Fundamentals of Small-Angle Neutron Scattering

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NCNR Summer School

Neutron Small Angle Scattering and Reflectometry from Submicron Structures
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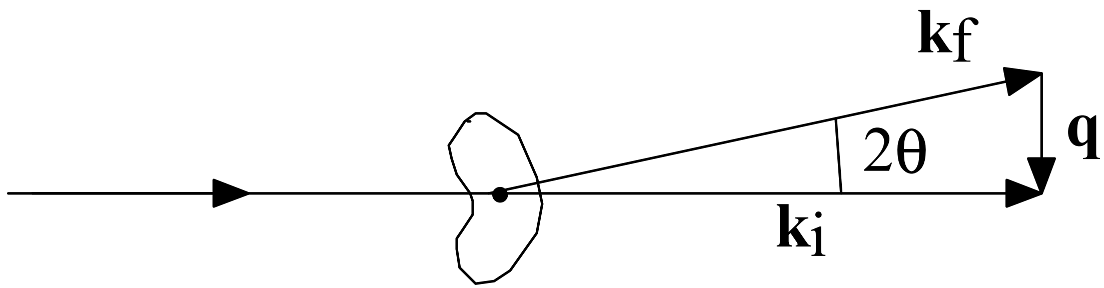
Outline

- Generalization of Atomic Scattering to a Continuum Model
    - Definitions
    - Scattering Length Density
    - Rayleigh-Gans Equation
    - Transmission

- Two - Phase Systems
    - Babinet's Principle
    - Scattering Invariant
    - Porod Limit

- Multi-Phase Systems
    - Approaches to Determining Structures

Small Angle Scattering



Constructive interference from structures in the direction of **q**

Diffraction length scale $d \approx 2\pi / q$

$$2\theta \approx \frac{\lambda}{d} \approx \frac{6\text{Å}}{60 \text{ to } 1000\text{Å}}$$

$$2\theta \approx 0.3° \text{ to } 5°$$

Scattering is at small angles - non-zero but smaller than classical diffraction angles

"Macroscopic" vs Atomic

- Previously defined atomic cross sections:

$$\sigma_{coh}\sigma_{inc}\sigma_{abs}\sigma = 4\pi\pi^2$$

- Easier to think in terms of material properties rather than atomic properties
- Define a "Scattering Length Density"

$$\rho(\vec{r}) = b_i\delta(\vec{r} - \vec{r}_i)$$

or

$$\rho = \frac{\sum_{i}^{n} b_i}{\overline{V}}$$

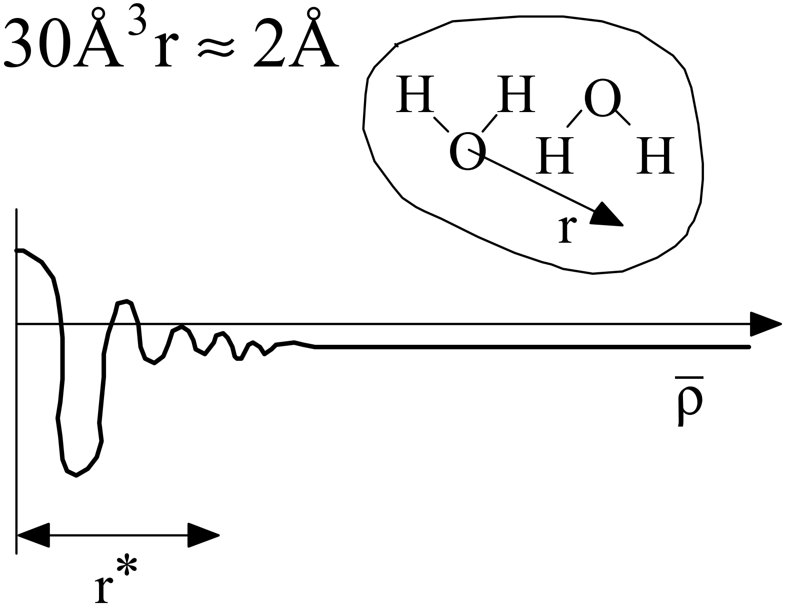
$\overline{V}$ is the volume containing the n atoms

What Length Scales Are Probed?

- Can we really use scattering length densities?

- consider H_2O : $\bar{v} \approx 30\text{Å}^3$ $r \approx 2\text{Å}$

$$\rho = \frac{\Sigma_i b_i}{\bar{v}}$$



$$1/q > r^* \quad r^* \approx 10\text{Å} \quad q \leq 0.1\text{Å}^{-1}$$

≈ 100 molecules

- We can use material properties rather than atomic properties when doing <u>small-angle</u> scattering

What Length Scales Are Probed?

- Then from:

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

- We can replace the sum over atoms with integral over the scattering length density

$$\sum_{i}^{N} b_i \rightarrow \int_V \rho(\vec{r})d\vec{r}$$

- Normalizing by sample volume and introducing scattering length density:

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

- "Rayleigh-Gans Equation"
- Inhomogeneities in $\rho(\vec{r})$ give rise to small angle scattering

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

Rayleigh-Gans Equation

- Different types of systems have a natural basis - and all are equivalent
- This is especially true if the scattering is from “countable” units:

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

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

Scattering from a Macroscopic Sample

$$\frac{d\sigma}{d\Omega}(\vec{q}) = \text{differential cross section}$$

- normalize by scattering volume

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{N}{V}\frac{d\sigma}{d\Omega}(\vec{q}) = \text{scattering per unit volume}$$

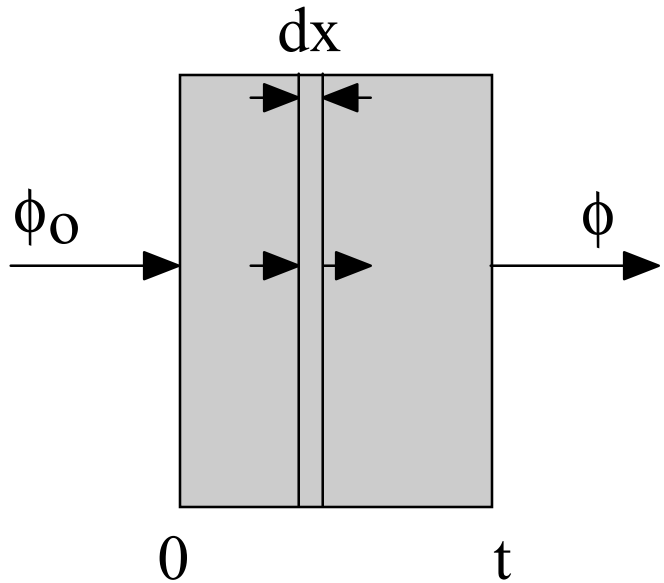
- Two contributions to measured signal:

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{d\Sigma_{coh}}{d\Omega}(\vec{q}) + \frac{d\Sigma_{inc}}{d\Omega}$$

- Incoherent scattering is not q-dependent and contributes only to the noise level, while absorption reduces the overall signal

$$\frac{d\Sigma}{d\Omega}(\vec{q}) \propto I(q) = \begin{matrix}\text{"Scattered Intensity"} \\ \text{(measured quantity)}\end{matrix}$$

Interaction of Neutron Beam with Macroscopic Sample



change in flux = incident flux • total cross section • thickness

$$-d\phi = \phi \cdot \Sigma \cdot dx$$

remember:

$$\Sigma = \sigma / \bar{V}$$

$$\Sigma_{total} = \Sigma_{coh} + \Sigma_{inc} + \Sigma_{abs}$$

Interaction of Neutron Beam with Macroscopic Sample

- Integrating over the sample thickness:

$$\int_{\phi_0}^{\phi} \frac{d\phi}{\phi} = -\Sigma \int_0^t dx \qquad \ln \frac{\phi}{\phi_0} = -\Sigma \cdot t$$

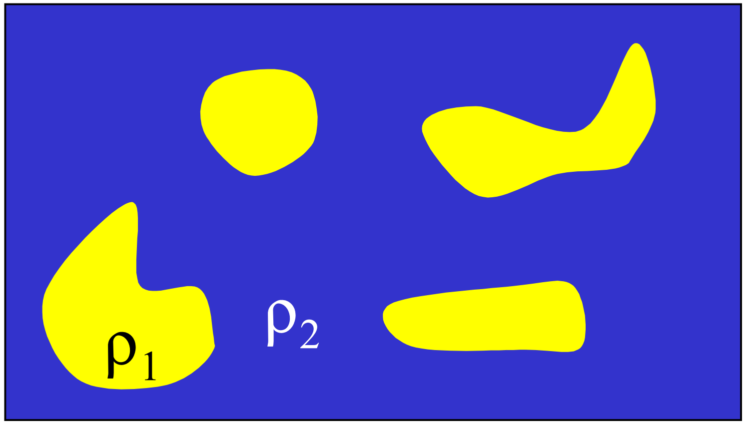
$$\frac{\phi}{\phi_0} = \text{transmission} = e^{-\Sigma \cdot t}$$

- Tempting to solve for optimal sample thickness:

$$t = 1/\Sigma \qquad \text{or} \qquad T_{opt} = 0.37$$

- but in practice ...
  - incoherent scattering background
  - multiple scattering
- Higher transmissions are desired

General Two-Phase System



- Incompressible phases of scattering length density ρ_1 and ρ_2

$$V = V_1 + V_2$$

$$\rho(r) = \begin{cases} \rho_1 \text{ in } V_1 \\ \rho_2 \text{ in } V_2 \end{cases}$$

General Two-Phase System

Then from the Rayleigh-Gans equation:

- break the total volume into two sub-volumes

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{1}{V}\left|\int_{V_1}\rho_1 e^{i\vec{q}\cdot\vec{r}}d\vec{r}_1 + \int_{V_2}\rho_2 e^{i\vec{q}\cdot\vec{r}}d\vec{r}_2\right|^2$$

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{1}{V}\left|\rho_1\int_{V_1}e^{i\vec{q}\cdot\vec{r}}d\vec{r}_1 + \rho_2\left\{\int_{V}e^{i\vec{q}\cdot\vec{r}}d\vec{r} - \int_{V_1}e^{i\vec{q}\cdot\vec{r}}d\vec{r}_1\right\}\right|^2$$

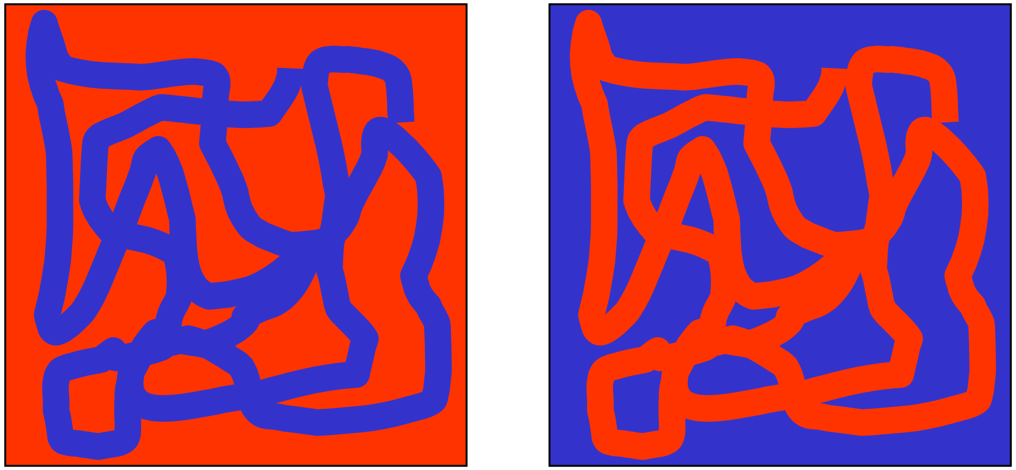
- So at non-zero q-values:

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{1}{V}(\rho_1 - \rho_2)^2\left|\int_{V_1}e^{i\vec{q}\cdot\vec{r}}d\vec{r}_1\right|^2$$

Material Properties
+
Radiation Properties

Spatial Arrangement
of Material

Babinet's Principle



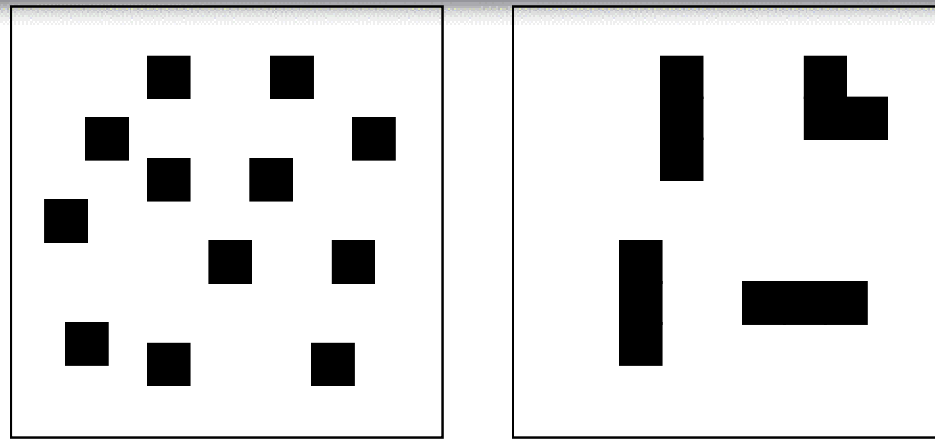
Two structures give the same scattering

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

*incoherent scattering may be different

- Contrast is relative
- Loss of phase information is $\rho_1 > \rho_2$?
- Very important in multi-phase systems
  - contrast matching / variation

Scattering Invariant



10% black / 90% white in each square

- Scattered intensity for each would certainly be different

$$\tilde{Q} = \int \frac{d\Sigma}{d\Omega}(\vec{q})d\vec{q} = (2\pi)^3 \overline{(\rho(\vec{r}) - \overline{\rho})^2}$$

- For an incompressible, two-phase system:

$$\frac{\tilde{Q}}{4\pi} \equiv Q^* = 2\pi^2 \phi_b (1 - \phi_b)(\rho_w - \rho_b)^2$$

•Domains can be in any arrangement

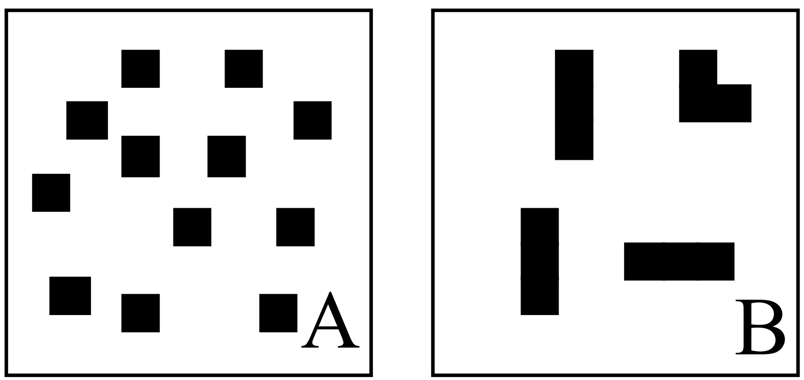
Guinier &Fournet, pp. 75-81.

Porod Scattering

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

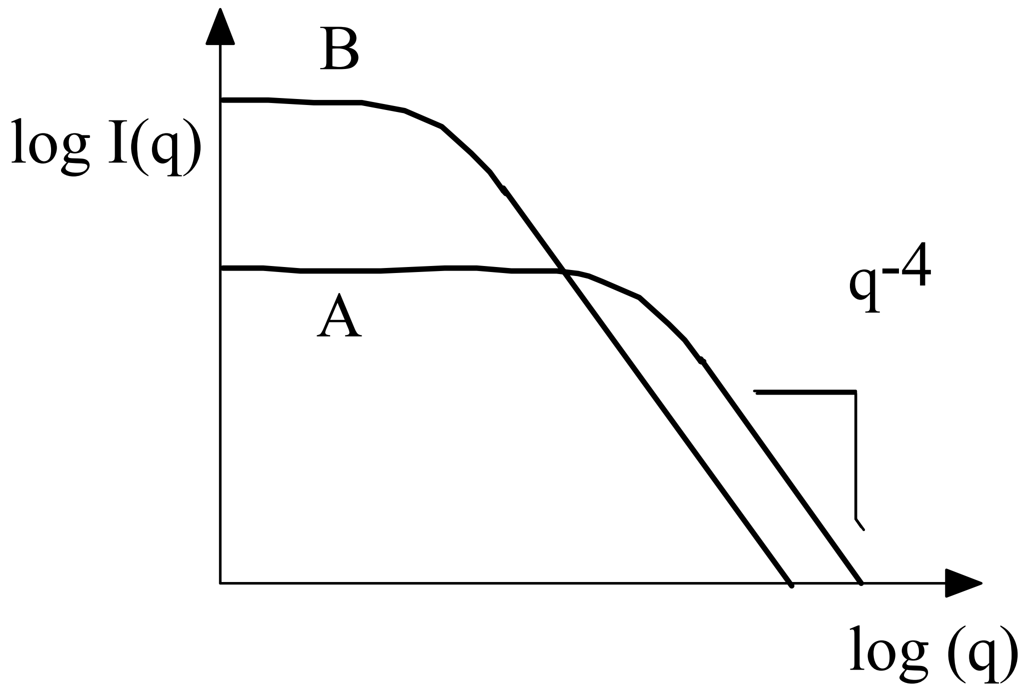
$$\frac{\pi}{Q^*} \cdot \lim_{q \to \text{large}} (I(q) \cdot q^4) = \frac{S}{V}$$

- S/V = specific surface area of sample



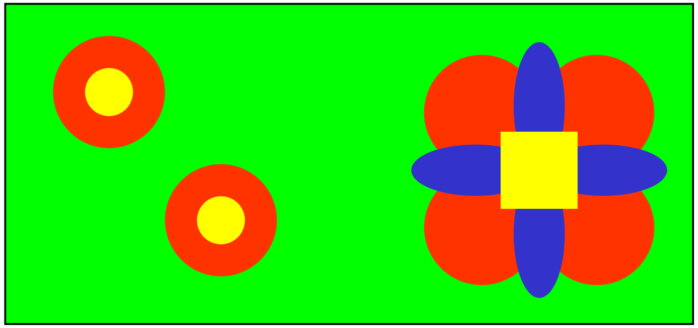
$$\frac{S_A}{V} > \frac{S_b}{V}$$

Porod Scattering



*Glatter & Kratky pp. 30-1.

Multi-Phase Materials



- "contrast" and "structure" terms can still be factored as for 2-phase system

$$\frac{d\Sigma}{d\Omega}(\vec{\mathbf{q}}) \rightarrow \frac{d\Sigma}{d\Omega}(q, \rho_i, S_{ij})$$

Multi-Phase Materials

- For 'p' different phases (0,p)

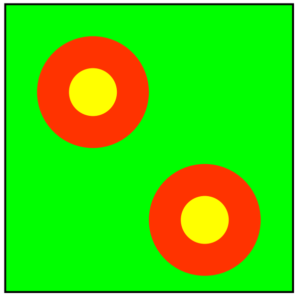
$$\frac{d\Sigma}{d\Omega}(q) = \sum_{i=1}^{p} (\rho_i - \rho_0)^2 S_{ii}(q) + \sum_{i<j} (\rho_i - \rho_0)(\rho_j - \rho_0) S_{ij}(q)$$

- Scattering is now a sum of several terms with possibly many unknowns (S_{ij}'s)

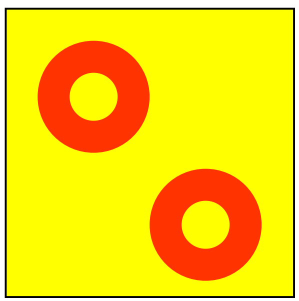
*Higgins & Benoit pp. 121-2.

Solving Multi-Phase Structures

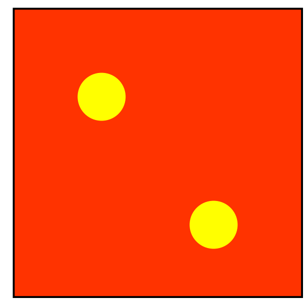
- Contrast Matching
  - reduce the number of phases ‘visible’



becomes…



or

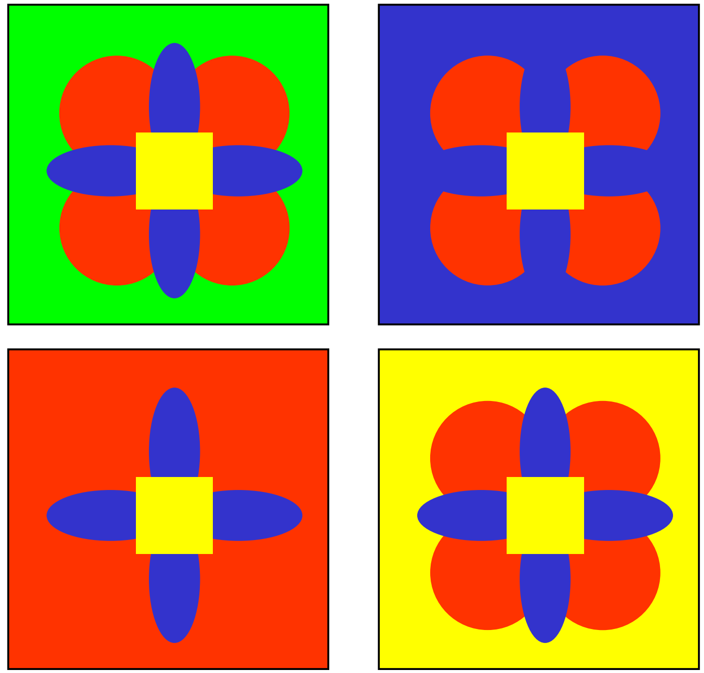


ρ solvent = ρ core
(shell visible)

ρ solvent = ρ shell
(core visible)

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

Solving Multi-Phase Structures



- A set of scattering experiments can yield a set of equations
  - of known contrasts and unknown ‘partial structure functions’
- Sturhmann Analysis

  Determine structure from R_g = F(contrast)

Summary

- General treatment of small-angle scattering:
  - Rayleigh-Gans equation
  - Scattering length density
  - Specialized for specific systems of interest

- Two-phase systems:
  - Relative scattering length density
  - Model independent results

- Multi-phase systems:
  - Advanced techniques
  - Control of contrast