Tales of X-ray scattering: Application and data analysis

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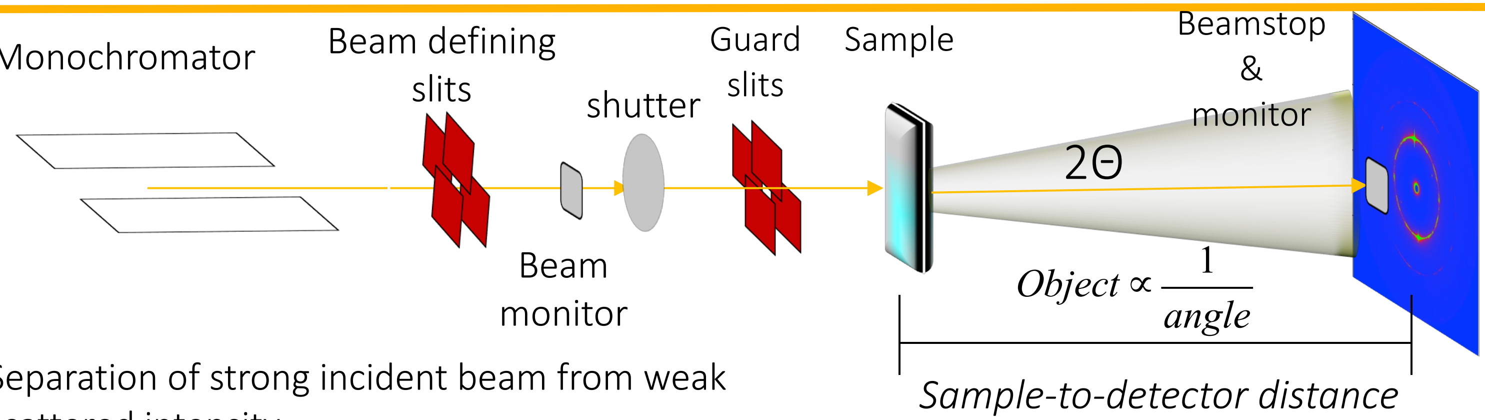
X-ray scattering reveals structural information on materials by observing the scattered intensity of an incident x-ray beam striking a sample as a function of incident angle, energy.

- The basics of scattering
- Instrumentation
- Scattering *vs.* direct imaging
- Tale 1. Self-assembled liquid crystals
- Tale 2. Nanocarbons
- Tale 3. Time-resolved SAXS
- Tale 4. Au NP polymer composites

The basics of small-angle x-ray scattering (SAXS)



- Separation of strong incident beam from weak scattered intensity
- Parasitic scattering

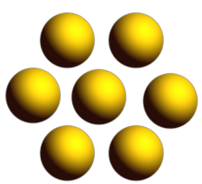
$$q = 4\pi \sin\Theta / \lambda$$

$$q = 2\pi / d$$

$$I(q) = N\,|F(q)|^2\,S(q)$$

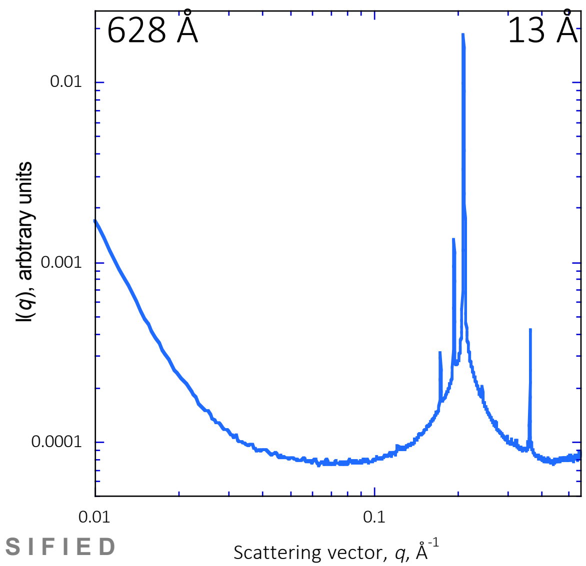
Form factor

Structure factor



Particle morphology

Particle-particle interactions
Long-range positional ordering

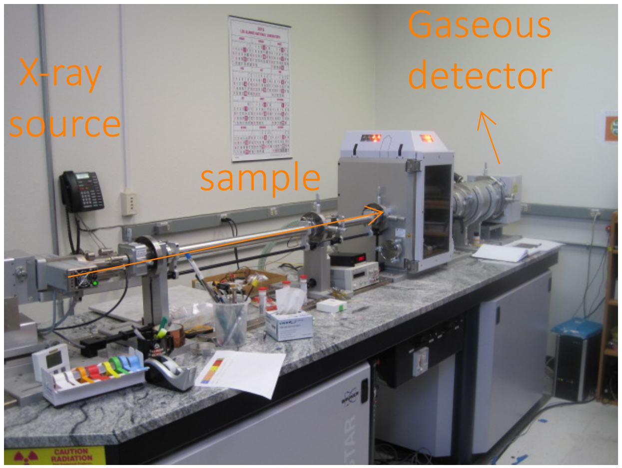


Circularly / azimuthally averaged data

X-ray scattering instrumentation

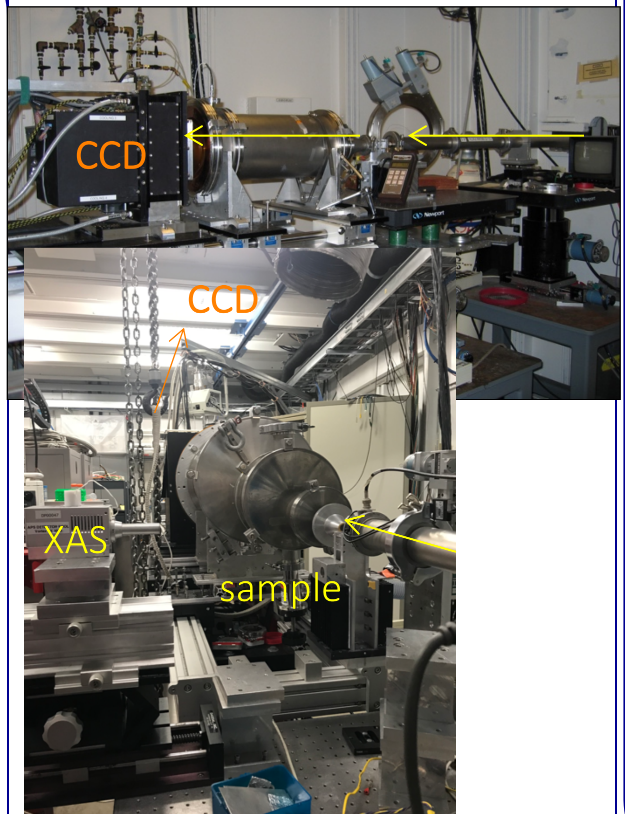
Laboratory SAXS/WAXS

Transmission SAXS @ CINT/LANL



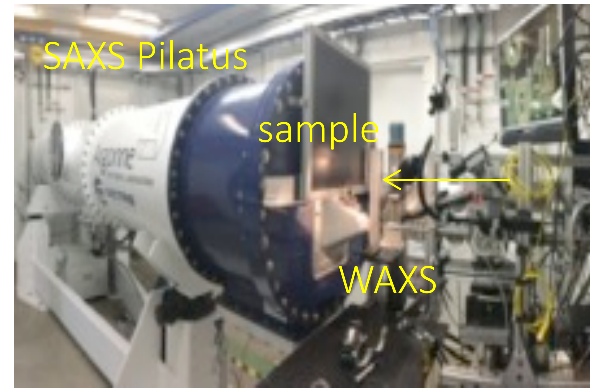
q = 0.01 = 0.2 Å^{-1}
(~ 628 Å – 31 Å)
KeV = 8.04

APS sector 12IDC
S. Seifert



q = 0.003 = 2.8 Å^{-1}
(~ 2,094 Å – 2.2 Å)
KeV = 4.5 - 36

APS sector 12IDB
Xiabing Zuo



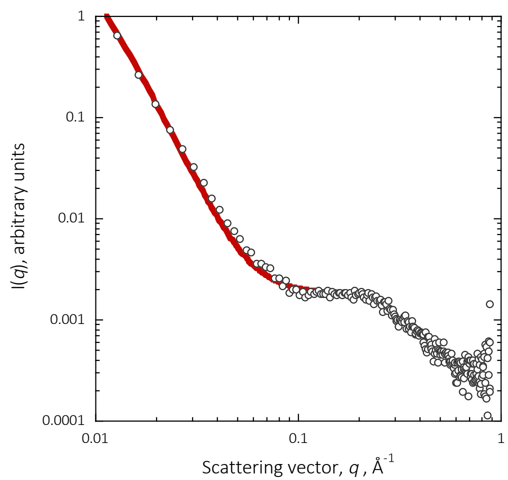
Simultaneous SAXS/WAXS
GISAXS/GIWAXS

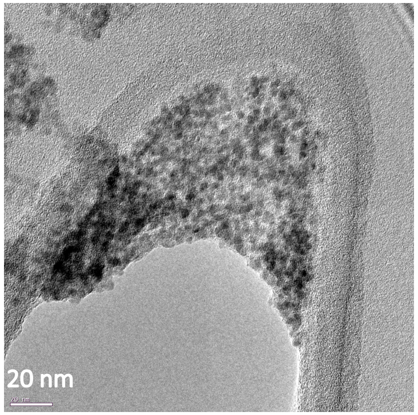
q = 0.003 = 2.8 Å^{-1}
(~ 2,094 Å – 2.2 Å)
KeV = 14

X-ray scattering vs. Electron microscopy

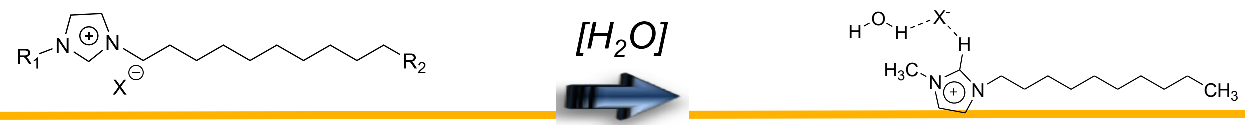
- Non-destructive (maybe)
- No special sample preparation required
- Flexible sample environments (full hydration)
- Amenable to *in-situ* / *operando* studies
- Provides atomic, molecular, nano- & mesoscale structure
- ns – fs time-resolved studies with synchrotron or free-electron laser x-ray sources
- Multi-modal materials characterization is fairly routine (spectroscopy + scattering)
- Gives an average (global) structure with statistics
- Data is given in reciprocal space
- Data interpretation can be challenging

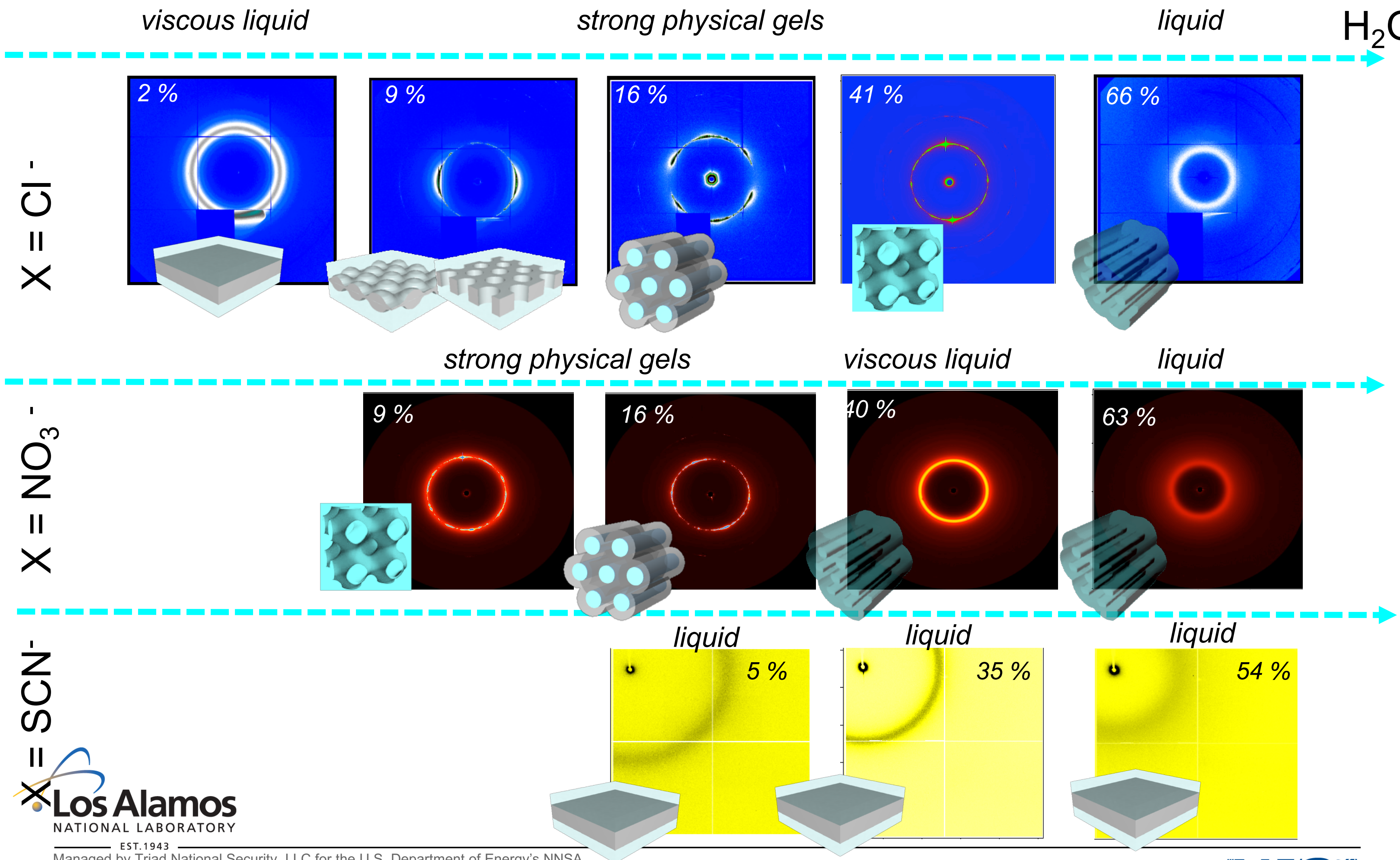
- Destructive
- Sample preparation required
- Samples are typically under vacuum
- Some *in-situ* cells now available (E-chem)
- Provides atomic to mesostructure images (same dimensional range as SAS)
- Direct imaging (real space)
- Image analysis is straightforward
- Can "find" what you are looking for





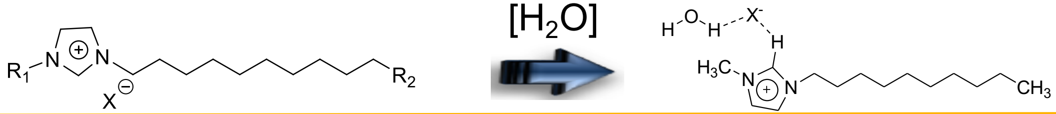
Nanostructure characterization of self-assembled amphiphiles by SAXS and WAXS

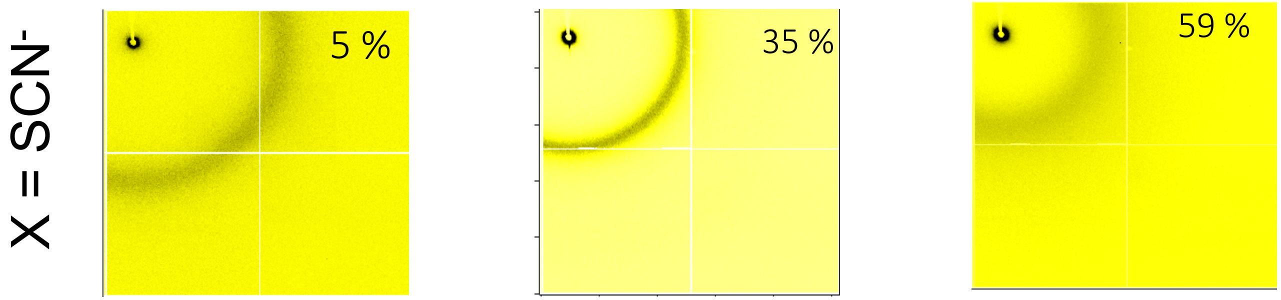


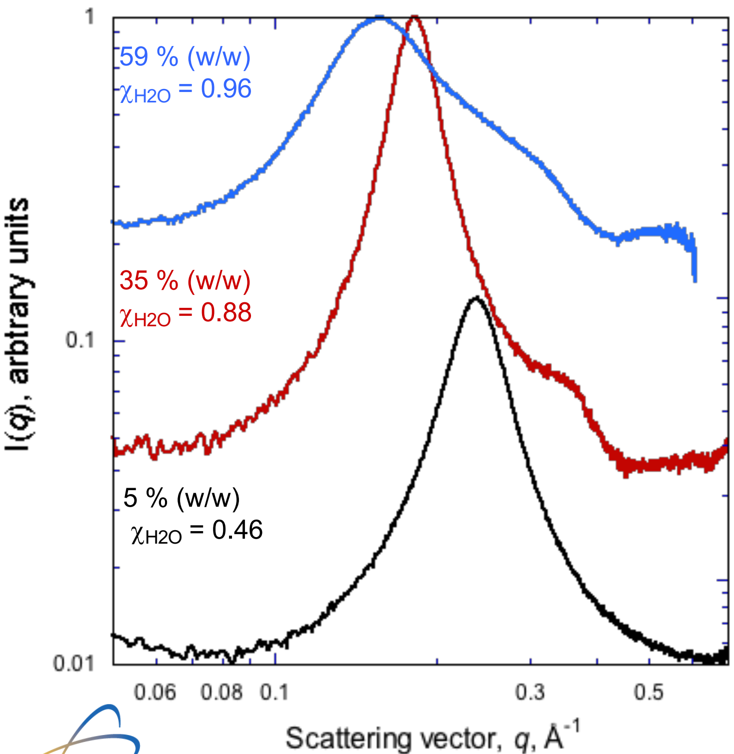


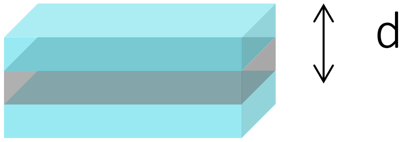
Nebgen, B.T. et al. Faraday Discussions, 2018, 206, 159-181.

Analysis of small-angle x-ray diffraction: The case of the weakly interacting anion









$n\lambda = 2d\sin\Theta$

q = 0.16 (001); 0.31 (002) Å^{-1} ; d = 2π/q = 39.1 Å

q = 0.18 (001); 0.36 (002) Å^{-1} ; d = 2π/q = 35.0 Å

q = 0.24 Å^{-1} ; d = 2π/q = 26.2 Å

- Lamellar structure independent of H_2O content
- Lattice dimension increases with increasing water
- Poor spatial coherence as indicated by FWHM of Bragg peak

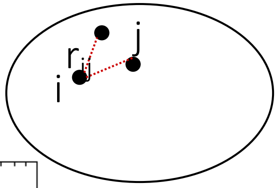
Nebgen, B.T. et al. Faraday Discussions, 2018, 206, 159-181.

Analysis of low q scattering to detail amphiphile aggregate morphology: A model independent approach

Pair distance distribution function (PDDF)

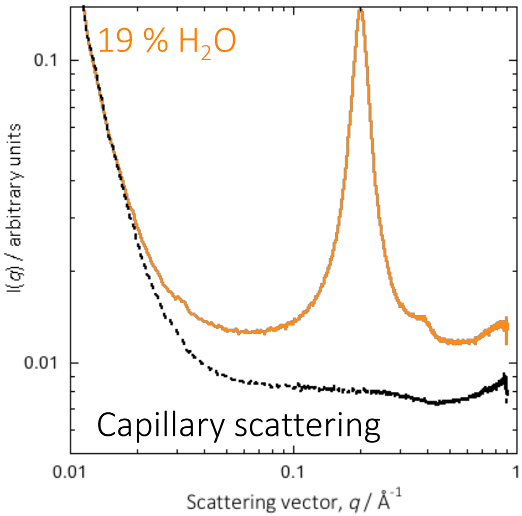
J. Illavsky, P. Jemian J. Appl. Cryst. 2009, 42(2), 347 – Irena

- Distribution of distances between all pairs of points within the particle weighted by the respective electron densities.
- P(*r*) is obtained by histogramming the distances between any pair of scattering elements within a particle

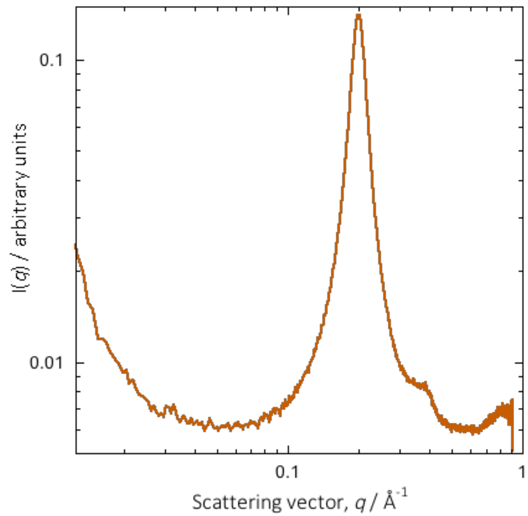


$$P(r) = r^2 \int_0^{\infty} I(q) \frac{\sin(qr)}{qr} 4\pi q^2 dq$$

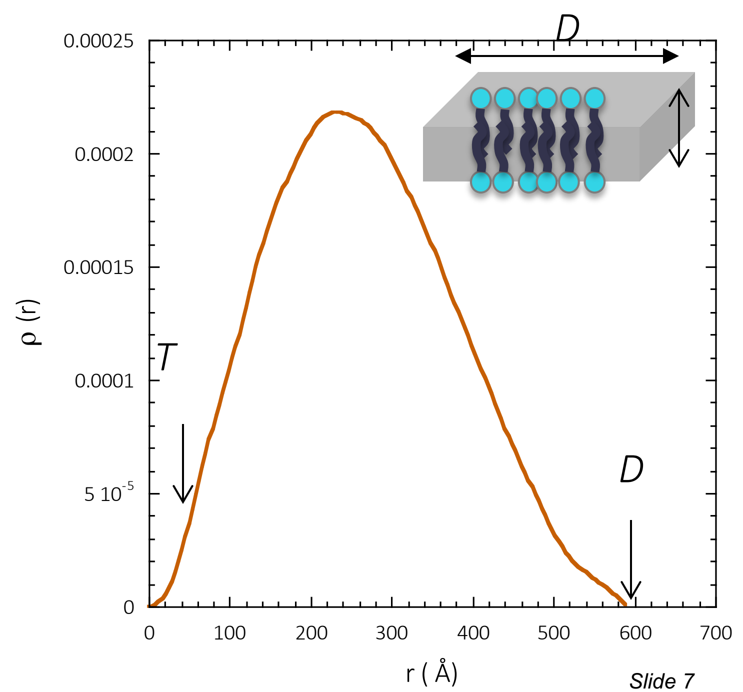
Uncorrected averaged data



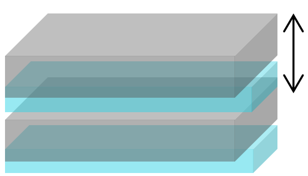
Background subtracted



"visible", real-space morphology of sheet



q = 0.20 $Å^{-1}$ (001); 0.40 $Å^{-1}$ (002)



d = 31.4 Å

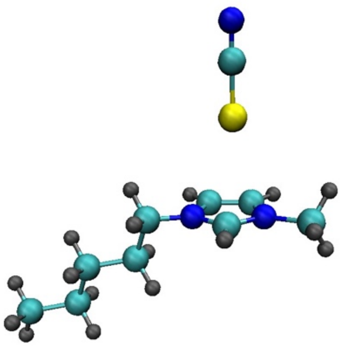
UNCLASSIFIED

Small Angle Scattering for Pharmaceutical Applications: From Drugs to Drug Delivery Systems. In: Chaudhuri B., Muñoz I., Qian S., Urban V. (eds) Biological Small Angle Scattering: Techniques, Strategies and Tips. Advances in Experimental Medicine and Biology, vol 1009. Springer, Singapore 2017

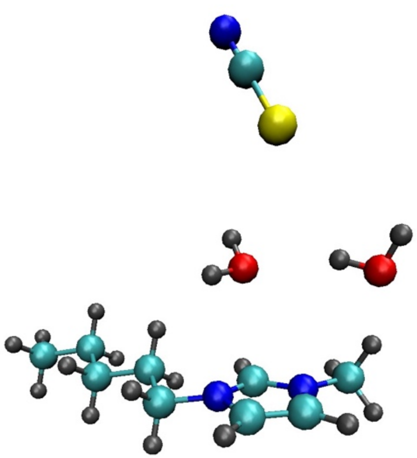
Combining MD simulations with wide-angle x-ray scattering to study molecular (solvent shell) structure: The case of a linear soft anion, SCN

Molecular Dynamics simulations reveal ionic domain (geometric configuration)

1st solvent shell structure

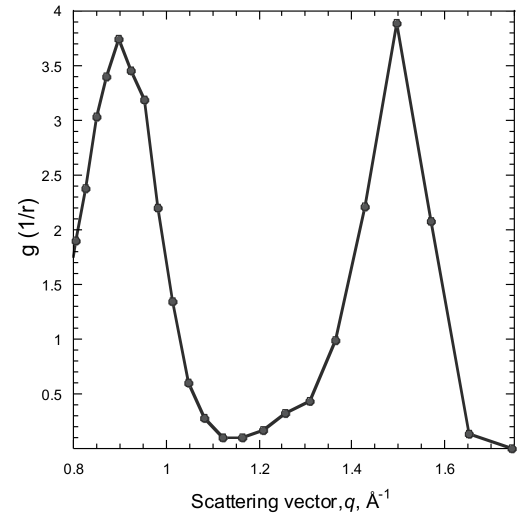


2nd solvent shell structure



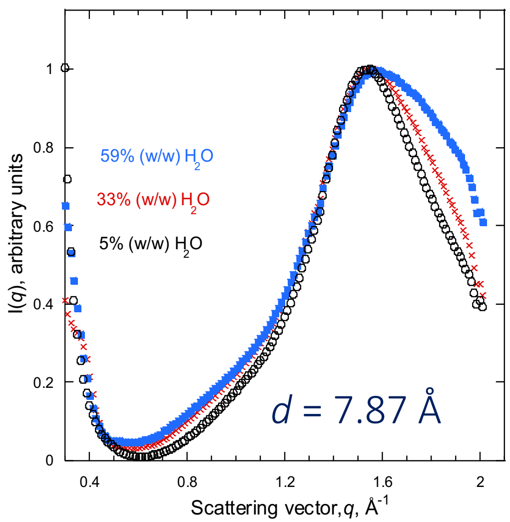
Theoretical radial distribution function (RDF)

d = 7.00 Å   *d* = 4.22 Å



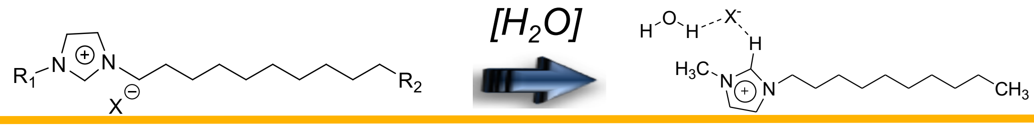
Exp'tl (WAXS)

d = 4.08 Å

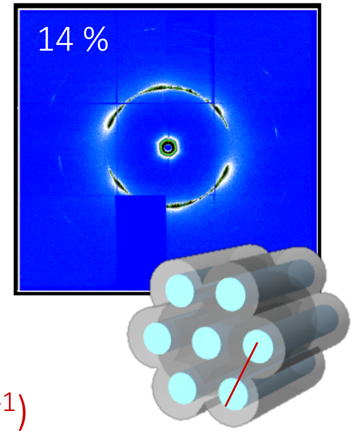


- Thiocyanate anion is positioned axially above / below the imidazolium ring
- Out-of-plane (axial) SCN prevents H-bonding to imidazolium → ***lack of gelation***
- Theory predicts significant secondary solvent shell structure - little preference for SCN to exist as nearest neighbors to imidazolium
- WAXS confirms first and second solvent shell structure

Analysis of small-angle x-ray diffraction: The case of the strongly interacting anion



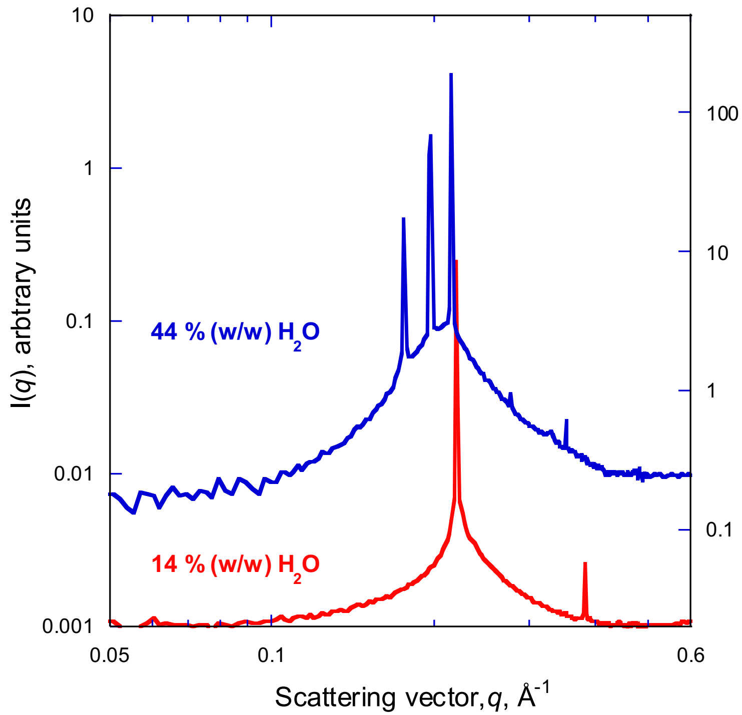
X = Cl -

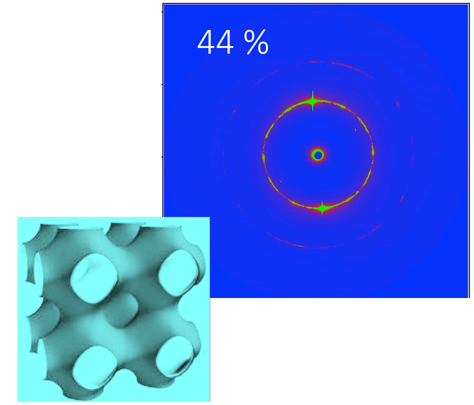


q (Å^{-1})	
0.220	√1
0.380	√3

$d = 2\pi/q = 28.6$ Å

$a = (2/\sqrt{3})d = 33$ Å





q (Å^{-1})		
0.172		√2
0.196	√2	
0.214		√4
0.278	√4	√6
0.332		√8
0.356	√8	

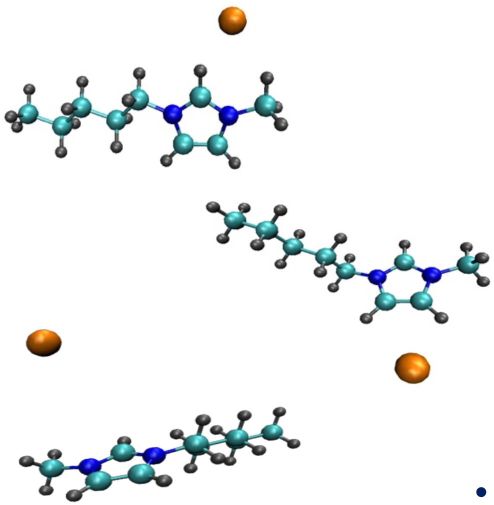
- Conversion from a well-ordered 2D hexagonal nanostructure to a mixture of 3-D cubic phases
- Puzzle – why higher symmetry with increasing water content?
- How does ionic domain structure lead to these nanostructures?

Nebgen, B.T. et al. Faraday Discussions, 2018, 206, 159-181.

Wide-angle x-ray (WAXS) scattering provides insight into solvent shell (molecular) structure: Spherical compact anion, Cl

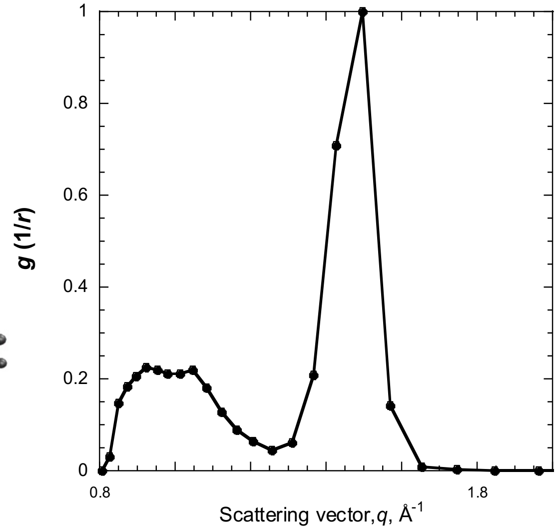
Molecular dynamics simulations reveal ionic domain (geometric configuration)

1st solvent shell structure



Theoretical RDF

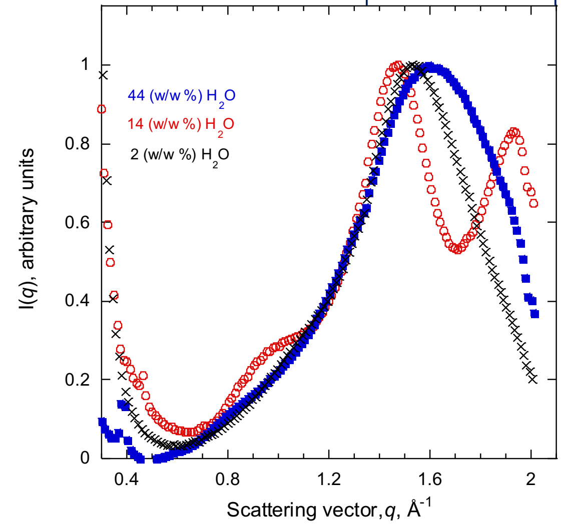
d = 4.22 Å

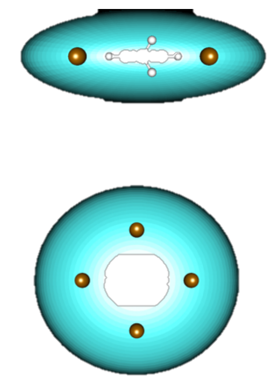


Exp'tl (WAXS)

ion pair for in-plane Cl^- = 4.27 Å

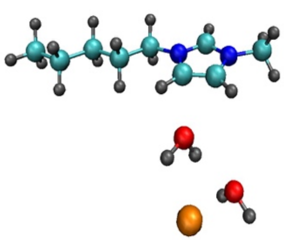
ion pair for out-of-plane Cl^- = 3.26Å





- MD simulations do not accurately determine the axial positioned Cl anion

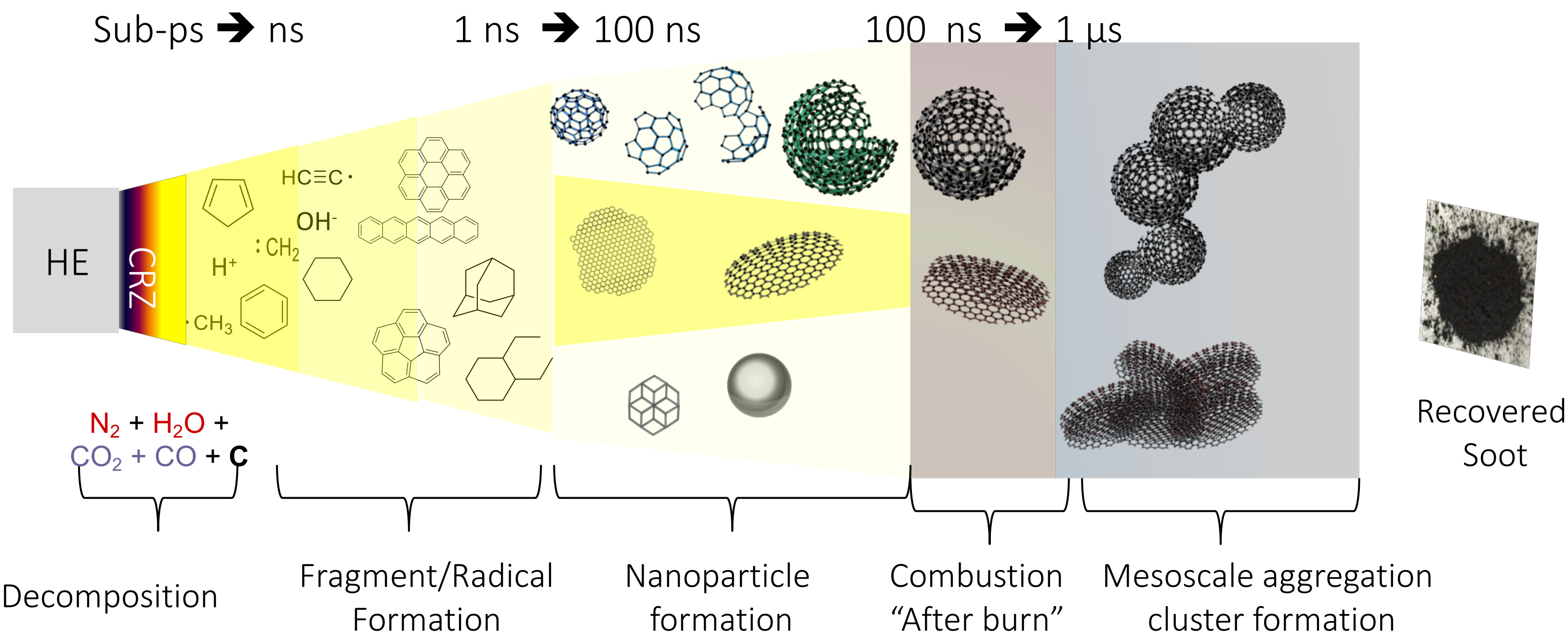
2nd solvent shell structure



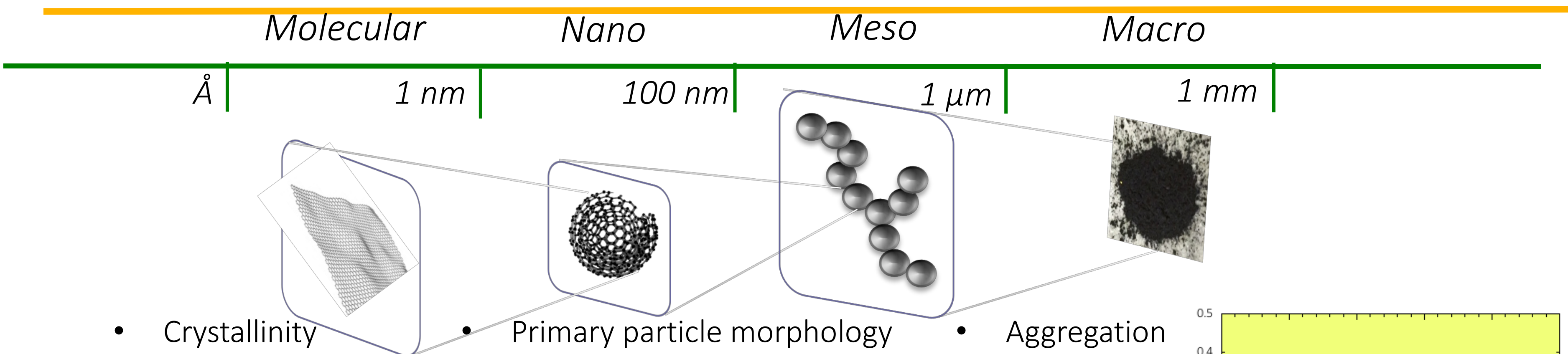
- 14 wt. % water – WAXS reveals 2 distinct anion cation distances in first solvent shell. Equatorial (4.27 Å) and axial chloride (3.26 Å). Also observed second solvent shell structure
- 44 wt. % water - correlation peak shifts to higher *q*, implying increased density from water infiltration into first solvent shell → extended network formation

Non-destructive analysis of detonation-derived carbons by x-ray scattering

- The science problem: How does the recovered solid carbon products from a detonation connect to the event?
- Science of signatures – nuclear forensics
- Fundamental shock induced chemical reactions
- Synthesis of novel nanocarbons using extreme conditions

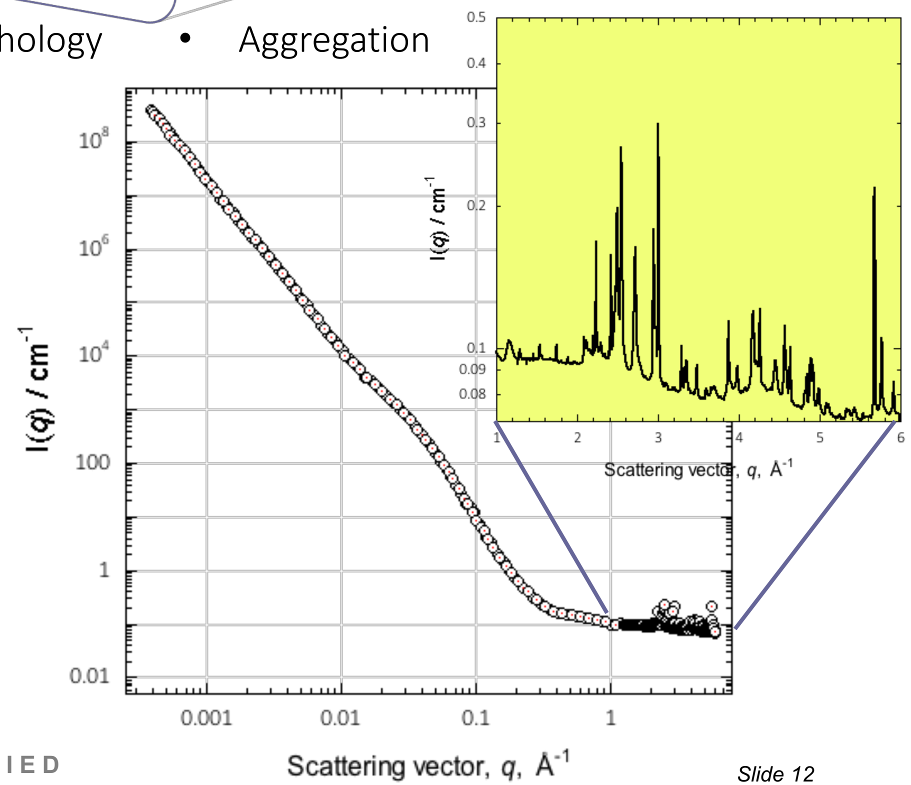


Evaluation of hierarchical structure using multi-decade x-ray scattering: Single component - carbon

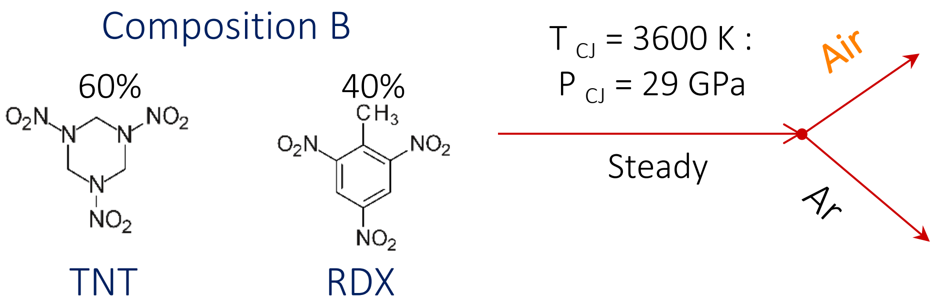


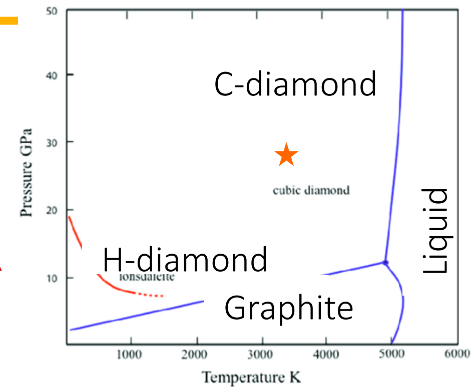
- Crystallinity
- Primary particle morphology
- Aggregation

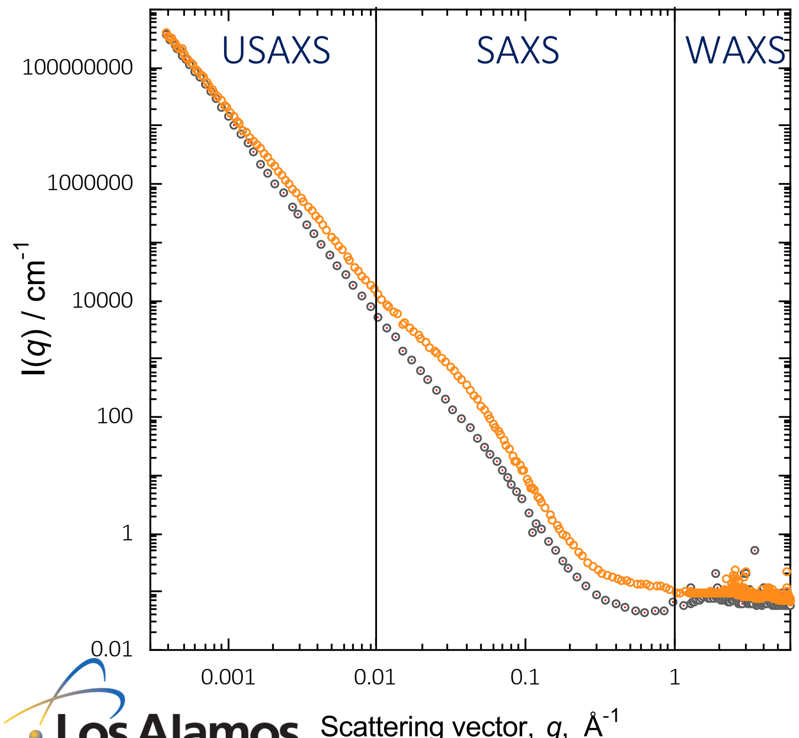
- Combined USAXS + SAXS + WAXS
- Bonse-Hart – pin-hole instruments at 9ID-C (Jan Ilvasky)
- "Stitched" scattering patterns provides structural information spanning length scales from 170 µm to 0.95 Å
- How to analyze multi-decade scattering (USAXS + SAXS)?



X-ray scattering patterns collected on unpurified soot recovered from detonating composition B







Observe differences in scattering patterns between detonation soot produced by detonating in air *vs.* inert atmospheres

How can we analyze the scattering patterns to understand the differences?

Evaluation of hierarchical structure in complex samples: Model independent approach

Beaucage's unified fit function

Model independent approach for identification of scattering entities within a complex sample

$$I(q) = G \exp(-q^2 R_g^2 / 3) + B(q^*)^{-P}$$

Guinier law + Porod power law

- Radius of gyration, R_g, for each structural level identified
- The R_g gives *a measure* of the average size of the scatter (primary particle or aggregate)

- The Porod exponent specifies the fractal nature of the scatter

Surface fractal if -3 < P < -4
Sharp interface P = -4
Mass fractal (Dimensionality law)

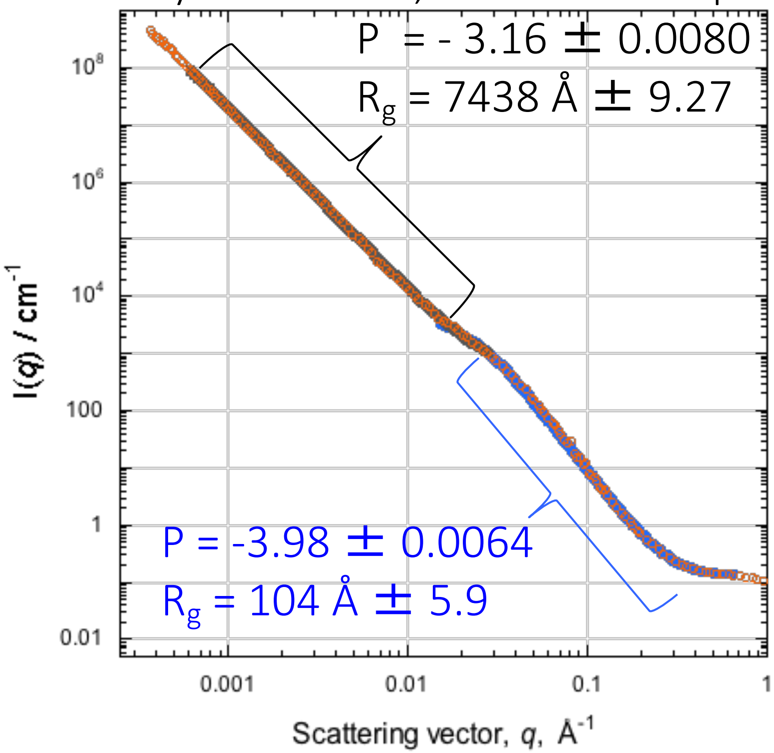
1D rods, P = -1
2D Platelets (lamellae), P = -2
3D spheres, P = -4

Beaucage G (2012) Combined Small-Angle Scattering for Characterization of Hierarchically Structured Polymer Systems over Nano-to-Micron Meter: Part IITheory. In: Matyjaszewski K and Möller M (eds.) Polymer Science:A Comprehensive Reference, Vol 2, pp. 399–409. Amsterdam: Elsevier BV.

Evaluation of composition B (unpurified) detonation soot using a model independent unified fit approach

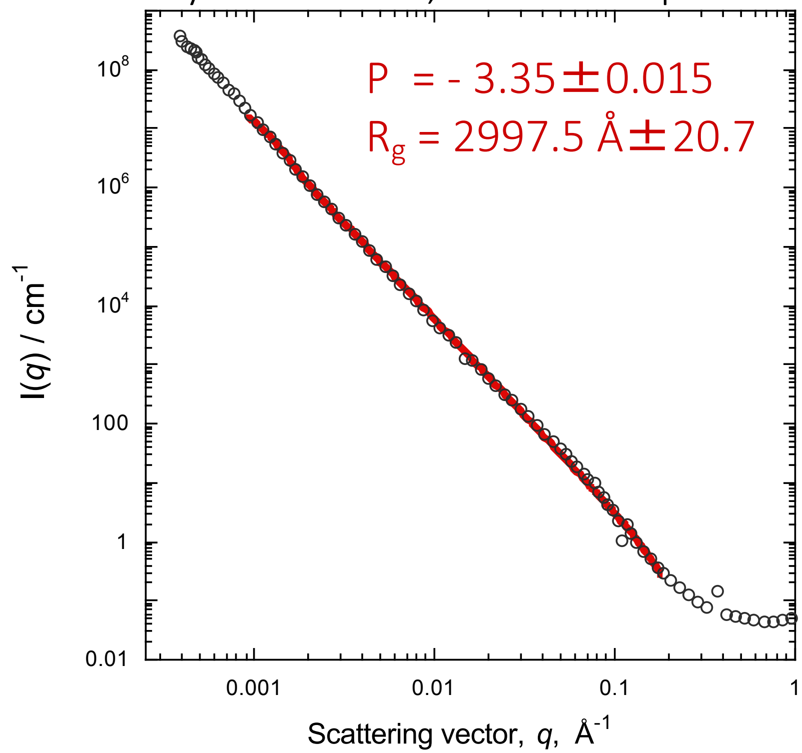
$$I(q) = G \exp(-q^2 R_g^2 / 3) + B(q^*)^{-P}$$

steady detonation, ambient atmosphere

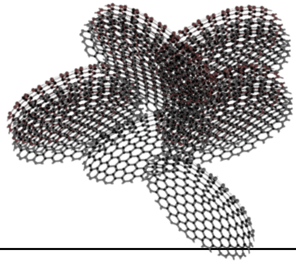


- 2-level fit (2 distinct populations) ➔ low degree of aggregation
- P ~ -4 ➔ Smooth interfaces & spherical 1° particles
- P = -3.2 ➔ Fractal aggregates/agglomerates

steady detonation, inert atmosphere



- 1-level fit (1 distinct populations) ➔ highly aggregated
- P = -3.3 Fractal

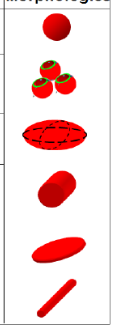


Determination of nanoparticle morphology using a model dependent approach. Nanoparticles recovered by detonation in inert atm

SAXS data collected on unpurified soot recovered from detonating composition B in an inert (Ar) atmosphere

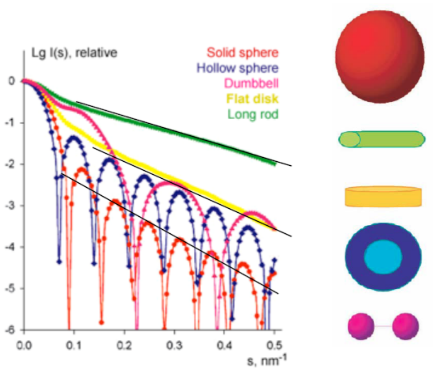
Common Form Factors of Shaped Objects (many more were computed numerically)

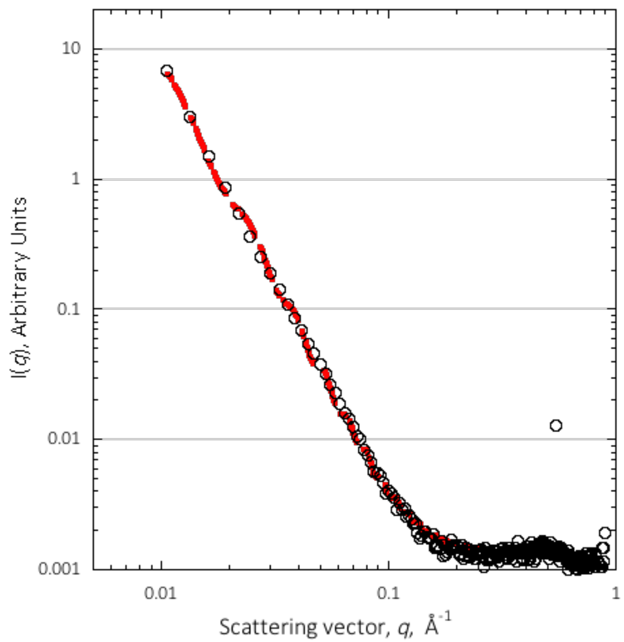
Morphologies	P(q) or $P^2(q)$ – depends on source	Morphologies
Spheres (radius :R)	$\frac{9}{(qR)^6}[\sin(qR) - qR\cdot\cos(qR)]^2 = A^2_{sph}(qR)$	
Spherical shells (outer radius: R_1 inner radius: R_2)	$\frac{[R_1^3\cdot A_{sph}(qR_1) - R_2^3\cdot A_{sph}(qR_2)]^2}{(R_1^3 - R_2^3)^2}$	
Triaxial ellipsoids (semiaxes: a,b,c)	$\int_0^1\int_0^1 A^2_{sph}[q\sqrt{a^2\cos^2(\pi x/2) + b^2\sin^2(\pi x/2)(1-y^2)_1 + c^2y^2}\,]\,dx\,dy$	
Cylinders (radius: R length: L)	$4\int_0^1 \frac{J_1^2[qR\sqrt{1-x^2}\,]}{[qR\sqrt{1-x^2}\,]^2}\frac{\sin^2(qLx/2)}{(qLx/2)^2}dx$ $J_1(x)$ is the first kind Bessel function of order 1	
Thin disk (radius: R)	By setting L = 0 $\quad \frac{2 - J_1(2qR)/qR}{q^2R^2}$	
Long rod (length: L)	By setting R = 0 $\quad \frac{2}{qL}\int_0^{qL}\frac{\sin(t)}{t}dt - \frac{\sin^2(qL/2)}{(qL/2)^2}$	



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

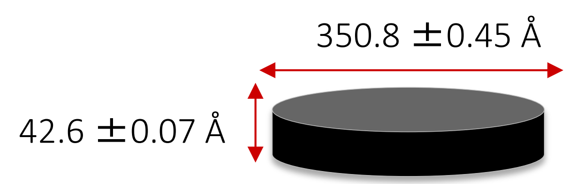
SAXS Scattering



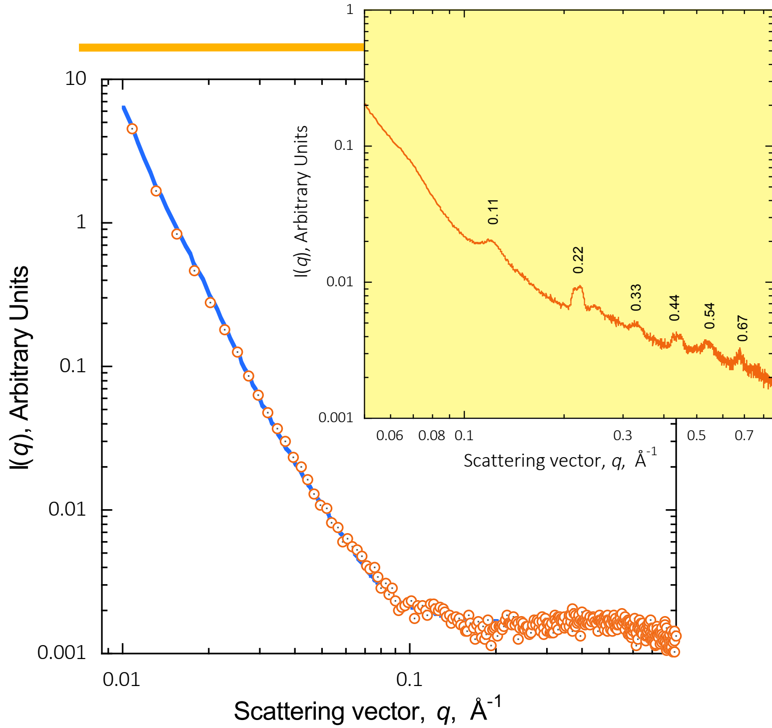


Selection of form factor can be made based upon unified fit results

Primary (nano)particles are well-modeled as circular discoidal particles

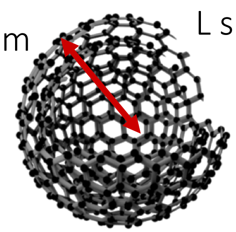


Determination of nanoparticle morphology using a model dependent approach. Nanoparticles recovered by detonation in air



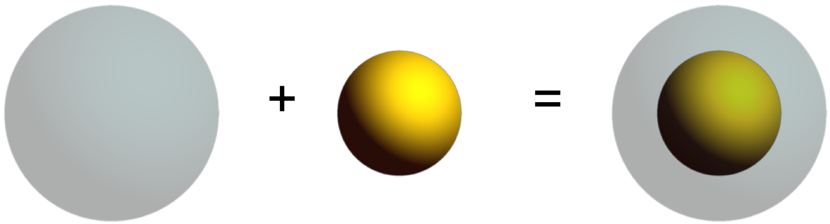
Hollow core - lamellar shell primary particle

R = 21.5 ± 1.7 nm



L shell = 13.4 ± 0.41 nm

Primary particles modeled as core-shell



$$P(q) = A(q)^2 / V^2$$

$$A(q)_{circle-shell} = \Delta\rho_{core}\left[\Delta\rho_{shell} V_{out}\phi(q, R_{out}) - (\Delta\rho_{shell} - \Delta\rho_{core}) V_{in}\phi(q, R_{in})\right]$$

$$V = \frac{4\pi R^3}{3}$$

$\Delta\rho_{core}$ = Excess scattering length density of the core

$\Delta\rho_{shell}$ = Excess scattering length density of the shell

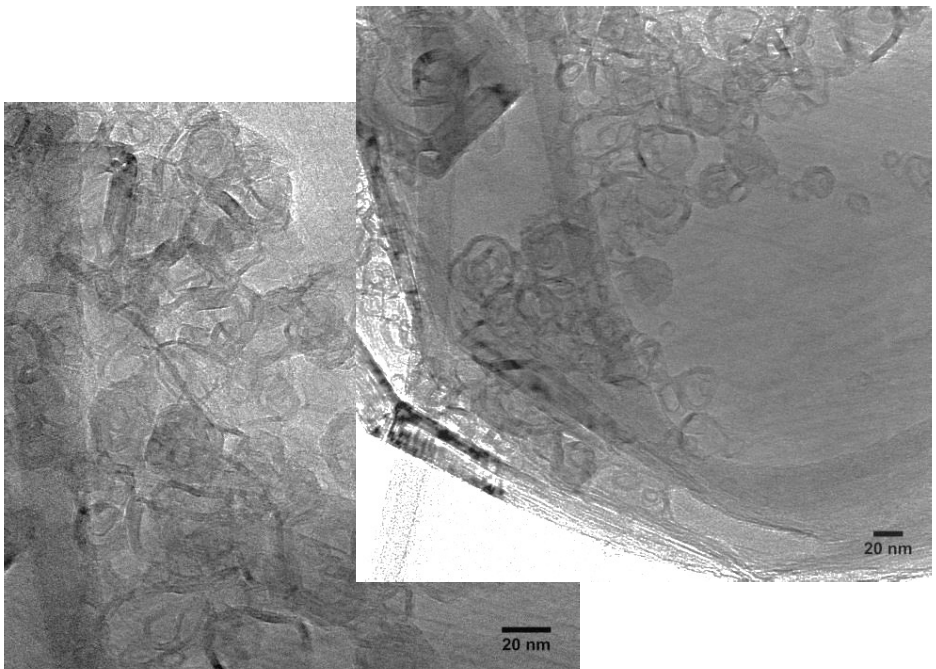
$$\phi(x) = \frac{3\left[\sin x - x\cos x\right]}{x^3}$$

- SAXS data is modeled by a spherical core-shell particle form factor (core is air and shell is carbon)
- Unified fit accurately predicts spherical morphology but doesn't account for shell structure

Direct / real-space imaging (TEM) confirms USAXS & SAXS

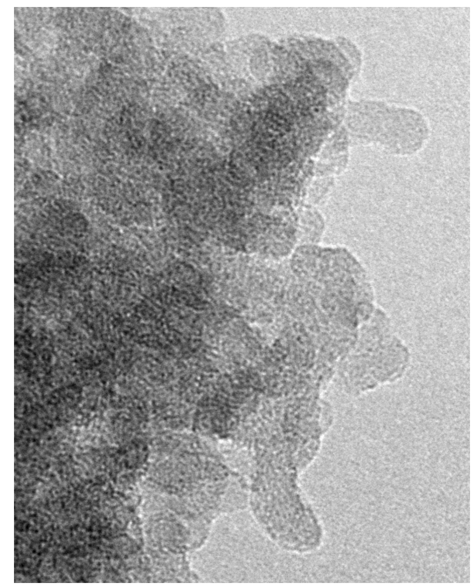
Comp B - Air

- Mesoscale structure - Loose aggregate
  - Diffusion limited cluster aggregation
  - Attractive particle interactions (oxidized surfaces?)
- Easily discern individual core shell hollow NPs



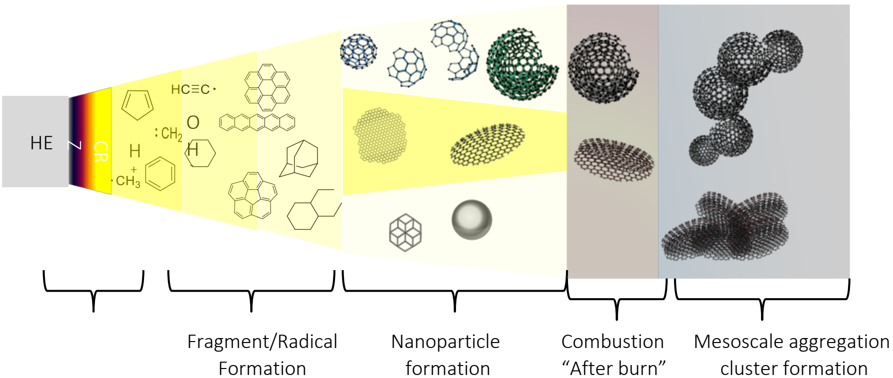
Comp B - Argon

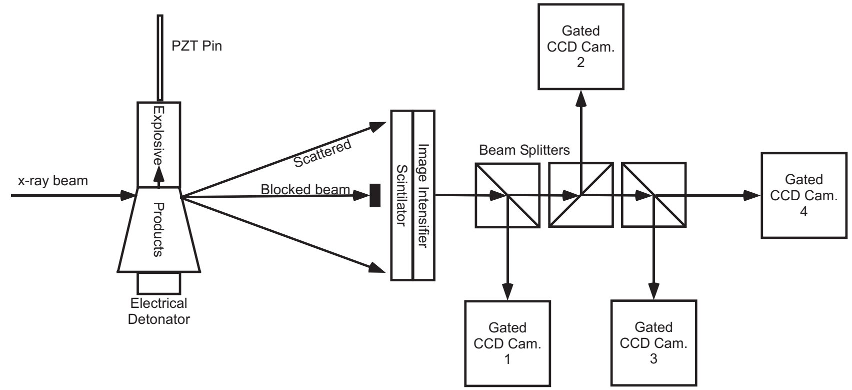
- Mesoscale structure - Tight/compact aggregate
  - Reaction limited cluster aggregation
  - Barrier to particle interaction
- Difficult to discern individual NPs
  - “outlying particles are deformed discs



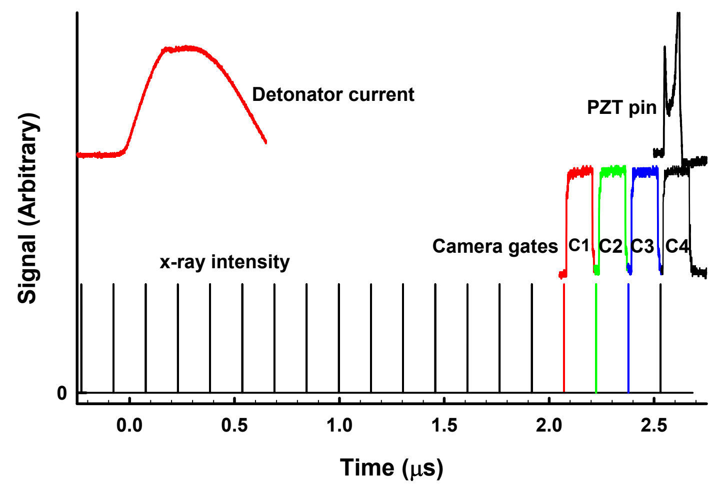
Time-resolved SAXS monitors the growth / assembly of carbon products behind the detonation front

SAXS instrument constructed for monitoring nascent carbon particle formation behind the detonation front



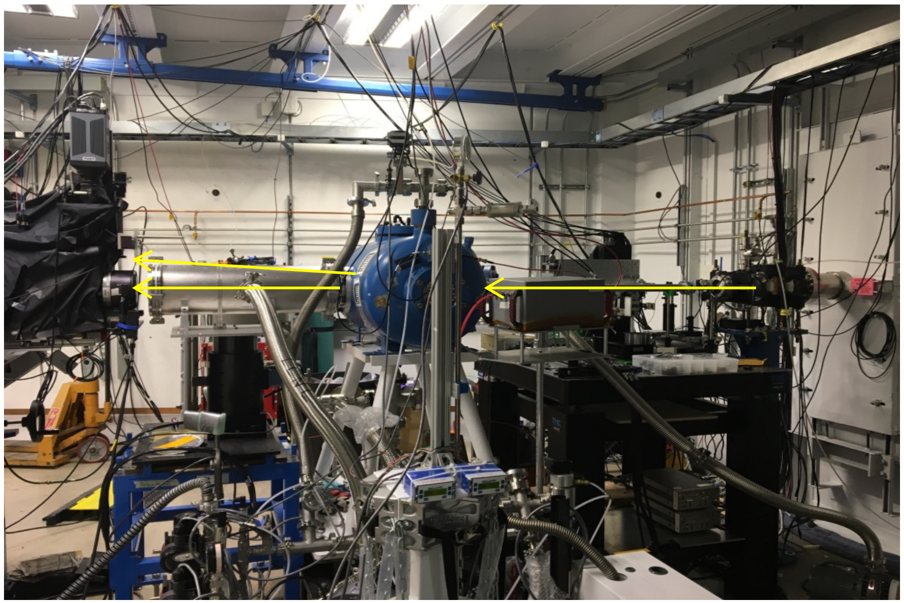


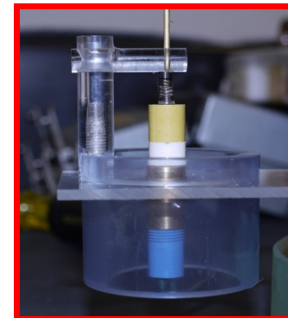
- Dynamic Compression Sector (35) – NNSA funded sector at APS/ANL
- First-of-a-kind experiments (only other attempt was in Russia)
- Required high flux (penetration through dense fluid & rapid dilution of particles due to fluid expansion) - pink beam (14.5kev or 23 keV)
- Required timing x-ray bunches to detonation wave passage and syncing camera gates to the x-ray bunches

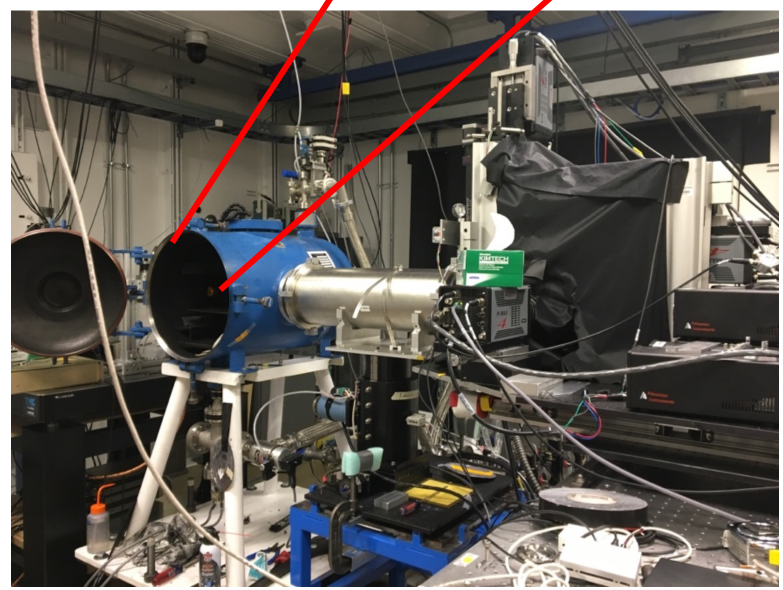


Gustavsen et al. J. Appl. Phys. 121, 105902 (2017)

Time-resolved SAXS monitors the growth / assembly of carbon products behind the detonation front



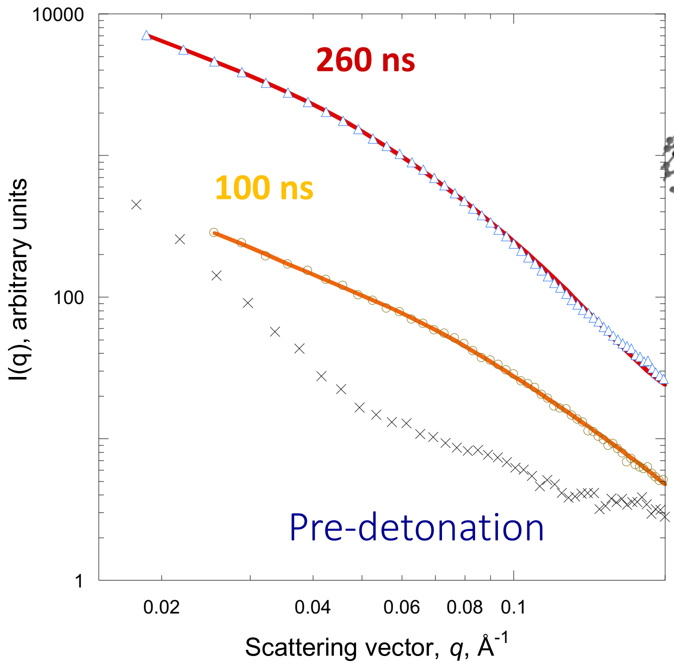




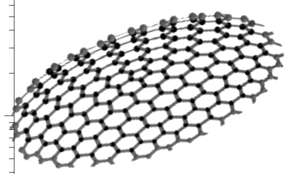
Gustavsen et al. J. Appl. Phys. 121, 105902 (2017)

Time-resolved SAXS on detonating composition B (in vacuo) reveals growth & assembly of carbon frameworks

Fractal clusters of disintegrated lamellae



Post-detonation



- Nano-sized flattened globules of carbon condensates (rough, multilayer ellipsoidal particles)
- Morphology is similar to shungite / Graphene QDs / C-dots

260 ns

Radius = 132.9 ±2.6 Å (13 nm)
Diameter = 26.6 nm
Thickness = 27.6 ± 0.8 Å (3 nm)

100 ns

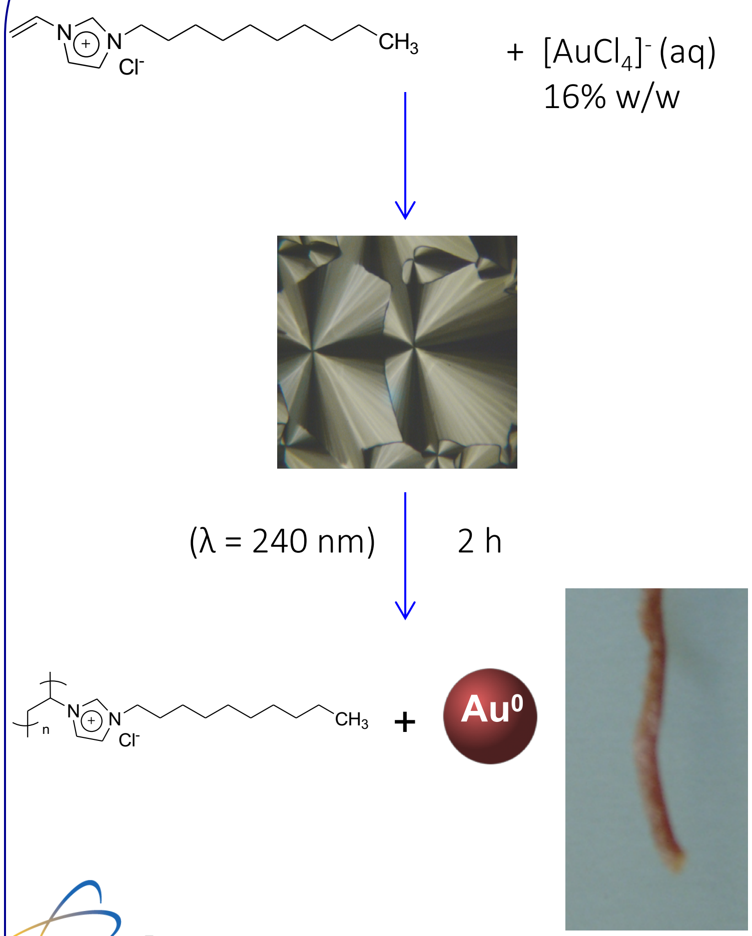
Radius = 88.2 ±3.0 Å (~ 9 nm)
Diameter = 17.6 nm
Thickness = 14.4 ± 2.6 Å (~ 1.5 nm)

Firestone, Dattelbaum, Podlesak, Gustavsen et al. AIP Conference proceedings, 1793, 030010 (2017)

Evaluation of multi-component systems by x-ray scattering: Plasmonic / Emissive QD polymer composites

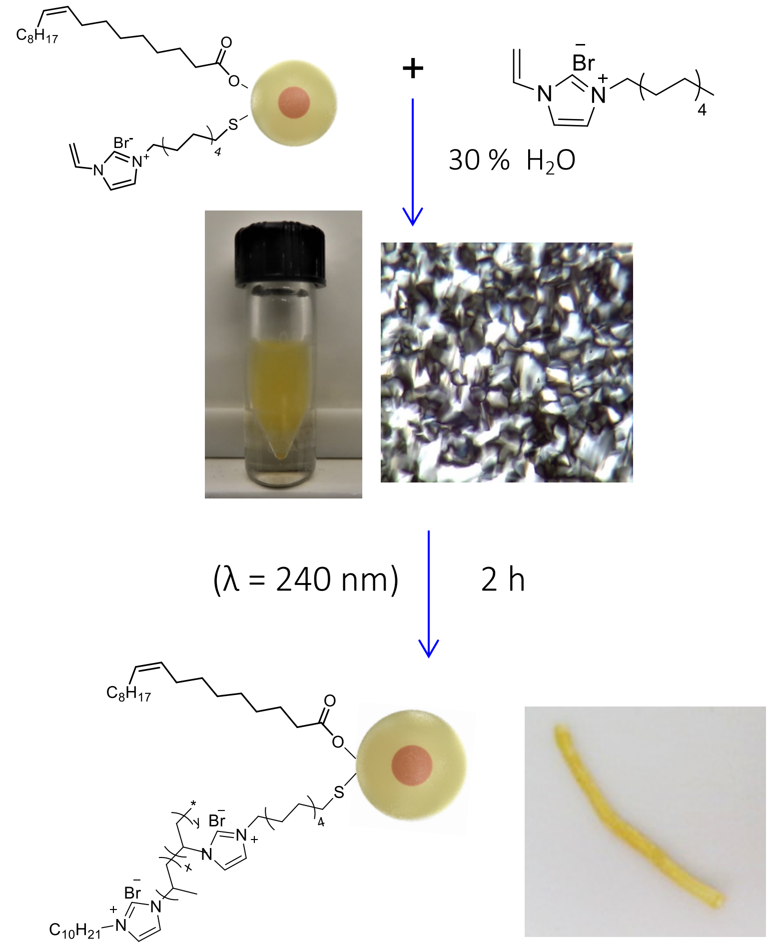
In-situ NP synthesis

Water-soluble NPs

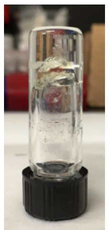


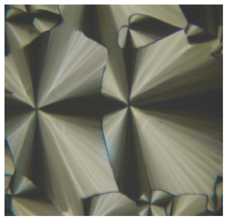
Ex-situ synthesized NPs

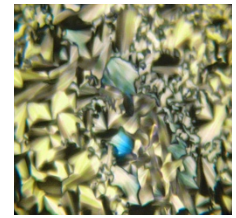
Organo-soluble NPs

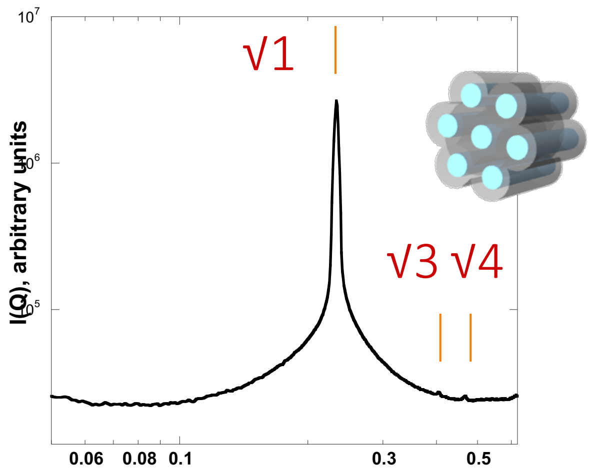


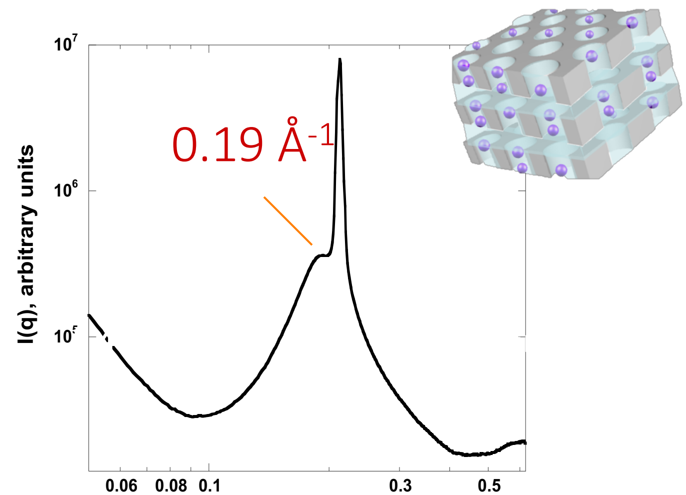
SAXS characterization of nanostructured plasmonic (Au NP)- poly(IL) composite











- Polymerization leads to a reduction in polymer symmetry (2HEX to Hexagonal Perforated Lamellar (HPL))
- Where are Au NPs? In the water channels? What is the size /shape of the *in-situ* synthesized Au NPs

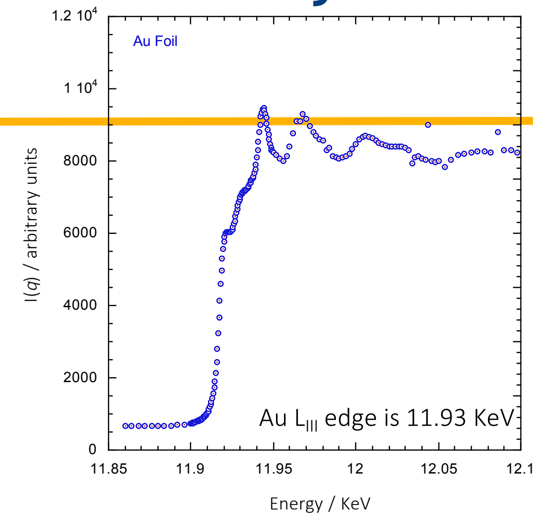
Batra, D. *et al.* Adv. Func. Mat. (2007,) 17, 1279

Lee, S.; J. Mater. Chem. (2009), 19(43), 8092-8101.

Lee, S. et al. ACS Appl. Mater. Interf. (2012), 4(5), 2311

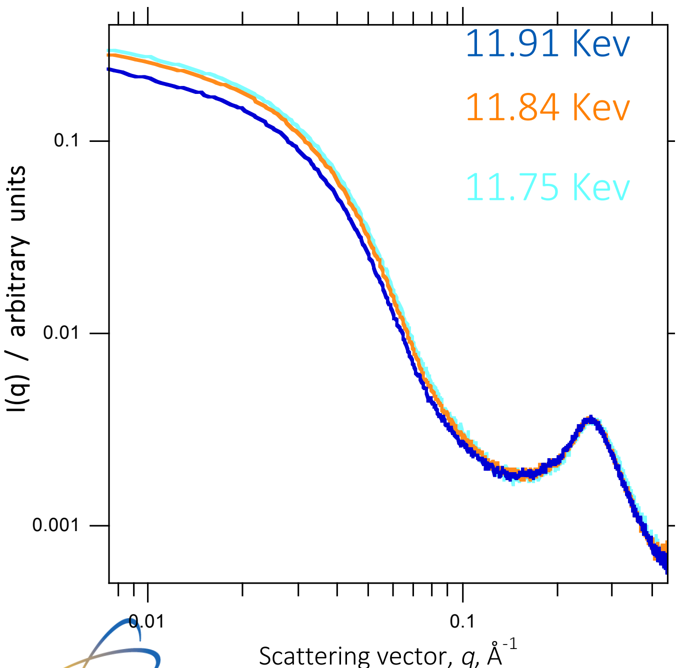
Element specific contrast in X-ray scattering : Anomalous X-ray Scattering (ASAXS)

$$F_n = f_0(q) + F'(E) + if''(E)$$



SAXS is a contrast technique / ASAXS is an element specific contrast technique

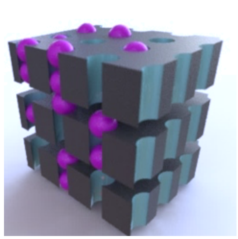
- Atomic scattering factor changes (anomalously) near the absorption edge of the element.
- Signal from the element in question can be distinguished from the rest of the sample
- Variation is achieved by measuring the scattering pattern at many different photon energies of the primary beam

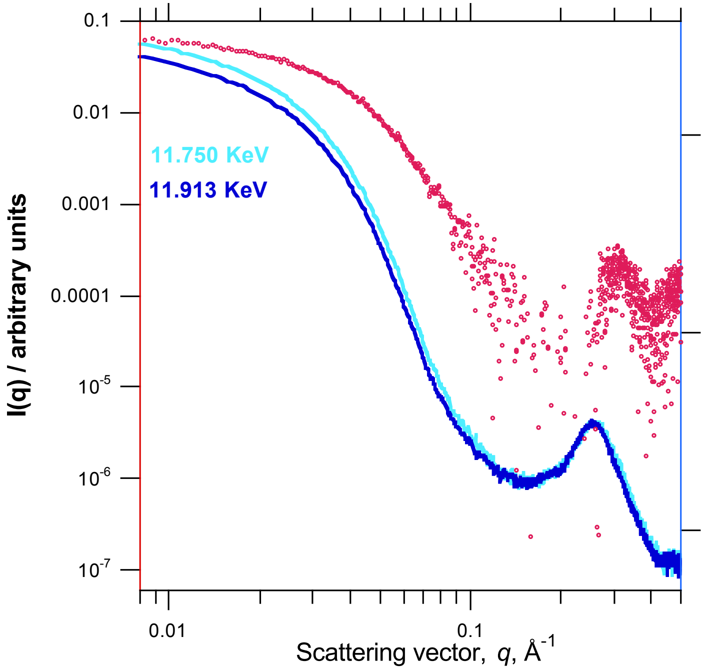


Observe I(q) vary with energy only in low q region

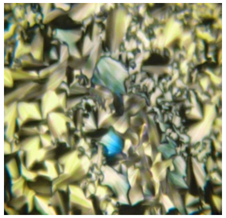
I(q) ↓ with KeV ↓

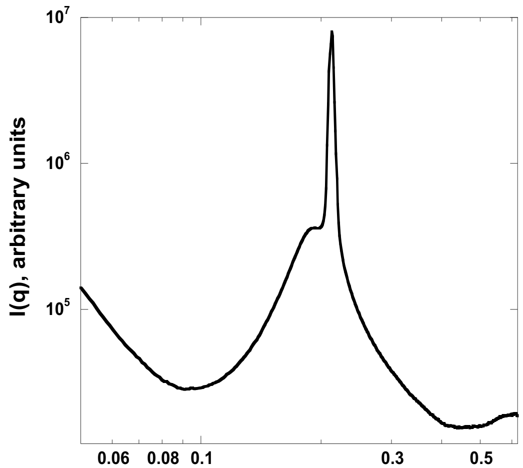
Au NPs reside in H_2O domain

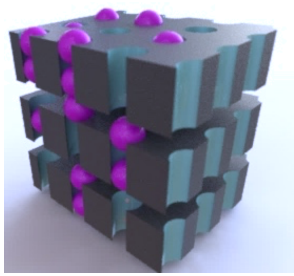




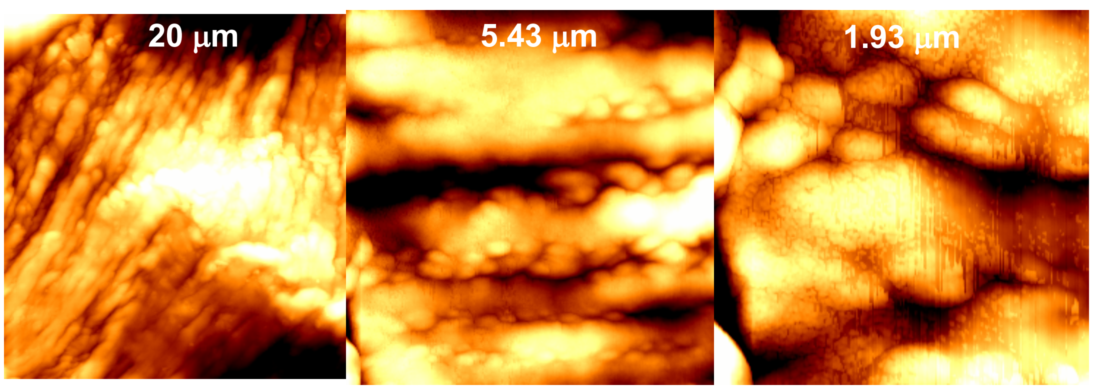
SAXS characterization of nanostructured plasmonic (Au NP)- poly(IL) composite







AFM confirms internal structure of Au NPs within water channels of a HPL structure



Guinier analysis of low q anomalous small-angle scattering yields polymer embedded Au NP morphology

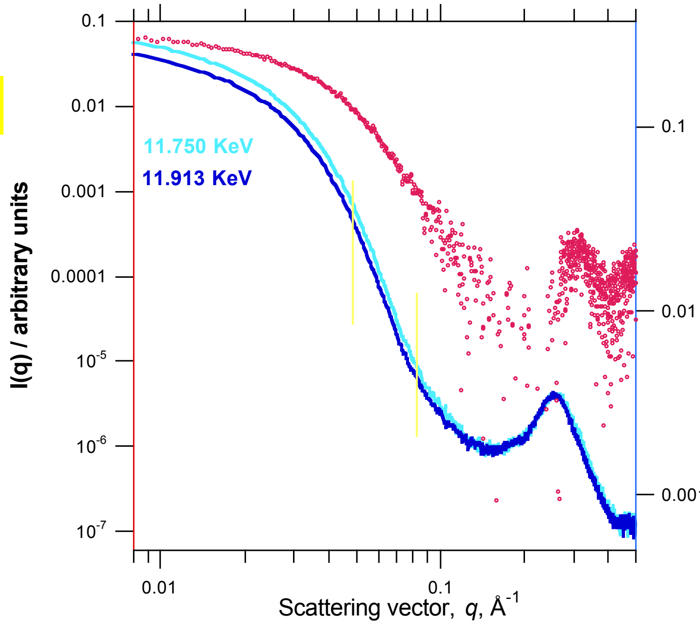
Guinier Approximation

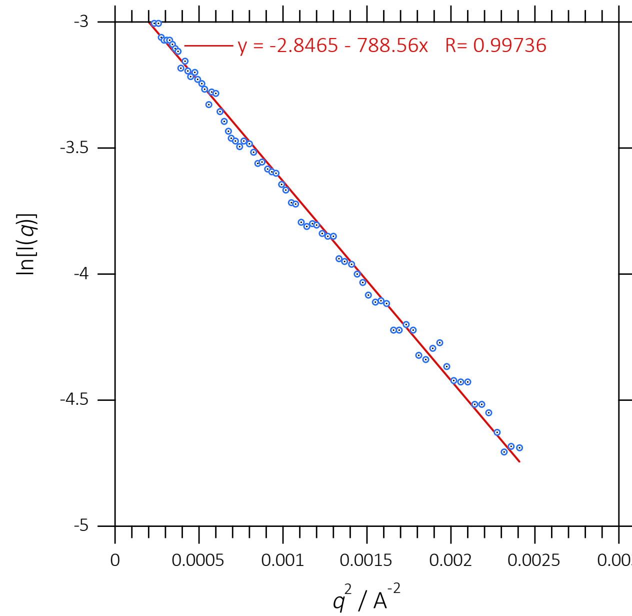
$I(q) = I(o) \exp(-1/3\ R_g^2\ q^2)$

$m = -R_g^2/3$ $R_g = \sqrt{3/5}\ R$

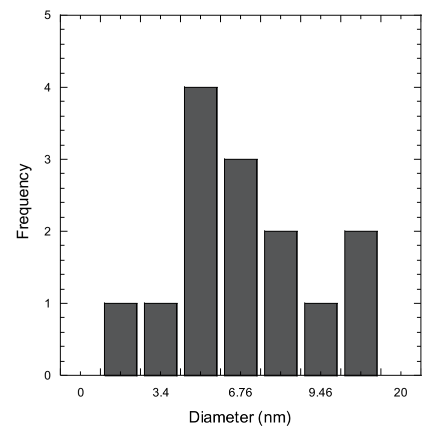
- Only valid if $q < 1/R_g$
- Matrix or solvent has been removed

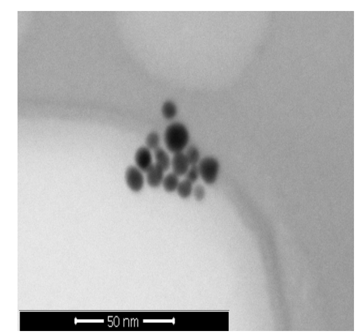
$R_g = 4.9$ nm
$R_{sphere} = 6.3$ nm





- Agreement with TEM





Final thoughts - go forth and scatter

- ✓ X-ray scattering is a powerful technique that can yield an enormous amount of structural information on complex materials
- ✓ The technique is well-suited for application to a wide range of soft /organic matter
- ✓ High quality data can be rapidly acquired at a synchrotron source.
- ✓ There are plenty of opportunities for further refining / improving our approaches to data analysis (i.e., automation for solving SAXS patterns analogous to single crystal structure determination)
- ✓ Software packages are available for data reduction and data analysis (J. Ilavsky – Irena)
- ✓ Strongly recommend collecting co-supporting structural data (EM, AFM, etc)
- ✓ Questions ?
- ✓ firestone@lanl.gov