Data Analysis of Hierarchical Systems

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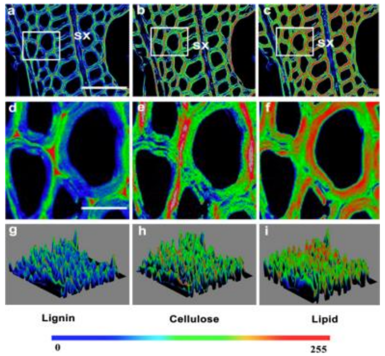
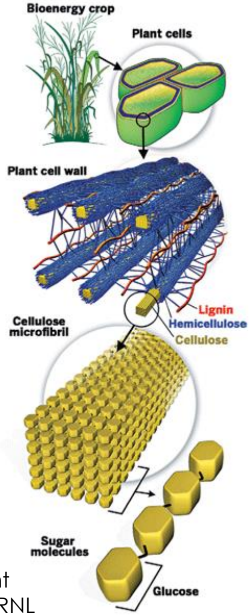
Example of Hierarchical Systems Around us

Plant Cell Wall

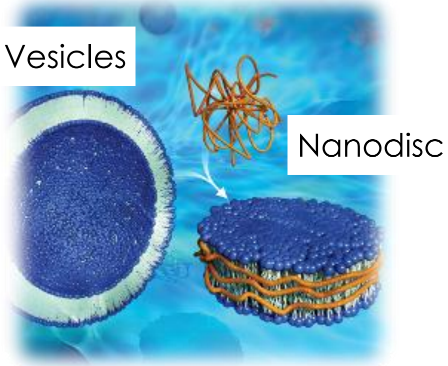


Plant Methods
17, 29 (2021).

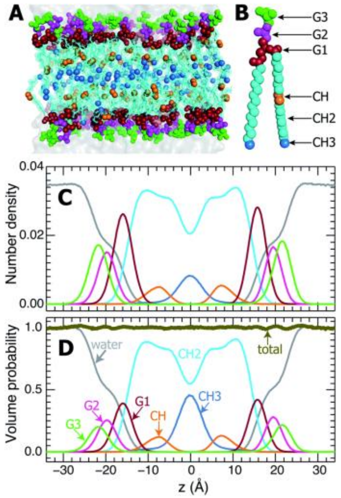


Genome Management
Information Systems/ORNL

Lipid Systems

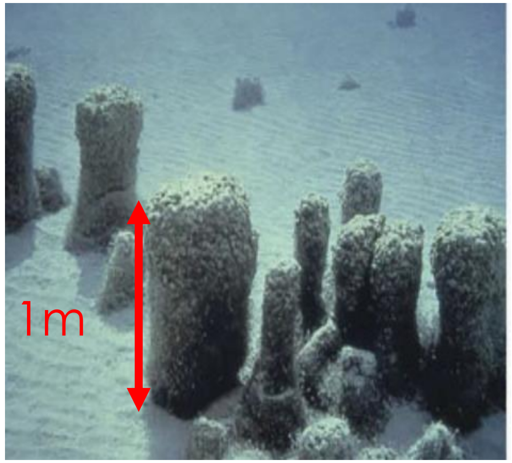


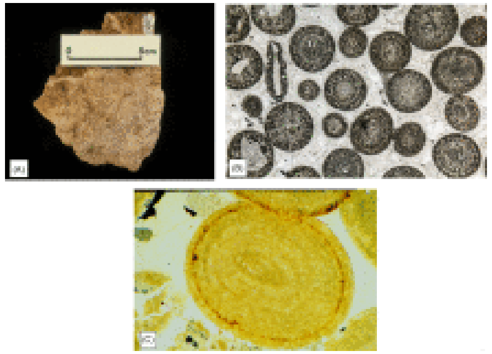
ACS Appl. Bio Mat. **4,** 4760–4768 (2021)



Soft Matter **10,** 3716–3725 (2014)

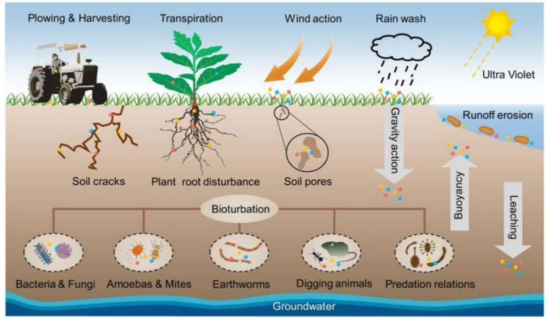
Sedimentary Rocks

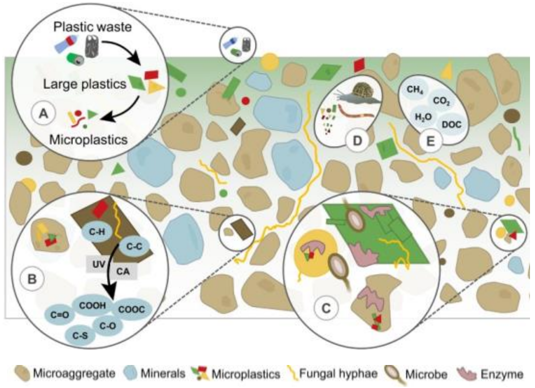




Encyclopedia of Geology 382-394 (2021)

Plastic/Soil Composites





Applied Soil Ecology **176,** 104486 (2022)

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Data Analysis Approaches Available

- Model Fit –

  Triblock Copolymer Structures in different Solvent Conditions

  - Debye Coil
  - Solid Sphere
  - Triblock Copolymer Micelle Structure

  Lipid Vesicles

  - Core-shell (or multi-shell)

- Shape-independent Fit - Guinier/power-law)

  Plant Cell Wall (powder sample state)

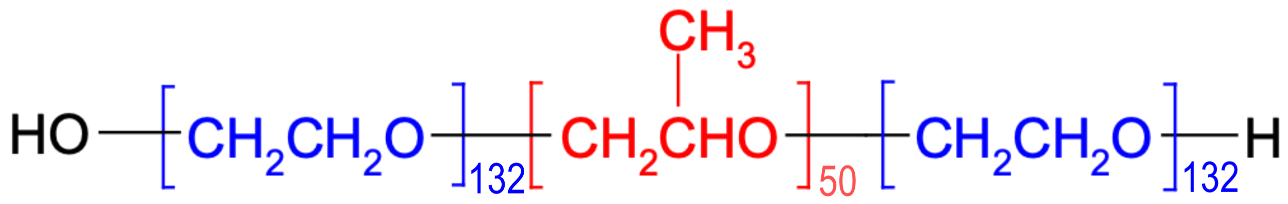
  - Unified Fit (Combination of Guinier and power-law functions)

- Composite Fit (A combination of Models and Shape-independent Approaches)

  Plant Cell Wall (Aligned state)

  - Cylinder Form Factor combined with Guinier and/or power-law functions

Amphiphilic Polymers - Drug Delivery

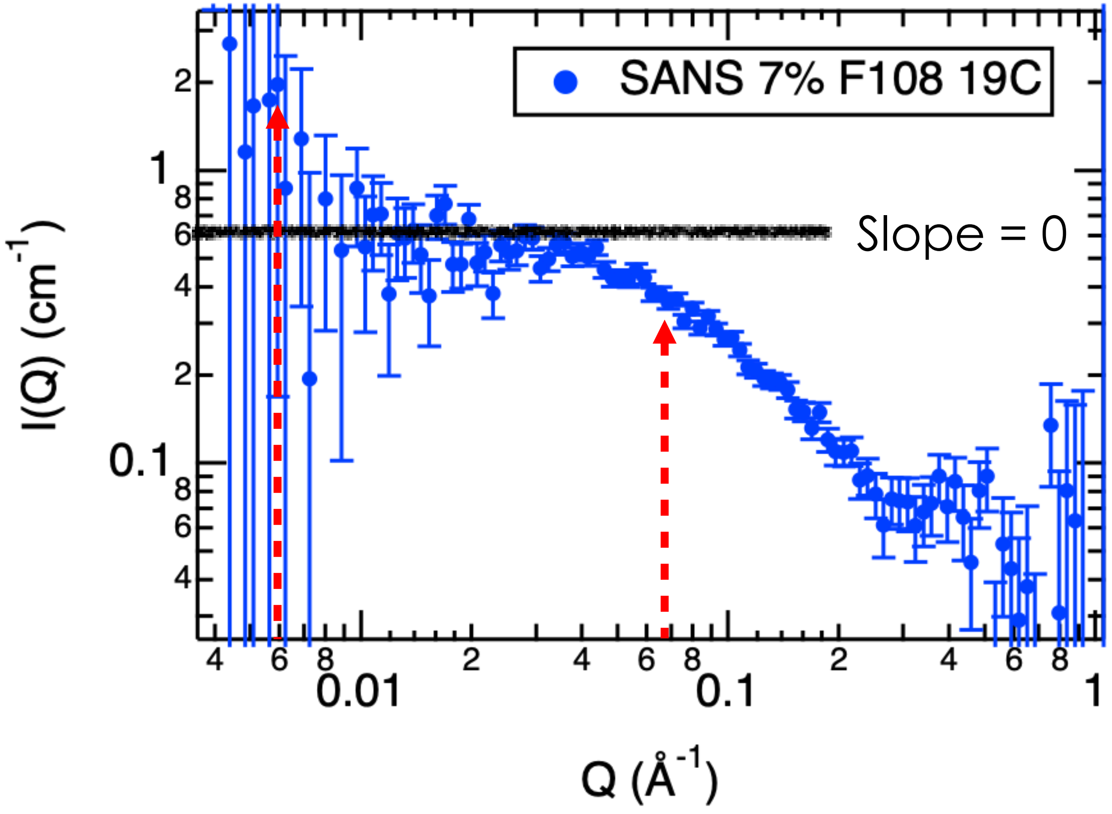


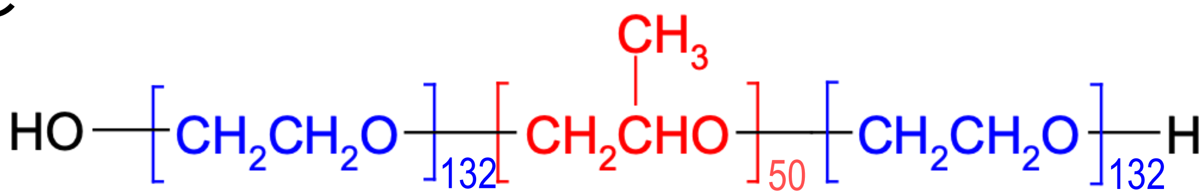
Pluronic F108

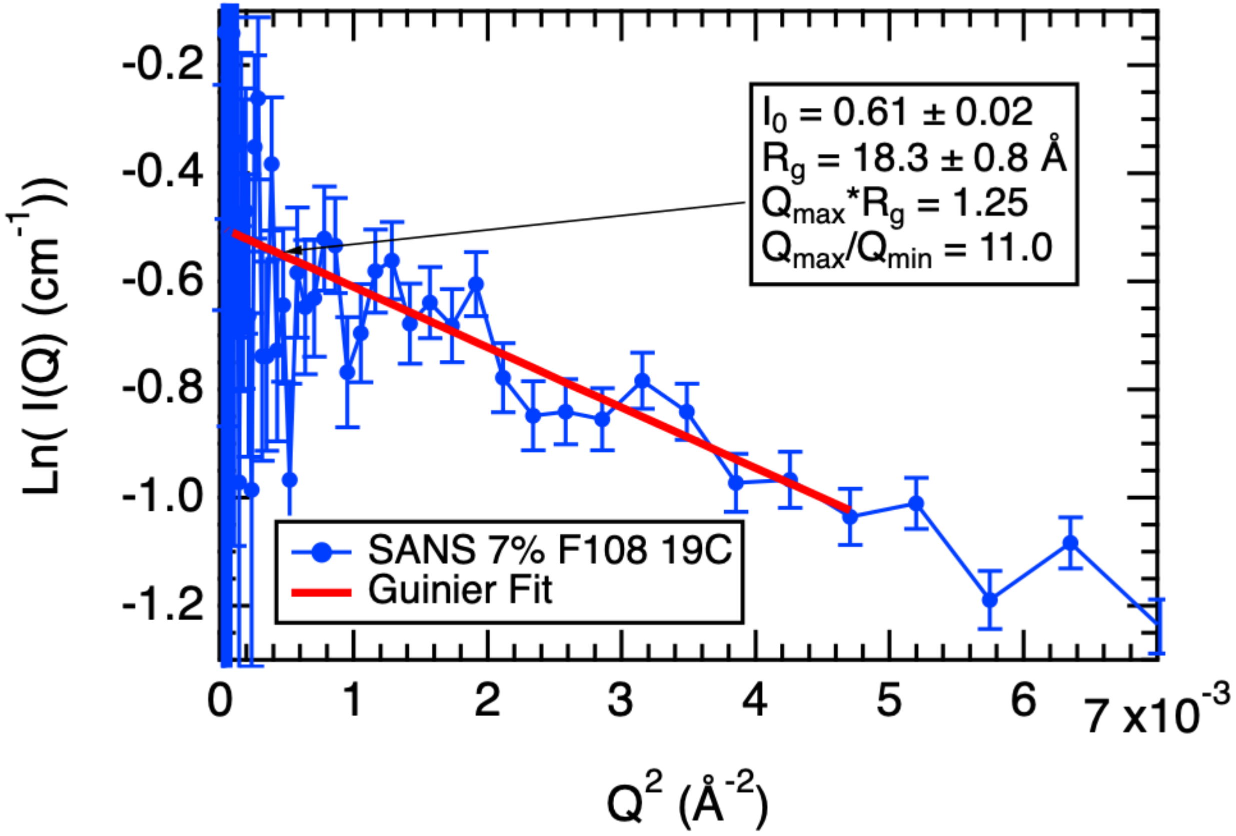
Hydrophilic
Hydrophobic

- Pluronic F108 7% solution in 0.1M sodium carbonate
- Molecular Weight (Mw) is 16400 Da
- Structure at room temperature (19 °C)

Guinier Analysis 7% F108 at 19 °C

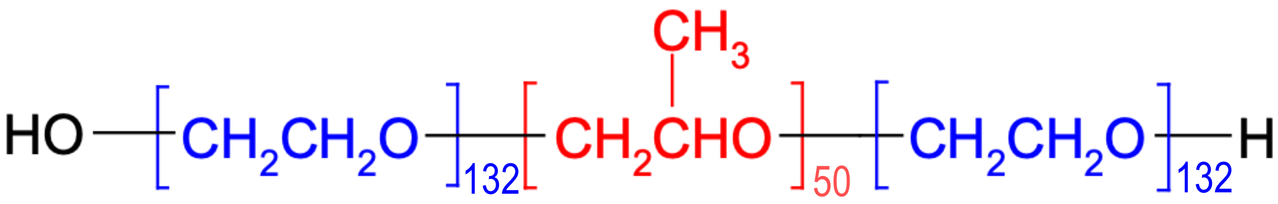


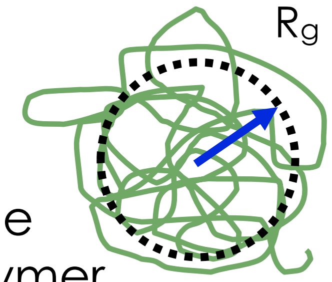




- Guinier analysis results
  - Globular particle and R_g ~ 18.3 Å
  - Q_{max} * R_g < 1.3
  - Q-range of straight line fit, Q_{max}/Q_{min} ~ 2.0+

Model Fits

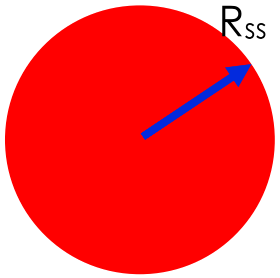




Debye Flexible
Gaussian Polymer

$$I(Q, R_g) = SF\frac{2[exp(-z) - 1 + z]}{z^2} + I_{bkg}$$

$$z = Q^2 R_g^2$$



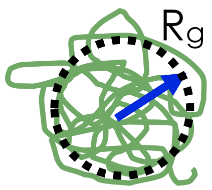
Solid Sphere

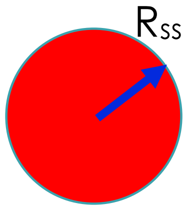
$$I(Q, R_{ss}) = SF(\frac{3[sin(z) - zcos(z)]}{z^3})^2 + I_{bkg}$$

$$z = QR_{ss}$$

- Models
  - Debye Flexible Gaussian Polymer (random conformations)
  - Solid Sphere (when low degree of solvent penetrates the particle)

Debye Flexible Gaussian Polymer vs. Solid Sphere

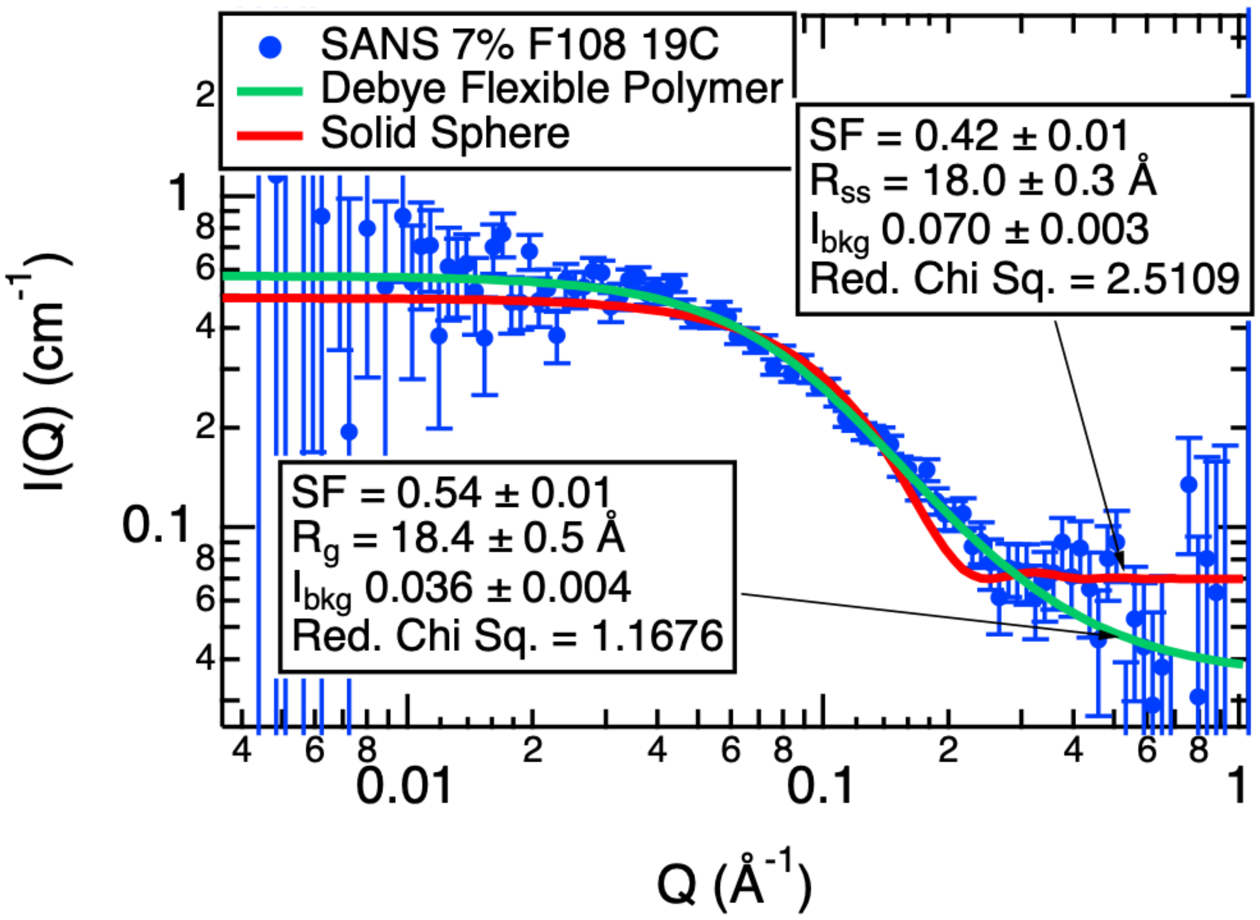




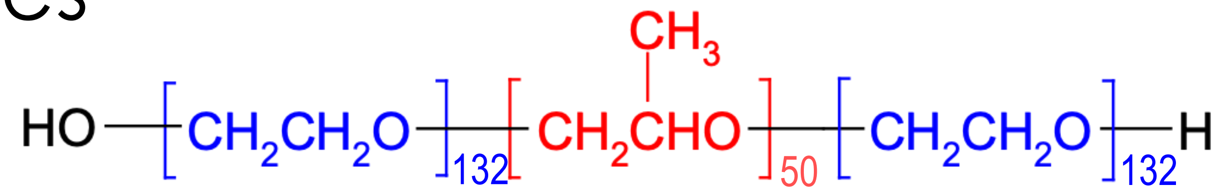
- F108 dissolved as individual polymers in solution of sodium carbonate

- High-Q region is highly sensitive to the surface morphology of the particle.

- **Debye flexible Gaussian polymer** function (High-Q PL exponent = 2) fits better than **solid sphere** (High-Q PL exponent = 4)



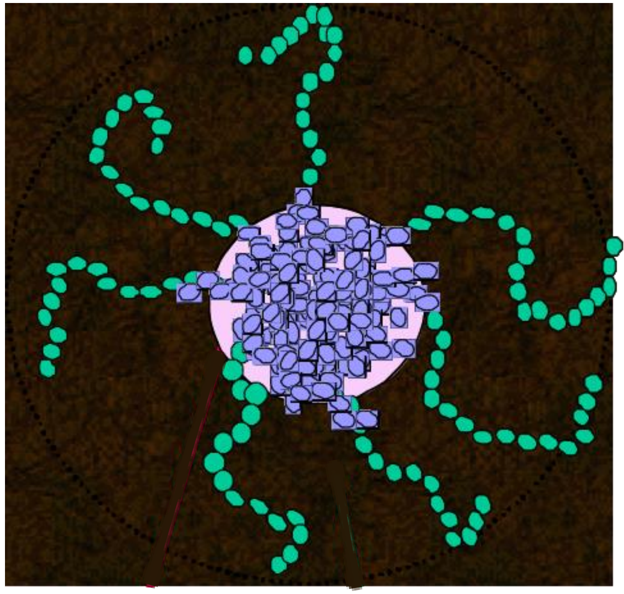
Self-Assembled Suprastructures



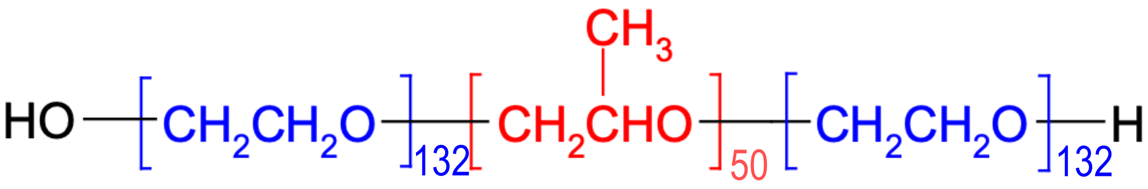
- Central core consists of the hydrophobic block of F108
- The tentacles are the hydrophilic blocks of F108
- Particle model
  - Spherical particle core for hydrophobic block
  - Debye Flexible Gaussian Polymer chain for hydrophilic blocks.
  - Interaction term- chain-chain and chain-Core
- Structure factor
  - Percus-Yevick structure factor (hard sphere approximation to enable developing an analytical expression)

Hydrophilic - PEO corona

Hydrophobic - PPO core



SANS data fit

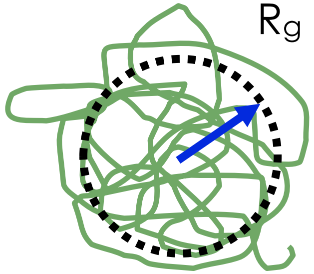


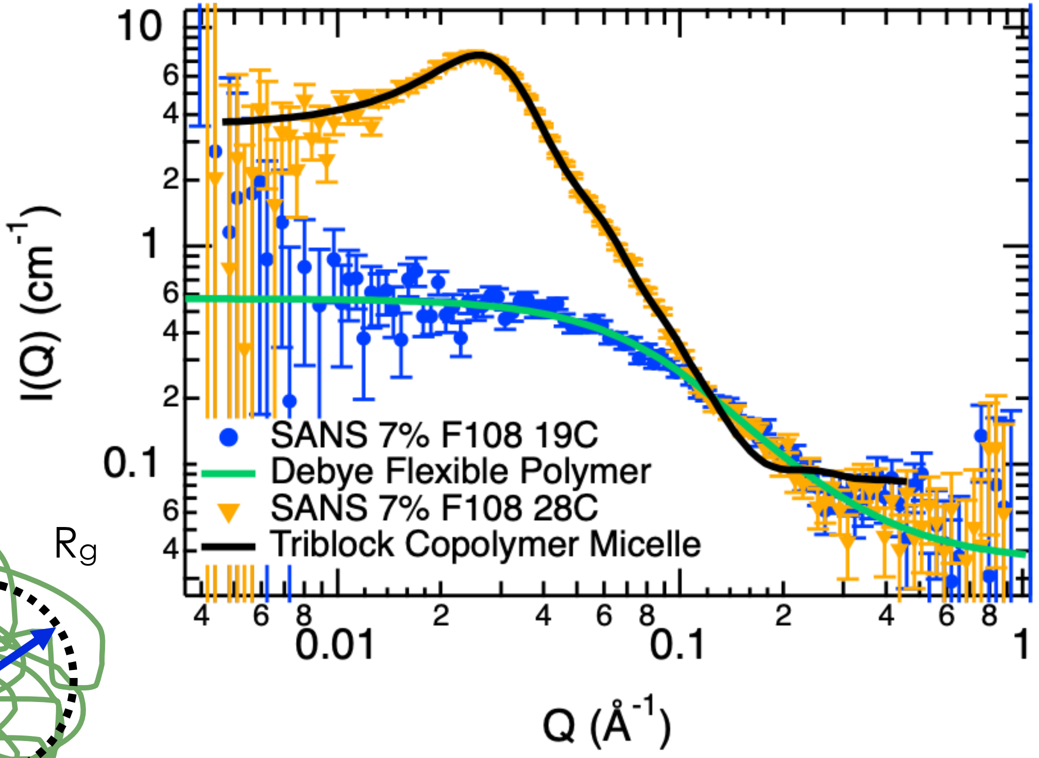
- Debye Flexible Gaussian Polymer Model
  - R_g (Å) 18.4 ± 0.5
- Triblock Copolymer Micelle Model
  - Aggregation (#) 13.1 ± 0.2
  - R_{core} (Å) 18.8 ± 0.3
  - R_{corona} (Å) 25.9 ± 0.6
  - Core Overlap Factor, d (#) 0.67 ± 0.02

  - Volume Fraction (#) 0.173 ± 0.003
  - Micelle-Micelle distance (Å) 209 ± 3

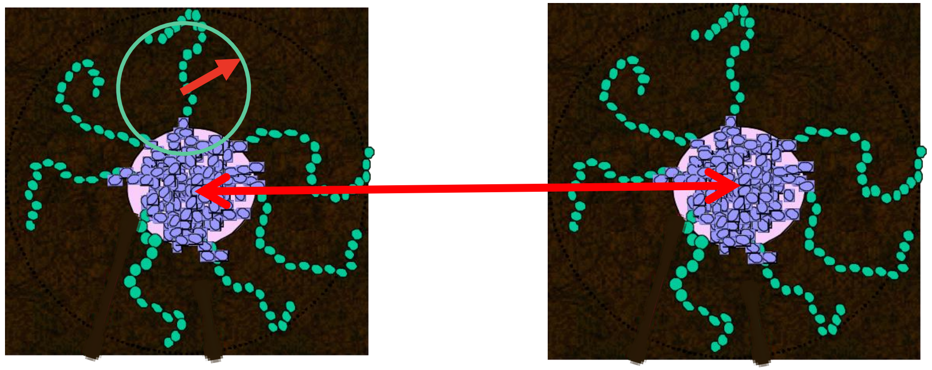
  - Particle diameter (Å) 72 ± 2

$= 2 \times [R_{core} + (d \times R_{corona})]$

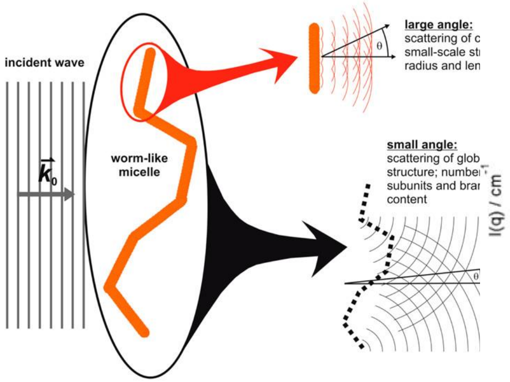


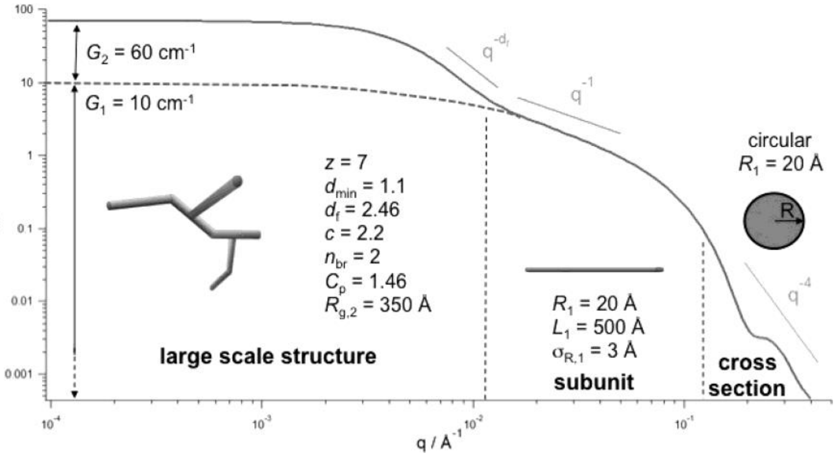


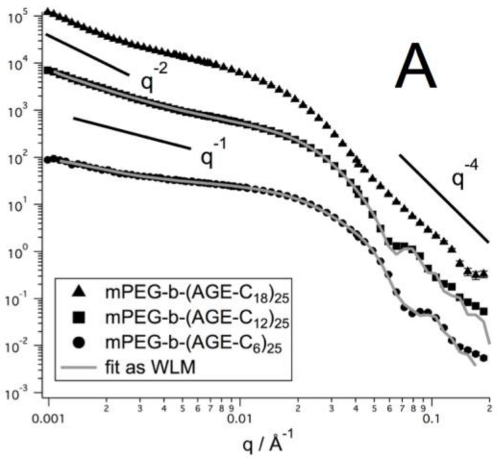
Hydrophilic - PEO corona
Hydrophobic - PPO core

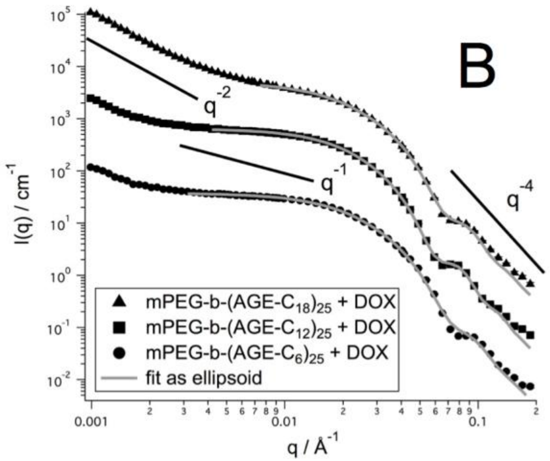


Drug release from Worm-like Micelles

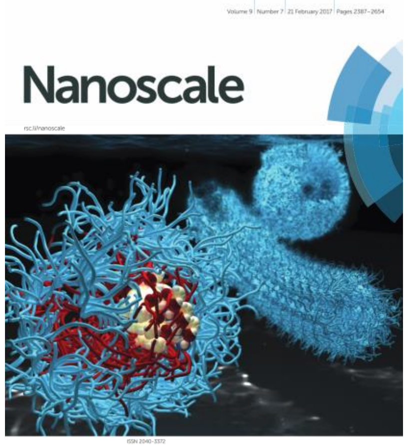








- Amphiphilic polymers as drug delivery for Cancer drug-DOX
- Worm like Micelles Structure is hierarchical
- Worm like Micelles transitions to Ellipsoidal Structure impeding efficient drug delivery



Le Dévédec, F., Her, S., Vogtt, K., Won, A., Li, X., Beaucage, G., Allen, C. **Nanoscale (2017) 9, 2417-2423**

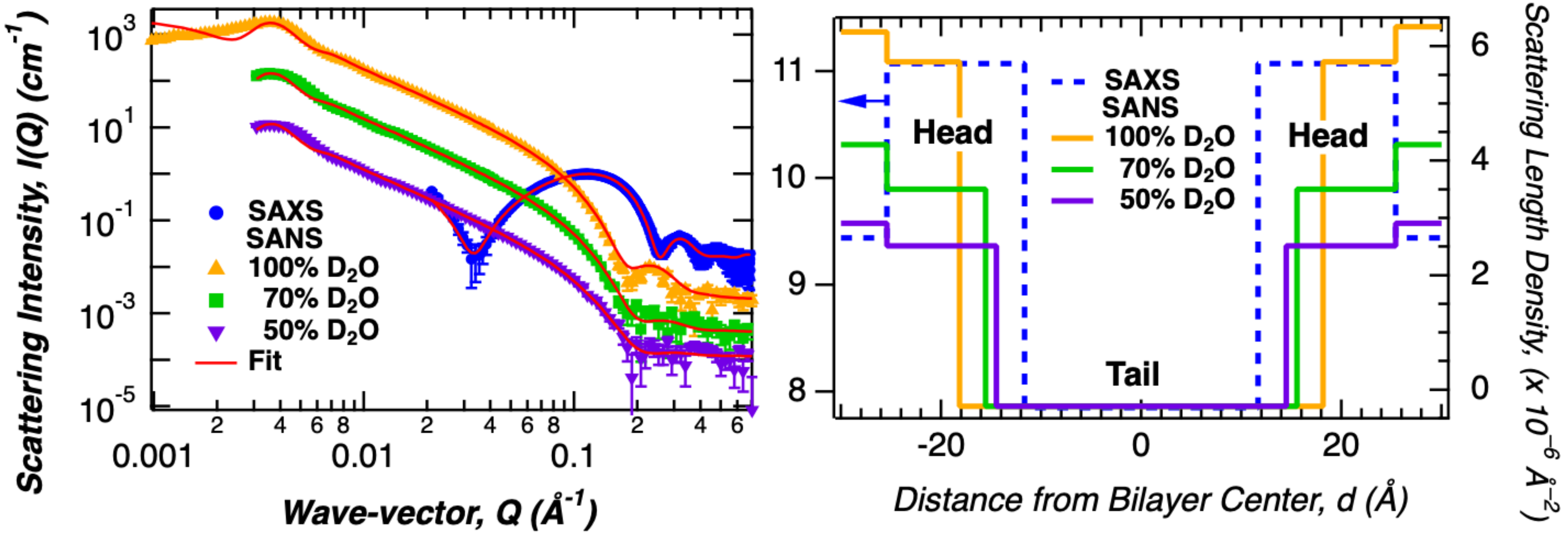
Vogtt, K., Beaucage, G., Weaver, M., Jiang, H. **Langmuir (2015) 31, 8228-8234**

Lipid Vesicles

- Slab Model
  - Core-multishell (Lipid Tail, Lipid Head, Solvent)

- SPD Model
  - Parsing of Lipid Molecule
  - Lipid Tail into 3 regions
  - Lipid Head into 3 regions
  - Solvent

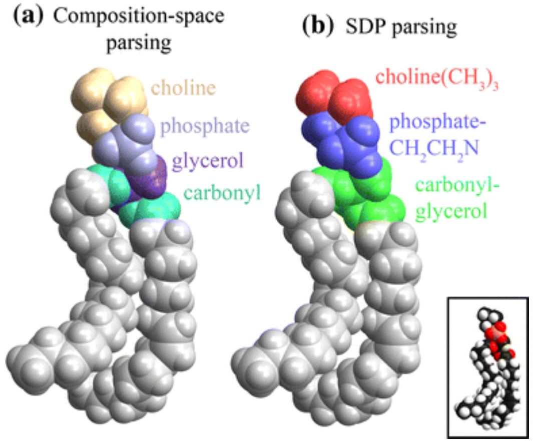
Contrast Variation improves data interpretation



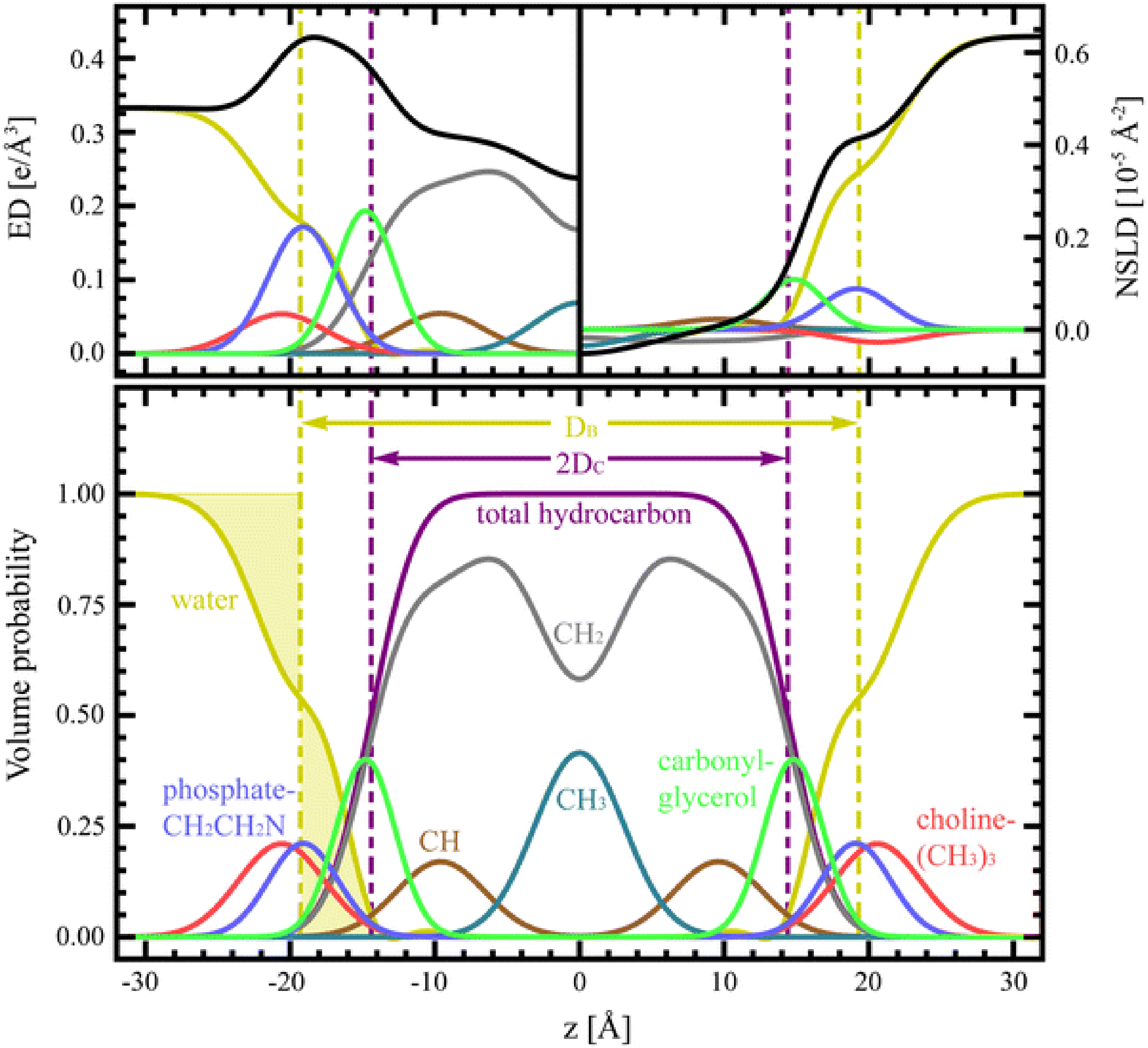
- Core-multishell Model
- Choice of solvent D_2O% is important to ensure head group region can be defined well

Smith, M.D., Pingali, S.V., Elkins, J.G., et al. **Green Chemistry (2020) 22, 8278-8288**

SDP Model



- Parsing different for SDP model
- To resolve several components, simultaneously fit 4-5 contrast conditions



Herberle, F., Pan, J., Standaert, R.F., et al. **Eur Biophys J (2012) 41, 875-890**

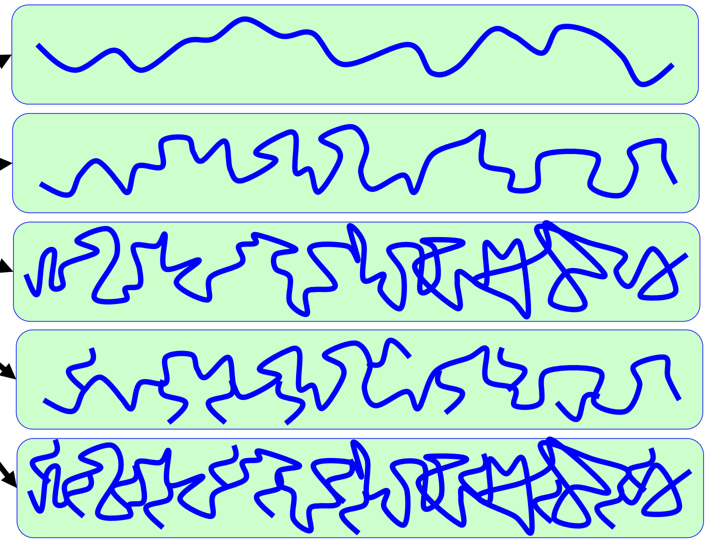
Plant Cell Wall

- Unified Fit Model (isotropic or random data)
- Composite (Form Factor + Power-law)

Fractal Slopes Interpretation

Fractal Type	Power-law Slope (Range)
Mass	– 1.0 to – 3.0 (Bulk)
Surface	– 3.0 to – 4.0
Porod	– 4.0
Diffuse-scattering	– 4.0 to – 5.0

Mass-fractal structures	Power-law slope
Polymers	
Polymer in good solvent	−1.5
Self-avoiding walk (linear swollen polymer)	−1.67
Random walk (polymer in theta solvent)	−2.0
Swollen branched polymer	−2.0
Randomly branched ideal polymer	−2.29
Non-equlibrium growth processes	
Multiparticle diffusion limited aggregate	−1.8
Percolation cluster	−2.5
Diffusion limited aggregate	−2.5
Low-dimensional objects (apparent mass fractals)	
Randomly distributed rods	−1.0
Randomly distributed lamellae or platelets	−2.0



Beaucage, G. **J Appl. Cryst. (1995) 28, 717-728**
Beaucage, G. **J Appl. Cryst. (1996) 29, 134-146**

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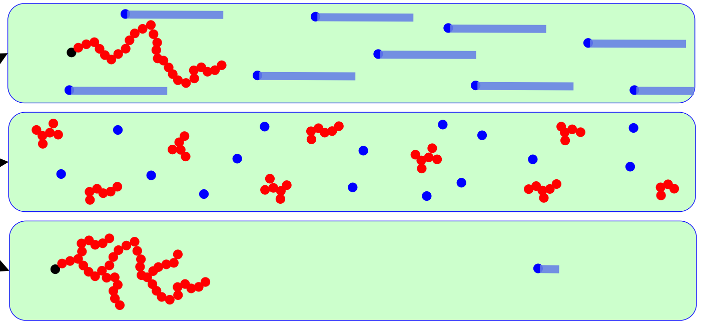

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Mass	– 1.0 to – 3.0
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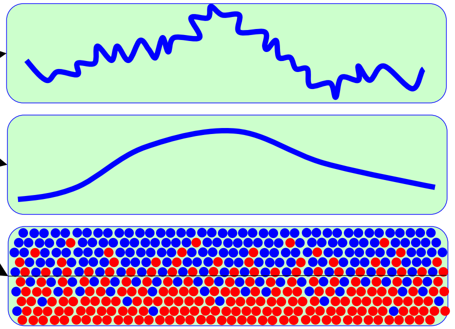
Porod	– 4.0
Diffuse-scattering	– 4.0 to – 5.0

Interface/ Surface (Surface, Porod, Diffuse-scattering)

Surface-fractal Power-law Scattering

		Surface Morphology
Maximally Rough	– 3.0	Crumpled Sheet
Smooth	– 4.0	Solid Sphere
Diffuse	– 5.0	Oil-Water



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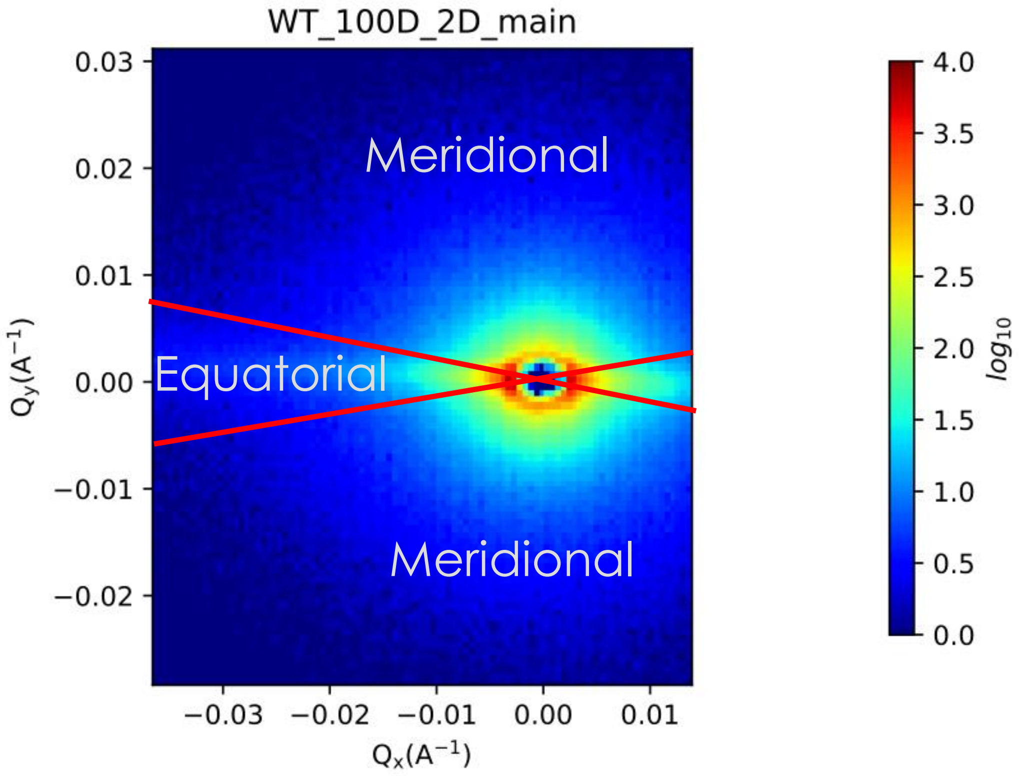
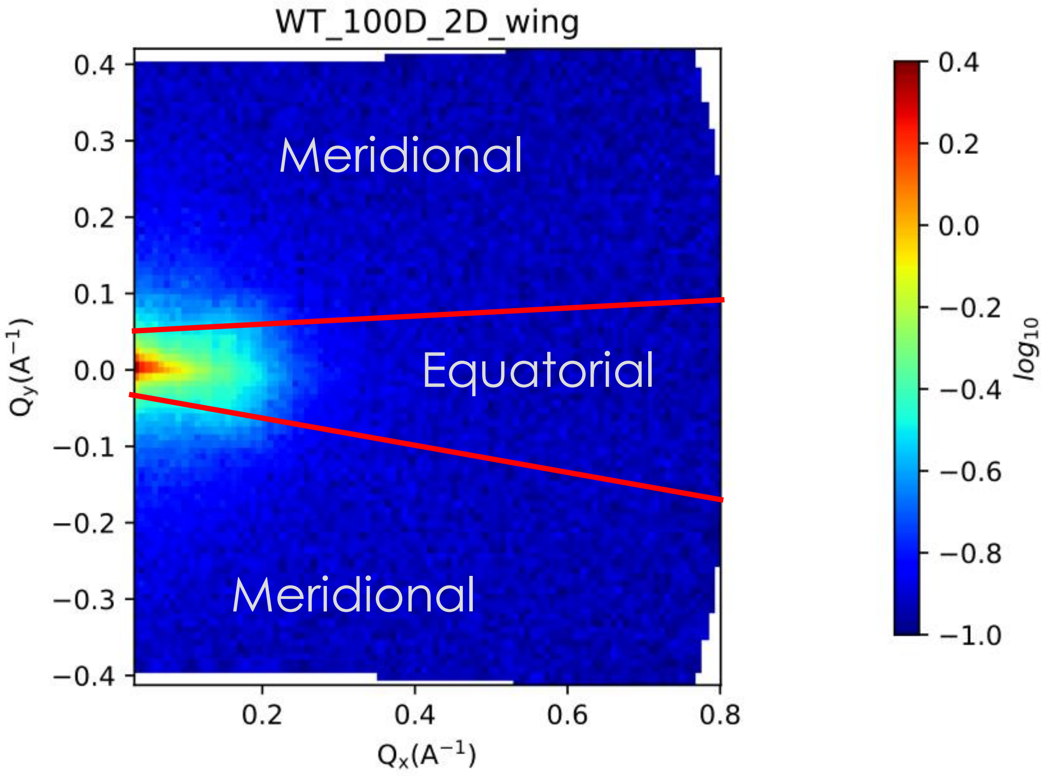
Plant Cell Wall

- Unified Fit
- Composite Model Fit

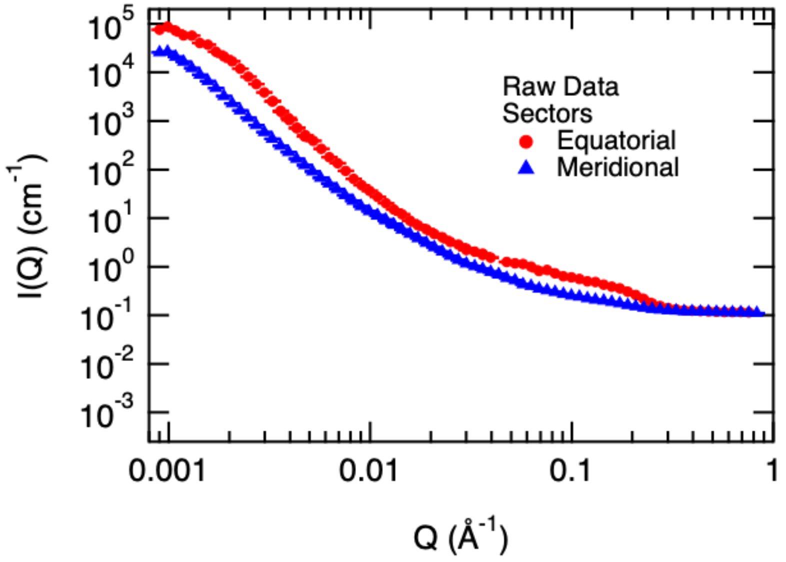
Anisotropic Data - Plant Cell Wall

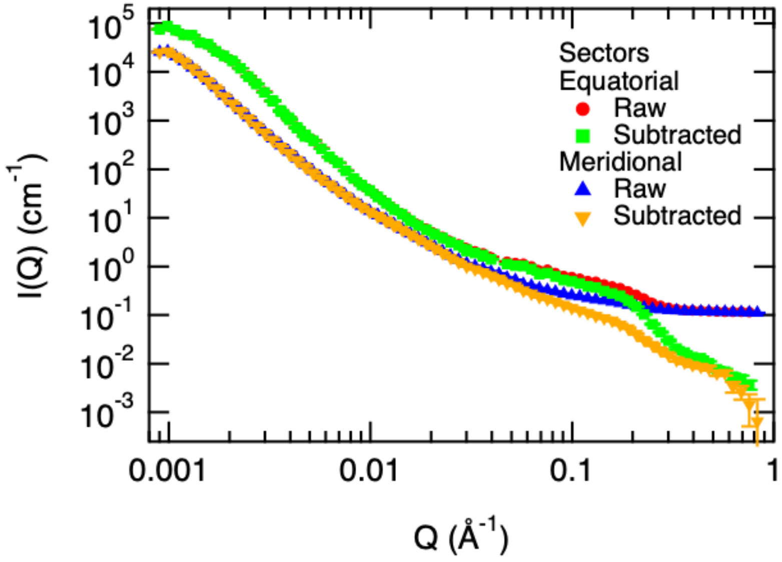


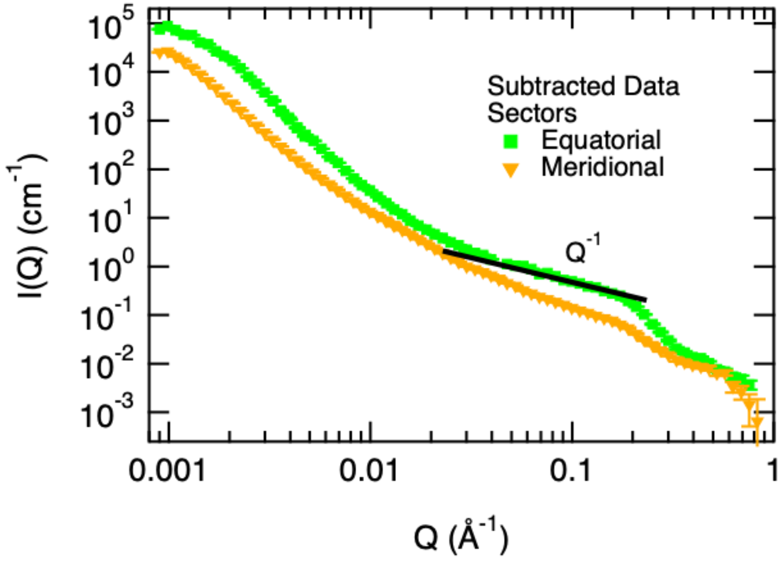


- Divide into sectors - Equatorial and Meridional

Anisotropic Data - Plant Cell Wall







- Solvent Scattering is the same
- Clear differences in structure based on direction of scatter

Questions?

Facility Acknowledgment Statement

- A portion of neutron scattering research presented as examples in this introduction used resources at the High Flux Isotope Reactor or Spallation Neutron Source, DOE Office of Science User Facilities, operated by the Oak Ridge National Laboratory.
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