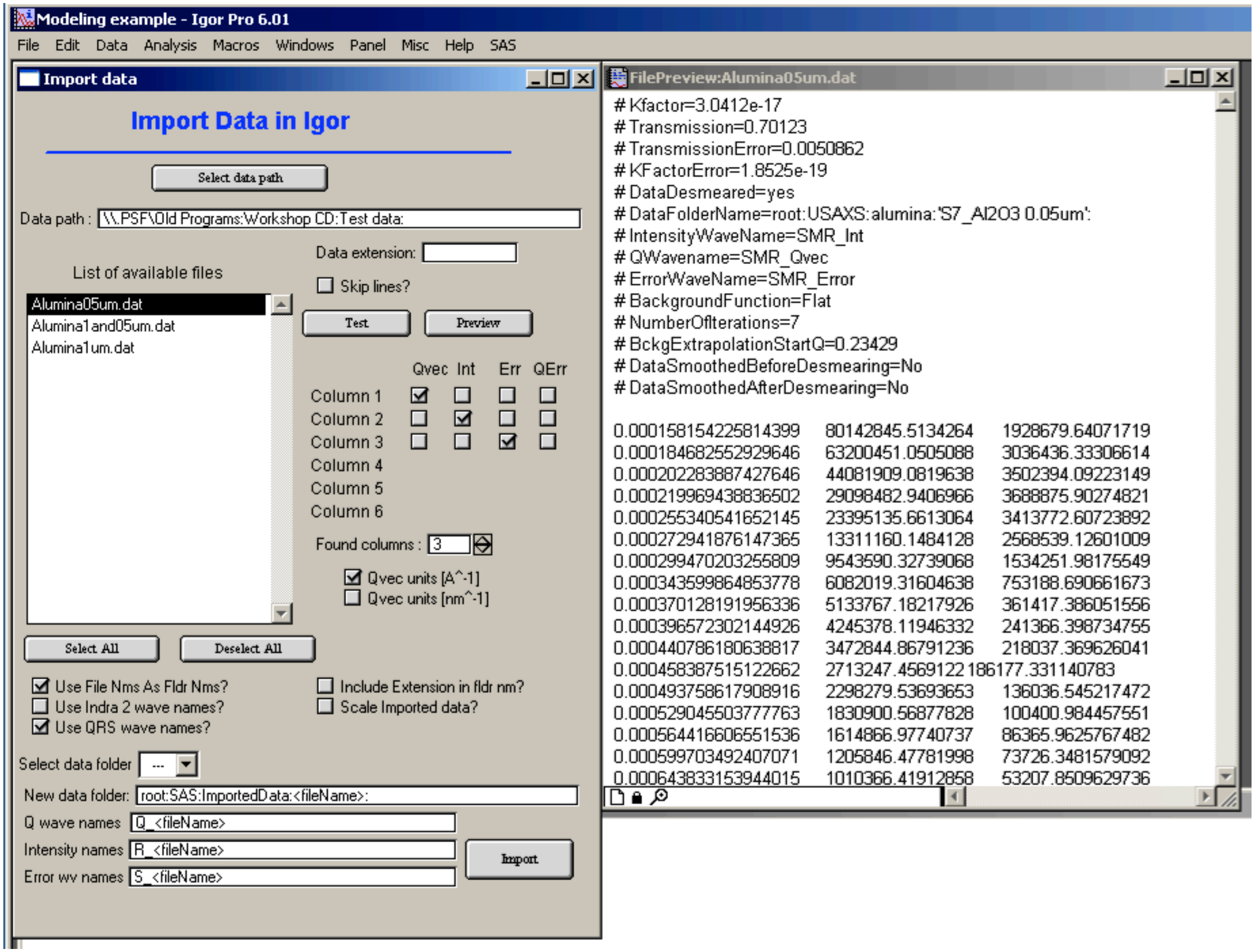


"Irena" data analysis package based on Igor Pro

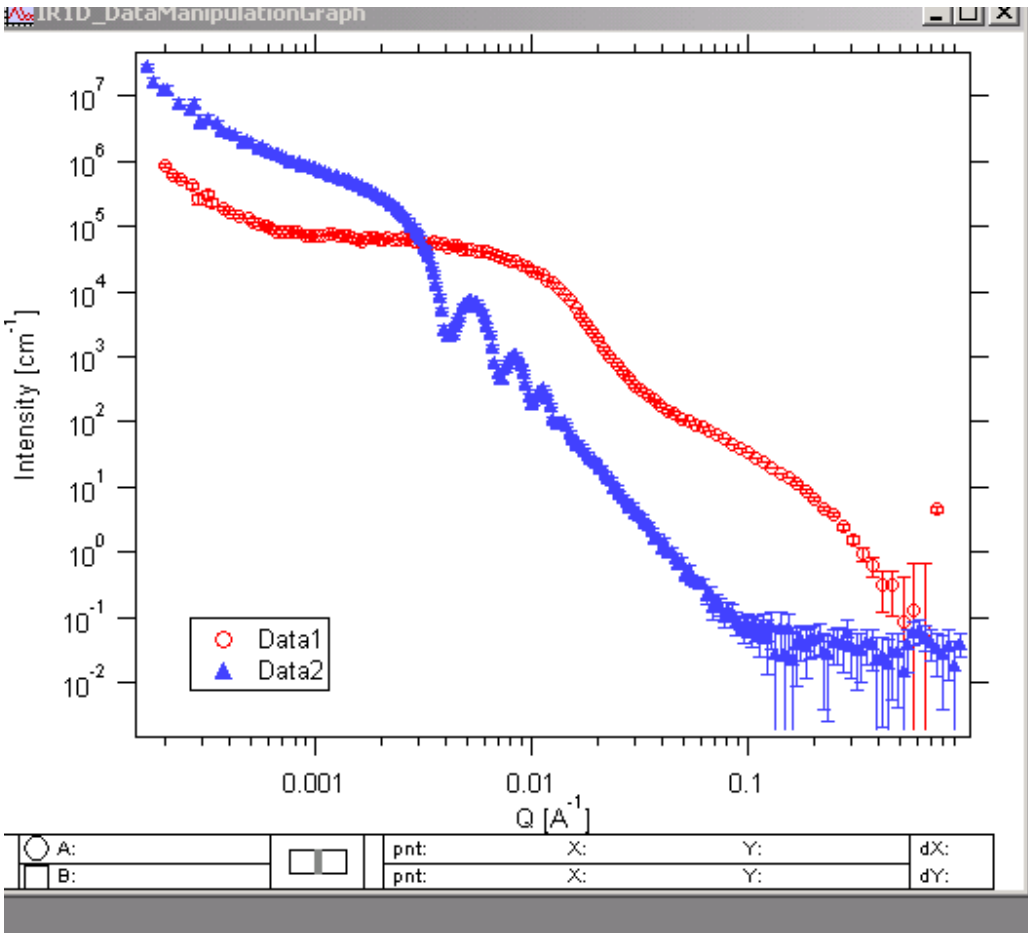
- Combines number of tools to one suit :
  - Import & export data (ASCII)
  - Modify & manipulate (subtract/divide/scale…)
  - Graph SAS data (save graphs, graph styles, some basic fitting, export graphics)
  - Model data using various models:
    - *Size distribution (dilute limit) using Maximum entropy, TNNLS, or regularization*
    - *Direct modeling with fitting (with selected structure factors)*
    - *Unified Fit model (Rg/Power law slopes)*
    - *Fractals*
    - *Debye-Bueche (gels)*
  - X-ray and neutron reflectivity tool (simple systems for up to 8 layers and no relationships between the layers)
  - Other tools:
    - *Calculate contrast (X-ray & neutron) incl. anomalous effects {Cromer-Liberman}*
    - *Desmear data for slit smeared instruments (USAXS, uses Lake method)*
    - *Etc…*
- Free for download - link from http://usaxs.xor.aps.anl.gov/
- **Manual has about 120 pages, please READ IT.**

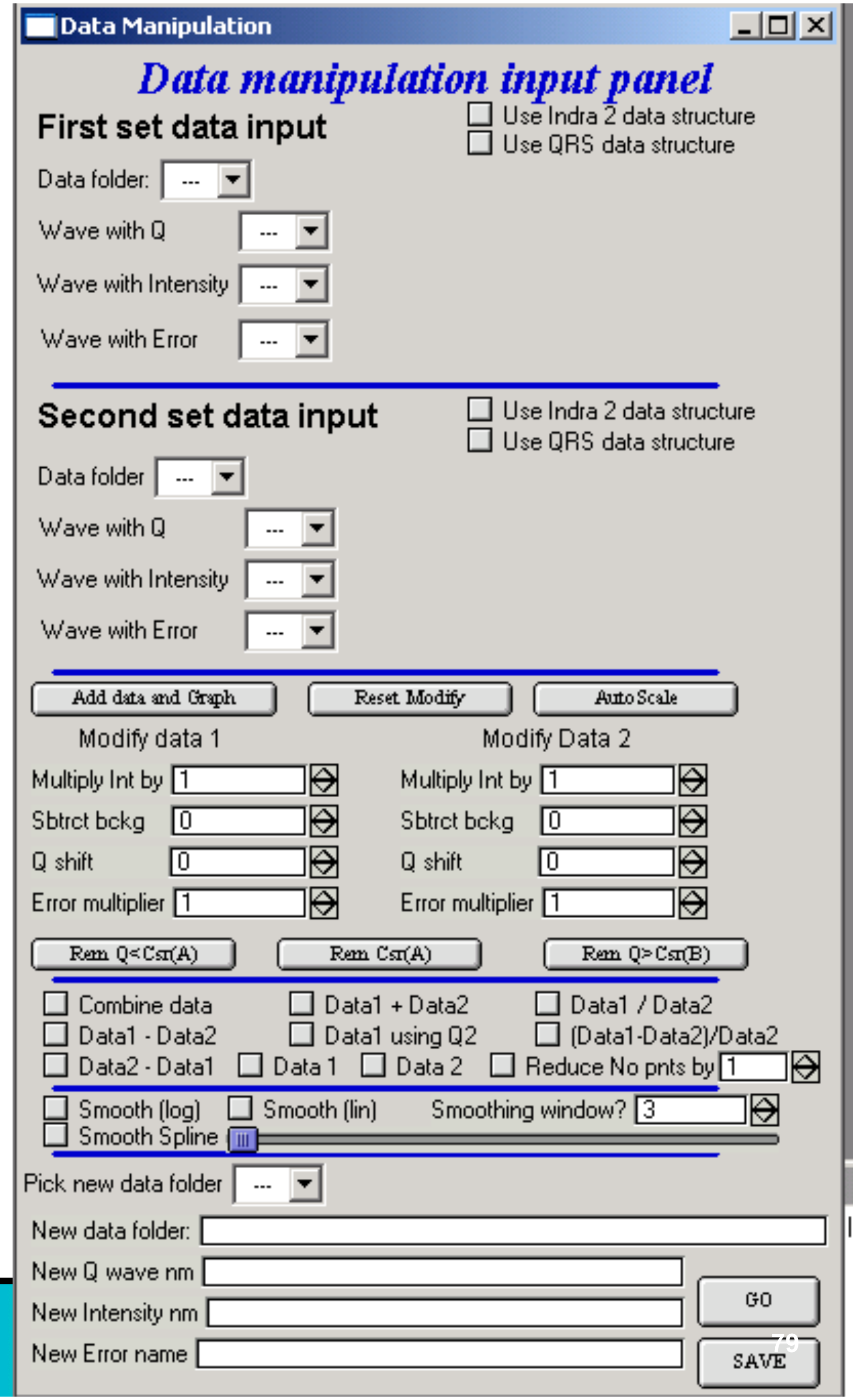
Data import tool

- Import ASCII data
  - Preview
  - Select columns
- Modify
  - Scale
  - Create errors
- Organize data

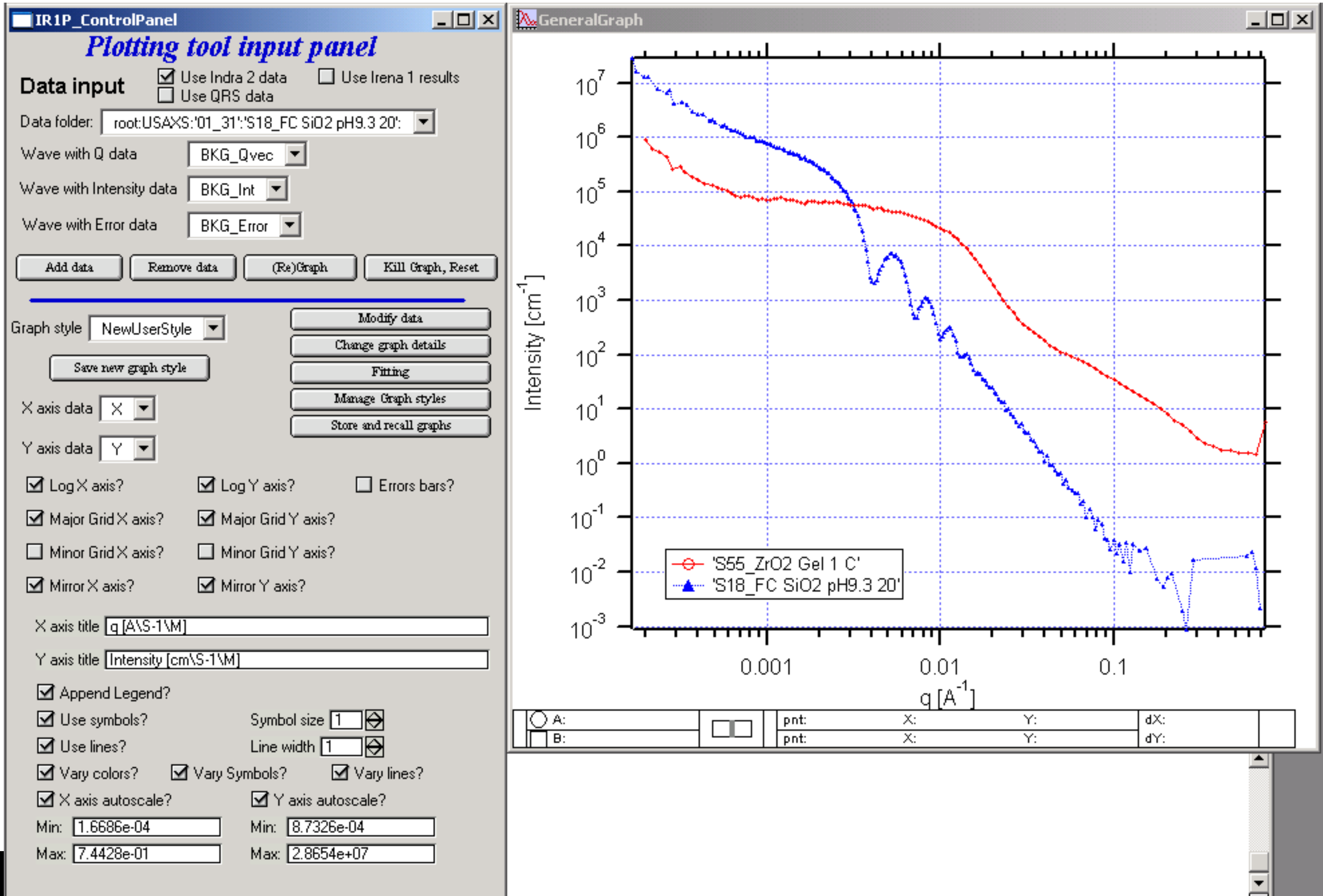


Manipulate data



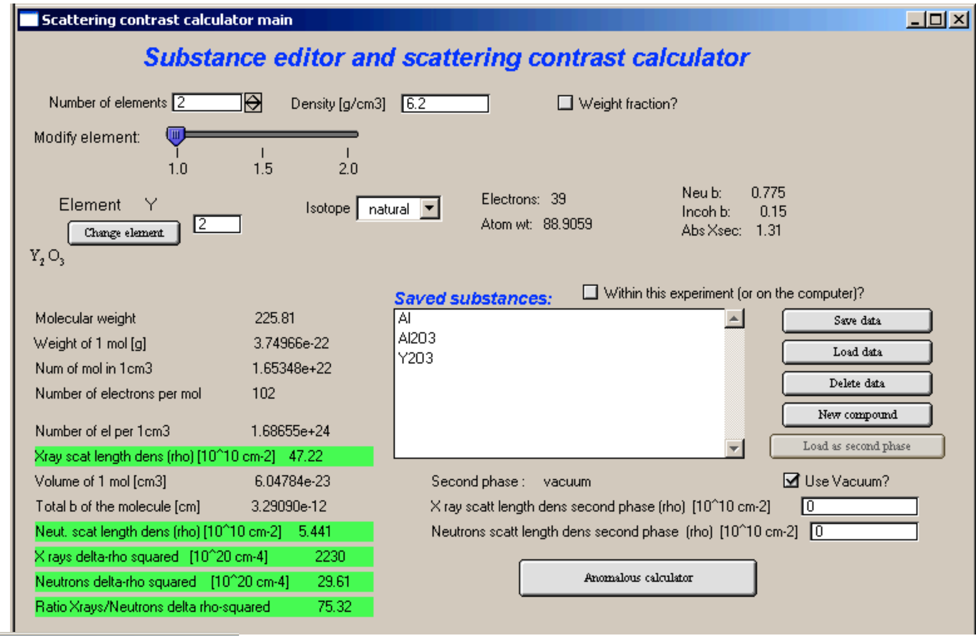


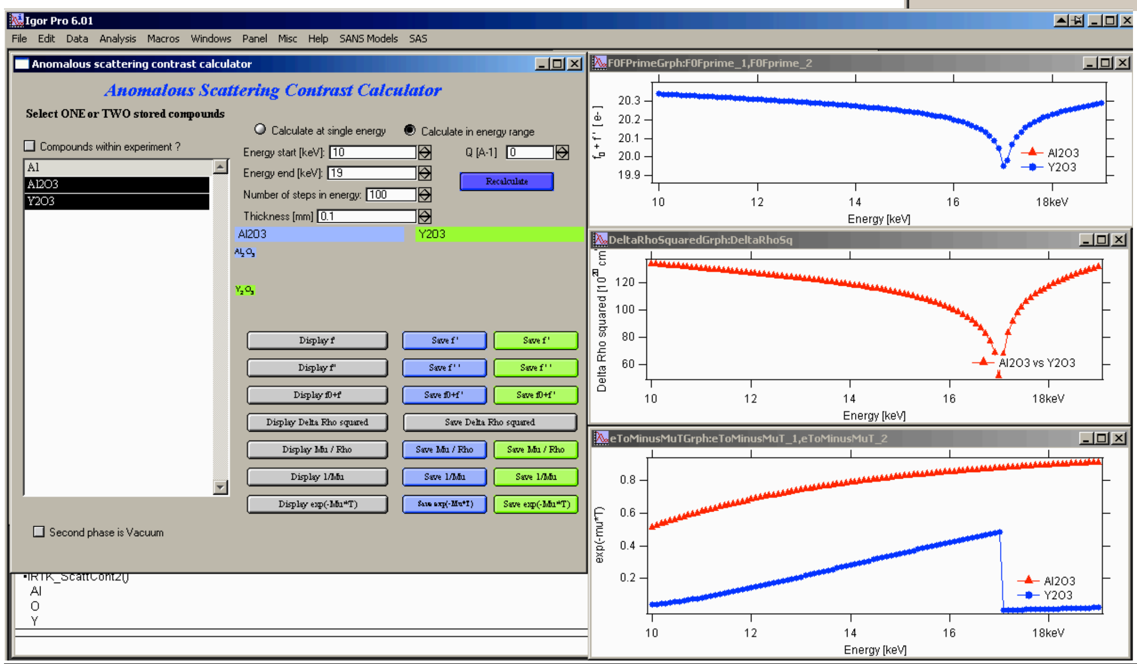
Example plotting tool



Scattering contrast calculator

Create & save "compounds"
Calculate X-ray scattering length density (free el. approx.)
Calculate neutron scat. length density





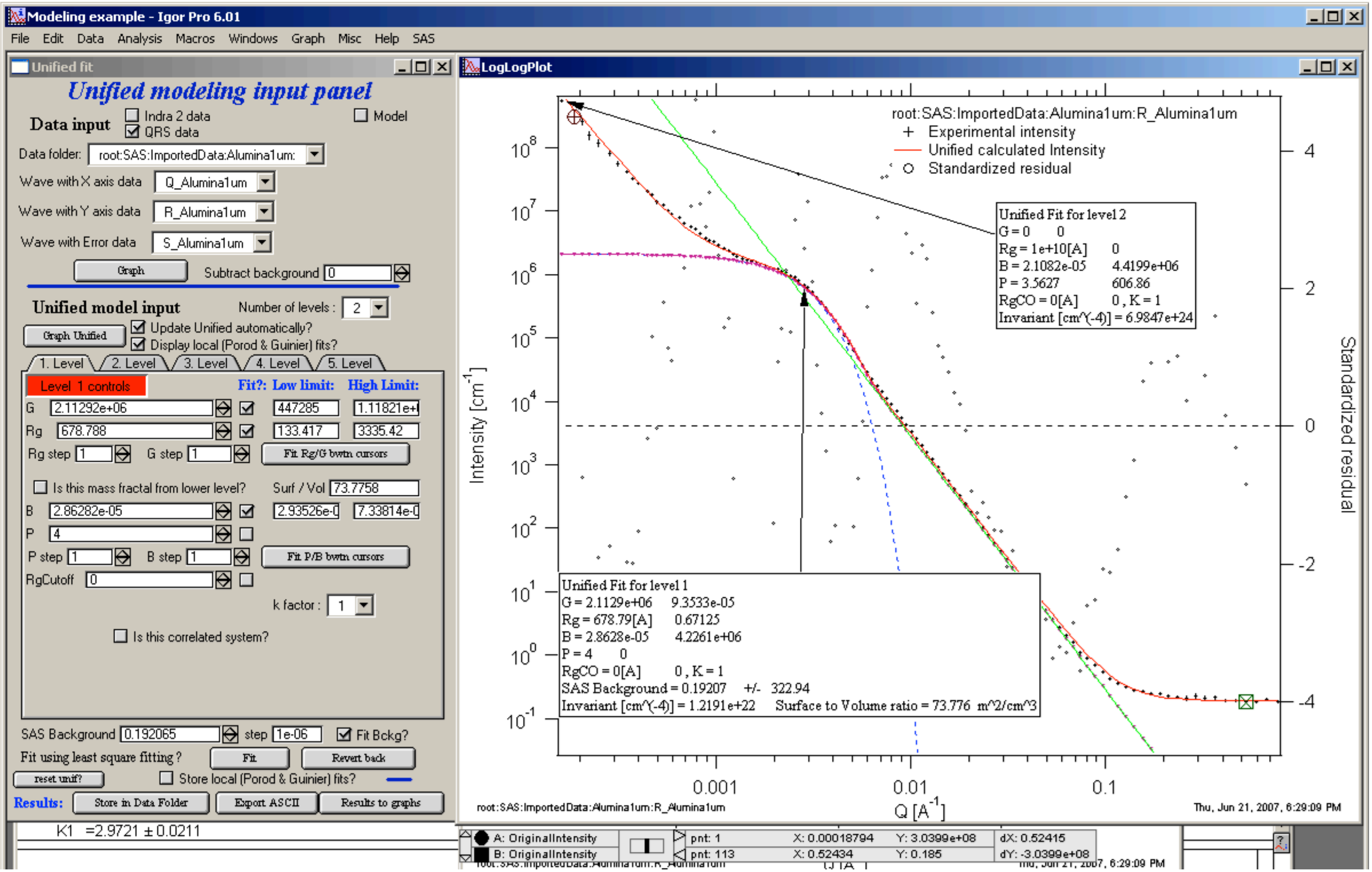
Cromer-Liberman code for Anomalous effects:
Calculate contrast
- at one energy
- in energy range

Calculate X-ray scattering length density (f_0, f', f")
Calculate transmission

Unified fit method
Small angle scattering – dilute limit…

- Represent "populations" or "levels" of structures in the sample by Rg (and pre-factor) & Power law slope (with pre-factor)
  - See references to Greg Beaucage work (http://www.eng.uc.edu/~gbeaucag/BeaucageResearchGroup.html)
- Structure factor "interferences" (~Hard sphere model)
- Very generic, very little knowledge about internal structure needed
- But only limited information is obtained.
  - Based on microstructure model can get details
    - *Fractals*
    - *Size distributions (e.g., parameters for assumed log normal size distribution)*
    - *Various shapes (form factors)…*
- Great tool for first look at the sample, sometimes the only tool really useful
- Fails for very narrow size distributions

Unified fit



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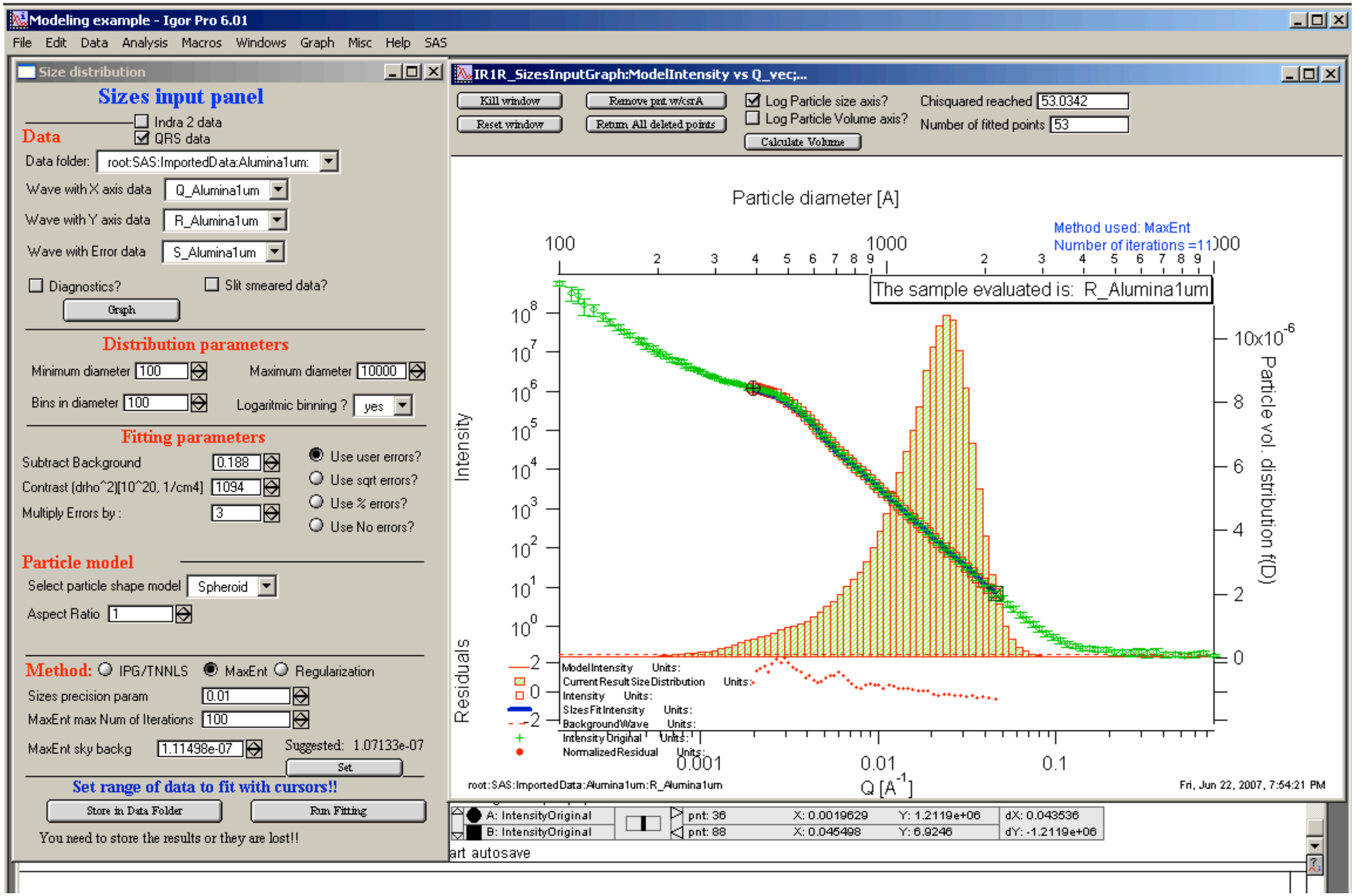
Size distribution example



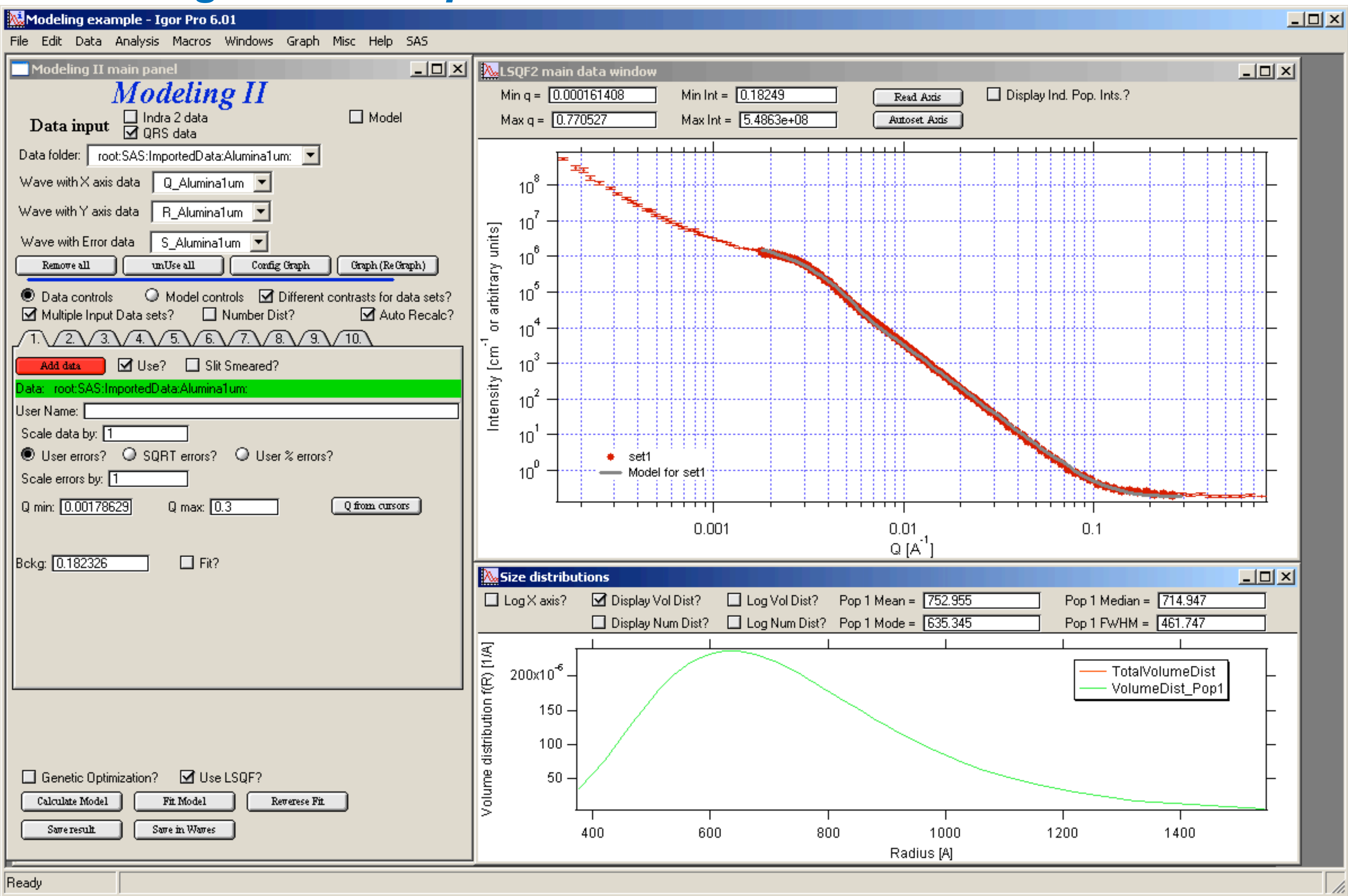
SAS modeling
Dilute limit with some structure factors included

- **Modeling I (old tool)**
  - Single input data set (Q-Int-error)
  - 5 populations of scatterers
    - *Contrast*
    - *Shape (~10 F(Q) available)*
    - *Gauss/Log-normal/LSW/power law distributions*
  - Dilute limit with optional of “interferences” (~ Hard sphere)
  - Least square or Genetic optimization fitting of parameters

- **Modeling II (new tool)**
  - Up to 10 input data sets (Q-Int-error)
  - 6 populations of scatterers
    - *Contrast*
    - *Shape (~10 F(Q) available)*
    - *Gauss/Log-normal/LSW/ power law distributions*
  - Dilute limit with optional 5 different S(Q)
  - Least square or Genetic optimization fitting of parameters

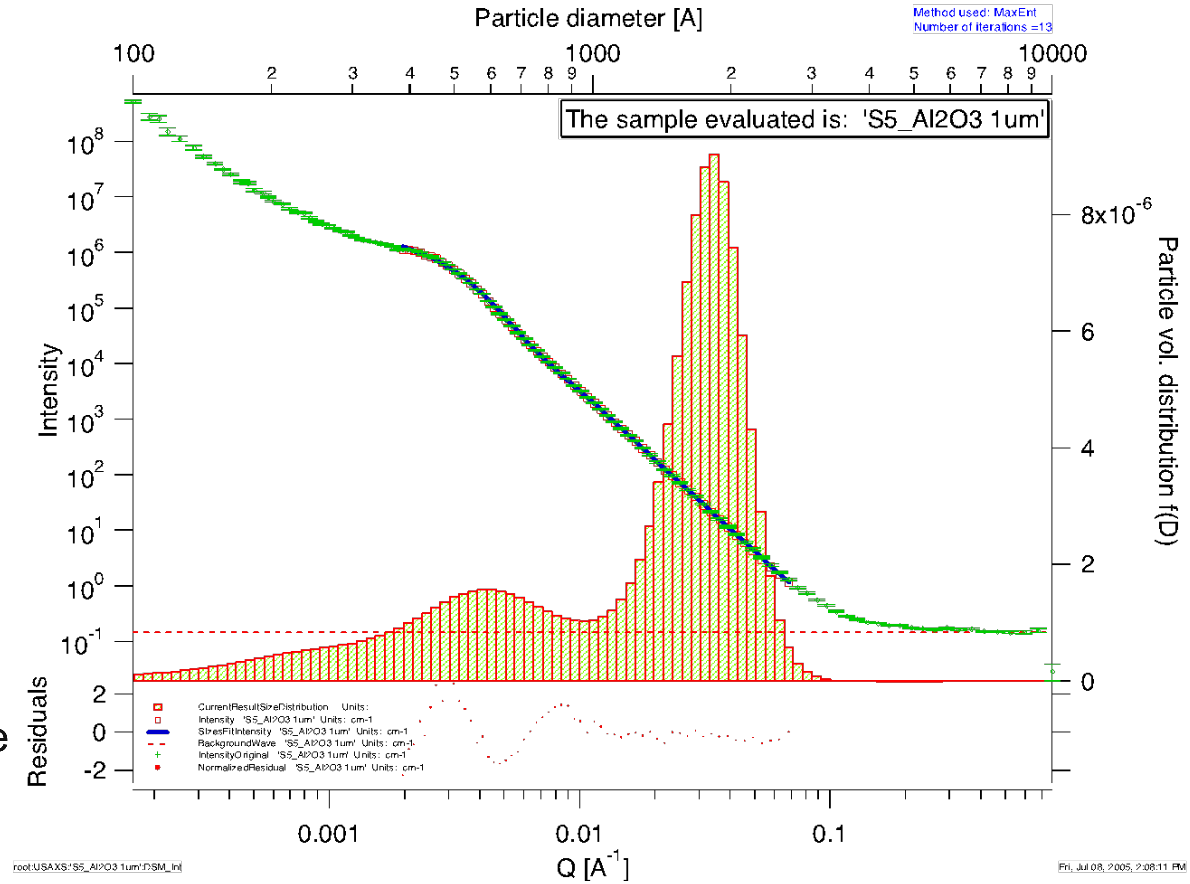
Genetic optimization: semi-Monte-Carlo method.
Particularly useful for narrow size distributions and reflectivity.
See manual for important details.

Modeling II - Data input controls



Size distribution – maximum entropy, regularization, or TNNLS/IPG
What is size distribution?

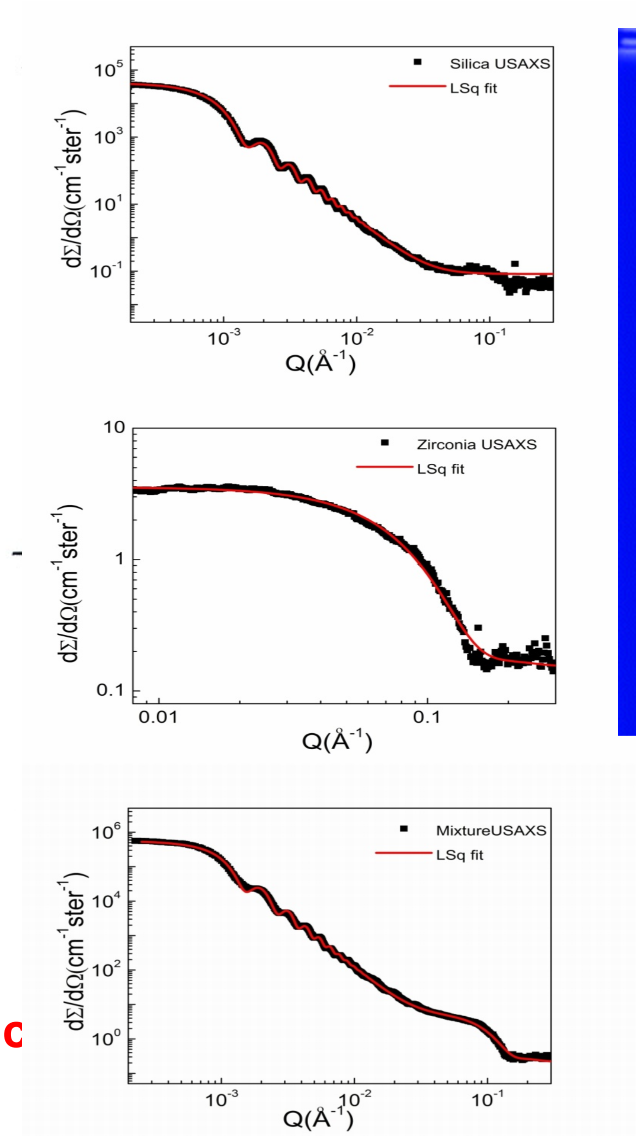
- Size distribution
  - Volume distribution
  - Number distribution
- How much volume -or- number of scatterers - is between
  R – dr & R + dr
  where 2*dr is width of the bin in radii (diameter)
- Total volume of particles –or- number of particles = area under the curve (between R_1 and R_2)
- In SAS often convenient to have log distribution of radii bins!

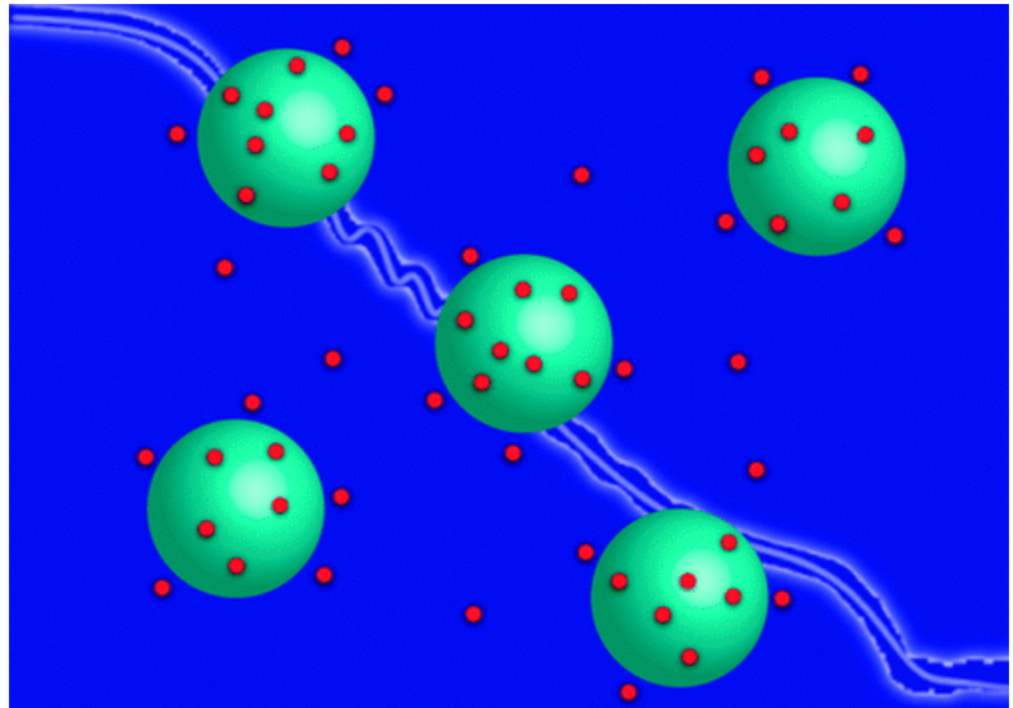


- Number of available particle shapes (F(Q)) including user defined F(Q) function
- Fast, easy – but all scatterers have to be same shape & contrast
- Uniqueness is achieved by use of the Maximum entropy method, TNNLS/IPG, or Regularization

Examples of science

Binary colloidal dispersion with large size asymmetry.





Mic

- Nanoparticles form a loose layer near the surface of the microspheres.
- Average nanoparticle to microsphere distance is close to Debye length.
- Nanoparticle concentration in the loose layer is much higher than that in the solution.

l. (2001) Proc. Natl. Acad. Sci. USA 98, 8950-8954

Arrangement of nanoparticles in the halo

1. Number of nanoparticles in the halo

$$N_{nano} = L_{halo} / L_{nano} = \frac{(\rho_{halo} - \rho_{solv})\frac{4}{3}\pi\left(R_3^{\ 3} - R_2^{\ 3}\right)}{(\rho_{nano} - \rho_{solv})\frac{4}{3}\pi R_{nano}^{\ \ 3}} = 1935.$$

2. 2D volume fraction of nanoparticles in the halo

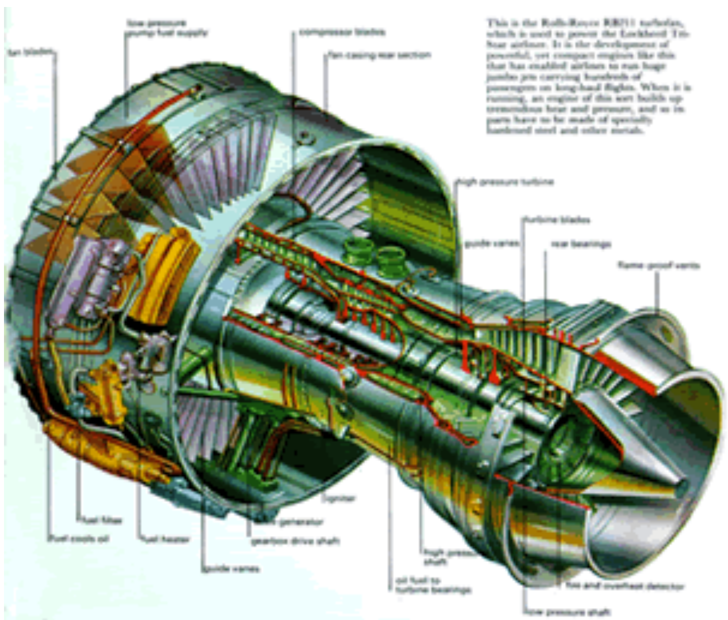
$$\phi_{area} = \frac{N_{nano}\pi R_{nano}^{\ \ 2}}{4\pi\left(\left(R_2 + R_3\right)/2\right)^2} = 0.039.$$

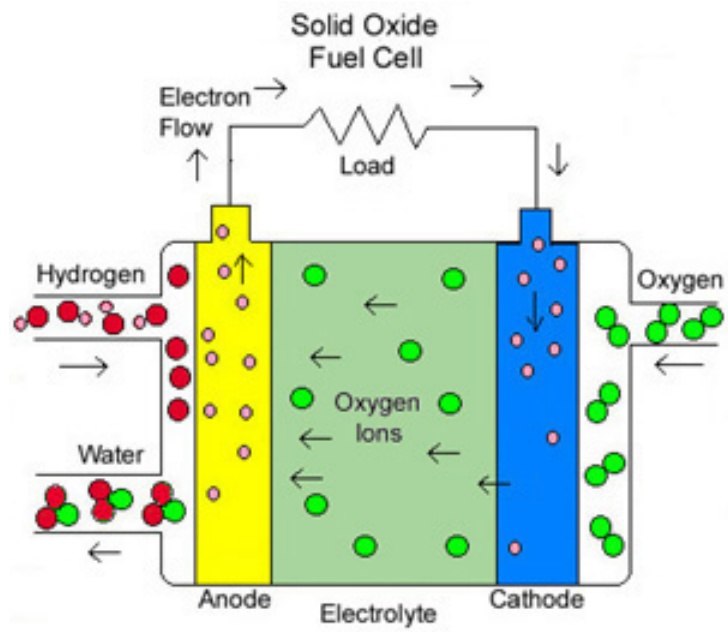
3. Nanoparticle separation distance with the halo

$$D = \left(\frac{\pi R_{nano}^{\ \ 2}}{\phi_{area}}\right)^{1/2} = 22.9nm \approx 8.9 R_{nano}$$

4. Absolute intensity→ 93% nanoparticles in the solution, 7% in the halo.
→ weak interaction between nanoparticles and microsphere.

Materials for Energy Generation

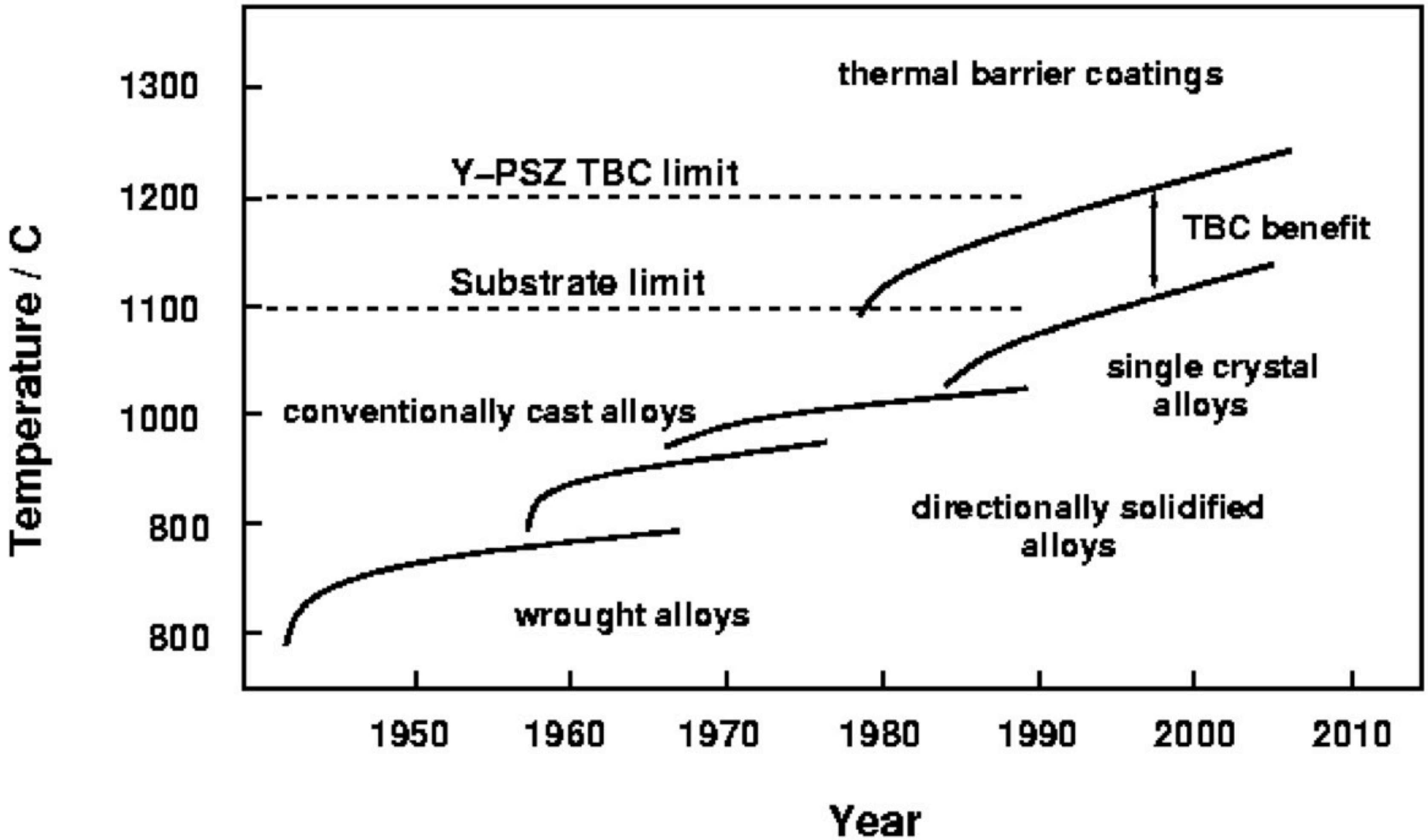




Most of the internal (hot environment) parts in jet engines are coated.
Trends - prime reliant coatings while increasing operating temperatures.
Plasma sprayed or EBPVD (DVD).

Environment friendly, efficient electric energy source.
Functional ceramic layers.
Trends – lower operating temperatures & increase life. Electrolyte reliability is very important.

Thermal barrier Coatings (TBC's) – never ending story?



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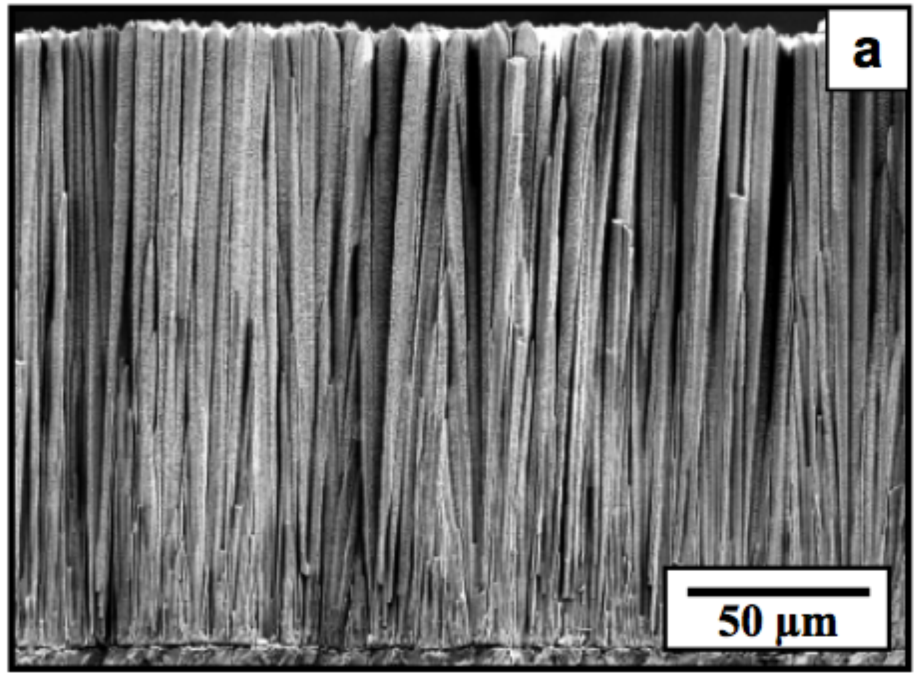
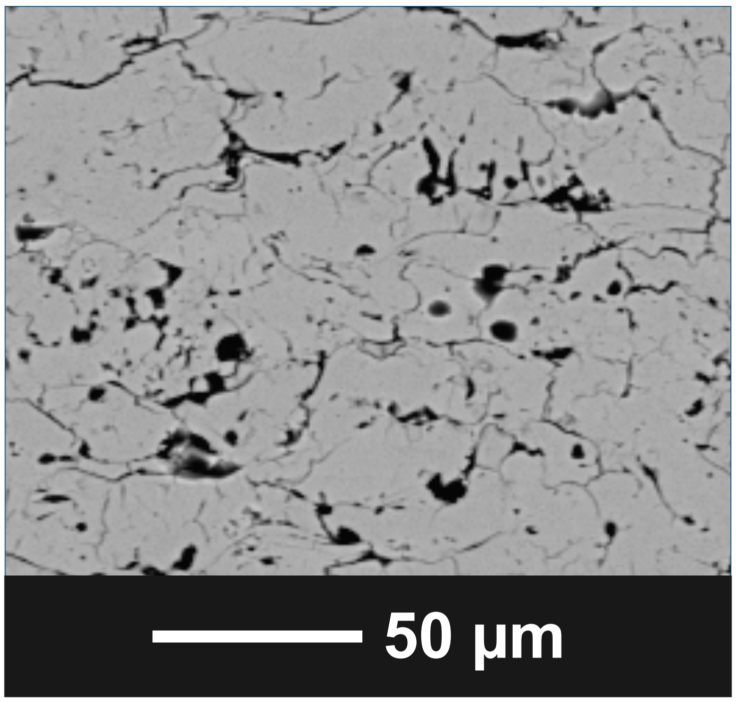
Complex designer void systems

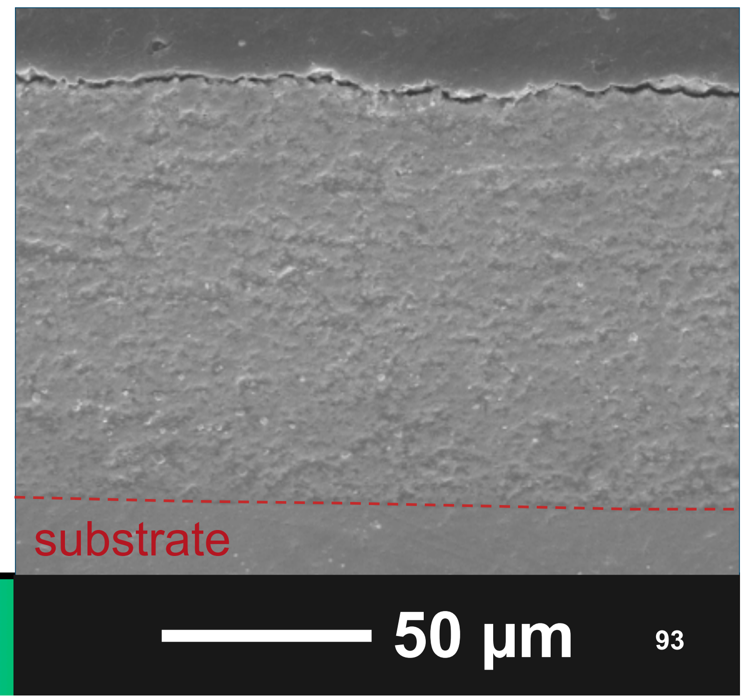
EBPVD
Complex sizes nano - micro



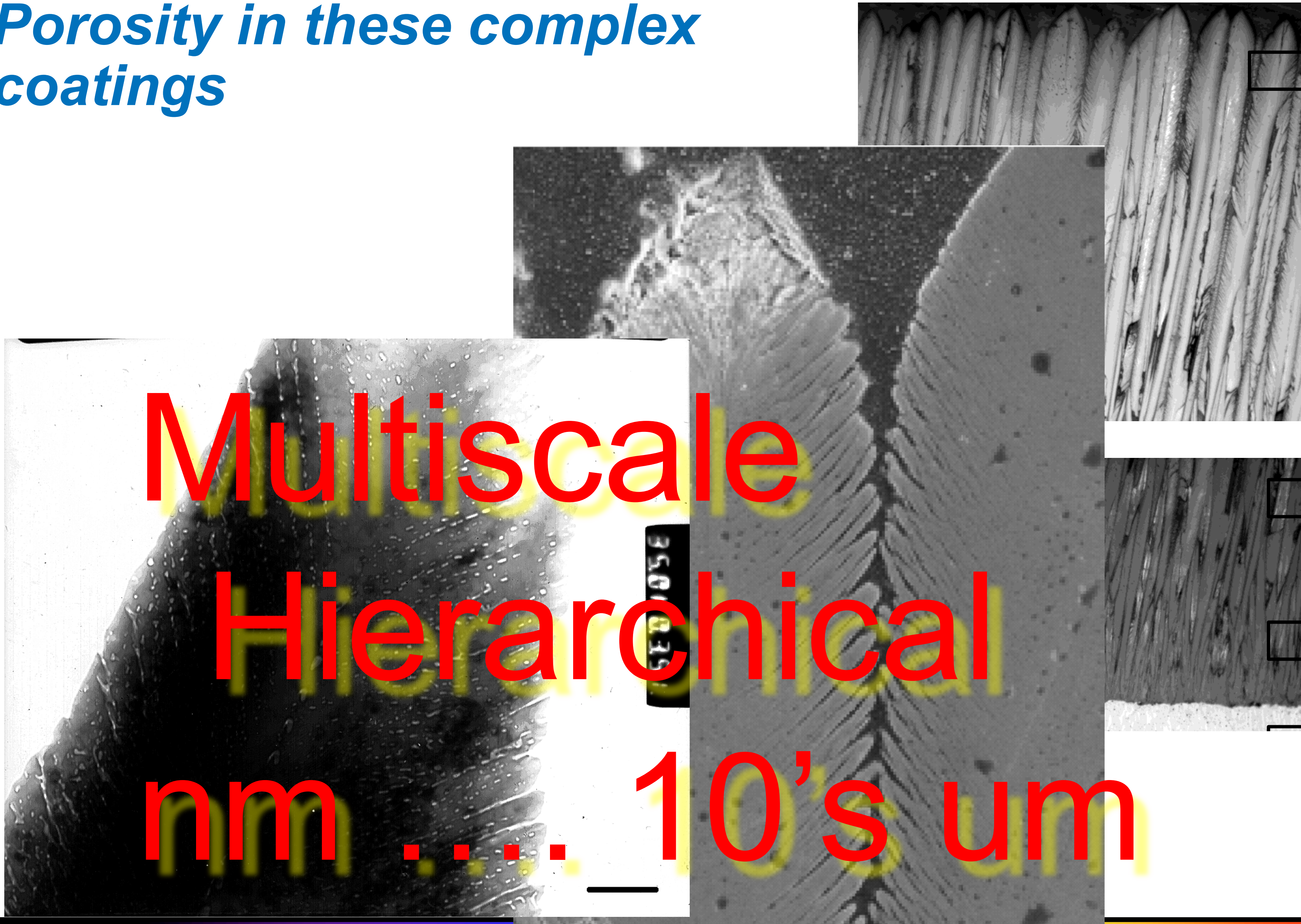
APS
micrometer-sized
8YSZ - d_{50} ~ 30000 nm



SPS
nanometer -sized
8YSZ - d_{50} ~ 50 nm



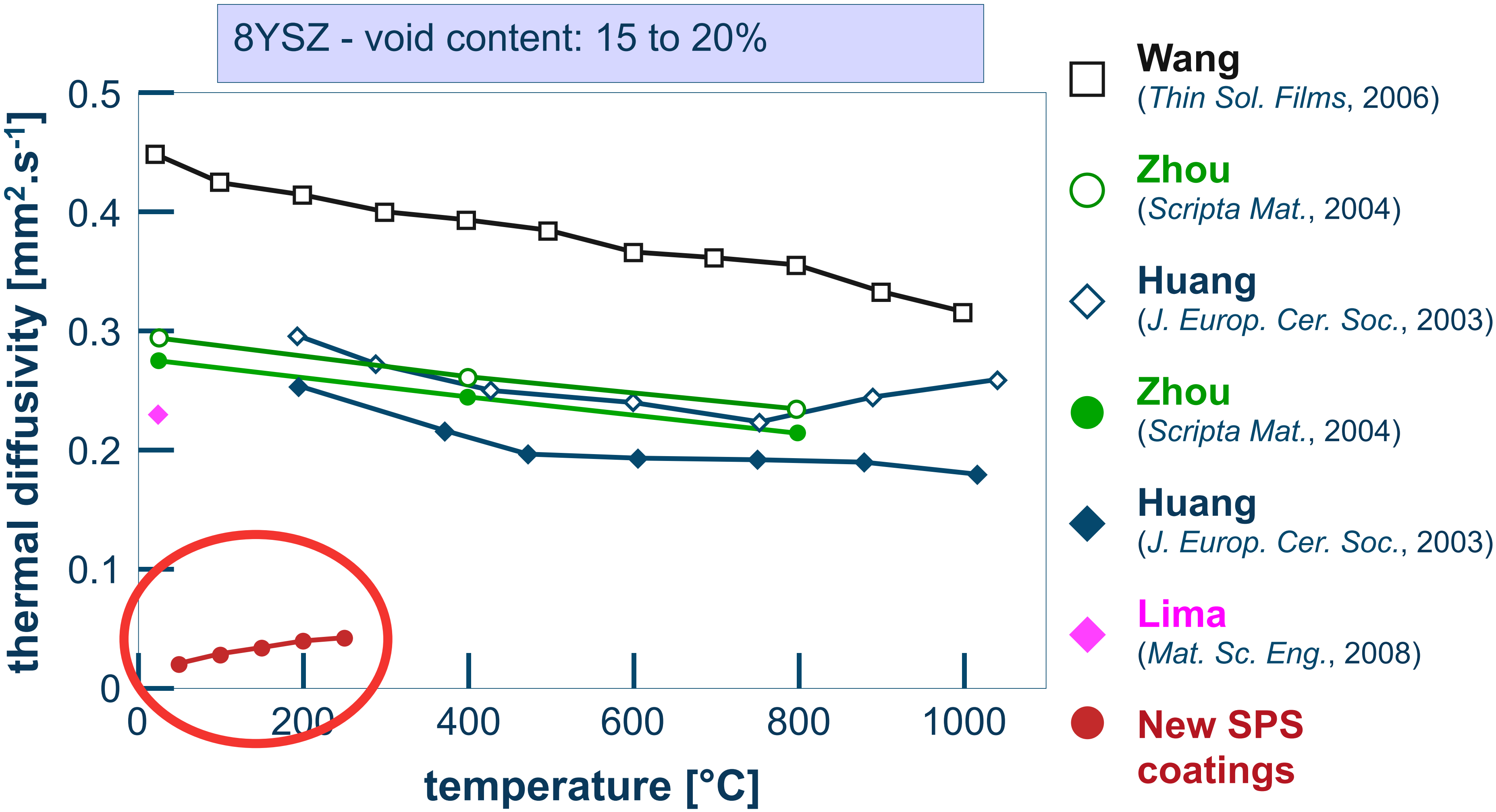
Porosity in these complex coatings

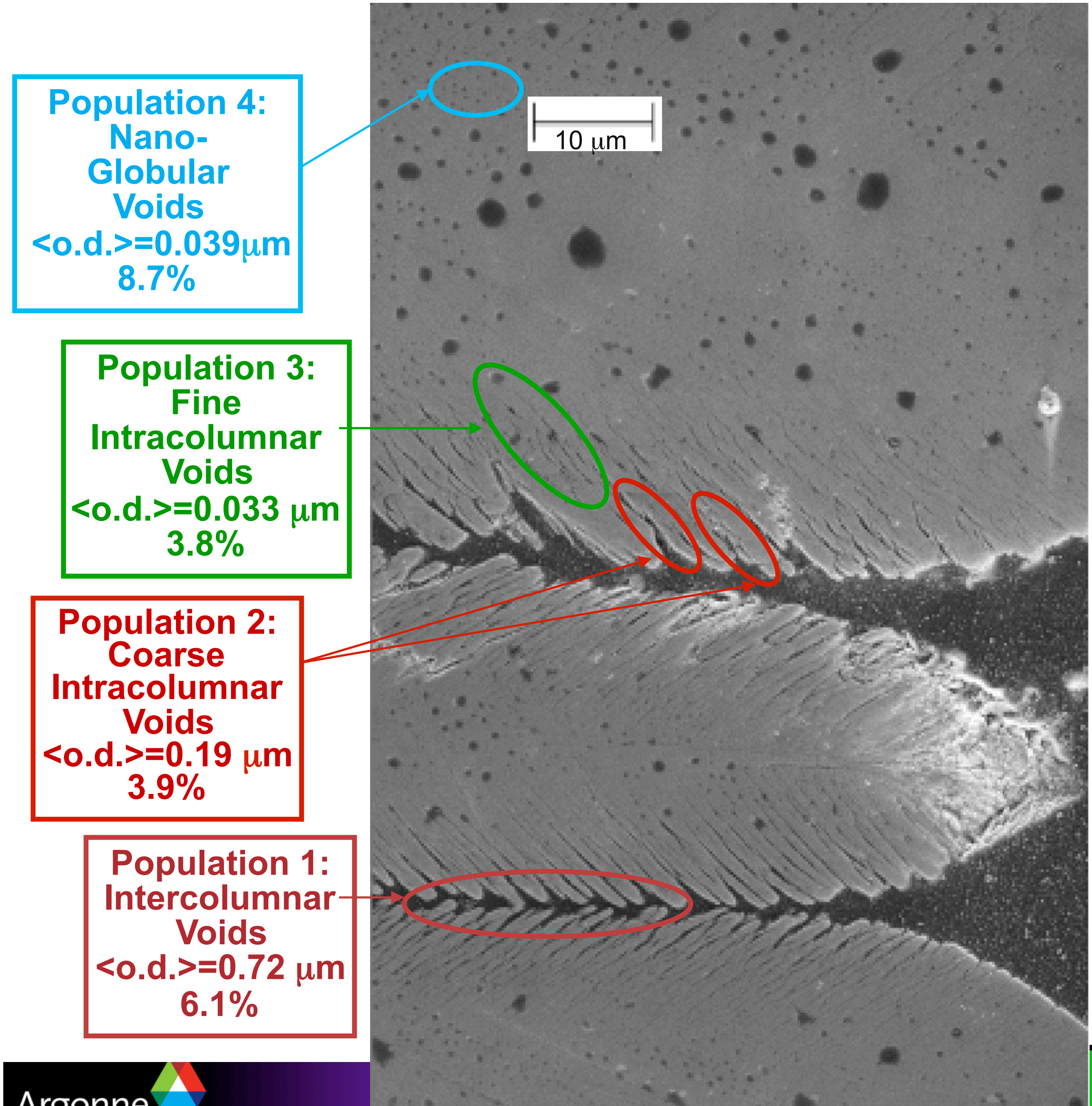


Application needs…

- Design the "best" microstructure for given application
  - Compromise among mechanical, thermal, … properties, SAFETY, and cost
  - Prefer development by modeling ("in computer process design")
  - Need to understand the manufacturing - microstructure – properties relationships
    - *As manufactured (kind of possible)*
    - *During application (difficult)*
  - Increase reliability and efficiency in application
  - Predict failure
- Need basic scientific understanding to guide us…

Thermal diffusivity measurement

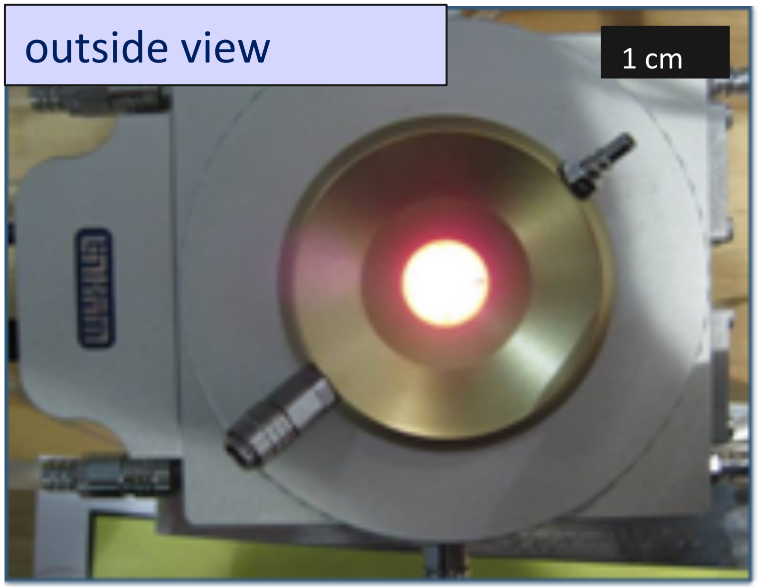


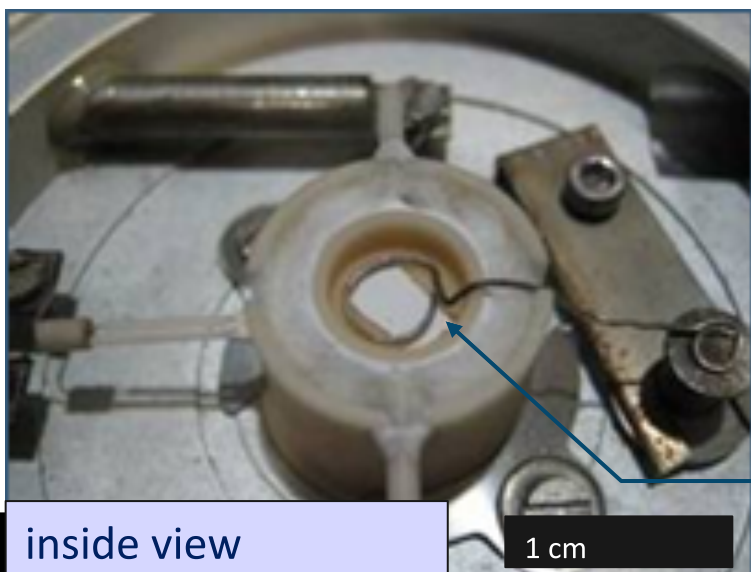


Example of ex-situ analysis:

- Full characterization of void system
- 2D collimated USAXS
- About 1 day of measurement
- About 1 month of analysis
- Single/few conditions

In-situ analysis – SPS coatings

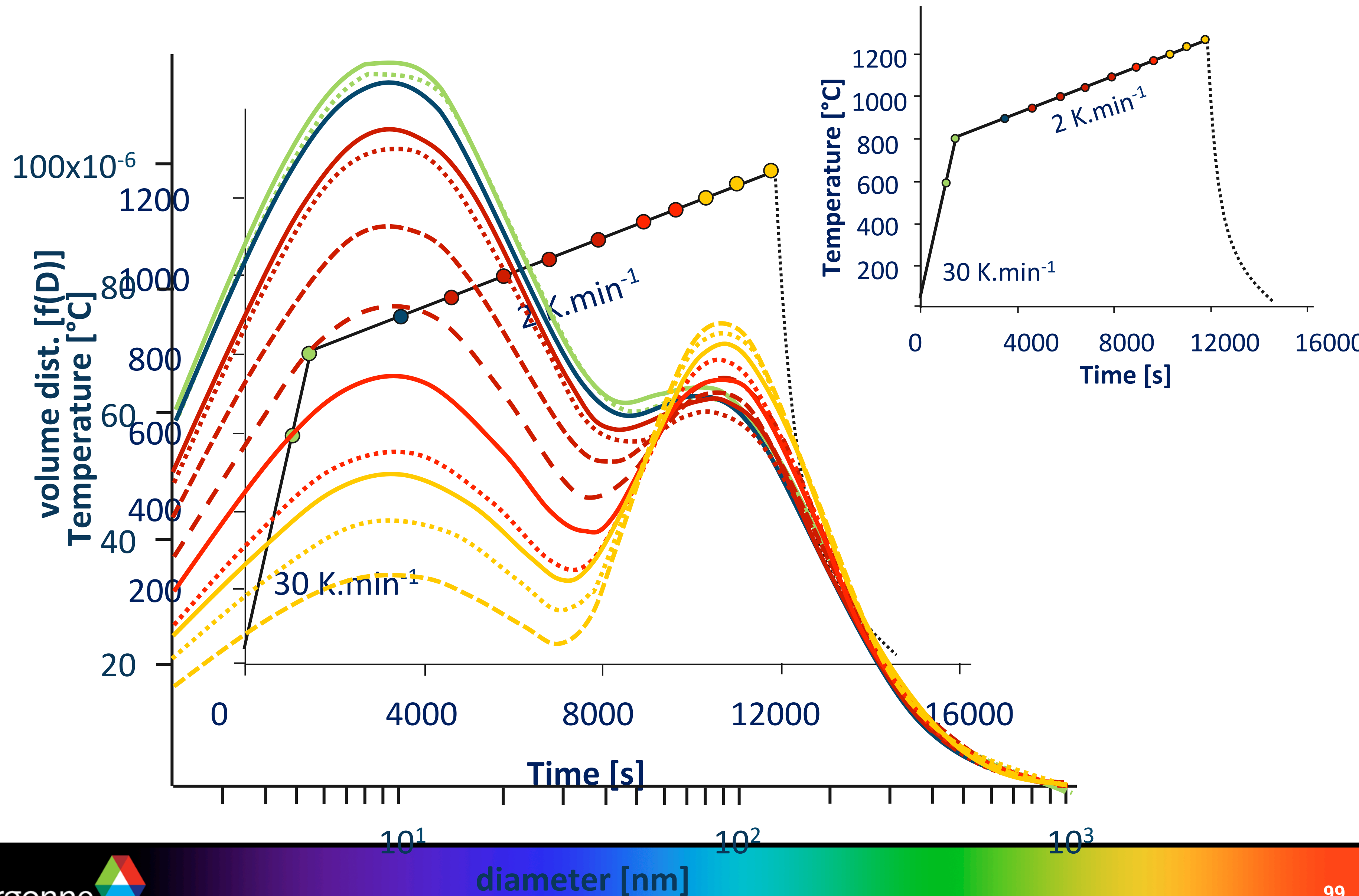




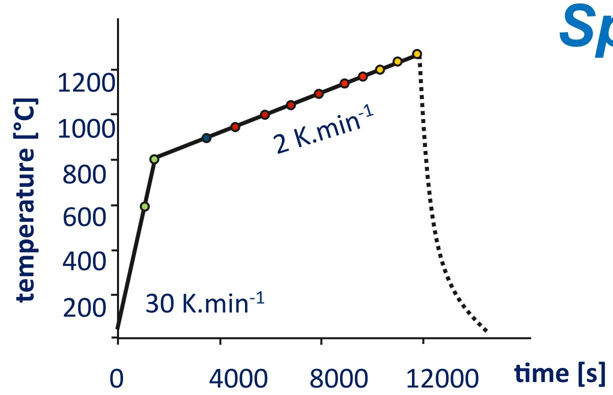
free-standing sample

- **Can study various parameters reflecting real-world conditions**
  - Time
  - Temperature
  - Chemistry (e.g., effect of Si, S, and various fuel compositions)
  - Real profiles with combination of above parameters

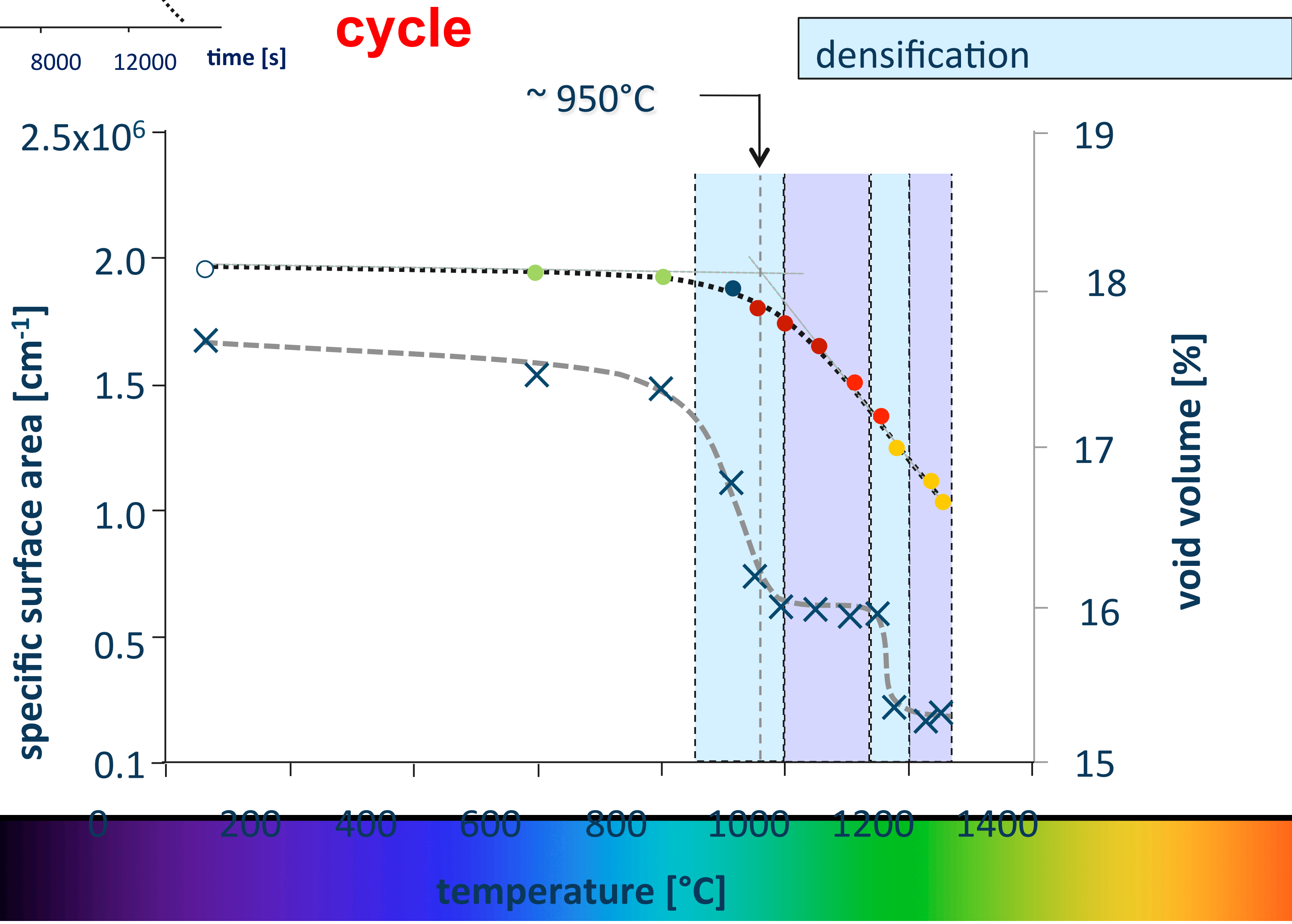
Modeled in-service microstructure changes



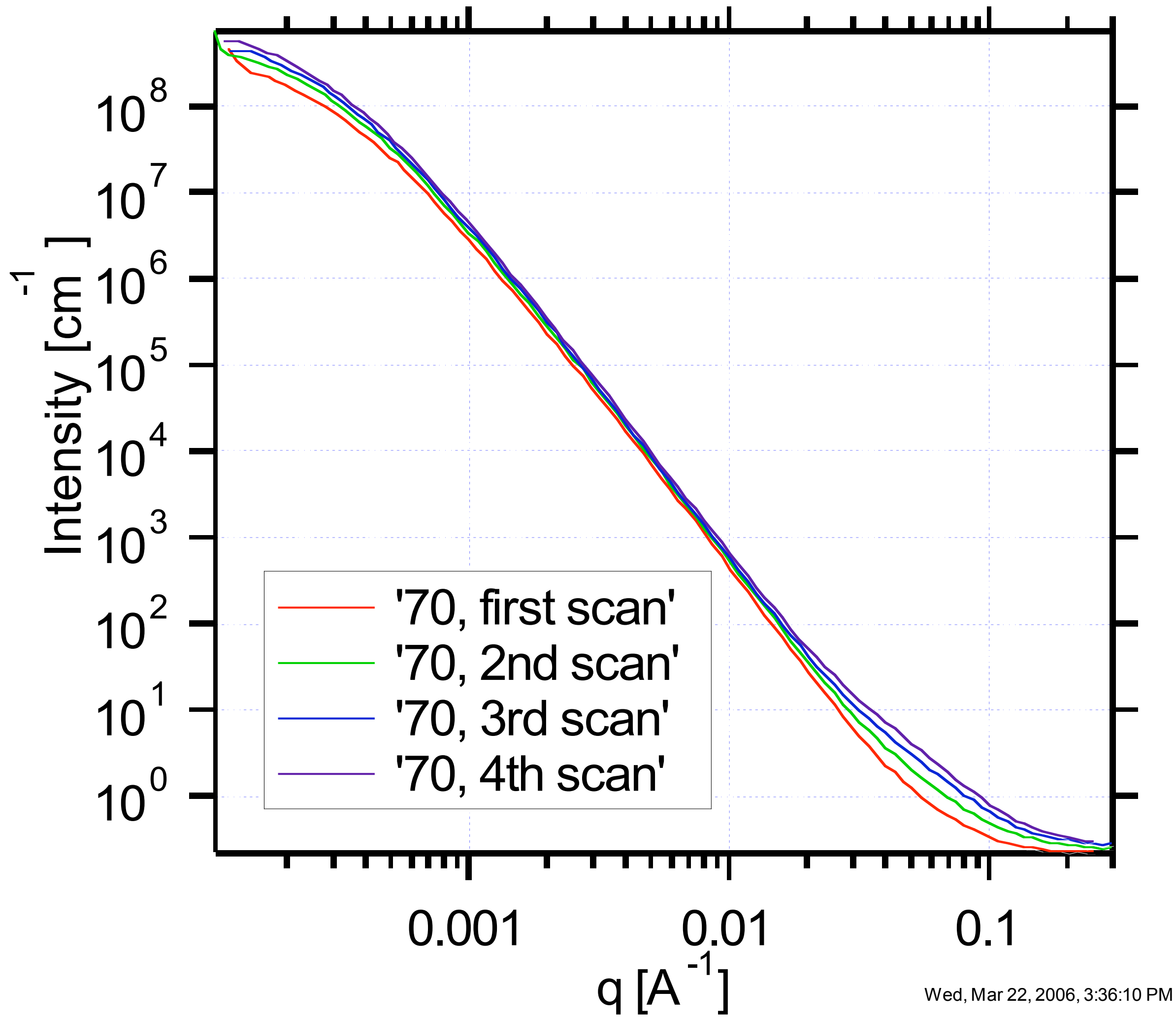
Specific surface area vs. void volume



These are important results for industry
This work is ongoing and scheduled next cycle

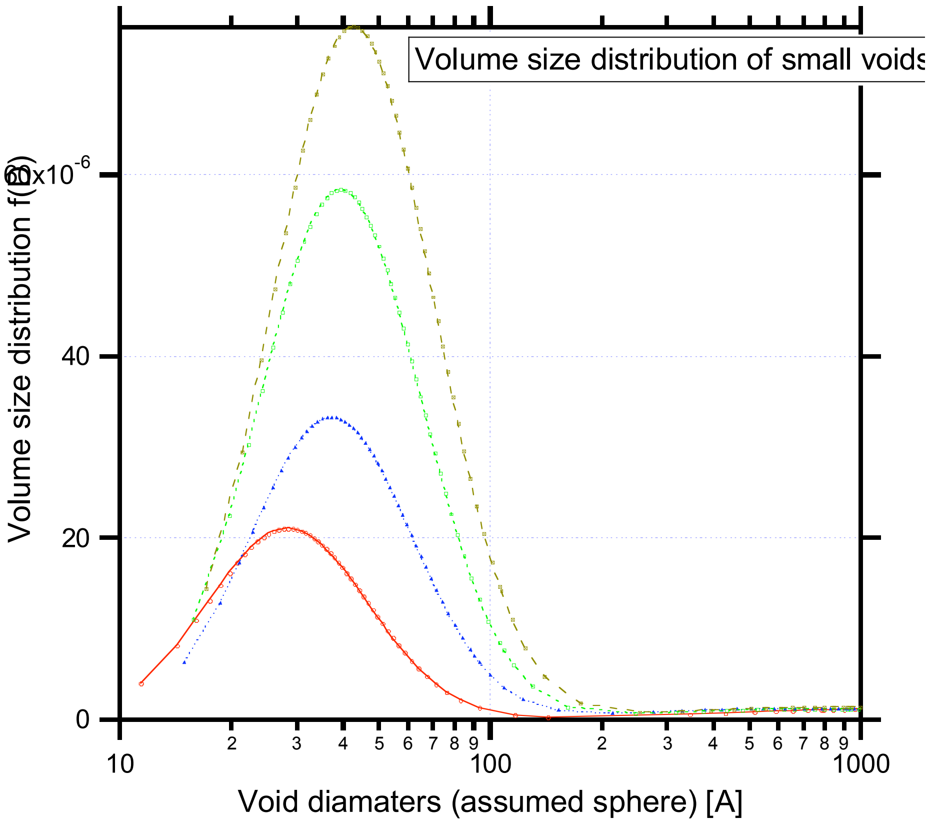


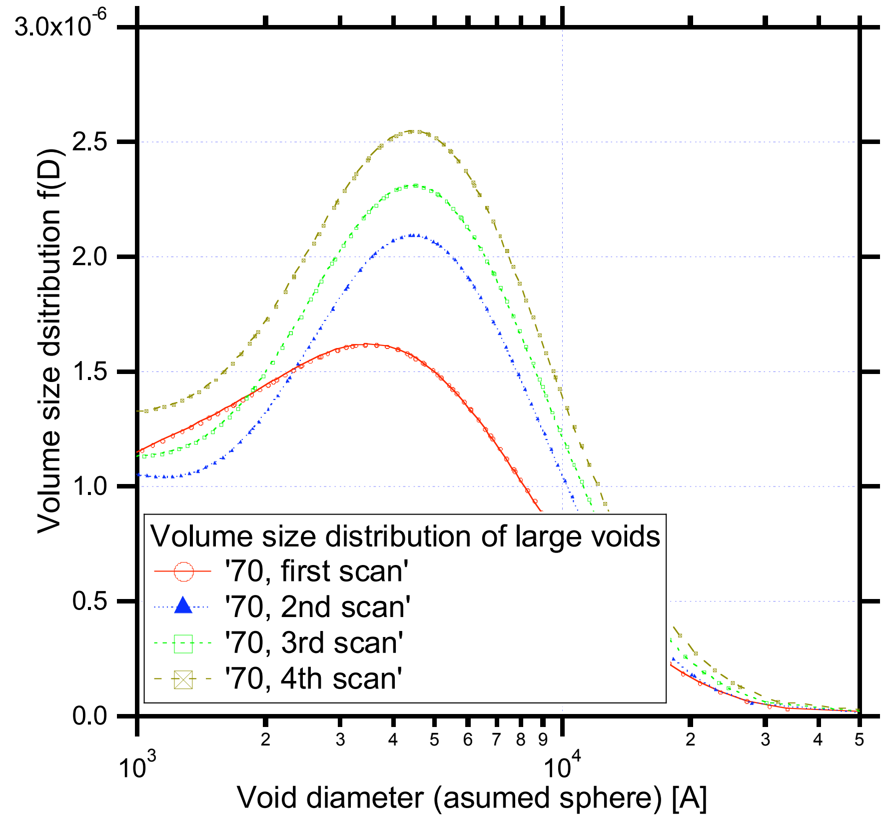
High explosives



USAXS data from in situ measurements of highly insensitive energetic materials based on 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Various TATB formulations experience an irreversible volume growth event that is a function of both temperature and time, generally referred to as ratchet growth. This affects significantly the detonation velocity of these highly insensitive explosives. Of particular concern are the voids in the nanometer to micron size scale intrinsically associated with the detonation process. Such small porosity in bulk material is not easily investigated using various techniques, however, ultra small angle scattering (USAXS) technique is ideally suited for characterization of structure on this scale in energetic materials. Presented data are from in situ experiment, each scan represents one thermal cycle between -30C and 80C. Graph is from work preformed by Trevor M. Willey, Tony van Buuren, and Jonathan R. I. Lee, LLNL.

High explosives





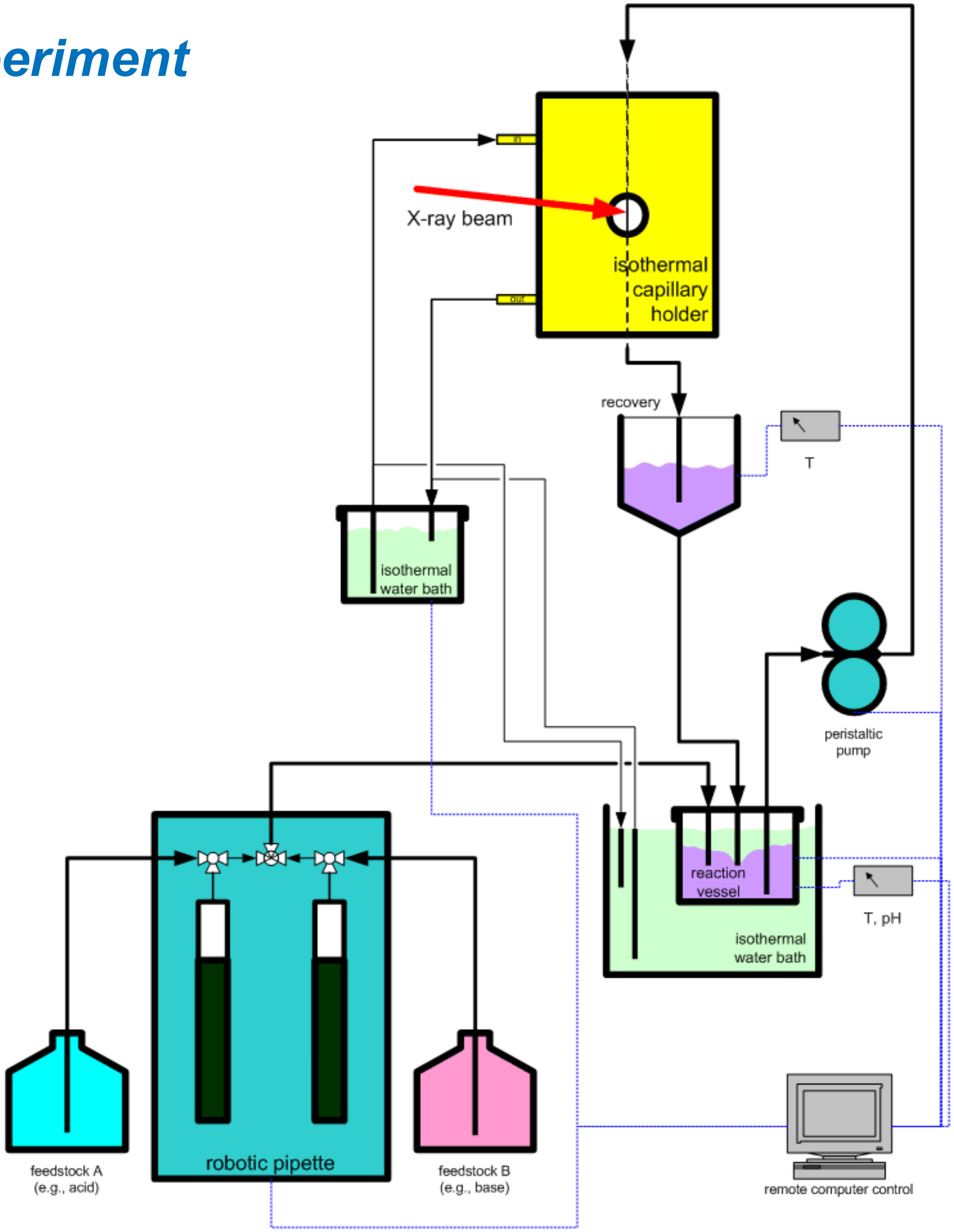
Small voids

Large voids

Quantitative results for large voids are very important for ratchet growth modeling efforts by LLNL. Nano voids were not known before…

Flow cell for this experiment

- isothermal experiments at 20, 25 and 35 °C
- reaction changes followed for up to 10 h
- periodic scans selected for modeling to represent observable reaction time line
- pH and temp recorded continuously



In situ ultrasmall-angle X-ray scattering study of solution-mediated precipitation of nanocrystalline ceria

A. J. Allen[1], V. A. Hackley[1], P. R. Jemian[2], J. Ilavsky[2], J. Raitano[3] and S-W. Chan[3]

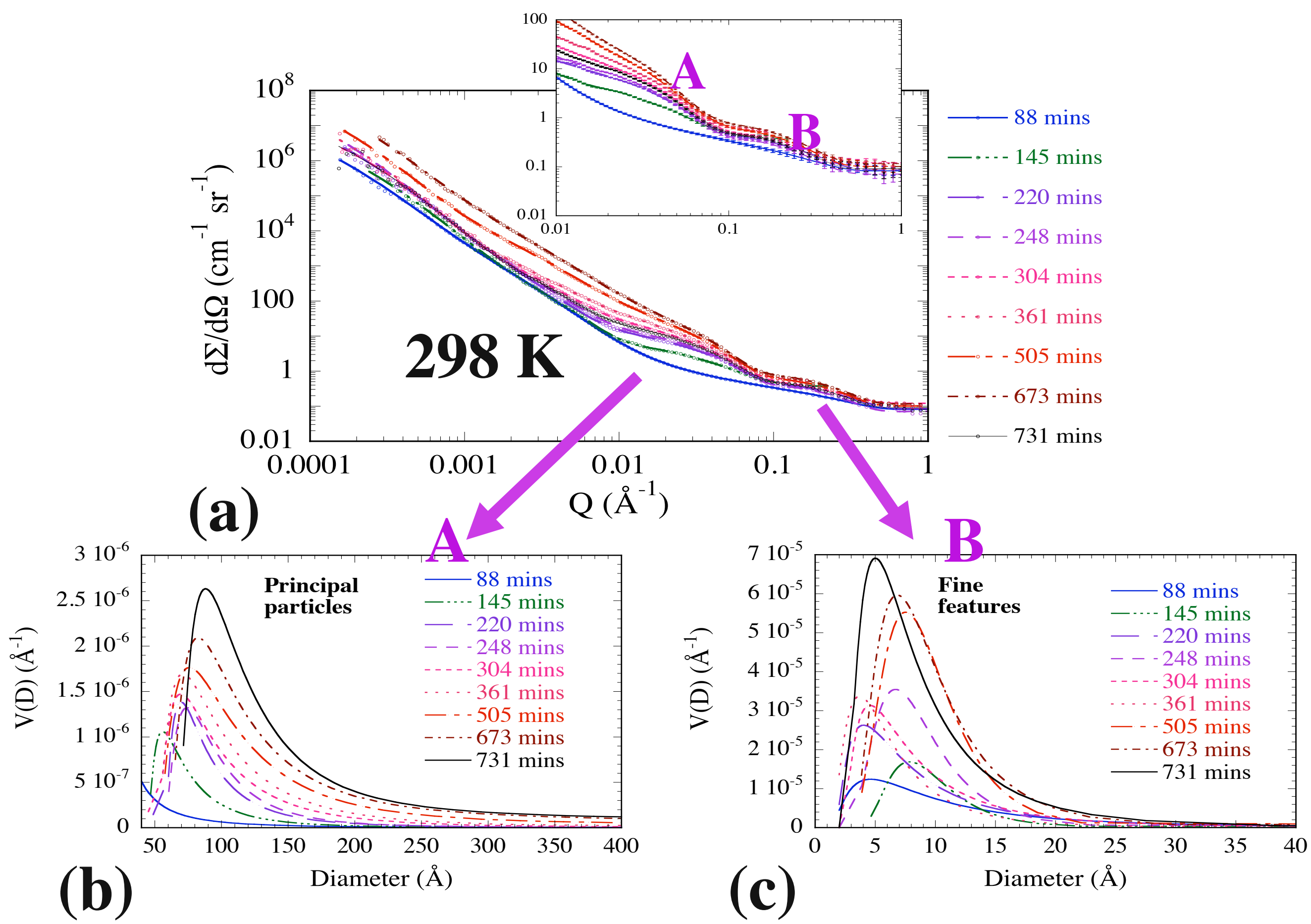
[1]National Institute of Standards and Technology, Gaithersburg, MD 20899-8520

[2]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

[3]Columbia University, New York, NY 10027

•Nano-CeO_2 has important potential applications:

3-way catalysts for vehicle emissions, SOFC electrolytes, gas sensors, optical coatings, CMP slurries, etc.



Conclusions….

Wrap up

- SAS investigations measure nanoscale microstructure
- Many different materials of technological importance can be investigated
- Wide range of instrumentation is available – need to choose wisely
- Data reduction tools are freely available
- Data analysis tools are also freely available – take advantage of this!
- Unique results not obtainable by other methods
- Complementary methods increase the information content which can be realized from a quantitative SAS investigation

Useful links – resources for SAS on the web

- APS SAS group – APS beamlines and useful links: http://small-angle.aps.anl.gov/
- NIST reactor data reduction & analysis software: http://www.ncnr.nist.gov/dva/index.html
- Indra & Nika (as presented in this talk): http://usaxs.xor.aps.anl.gov/staff/ilavsky/
- Dmitri Svergun (GNOM) http://www.embl-hamburg.de/ExternalInfo/Research/Sax/
- ESRF software: http://www.esrf.eu/UsersAndScience/Experiments/TBS/SciSoft

Organizations

IUCr SAS	http://www.iucr.org/iucr-top/iucr/csas.html
ANL SAS SIG	http://small-angle.anl.gov
USAXS	http://usaxs.aps.anl.gov

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