

27.0 <u>Å</u>

### **Small-angle Scattering for Every Problem?**

#### **Materials science review of SAS Applications**



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#### Advanced Photon Source ("APS"), www.aps.anl.gov



#### Purpose of this presentation

- Entertain ...
- Educate...
- Raise your SAXS know-how ...
  - Understand the theory limits
  - Understand the experiment
    - Capabilities
    - Limitations
  - Understand the software limitations
  - ••
- NOT : make you SAXS experts. Need more time and experiments.

## **BUT**:

### **Managing your SAXS expectations**

#### Quickly about me:

- Over 30 years experience in X-ray (diffraction/scattering) fields.
- Over 20 years of experience in the SAXS/SANS fields.
- Over 15 years experience as beamline scientists.
- PhD in Materials Science and Engineering
  - Thermally sprayed coatings I actually made stuff with my hands!
  - MS in Physics MS thesis was diffraction (Debye-Waller factor)
  - Used SANS (MSANS) for ~10 years
  - Mostly SAXS (USAXS) for more than 15 years
- Since 1999 Instrument scientist on USAXS at the APS
  - Unique instrument among SAXS devices :

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The largest range of Q vectors covered on any single instrument in the World about 5 decades
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today

- Many, many users (many, many sleepless nights)
- Extremely versatile from "Chocolate to Plutonium in one week"
- Since 2001 author of SAXS analysis and data reductions software packages:
  - Irena, Nika, Indra, Clementine...
- Since ~2004 provide SAXS/SANS user community with absolute intensity standard (Glassy carbon)
  - This year should become NIST standard.

#### Typical challenges of the SAXS/SANS technique

- Wrong Problem
  - Too complex system?
  - Not enough contrast?
- Wrong instrument selection
  - Wrong Q range?
  - Sensitivity time resolution beam size X-ray energy …
  - Transmission (= X-ray energy selection)
  - X-ray damage to sample
- Wrong analysis expectations
  - No supporting information (Imaging, other measurement techniques)
  - No justified model
  - Unreasonable expectations
  - Model fitting not unique

### Small-angle scattering primer



#### Introduction

- Small-angle scattering is ....
  - Well known technique
  - Old technique
  - Something everyone <u>believes</u> they understand really well
  - ... and many (most?) do not.

### If the model is incompatible with your data, it is not the data you need to change. The fact, that A model fits your data, it is NOT proof that it is THE appropriate model.

FYI: Recommending Ilavsky as reviewer for your manuscript may not be the best idea, especially if you abused *Irena* ... ③

### History of SAXS is long... (< 1936)

Krishnamurty (1930) Hendricks (1932) Mark (1932) Warren (1936)



carbon black

Observation of scattering from powders, fibers, and colloidal dispersions



Molten silica – silica gel

From presentation of Y. Amemiya, courtessy to Dr. I.L.Torriani

### History (> 1936)





Single crystals of Al-Cu hardened alloy

#### <u>A. Guinier</u> (1937, 1939, 1943)

Interpretation of inhomogeneities in Al alloys "G-P zones", introducing the concept of "particle scattering" and formalism necessary to solve the problem of a diluted system of particles.

#### <u>O. Kratky</u> (1938, 1942, 1962)

<u>G. Porod</u> (1942, 1960, 1961)

Description of dense systems of colloidal particles, micelles, and fibers.

Macromolecules in solution.





From presentation of Y. Amemiya, courtessy to Dr. I.L.Torriani





#### <u>MY Instrument & the competition</u> USAXS + SAXS + WAXS (in less than 5 minutes!



#### Comparison of USAXS/pinSAXS/WAXS capabilities



That is great, so what's the problem?

#### Real space and Reciprocal Space



= Patterson Function per volume

### Theory follows... But: Concentrate on the global picture!

Comment: this is generally assuming **ISOTROPIC** systems Things get much more complex when anisotropy needs to be included...





SAS mea	- Sizes sured $q = 4\pi \frac{\text{Si}}{-}$	X-ray source Bragg angle = $\theta$ Samp $dn(\theta)$ $d = \frac{2}{\lambda}$	X-ray detector $\theta$ $\theta$ $\theta$ $\theta$ $\theta$ $\theta$ $\theta$ $\theta$
	Q [A <sup>-1</sup> ]	D [nm]	20 [deg] 12keV
	1	0.6	10
	0.1	6	1
	0.01	60	0.1
	0.001	600	0.01
	0.0002	3000 (3 um)	0.001
	Detector dynam	nic range is important – Inter	nsity q

#### Pair-distance distribution function

#### Scattering intensity:

#### Pair distance distribution function :PDDF

the set of distances joining the volume elements within a particle, including the case of non-uniform density distribution.

Particle's <u>SHAPE</u> and maximum **DIMENSION**.



## The simplest, the most symmetric particle in small-angle scattering = <u>sphere</u>



#### Calculated *p(r)* for different particle shapes



D. SVERGUN and M. KOCH, Rep. Prog. Phys. 66.10 (2003) 1735–1782

#### **Common Form Factors of Particular Shapes**

Morphologies	P(q)	Morphologies
Spheres (radius :R)	$\frac{9}{(qR)^6}[\sin(qR) - qR \cdot \cos(qR)]^2 = A_{sph}^2(qR)$	
Spherical shells (outer radius: $R_1$ inner radius: $R_2$ )	$\frac{[R_1^3 \cdot A_{sph}(qR_1) - R_2^3 \cdot A_{sph}(qR_2)]^2}{(R_1^3 - R_2^3)^2}$	20
Triaxial ellipsoids (semiaxes: a,b,c)	$\int_{0}^{1} \int_{0}^{1} A_{sph}^{2} \left[q \sqrt{a^{2} \cos^{2}(\pi x/2) + b^{2} \sin^{2}(\pi x/2)(1-y^{2})_{1} + c^{2} y^{2}}\right] dx dy$	
<b>Cylinders</b> (radius: R length: L)	$4\int_{0}^{1} \frac{J_1^2[qR\sqrt{1-x^2}]}{[qR\sqrt{1-x^2}]^2} \frac{\sin^2(qLx/2)}{(qLx/2)^2} dx$ J <sub>1</sub> (x) is the first kind Bessel function of order 1	
Thin disk (radius: R)	By setting L = 0 $\frac{2 - J_1(2qR)/qR}{q^2R^2}$	
Long rod (length: L)	By setting R = 0 $\frac{2}{qL}\int_{0}^{qL}\frac{\sin(t)}{t} dt - \frac{\sin^2(qL/2)}{(qL/2)^2}$	

"Structure Analysis by Small Angle X-Ray and Neutron Scattering" L. A. Feigen and D. I. Svergun

<sup>2015</sup> SAS - Theory and Applications, Jemian





#### Dilute, Randomly-dispersed monodisperse Rods



### Dilute systems

Dilute = independent scatterers = NO interparticle effects

Total intensity = sum of individual particle scattering

$$I(q) \propto \frac{N}{V} V_{particle}^2 (\rho_1 - \rho_2)^2 P(q) S(q)$$

P(q) = Form factor - SHAPE and SIZE information
P(q) is dimensionless and P(0) = 1
P(q) for simple shapes can be found in all texts
Intensity from monodisperse spheres .....

## Non-Dilute systems and S(q)

Scattering (Interference) determined by spatial dimensions



Rk - Rj 🔵

Rj

Kk

#### **Form Factor -** P(q)

particle size and shape (intraparticle)

**Structure Factor -** S(q) interparticle correlations

function of local order and interaction potential; complex if correlation between position and orientation

# Structure Factor: common spacing(s) between scatterers

- As concentration increases, these assumptions are removed:
  - [x] Dilute (non-interacting)
  - [x] Randomly dispersed

$$\frac{d\Sigma}{d\Omega}(Q) = P(Q) S(Q)$$

- BUT, you *must* assume:
  - Monodisperse
  - Common morphology
- Ok in biology
- Not common in materials science
   2015 SAS Theory and Applications, Jemian



Advances in Colloid and Interface Science 70 (1997) 171-210

#### S(Q): Concentration effect

Low concentration, gas-like, S(Q)=1

Higher concentration, liquid-like, S(Q) oscillates about 1

High concentration, crystal-like, diffraction peaks



### How dilute is 'dilute'

#### Consider R = 100 Å hard spheres

Volume Fraction	Avg. Sep.(Å)	Radius from Guinier (Å)
10-4(0.01%)	3500	100.0
10-3(0.1%)	1600	<b>99.7</b>
$10^{-2}(1\%)$	750	93.3
10-1(10%)	350	5.4

#### Why not just study dilute ?

- 1. Intensity may be too low (measure concentration series) or
- 2. Sample i.e. P(q) may change

#### Example data showing structure factor: 1 um spheres, monodisperse, dried powder



#### Colloidal Silica (Ludox TM50) in water showing S(Q)

![](_page_28_Figure_1.jpeg)

![](_page_29_Picture_0.jpeg)

Colloidal Silica in Epoxy

![](_page_29_Figure_2.jpeg)

#### Fractals = may be the most abused term in SAS

fractal objects present the same structure on any length scale (= over many decades in sizes!!!!).

Mass fractal: Menger sponge, mass fractal dimension  $D_m$ = 2.72

![](_page_30_Picture_3.jpeg)

http://commons.wikimedia.org/wiki/File:Menger-Schwamm-Reihe.jpg

Surface fractal: Koch snowflake, surface fractal dimension  $D_s = 1.26$  (in  $d_e = 2$ )

![](_page_30_Picture_6.jpeg)

![](_page_30_Figure_7.jpeg)

![](_page_30_Figure_8.jpeg)

http://upload.wikimedia.org/wikipedia/commons/8/8e/KochFlake.png

2013 APS Beyond Rg: SAS - Theory and Applications, Jemian

# Fractals in small-angle scattering: power law analysis of *I(Q)*

![](_page_31_Figure_1.jpeg)

 $D_m$  = mass fractal dimension  $D_s$  = surface fractal dimension  $d_e$  = Euclidian dimension (3 in real life)

Many SAXS curves follow a power law

 $\mathsf{I}(q) \propto q^{-\alpha}$ 

Mass fractal:  $\alpha = D_m \qquad (0-3)$ 

Surface fractal:  $\alpha = 2d_{e} - D_{s}$  (6 - D<sub>s</sub>, when  $d_{e} = 3$ )

Shape	D <sub>m</sub>	$D_s$	
Line	1	0	
Platelet	2	1	
Sphere	3	2	Porod law
			$I(q) \propto q^{-4}$

#### There are fractals in nature: e.g., soils, sandstones, rock - voids structure

![](_page_32_Figure_1.jpeg)

Prairie soils can contain significantly more organic matter than farmed (cultivated) soils. It is not known why, what the difference in organic matter arrangements are. By studying samples with organic matter and after burning off the organic matter over wide **q**/intensity range (including USANS) we were able to quantitatively find organic matter location.

#### Scattering length density

- Measure of interaction difference of radiation with atoms/molecules in scatterer (density inhomogeneity) and its surroundings
- Scattering is due to a difference in:
  - X-ray: refractive index,  $r_{e}$  f
  - neutron: nuclear (and magnetic) scattering length

$$\rho_{sld} = \frac{n}{V}b \qquad \Delta \rho = r_{e-}\sum_{Z} \Delta c_{Z} f_{Z}$$

- n: number of atoms/molecules
- V: unit volume
- b: scattering length
- $r_{e}$ : Thompson radius of an electron, 2.818 fm
- *f*: atomic scattering factor

![](_page_33_Picture_11.jpeg)

![](_page_33_Picture_12.jpeg)

Precipitation in commercial Waspaloy

![](_page_33_Figure_14.jpeg)

Source: http://commons.wikimedia.org/wiki/File:Menger\_sponge\_(Level\_1-4).jpg

#### **Babinet's Principle**

- Two structures give the same scattering (\*)
- Contrast is relative
- Loss of phase information
- Very important in multi-phase systems for contrast matching or variation

![](_page_34_Picture_5.jpeg)

![](_page_34_Picture_6.jpeg)

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(\vec{\mathbf{q}}) \propto \left(\rho_1 - \rho_2\right)^2$$

#### \*incoherent scattering may be different

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#### **Contrast Variation**

![](_page_35_Picture_1.jpeg)

When the monster came, Lola, like the peppered moth and the arctic hare, remained motionless and undetected. Harold, of course, was immediately devoured.

Needed when more than one type of scatterer is present

•Vary  $|\Delta \rho|^2$  of one type, holding others constant

Anomalous scattering (X-ray & neutron)

- Isotope substitution (neutron)
- Isomorphous replacement

...

- Magnetic scattering (neutron)
- Concentration variation (X-ray & neutron)
## Anomalous Small-Angle X-ray Scattering

- Why anomalous SAXS?
  - Element-specific contrast variation
  - Use to separate population distributions of scatterers
- Will ASAXS solve every problem?
  - Not even close
  - The easy problems are already taken



# X-ray photon Energy selection for ASAXS contrast variation study

Calculate the scattering contrast of the major populations Choose energies so that  $|\Delta \rho(E)|^2$  are evenly-spaced

$$\Delta \rho_k(E) = r_e(E) \sum_{Z} \Delta c_Z \left[ Z + f'_Z(E) + i f''_Z(E) \right]$$

X-ray scattering contrast of scatterers in SN-88 near the Yb L<sub>III</sub> edge



X-ray photon energy, eV, from  $L_{III}$  absorption edge

## **Optimal sample thickness**

$$I(Q) = I_0 \Omega t \ e^{-\mu t} \ \frac{d\Sigma}{d\Omega}(Q)$$

measured intensity

$$\max(I(t)): t = 1/\mu, e^{-\mu t} = 0.37$$

Optimal thickness due to absorption

In practice, I(Q) can show presence of...

- incoherent scattering background
- multiple scattering

Higher transmissions are typically desired:

- Lower sample thickness, t
- Lower absorption, μ (use higher X-ray energy)

# Absolute SAS Cross-Section $d\Sigma/d\Omega$

J Appl Cryst **5** (1972) 315-324, **16** (1983) 473-478 Acta Metall Mater **39**.11 (1991) 2477-2487

$$I(Q) = I_0 \Omega t \ e^{-\mu t} \ \frac{d\Sigma}{d\Omega}(Q)$$

I(Q): intensity, arbitrary units

- $I_0$ : apparent source intensity, arbitrary units
- $\varOmega$  : solid angle subtended by detector
- *t*: sample thickness
- $\mu$  : linear absorption coefficient
- $d\Sigma(Q)/d\Omega$  : differential scattering cross-section per unit volume per unit solid angle

# Multiple scattering ugly beast complicating our life

Important for samples with : high scattering contrast, high volume of scatterers, large scatterers. On devices with long wavelength (multi-A neutrons?).



# How to identify:

Profile at low-q depends on:

- Wavelength or
- Sample thickness

Challenge:

Shape changes Absolute intensity difficult

Work around:

Truncate data at low-q and use only higher Q value data.

#### <u>Fix</u>:

Make sample thinner or wavelength shorter.



In this example, 1um thick sample is probably close to single scattering, but the thicker samples exhibit multiple scattering.

# Quantitative SAXS (SANS) data Glassy carbon standard

If we can place intensity on absolute scale [cm<sup>2</sup>/cm<sup>3</sup> or cm<sup>2</sup>/g]

Absolute volume of scatterers [cm<sup>3</sup>/cm<sup>3</sup> or cm<sup>3</sup>/g] Specific surface areas [cm<sup>2</sup>/cm<sup>3</sup> or cm<sup>2</sup>/g] Contrast, density analysis

...

# **Advantages of Quantitative SAS**

- Sampling volume large compared to features investigated: <u>Statistically Significant Sampling</u>
  - Sample volume typically  $10^{-12} 10^{-10} \text{ m}^3$
  - Scatterer size typically 10<sup>-9</sup> 10<sup>-6</sup> m
  - 10<sup>3</sup> 10<sup>13</sup> 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  $N_{V} = \sum_{i} \frac{f_{i}(D) \Delta D_{i}}{\left(\frac{\pi}{6}\right) D_{i}^{3}}$ 



## **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 : <u>ilavsky@aps.anl.gov</u> or just ask me here).
- At least 90 samples shipped in last ~ 6 years.

### **USAXS/SAXS** data comparison



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

# Radius of gyration, R<sub>g</sub>

- Radius of gyration, R<sub>g</sub>, is the name of several related measures of the size of an object, a surface, or an ensemble of points *of any geometry*. It is calculated as the root mean square distance of the object's parts from its center of gravity.
- In polymer physics, the radius of gyration is proportional to the root mean square distance between the parts of the object:
   2b
   2a



### **Example Fit to Guinier Approximation**



50



### Morphology of Dimosil® Tire-Tread Silica



# Monodispersed SAXS: Biological SAXS (proteins) & some materials science

# Ellipsoids







From presentation of Y. Amemiya, courtesy to Dr. I.L.Torriani



Source EMBL summer SAXS school course

# Real BIO SAXS = monodispersed systems ....

# Effect of the hydration shell, X-rays

lg I, relative





# SANS data for mono-dispersed, multi-shell spherical scatterers



Multiple shell model (4 shells)

#### Lot of parameters...

- Shell SLD
- Shell thicknesses
- Core radius
- SANS Smearing effect very important (good model?)
- <u>How robust this solution is?</u>



# Polydisperse cases -"Real world materials"



# Mostly we will show you extreme case of complex systems - BUT - successes ...



1530 Å<sup>3</sup>

U<sub>60</sub> aggregates after 8 hour aggregation induced by addition of Group I cations (Li, Na, K,..).
Peter Burns group, U Nottre Dame, IN

Whole graph –
USAXS&SAXS combined

SAXS/SANS

### Metallurgical example Polydispersed system & structure factor in base material, which also scatters



### Hierarchical Structure from Scattering



# Scattering from a polymer chain



# Now throw in the problem anisotropy and lots of things start breaking down

- Need to analyze 2D cut through 3D distribution of intensity
  - Difficult to get absolutely calibrated
  - Difficult to reconstruct meaningful intensity profiles
- Not many models available publically
- Typical = Fiber scattering
- Example here is EB PVD coatings layer of ceramics grown on the surface

# Complex designer void systems <sub>EBPVD</sub>

**Complex sizes** 

nano - micro

APS micrometer-sized 8YSZ - d<sub>50</sub> ~ 30000 nm



50 µm

SPS nanometersized 8YSZ - d<sub>50</sub> ~ 50 nm







Population 3: Fine Intracolumnar Voids <o.d.>=0.033 μm 3.8%

Population 2: Coarse Intracolumnar Voids <o.d.>=0.19 μm 3.9%

> Population 1: Intercolumnar Voids <o.d.>=0.72 μm 6.1%



65



## Anisotropy modeling



Thermally cycled microstructure shows evolution of different void components in EB-PVD Coatings



Thermally Cycled 0.00029 Å<sup>-1</sup>

Thermally Cycled 0.000723 Å<sup>-1</sup>



## Wrap up: SAS Theory and Applications

- SAS investigations measure nanoscale structure
- Many different materials of technological importance can be investigated
- Contrast variation methods possible
- Statistically significant results
- Unique results not obtainable by other methods
- Complementary methods increase the information content which can be realized from a quantitative SAS investigation



# Instrumentation

- Basic design of typical SAXS instrument
  - Pinhole SAXS
  - Other geometries (Kratky, Bonse-Hart)
- APS instrumentation
  - 5ID beamline SAXS
  - 12ID SAXS
  - 15ID USAXS/SAXS

# **Small- and Wide-Angle X-ray Scattering Measurements**



## Typical(?) synchrotron SAXS instrument = pinhole

#### • Camera-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



73



#### **5ID-D SAXS Parameters**

#### SAXS at DuPont-Northwestern-Dow CAT's 5ID-D station

APS Undulator A insertion device	
Si(111) monochromator	7 keV to 18 keV (1.8 Å to 0.7 Å)
1:1 horizontal bent mirror focusing	Rh, Glass, or Pt
Standard slit-based pinhole geometry	Beam size $\rightarrow$ 50 $\mu m$ $\times$ 50 $\mu m$ to 1 mm $\times$ 2.5 mm
Wide range of camera lengths available	136 mm to 10,000 mm
Momentum transfer over three orders	0.001 Å <sup>-1</sup> to 5 Å <sup>-1</sup> (6200 Å to 1.26 Å)

#### **Detectors**



#### Sample Environments


## SAXS at DuPont-Northwestern-Dow CAT's 5ID-D station

## Coming Soon High speed SAXS/MAXS/WAXS



## Slit –smeared cameras: Kratky camera, Bonse-Hart Camera

Commercially available, e.g. Kratky camera: <u>http://www.hecus.at/</u> Bonse-Hart Camera : Rigaku : <u>http://www.rigaku.com/saxs/ultra.html</u>



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



## USAXS/SAXS/WAXS - now at APS sector 9ID



Δ