Analysis of SANS and USANS Data

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NCNR Summer School

Neutron Small Angle Scattering and Reflectometry

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CHRNS Center for High Resolution Neutron Scattering NIST

Outline

- Basic Equations
- Model-independent methods

  Guinier, Porod, Invariant
- Non-Linear Model Fitting

  Particles, Polymers, Materials
- Global Fitting
- Anisotropic Scattering
- Transforms
- Ab initio modeling

Easy

↓

More involved

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The Basics

Starting from: $$\frac{d\sigma}{d\Omega}(\vec{\mathbf{q}}) = \frac{1}{N}\left|\sum_{i}^{N} b_i e^{i\vec{\mathbf{q}}\cdot\vec{\mathbf{r}}}\right|^2$$

- We can replace the sum over atoms with an integral over the scattering length density $$\sum_{i}^{N} b_i \rightarrow \int_V \rho(\vec{\mathbf{r}})d\vec{\mathbf{r}}$$

- Normalizing by sample volume and introducing scattering length density

$$\boxed{\frac{d\Sigma}{d\Omega}(\vec{\mathbf{q}}) = \frac{N}{V}\frac{d\sigma}{d\Omega}(\vec{\mathbf{q}}) = \frac{1}{V}\left|\int_V \rho(\vec{\mathbf{r}})\, e^{i\vec{\mathbf{q}}\cdot\vec{\mathbf{r}}}\, d\vec{\mathbf{r}}\right|^2}$$

- Inhomogeneities in $\rho(\vec{\mathbf{r}})$ give rise to small angle scattering

$\Sigma = \sigma/V$ is the "macroscopic cross section"

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Scattering Basis

Different systems each have a natural basis - and all are equivalent

- This is especially true if the scattering is from "countable" units

$$\left| \int_V f(\vec{\mathbf{r}})\, d\vec{\mathbf{r}} \right|^2 \rightarrow \sum_i^N \sum_j^N f(\vec{\mathbf{r}}_i - \vec{\mathbf{r}}_j)$$

Polymers	monomer unit
Particulates	per particle
Proteins	polypeptide subunits

- A statistical description may also be appropriate

$$\rho(r) \rightarrow \gamma(r)$$

Non-particulate	correlation function

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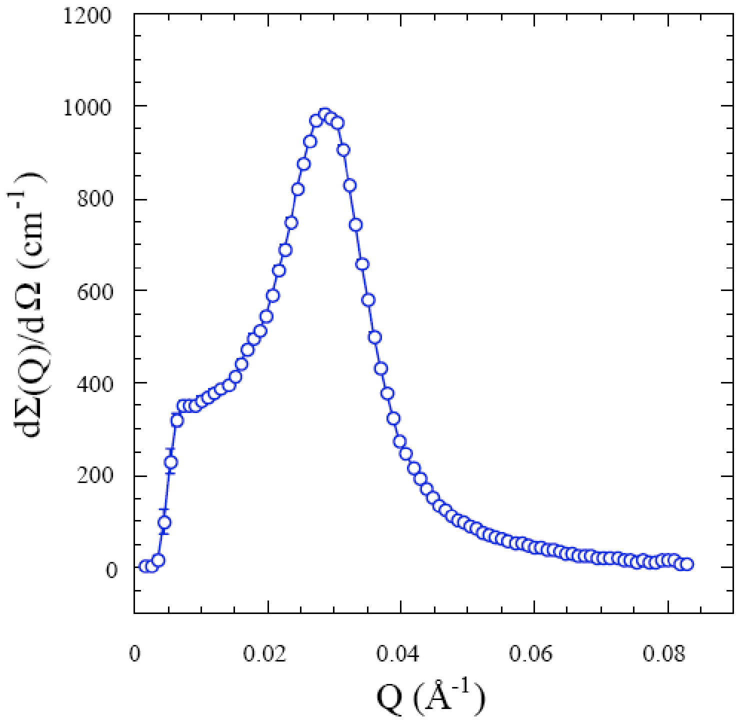
Measured Intensity

After reducing the raw data - you will typically have:

I(Q) vs. Q

Units of intensity are cm^{-1} $ster^{-1}$

Units of Q are $length^{-1}$



$$I(Q) = \frac{8\pi\xi^3(\Delta\rho)^2\phi(1-\phi)}{(1+(Q\xi)^2)^2}$$

$$I(Q) = \frac{\phi}{V_p}\left[\frac{3V_p(\Delta\rho)(\sin(QR) - QR\cos(QR))}{(QR)^3}\right]^2$$

$$I(Q) = \frac{2\phi(\Delta\rho)^2 Z v_m (e^{-x} + x - 1)}{x^2} \qquad x = (QR_g)^2$$

Model Independent Analysis

What information can you obtain?

- Invariant
  - volume fraction, data consistency
- Porod Limit
  - specific surface area, surfactant head group area
- Guinier Analysis
  - general or specific dimensions
- I(Q=0)
  - particle volume, molecular weight

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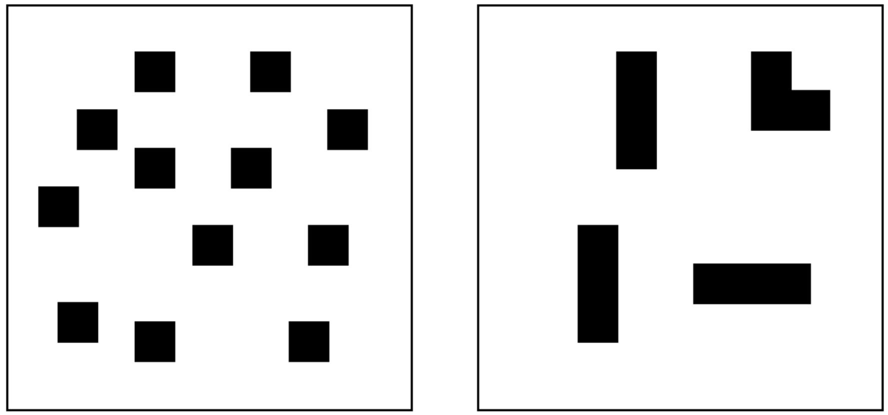
Scattering Invariant



10 % black
90 % white
in each square

- Scattered intensity for each would certainly be different

$$Q_I \equiv \int_0^\infty q^2 \frac{d\Sigma}{d\Omega}(q)\, dq$$

- For an incompressible, two-phase system:

$$Q_I = 2\pi^2 \Delta\rho^2 \phi(1-\phi)$$

- Domains can be in any arrangement

*Guinier and Fournet, pp. 75-81.

**Need “wide” Q-range to do integration

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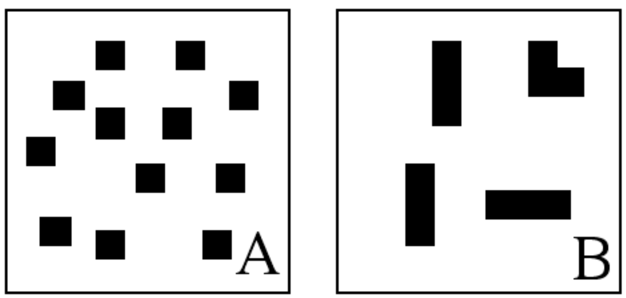
Porod Scattering

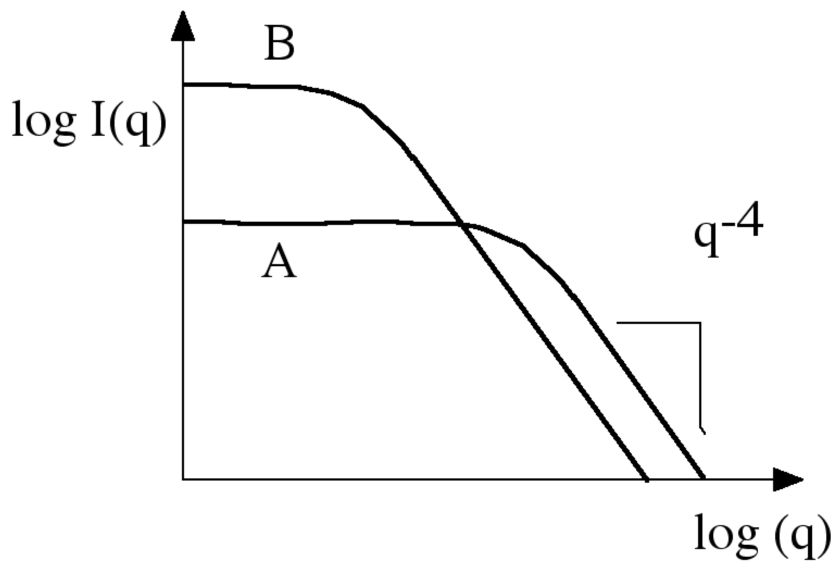
- At large q: $I(q) \propto q^{-4}$

$$\lim_{q\to\infty} \frac{d\Sigma}{d\Omega}(q) \equiv C_p \big/ q^4 = 2\pi\, \Delta\rho^2\, S_V \big/ q^4$$

S_V = specific surface area of sample



$$\frac{S_A}{V} > \frac{S_b}{V}$$



*Glatter and Kratky, pp. 30-31.

**Need "sharp" interface and "high" Q

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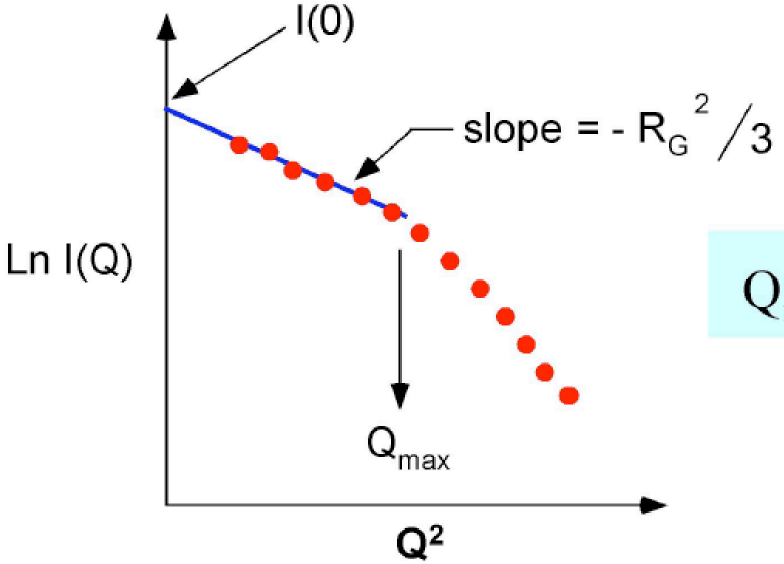
Guinier Analysis

Guinier Approximation:

$$I(Q) \cong I(0)e^{-\frac{1}{3}R_G^2 Q^2}$$

Guinier Plot:

$$\ln[I(Q)] = \ln[I(0)] - Q^2 R_G^2 / 3$$



$$Q_{max} R_G \leq 1$$

Guinier Radius = R_g
= RMS distance from "center of scattering density"

Sphere:

$$R_g^2 = \frac{3}{5} R^2$$

Cylinder:

$$R_g^2 = \frac{L^2}{12} + \frac{d^2}{8}$$

Gaussian Coil:

$$R_g^2 = \frac{1}{6}\langle L^2 \rangle$$

**Need "dilute" particles and "low" Q

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Zero angle scattering

$$I(Q=0) = \frac{1}{V}\left(\int_V \rho(\vec{r})d\vec{r}\right)^2$$

becomes

$$I(Q=0) = \frac{N}{V}(\rho_p - \rho_o)^2 V_p^2$$

for N uniform particles in volume V, each with SLD ρ_p and volume V_p

In terms of concentration:

$$c(mg/ml) = \frac{N}{V}\rho V_p$$

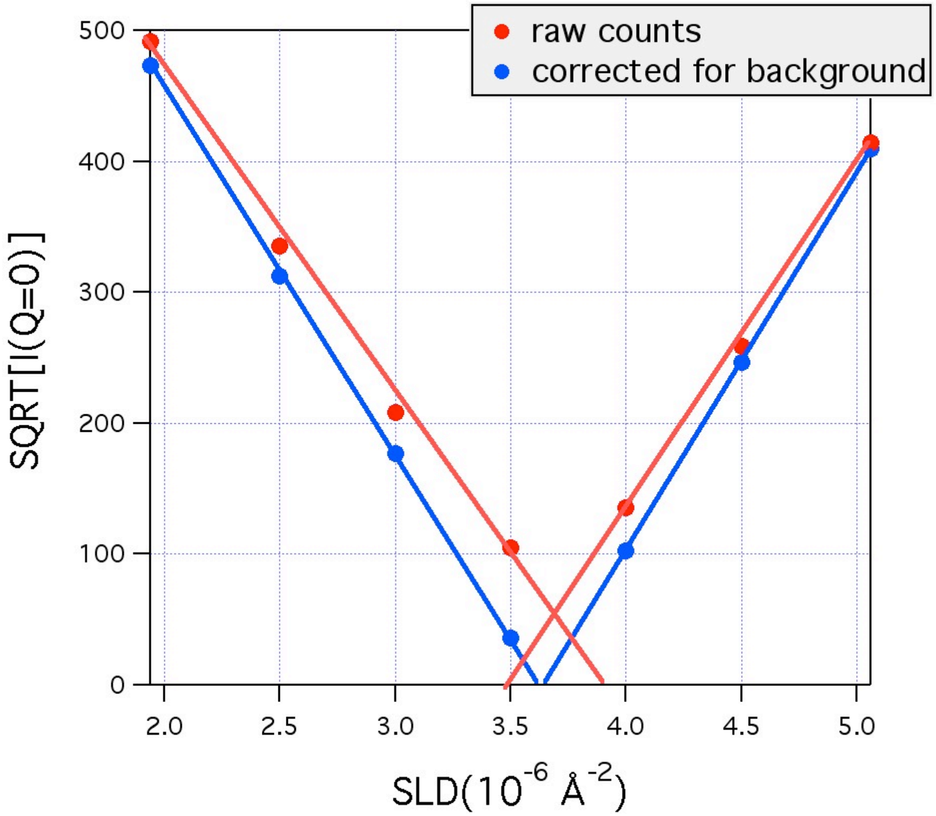
$$M_w = \rho V_p N_A \qquad \rho = mass\ density$$

$$I(Q=0) = \frac{cM_w}{\rho N_A}(\rho_p - \rho_o)^2$$

**Need “dilute” particles and “low” Q

Determining the Contrast Match Point

$$I(Q=0) = \frac{N}{V}(\rho_p - \rho_o)^2 V_p^2$$



- Make several measurements at different solvent SLDs
- Keep the same concentration
- Extrapolate data to I(Q=0)
- Plot sqrt(IQ=0) vs. SLD

- Don't forget to correct for the incoherent background contribution

- For composite particles, I(Q=0) will never reach zero - but it will be a minimum at the average particle contrast

**Need "dilute" particles and "low" Q

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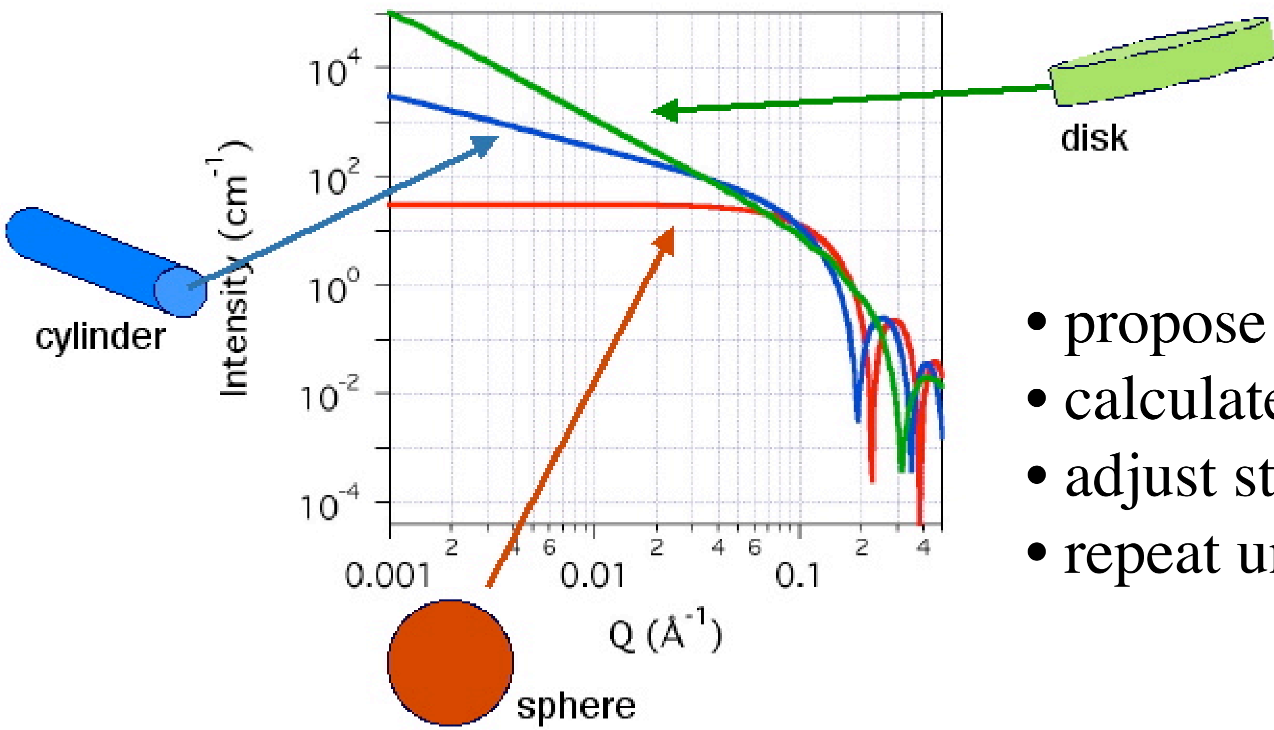
Non-Linear Model Fitting

One of the most commonly used methods
- a “forward” calculation
- many structures and interactions to choose from

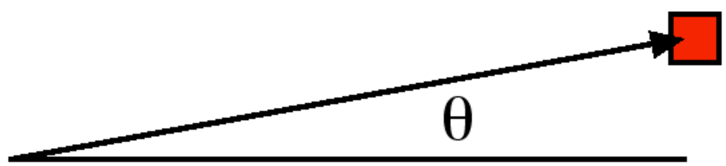


- propose a structural model
- calculate I(Q)
- adjust structural parameters
- repeat until done

Resolution

All measured data is affected to some extent by the instrument configuration = “Resolution Smearing”

“True” I(Q) -> $I_s(Q)$



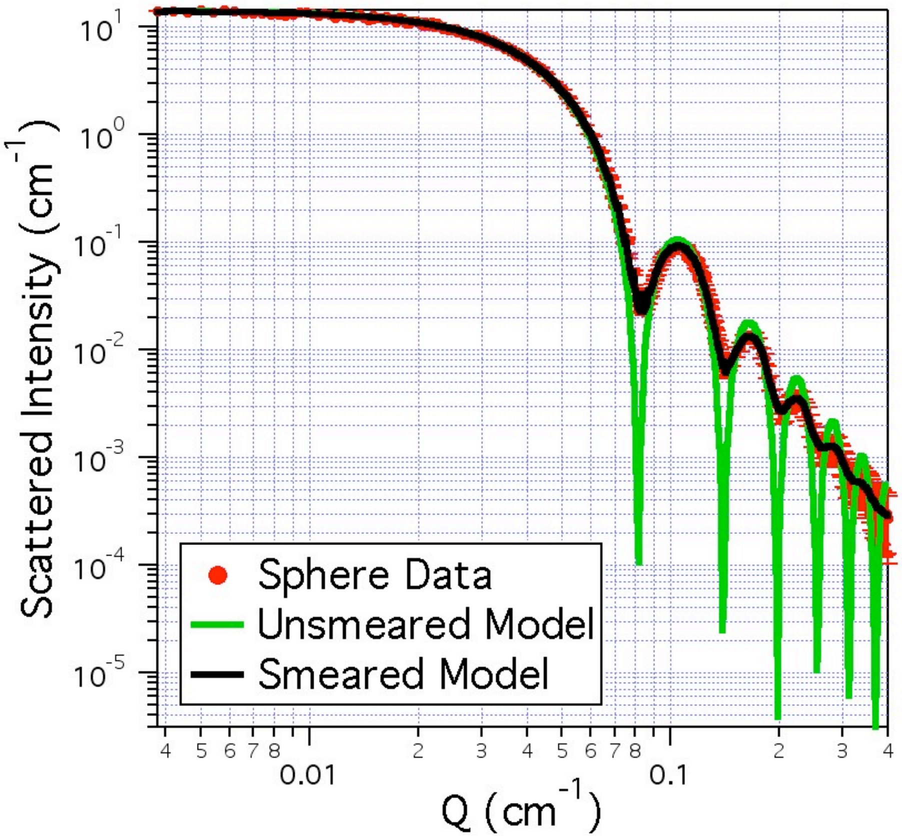
$$Q = \frac{4\pi}{\lambda}\sin(\theta/2)$$

- SANS uses pinhole collimation
- USANS uses slit collimation (more significant smearing)

Resolution effects should NEVER be ignored during analysis

- NCNR tools make it easy to include resolution

Non-Linear Model Fitting



Point	parameters_sf	coef_sf	smear_coef_sf
0	scale	0.05	0.05
1	Radius (A)	55	55
2	contrast (Å-2)	2e-06	2e-06
3	bkgd (cm-1)	0	0

- Non-linear least squares fitting to experimental data

- Use all the information you can to reduce the number of free model parameters
  - -SLD's
  - -Concentrations
  - -Lengths

- A "good" fit does not necessarily guarantee a perfect representation of the structure in the sample

**Need knowledge of sample and model

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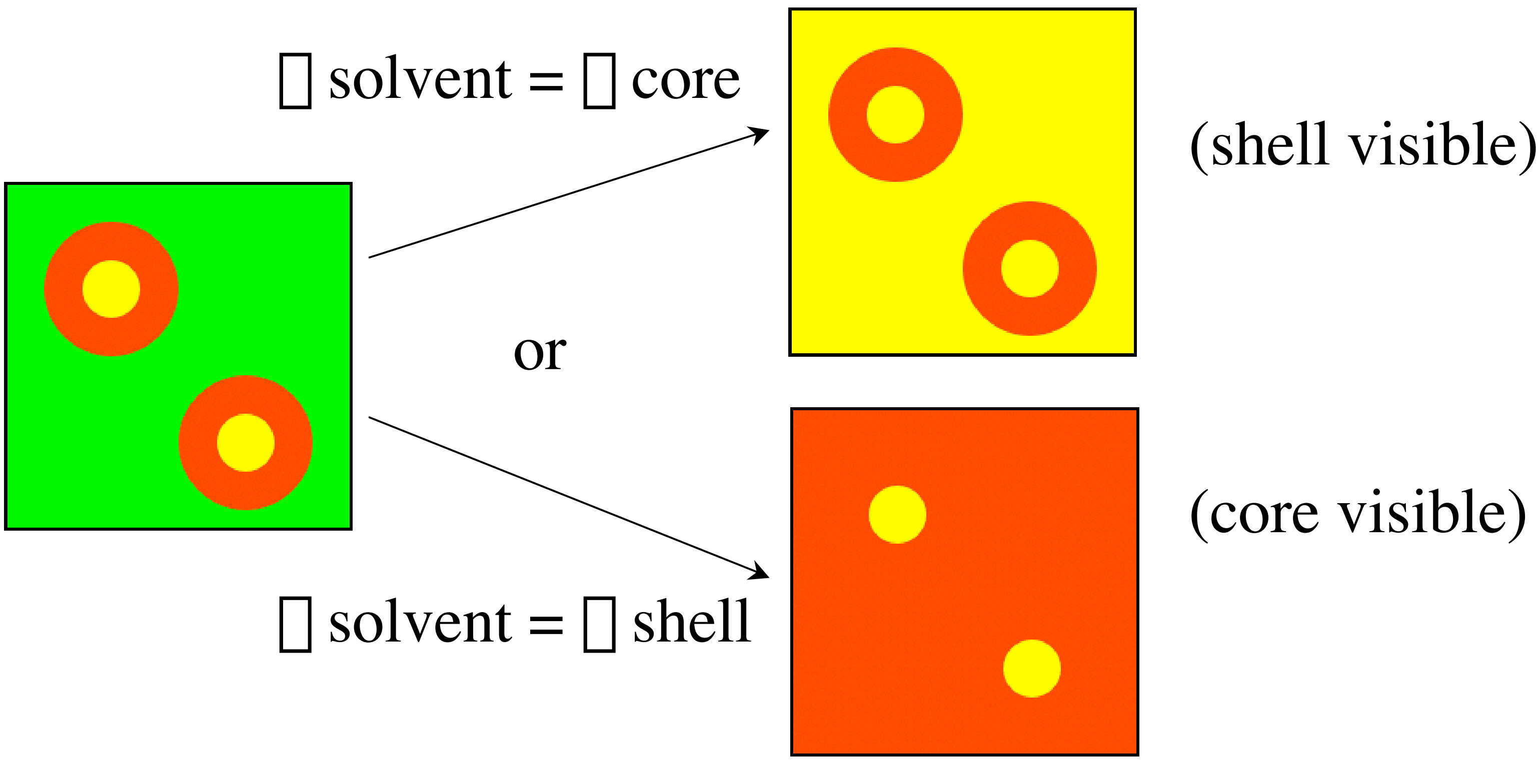
Contrast Variation

Contrast Matching

reduce the number of phases “visible”

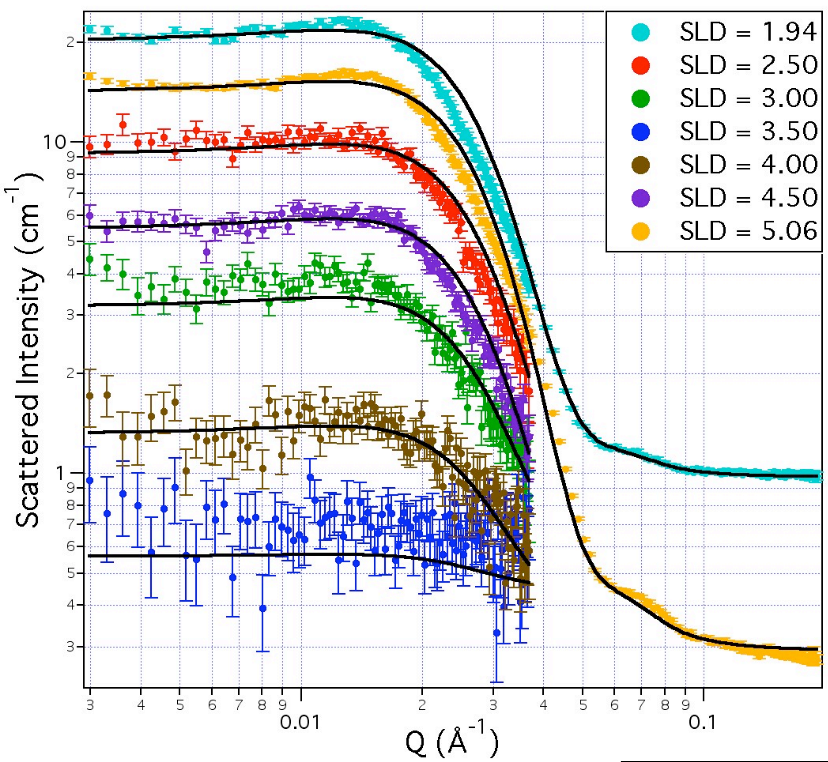


- The two distinct two - phase systems can be easily understood

Global Fitting

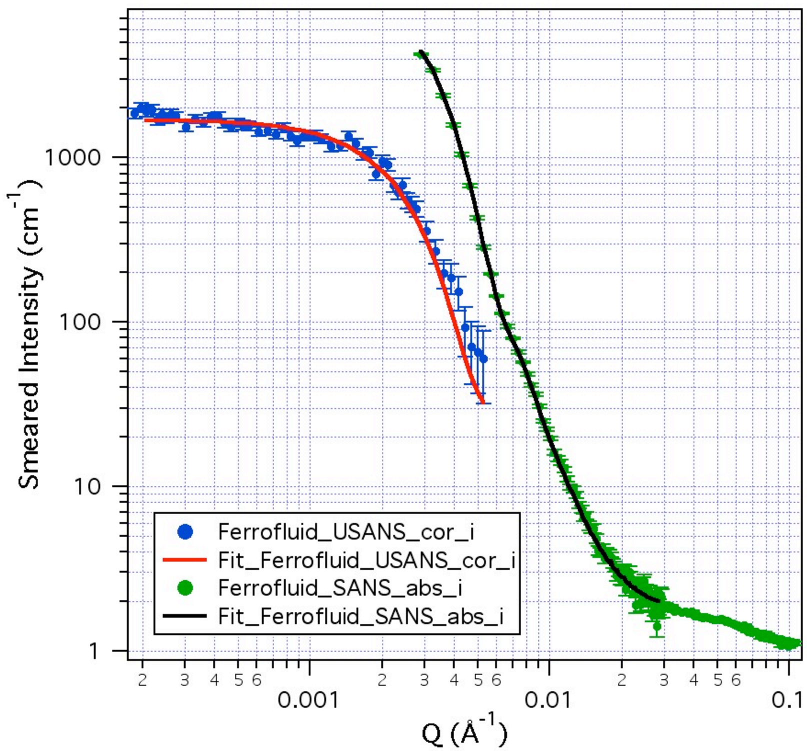
Contrast variation

- same particles, different solvent
- R, $□_p$, □ are the same
- $□_{solv}$, background are different



SANS + USANS data

- same sample (same cell)
- all parameters are the same
- smearing, scaling different



**Need "correct" model

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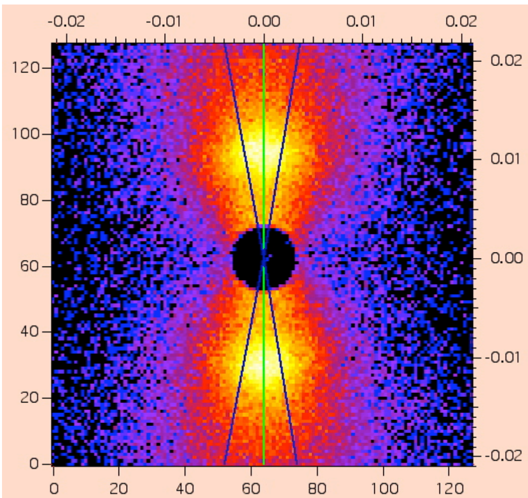
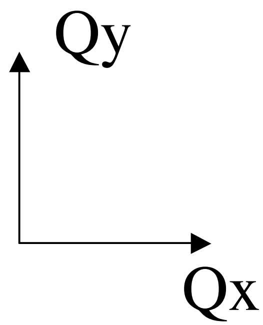
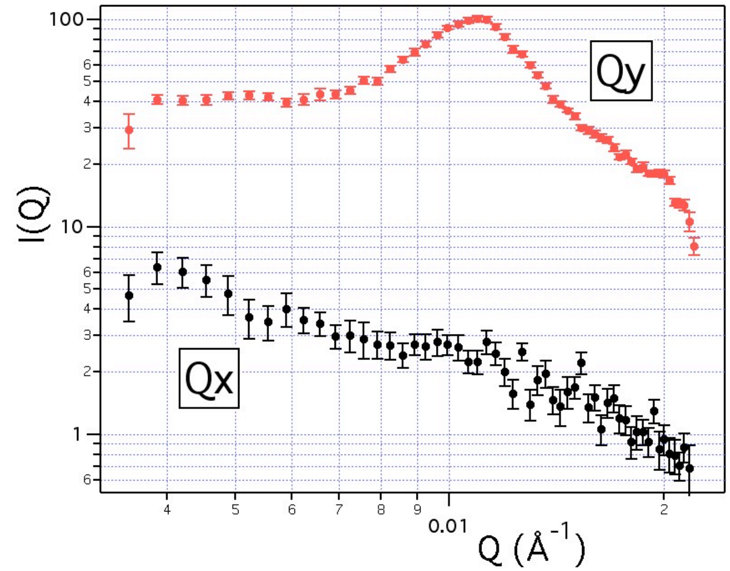
Anisotropic Scattering

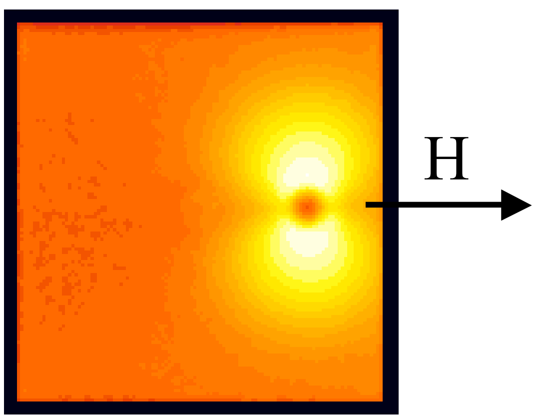
Elongated particles aligned by shear







Magnetic domains under an applied field



$$I(Q) \propto (\Delta\rho^2 + \Delta M^2 \sin^2 \phi) P(Q) S(Q)$$

□M = magnetic contrast

Analyze as a 2D pattern I(Q,□)

Transforms - p(r)

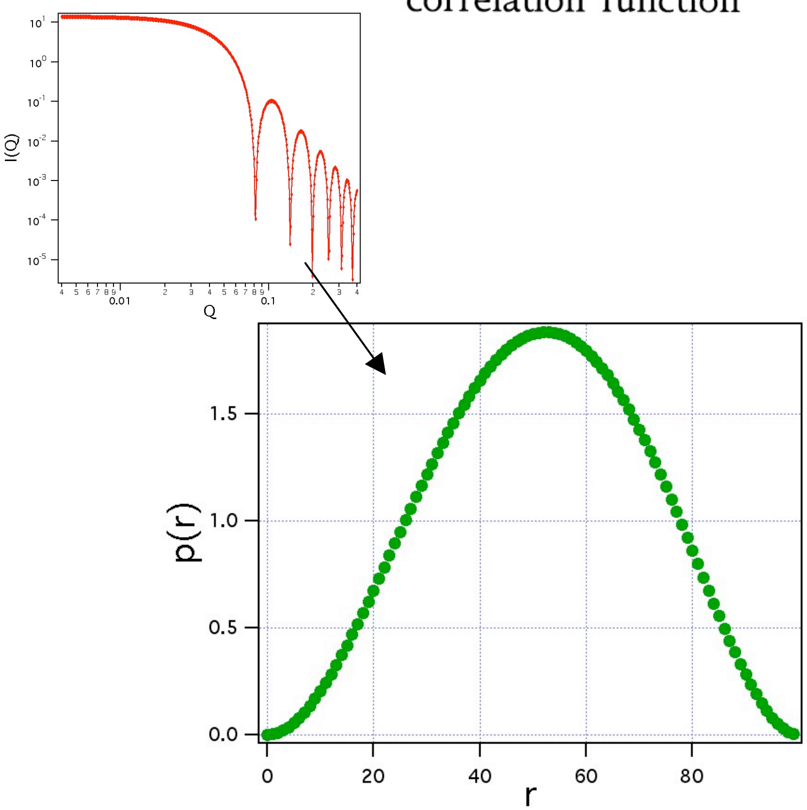
Distance Distribution Function: p(r)

average over orientations

$$I_p(Q) \propto \left\langle \int \gamma(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} \, d\vec{r} \right\rangle = 4\pi \int r^2 \gamma(r) \frac{\sin(Qr)}{Qr} dr$$

correlation function

p(r) is the probability that 2 randomly chosen points are at a distance r apart



If I(Q) is measured over a wide enough Q-range, then one can compute p(r) as the inverse transform:

$$p(r) = \frac{1}{2\pi^2} \int_0^\infty I(Q)(Qr)\sin(Qr)\, dQ$$

For a sphere:

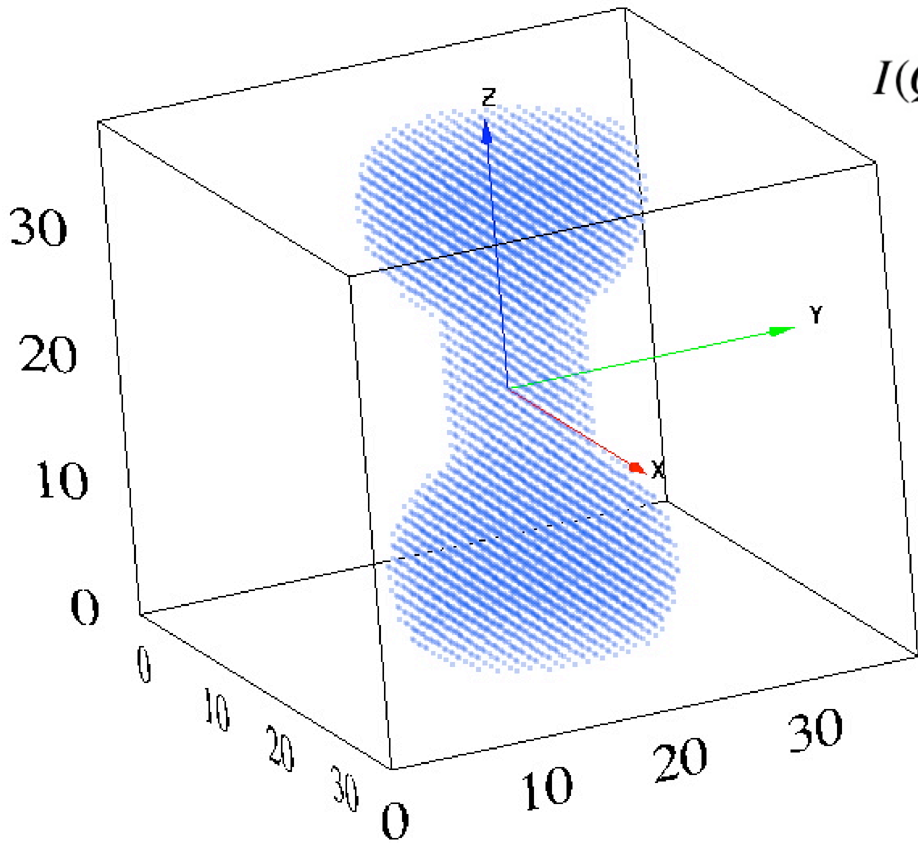
$$p(r) = 12x^2(2 - 3x + x^3) \qquad x = r/D$$

*See: D. Svergun, O. Glatter

**Need "dilute" particles and "wide" Q-range

Ab initio methods

- Calculate I(Q) for complex structures
  - Biological molecules made up of subunits
  - non-standard geometric shapes



$$I(Q) = \sum_{i=1}^{n} I_i(Q) + 2\sum_{i\neq j}\sum F_i(Q)F_j(Q)\frac{\sin(Qr_{ij})}{Qr_{ij}}$$

- fill volume with spheres on a grid
- need distance between every pair
- can be computationally intensive
- can optimize shape

- packages available (D. Svergun)

**Need “dilute” particles and “burly” computer

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Summary

- Start Simple

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- Work up to more complex

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- Must use all other information available
- Must always make physical sense
- Must always check that approximations are valid
  - -dilute, random, length scales, etc.

- Many tools available at the NCNR
- Many tools available on the web

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