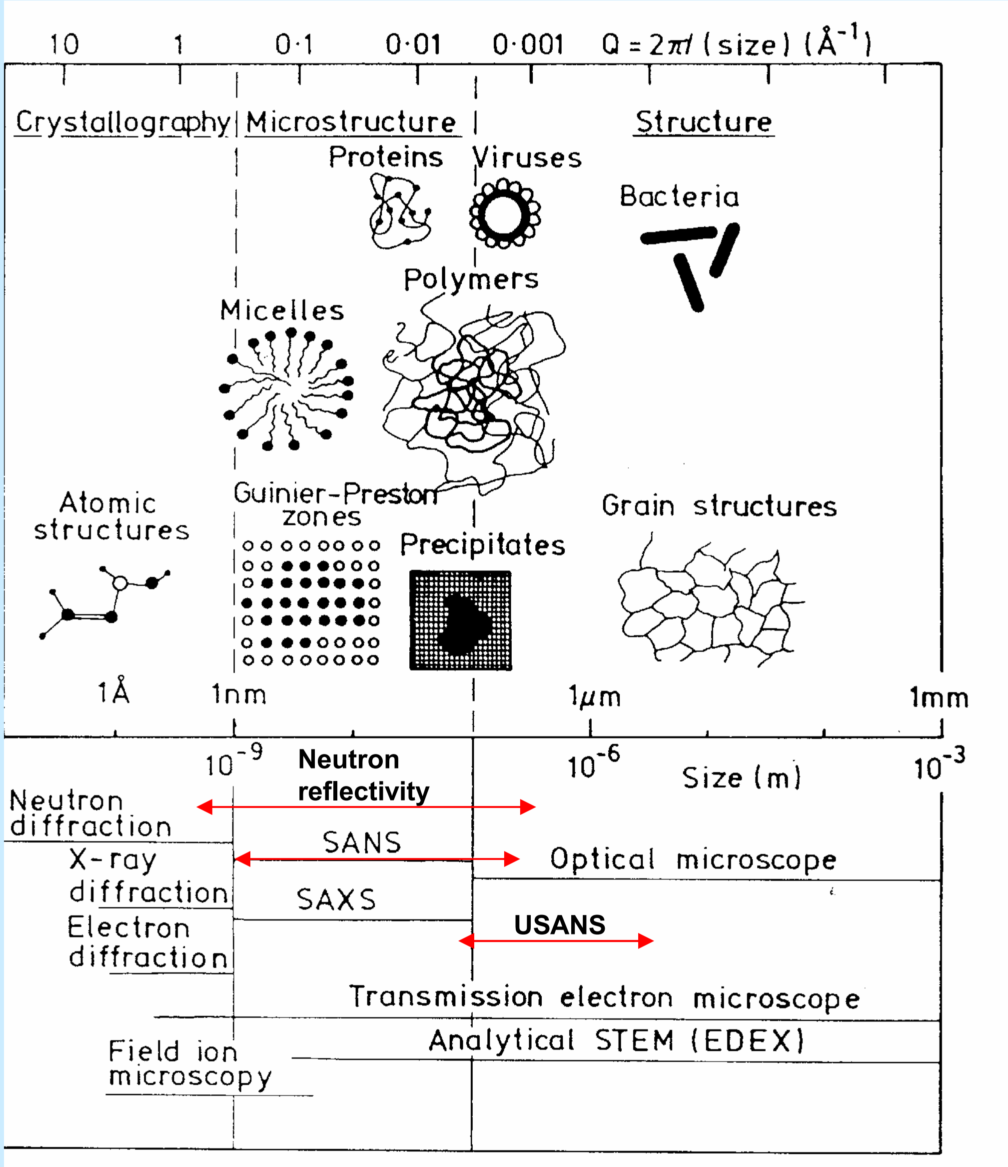
Fundamentals of Small-Angle Neutron Scattering

SANS: A Tool for Relating Nanoscale Structure to Bulk Properties

Charles Glinka
NIST Center for Neutron Research
Gaithersburg, Maryland

(http://www.ncnr.nist.gov)

Techniques for the Measurement of Microstructure



SANS or SAXS?

	SANS	SAXS
Source of scattering	Differences in scattering length density	Differences in electron density
Sources	Few and weak	Many and strong
Size scale	1 nm - 1000 nm	1 nm – 1000 nm

SANS or SAXS?

	SANS	SAXS
Special Features	• D labeling and H/D contrast variation • Magnetic scattering • Conducive to extreme envivonments • nondestructive	• msec resolution for time-resolved measurements •Superior Q-resolution •Anomalous scattering •Small sample size

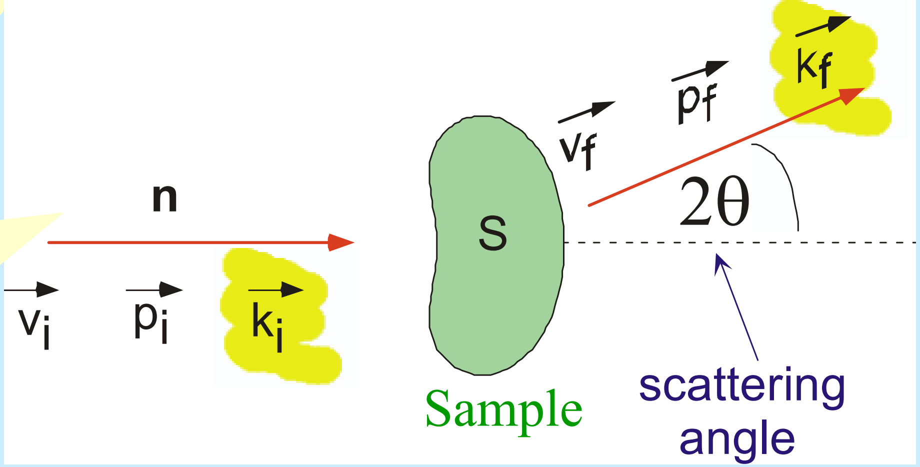
SANS or SAXS?

	SANS	SAXS
Complications	• Incoherent scattering • H/D isotope effects	• Radiation damage to some samples • Parasitic scattering • Fluorescence • Beam stability

Concepts Common to SANS and Neutron Reflectometry

For a steady state source

Collimated beam of monochromatic neutrons incident on sample, S

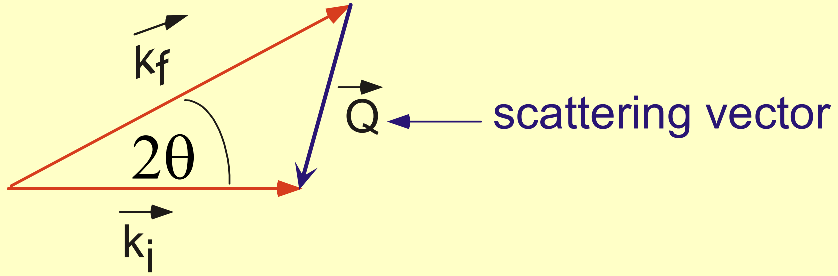


Scattered neutrons counted as a function of scattering angle, 2θ

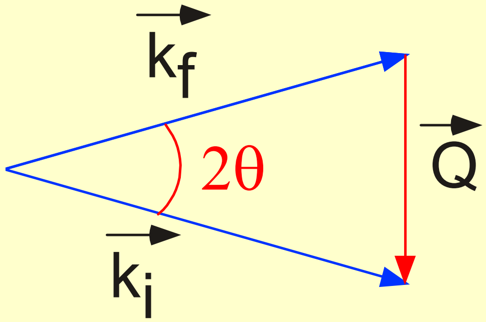
Incident neutron wave vector, $\left|\vec{k}_i\right| = \frac{2\pi}{\lambda_i}$

Scattering Triangle

$$\boxed{\vec{k}_i - \vec{k}_f = \vec{Q}}$$



For elastic scattering $(k_i = k_f = 2\pi/\lambda)$



$$\vec{Q} = \vec{k}_i - \vec{k}_f$$

$$\left|\vec{Q}\right| = 2k\sin\theta$$

$$Q = \left(\frac{4\pi}{\lambda}\right)\sin\theta$$

Recall Bragg's Law $\longrightarrow$ $\lambda = 2d\sin\theta$

or $$d = \frac{\lambda}{2\sin\theta} = \frac{2\pi}{\left(\frac{4\pi}{\lambda}\right)\sin\theta} = \frac{2\pi}{Q}$$

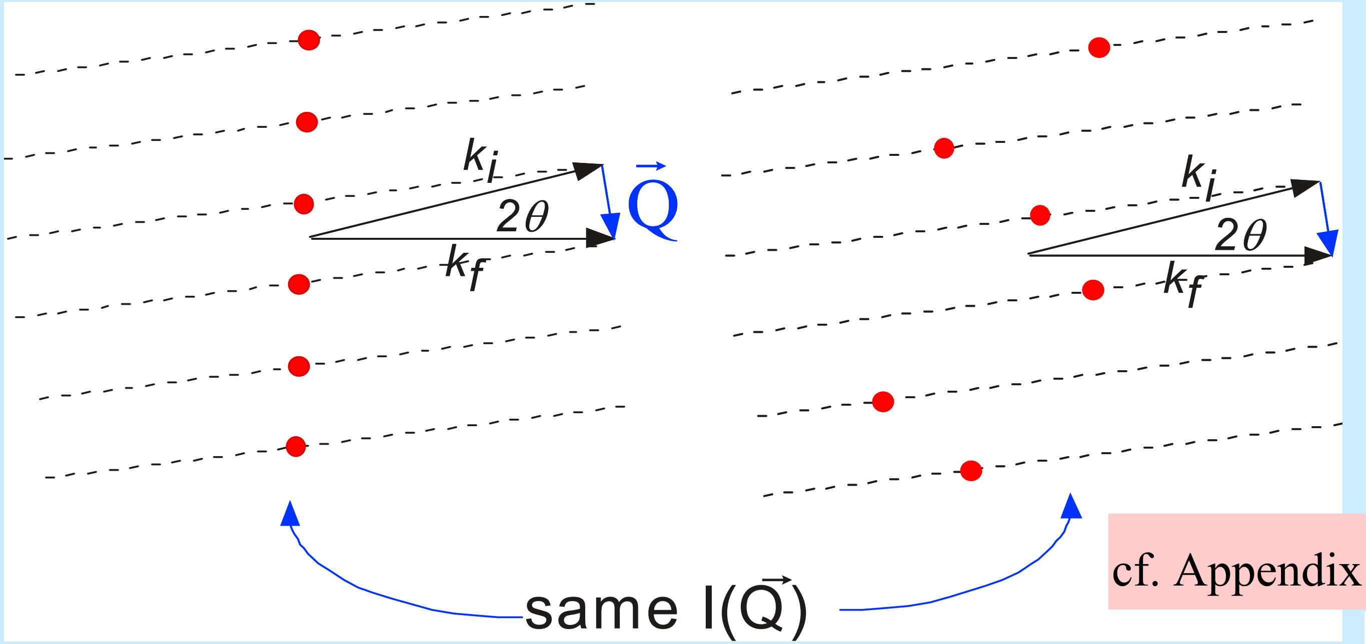
In general, diffraction (SANS or NR) probes length scale

$$d \approx \frac{2\pi}{Q}, \quad \text{for small scattering angles, } d \approx \frac{\lambda}{2\theta}$$

In general, diffraction (SANS or NR) probes length scale

$$d \approx \frac{2\pi}{Q}, \quad \text{for small scattering angles, } d \approx \frac{\lambda}{2\theta}$$

More specifically, diffraction (SANS or NR) probes structure in the direction of $\overrightarrow{Q}$, on a scale, $d \approx 2\pi / |\vec{Q}|$

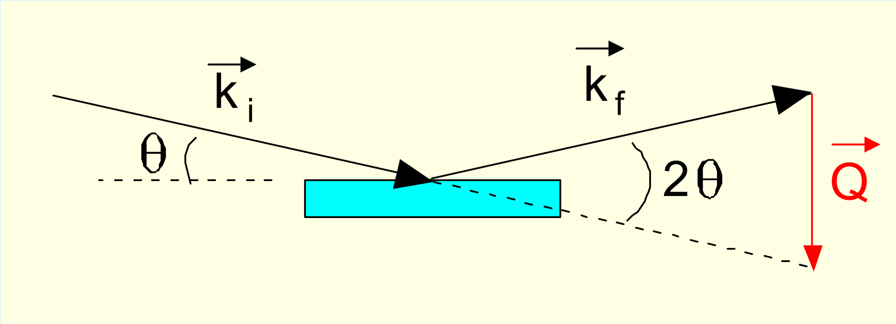


cf. Appendix A.

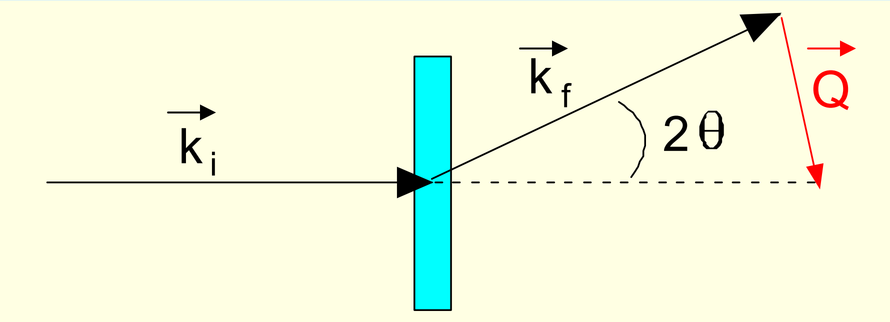
Diffraction Probes Structure in the Direction of $\vec{Q}$

$$\vec{k}_i - \vec{k}_f = \vec{Q}$$

Specular Reflection Geometry



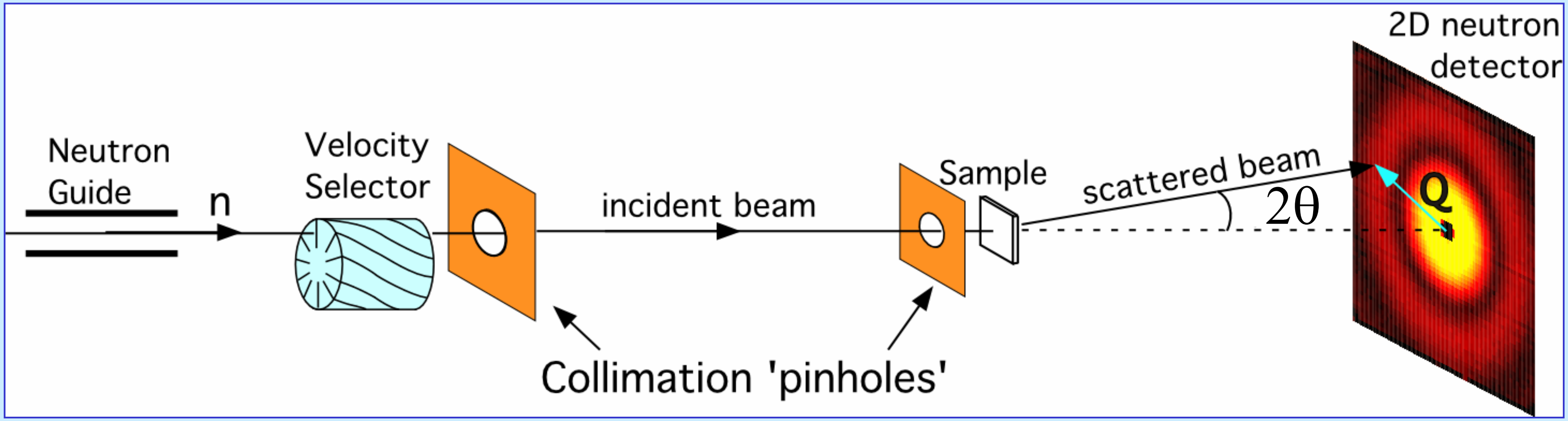
SANS Geometry



Reflectivity probes structure perpendicular to surface (parallel to Q), and *averages over structure in plane of sample.*

SANS probes structure in plane of sample (parallel to Q), and *averages over structure perpendicular to sample surface.*

SANS Instrument Schematic



Small-Angle Neutron Scattering (SANS) probes structure on a scale *d* , where

$$d \approx \frac{\lambda}{2\theta}$$

(wavelength)

(scattering angle)

$0.5 \text{ nm} < \lambda < 2 \text{ nm}$ (cold neutrons)

$0.1° < \theta < 10°$ (small angles)

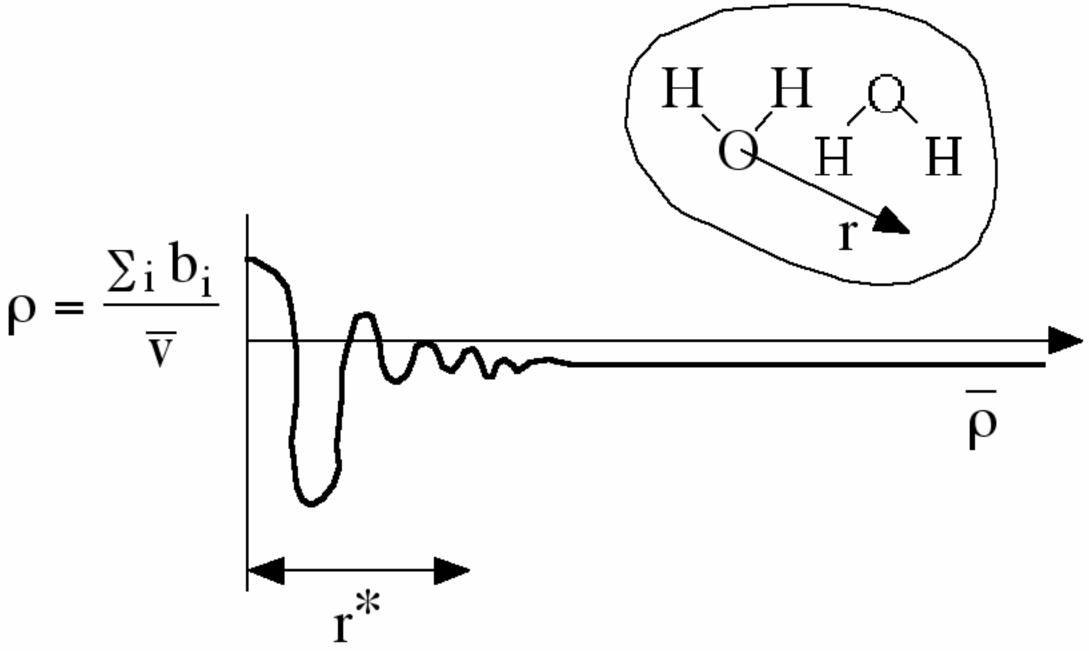
$1 \text{ nm} < d < 300 \text{ nm}$

SANS Fundamentals

- For Length Scale Probed by SANS Can Use Continuum Approximation

- consider H_2O, v ~ 30 $Å^3$, r ~ 2 Å

Scattering Length Density



neutrons X rays

$b \longrightarrow Z r_e$

$\frac{1}{q} > r^*$ $r^* \approx 10 \dot{A}$ $q \le 0.1 \dot{A}^{-1}$ (> 100 H_2O molecules)

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

SANS Fundamentals

- Inhomogeneities in scattering length density, ρ(r), give rise to small-angle scattering

- Angular dependence of scattering, I(q), is given by:

$$\mathrm{I}(\vec{\mathbf{q}}) = \frac{1}{V}\left|\int_V \rho(\vec{\mathbf{r}})e^{i\vec{\mathbf{q}}\cdot\vec{\mathbf{r}}}\,d\vec{\mathbf{r}}\right|^2$$

Rayleigh-Gans eqn.

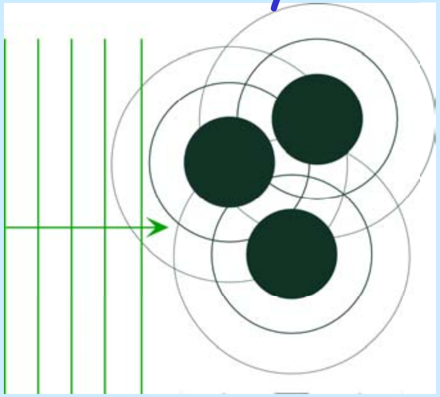
Entire volume of sample

SANS Fundamentals: Coherent vs. Incoherent Scattering

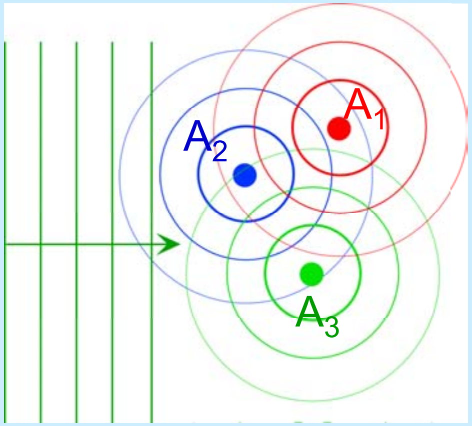
Consider scattering from N atoms of a single element, ${}^{A}_{Z}X$

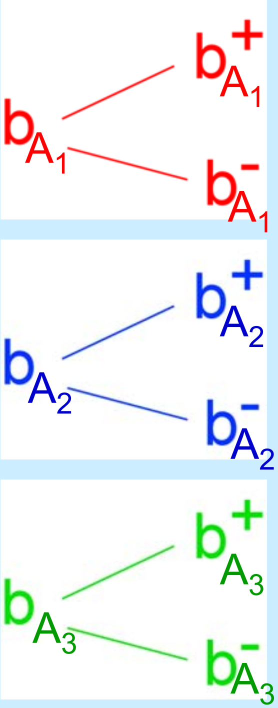
$$I(\vec{q}) = \frac{1}{V}\left|\sum_{i}^{N} b_i e^{i\vec{q}\cdot\vec{r}_i}\right|^2$$

X rays



Neutrons





atomic number

electron radius

atom form factor

$$Z\, r_e\, f(\theta)$$

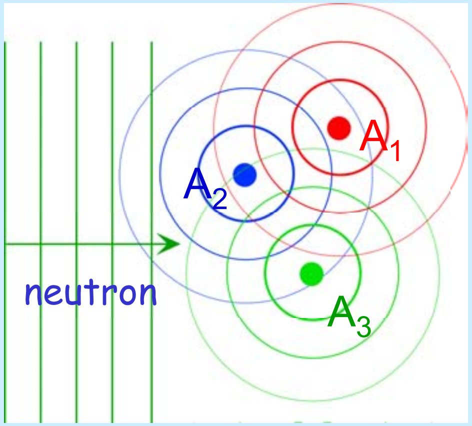
scattering length

scattering lengths, b's, depend on isotope *and* isotope spin

SANS Fundamentals: Coherent vs. Incoherent Scattering

Consider scattering from N atoms of a single element, ${}^{A}_{Z}X$

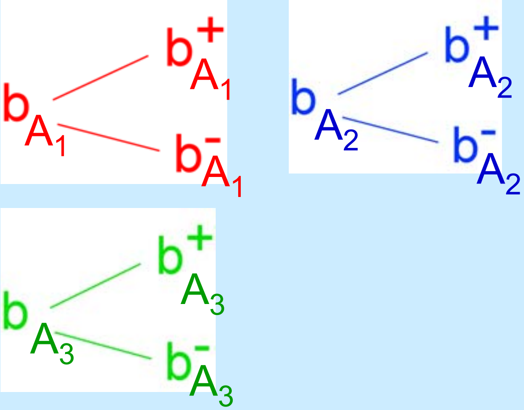
$$\mathrm{I}(\vec{\mathrm{q}})=\frac{1}{\mathrm{V}}\left\langle\left|\sum_{i}^{N}\mathrm{b}_{\mathrm{i}}e^{i\vec{q}\cdot\vec{r}_i}\right|^2\right\rangle$$



$$\mathrm{I}(\vec{\mathrm{q}})=\frac{1}{\mathrm{V}}\left\langle\sum_{i,j}^{N}\mathrm{b}_{\mathrm{i}}\mathrm{b}_{\mathrm{j}}e^{i\vec{q}\cdot\left(\vec{r}_i-\vec{r}_j\right)}\right\rangle$$

Since b's are uncorrelated with the atom positions

$$\mathrm{I}(\vec{\mathrm{q}})=\frac{1}{\mathrm{V}}\sum_{i,j}^{N}\left\langle\mathrm{b}_{\mathrm{i}}\mathrm{b}_{\mathrm{j}}\right\rangle\left\langle e^{i\vec{q}\cdot\left(\vec{r}_i-\vec{r}_j\right)}\right\rangle=\mathrm{I}_{\mathrm{Coh}}\left(\vec{q}\right)+\mathrm{I}_{\mathrm{Incoh}}\left(\vec{q}\right)$$



where

$$\mathrm{I}_{\mathrm{Coh}}(\vec{\mathrm{q}})=\frac{1}{\mathrm{V}}\left\langle\mathrm{b}\right\rangle^2\sum_{i,j}^{N}\left\langle e^{i\vec{q}\cdot\left(\vec{r}_i-\vec{r}_j\right)}\right\rangle$$

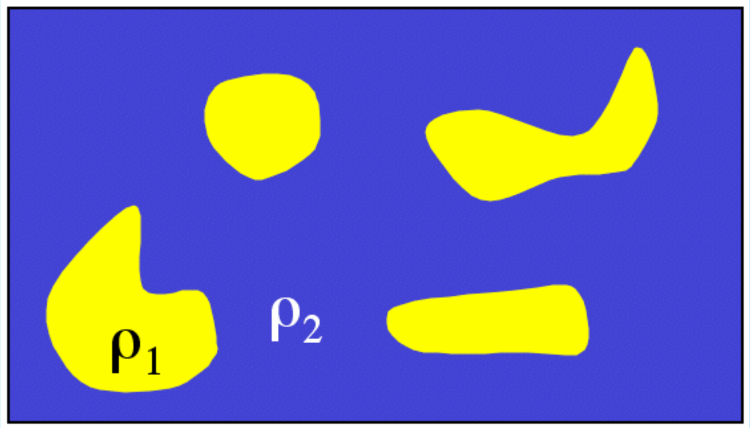
structural information

$$\mathrm{I}_{\mathrm{Incoh}}(\vec{\mathrm{q}})=\frac{1}{\mathrm{V}}\left(\left\langle\mathrm{b}^2\right\rangle-\left\langle\mathrm{b}\right\rangle^2\right)\sum_{j,j}^{N}\left\langle\underbrace{e^{i\vec{q}\cdot\left(\vec{r}_j-\vec{r}_j\right)}}_{1}\right\rangle$$

no structural information

scattering lengths: depend on isotope *and* isotope spin

General Results for a Two-Phase System



‘phase’ in this context refers to scattering length density

- Incompressible phases of scattering length density ρ_1 and ρ_2

$$V = V_1 + V_2$$

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

From the Rayleigh-Gans equation:

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

break total volume
into two sub-volumes

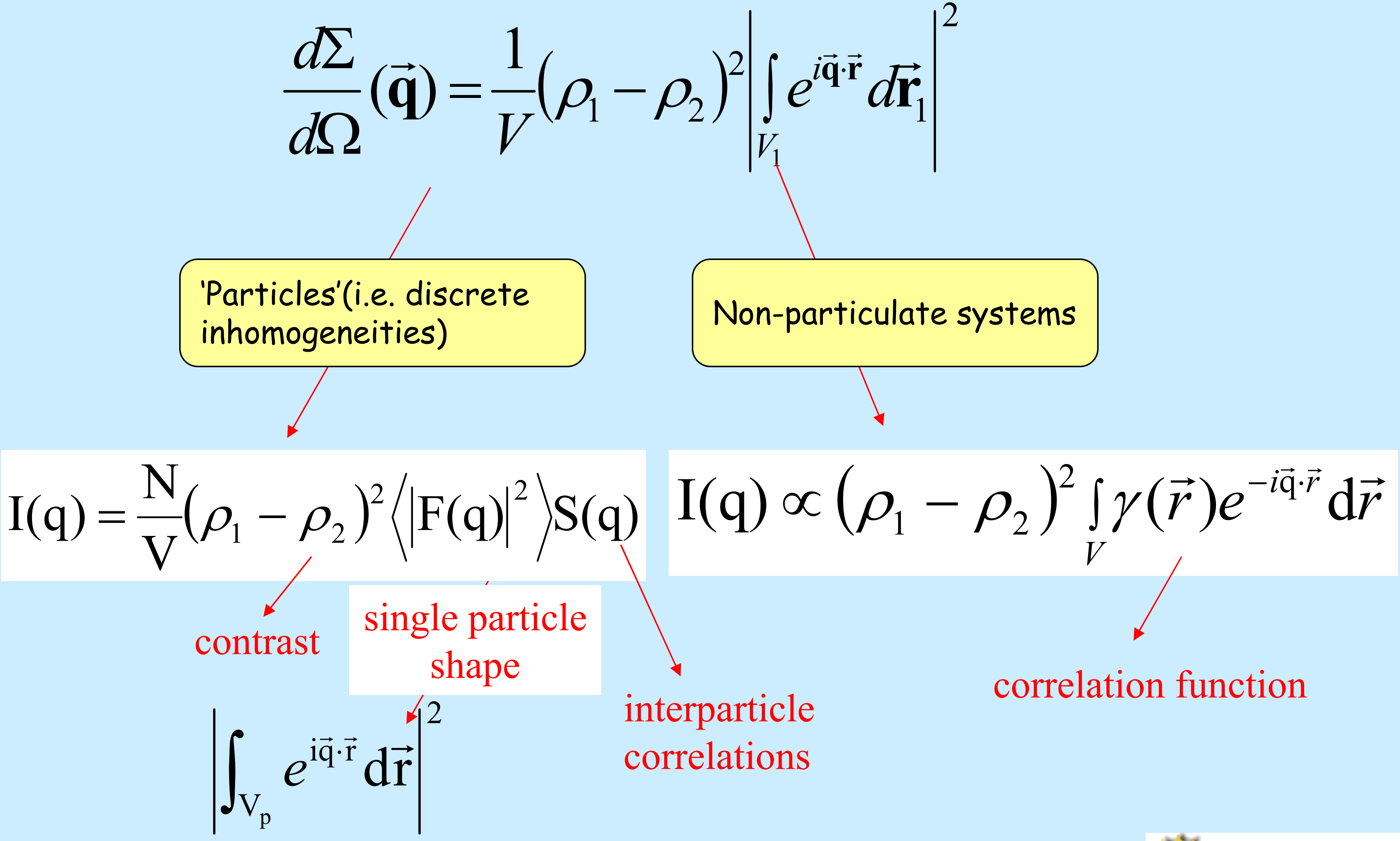
$$\mathrm{I}(\vec{\mathbf{q}}) = \frac{1}{V}\left| \rho_1 \int_{V_1} e^{i\vec{\mathbf{q}}\cdot\vec{\mathbf{r}}}\, d\vec{\mathbf{r}}_1 + \rho_2 \left\{ \int_{V} e^{i\vec{\mathbf{q}}\cdot\vec{\mathbf{r}}}\, d\vec{\mathbf{r}} - \int_{V_1} e^{i\vec{\mathbf{q}}\cdot\vec{\mathbf{r}}}\, d\vec{\mathbf{r}}_1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

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

Contrast Factor
(depends on materials
and radiation properties)

Spatial arrangement
of material

General Results for a Two Phase System



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

'Particles'(i.e. discrete inhomogeneities)

Non-particulate systems

$$\mathrm{I(q)} = \frac{\mathrm{N}}{\mathrm{V}}(\rho_1 - \rho_2)^2 \left\langle \left|\mathrm{F(q)}\right|^2 \right\rangle \mathrm{S(q)}$$

$$\mathrm{I(q)} \propto (\rho_1 - \rho_2)^2 \int_V \gamma(\vec{r}) e^{-i\vec{\mathrm{q}}\cdot\vec{r}} \mathrm{d}\vec{r}$$

contrast

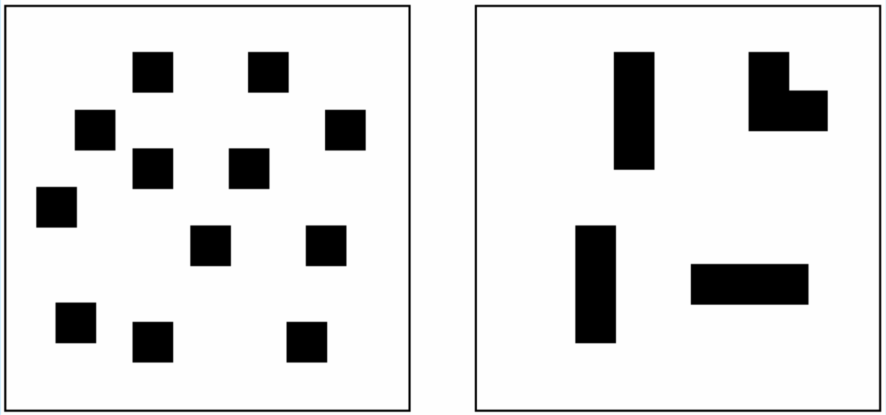
single particle shape

$$\left| \int_{\mathrm{V_p}} e^{\mathrm{i}\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}} \mathrm{d}\vec{\mathrm{r}} \right|^2$$

interparticle correlations

correlation function

Scattering Invariant



10 % black
90 % white
in each square

- Scattered intensity for each would certainly be different

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

- For an incompressible, two-phase system:

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

- <u>Domains can be in any arrangement</u>

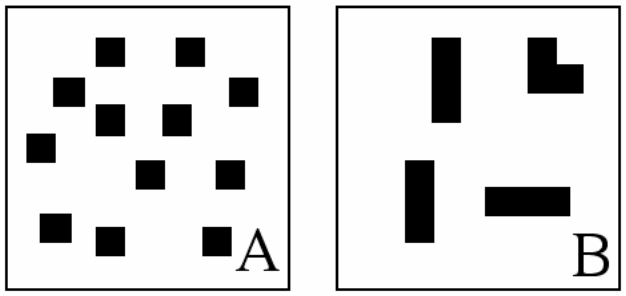
*Guinier and Fournet, pp. 75-81.

Porod Scattering

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

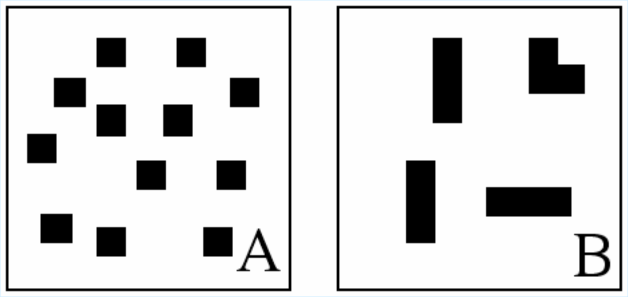
$$\frac{\pi}{Q^*} \cdot \lim_{q \to \mathrm{large}} \left(I(q) \cdot q^4\right) = \frac{S}{V}$$

S/V = specific surface area of sample

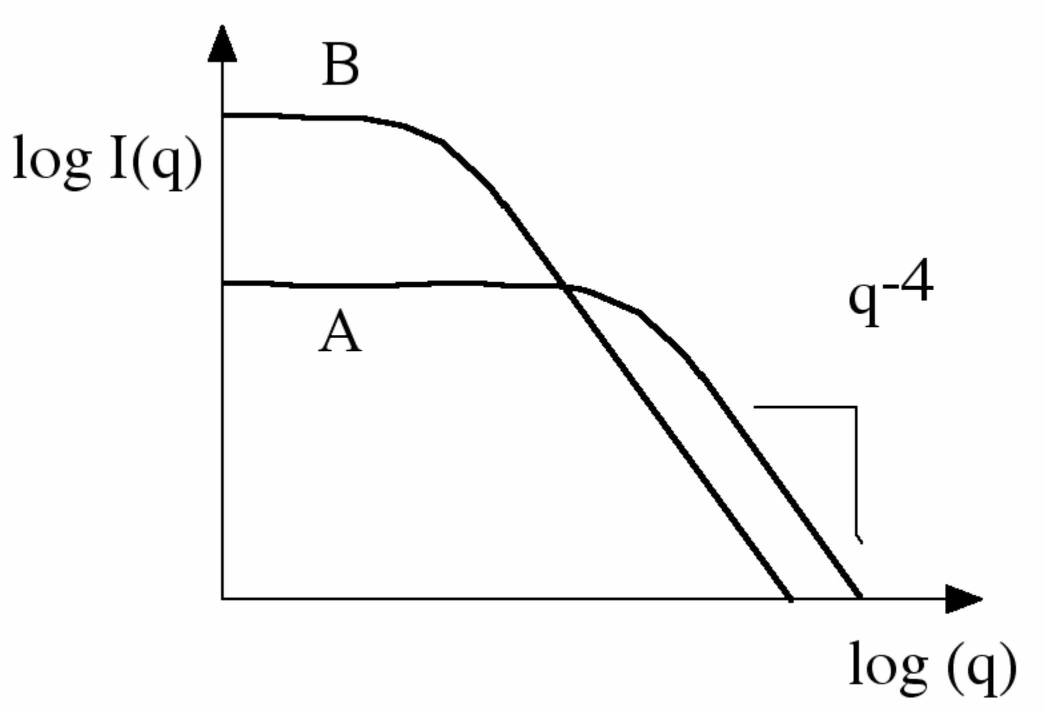


$$\frac{S_A}{V} > \frac{S_b}{V}$$

Porod Scattering



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



*Glatter and Kratky, pp. 30-31.

SANS and Thermodynamics

Thermal density fluctuations also produce small-angle scattering

$$\mathrm{I}(0) = \frac{\rho^2}{\mathrm{V}} k\mathrm{T}\, \beta_{\mathrm{T}}$$

Isothermal compressibility

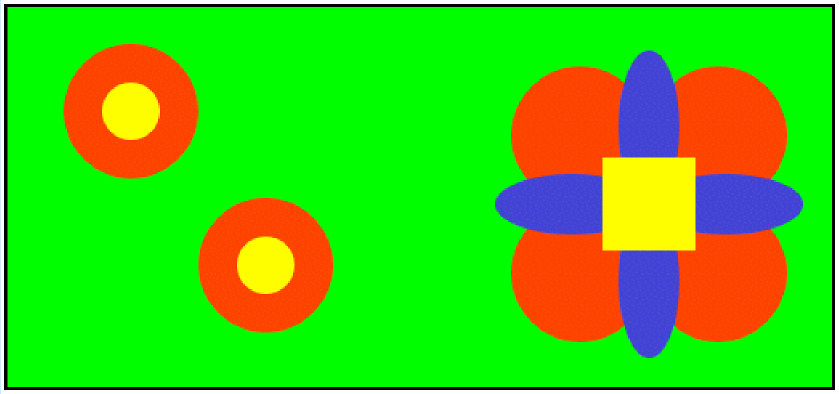
Composition fluctuations also produce small-angle scattering

$$\mathrm{I}(0) = \frac{\Delta\rho^2}{\mathrm{V}} k\mathrm{T} \,/\, \frac{\partial^2 G_m}{\partial \phi^2}$$

Curvature of Free Energy of Mixing

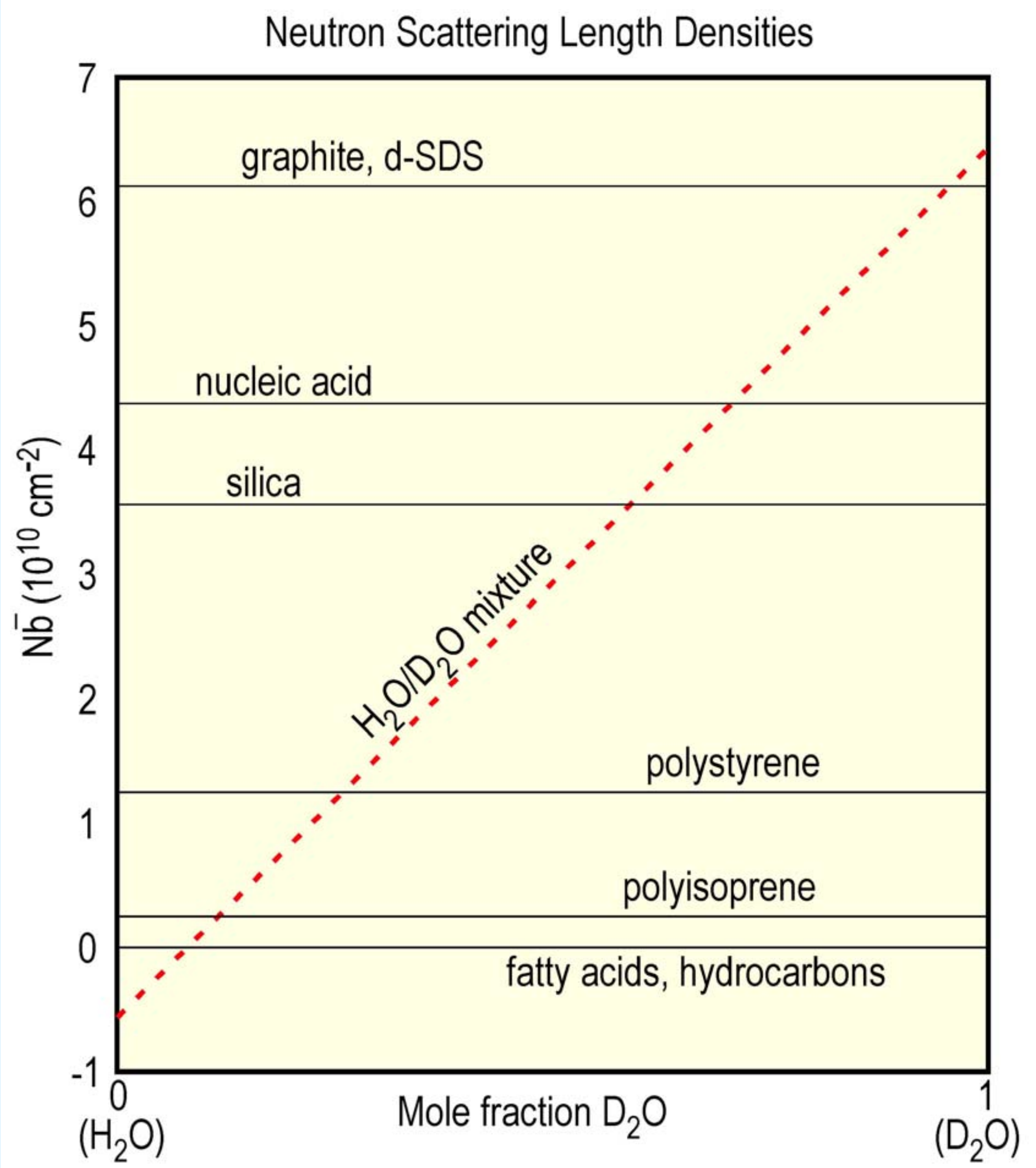
Ref: *Introduction to Polymer Physics*, M. Doi, 1996

Multi-Phase Materials

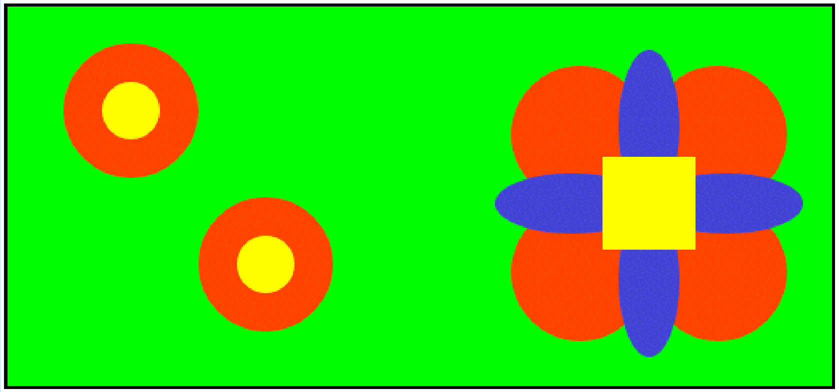


- “contrast” and “structure” terms can still be factored as for 2 - phase systems

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


Neutron Scattering Length Densities
7
6
5
4
3
2
1
0
-1
Nb̄ (10¹⁰ cm⁻²)
graphite, d-SDS
nucleic acid
silica
H₂O/D₂O mixture
polystyrene
polyisoprene
fatty acids, hydrocarbons
0
(H₂O)
Mole fraction D₂O
1
(D₂O)

Multi-Phase Materials



- for ‘p’ different phases in a matrix ‘0’

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

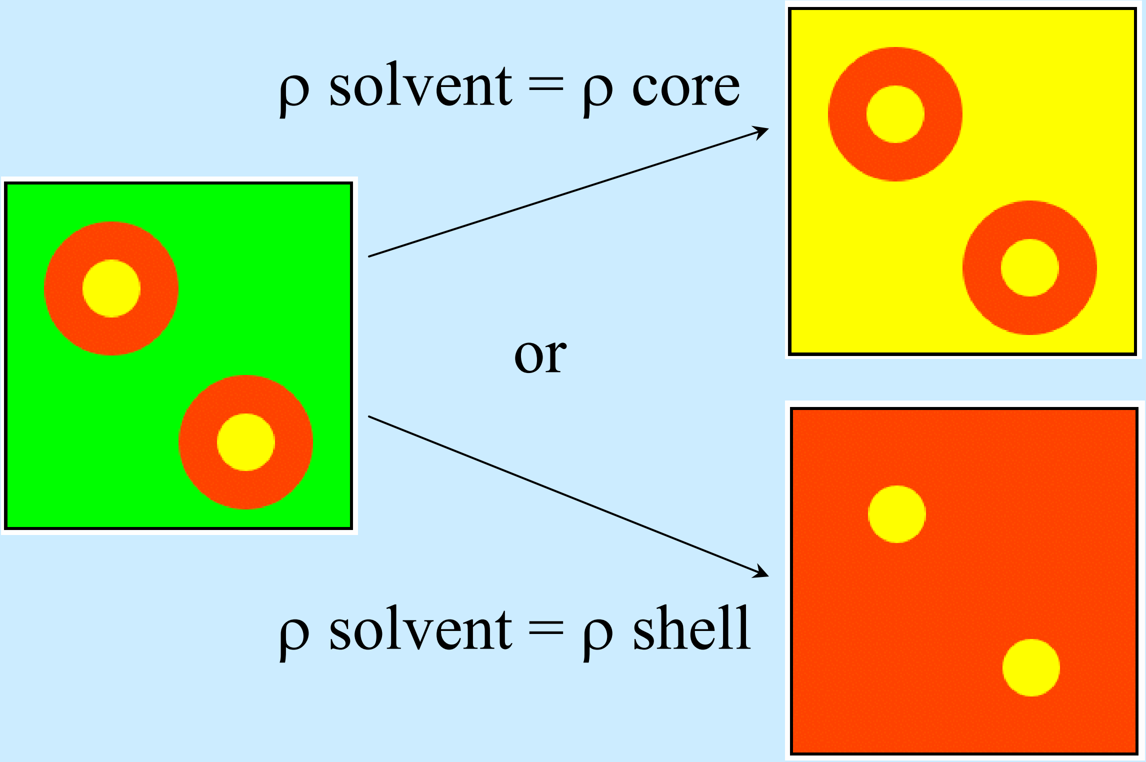
- Scattering is now a sum of several terms with possibly many unknown S_{ij}’s

*Higgins and Benoit, pp. 121-122.

Solving Multi-Phase Structures

Contrast Matching

reduce the number of phases “visible”



ρ solvent = ρ core

(shell visible)

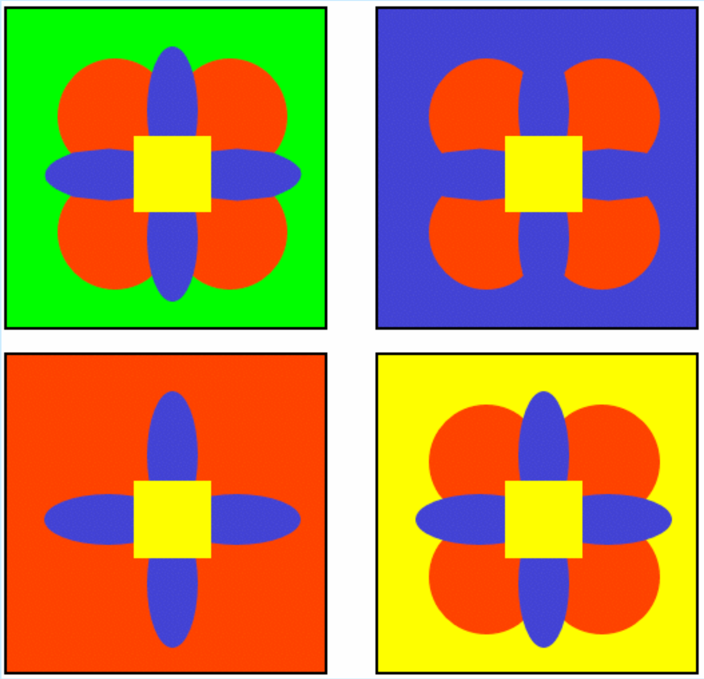
or

ρ solvent = ρ shell

(core visible)

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

Contrast Variation



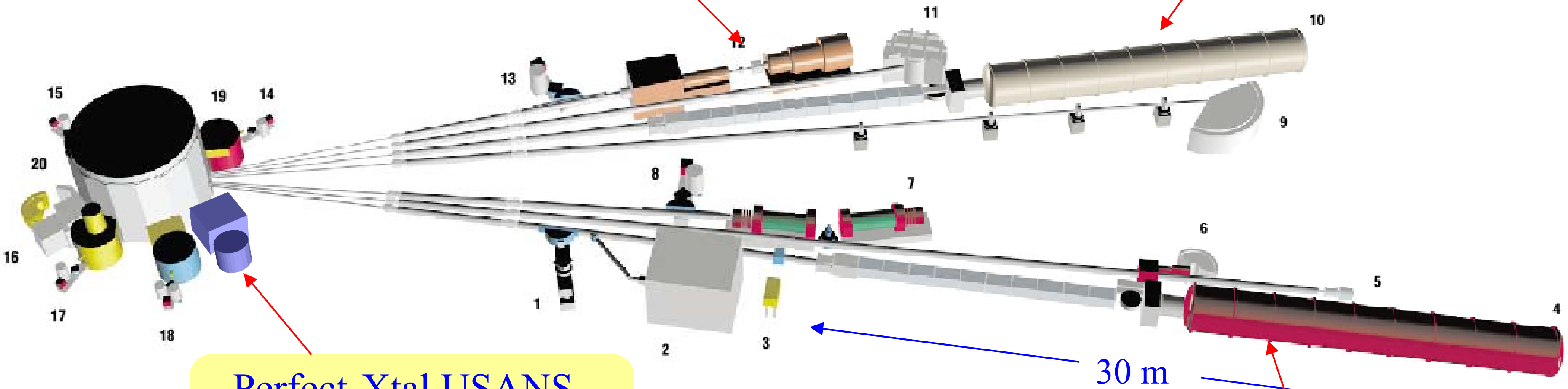
- A set of scattering experiments can yield a set of equations of known contrasts and unknown ‘partial structure functions’

- Sturhmann Analysis
  Determine structure from Rg = f (contrast)

NIST Center for Neutron Research (NCNR)

- 20 MW Reactor (4 x 10^{14} n/cm^2-s peak thermal flux)
- Large liquid H_2 cold source (25 K)
- 21 beam facilities (7 thermal, 14 cold)
- 6 irradiation facilities

SANS Instrumentation at the NCNR



8-m Pinhole SANS

$0.05 \text{ nm}^{-1} < Q < 0.5 \text{ nm}^{-1}$

CHRNS 30-m SANS

$0.010 \text{ nm}^{-1} < Q < 6 \text{ nm}^{-1}$

Perfect-Xtal USANS

$5 \times 10^{-4} \text{ nm}^{-1} < Q < \sim .01 \text{ nm}^{-1}$

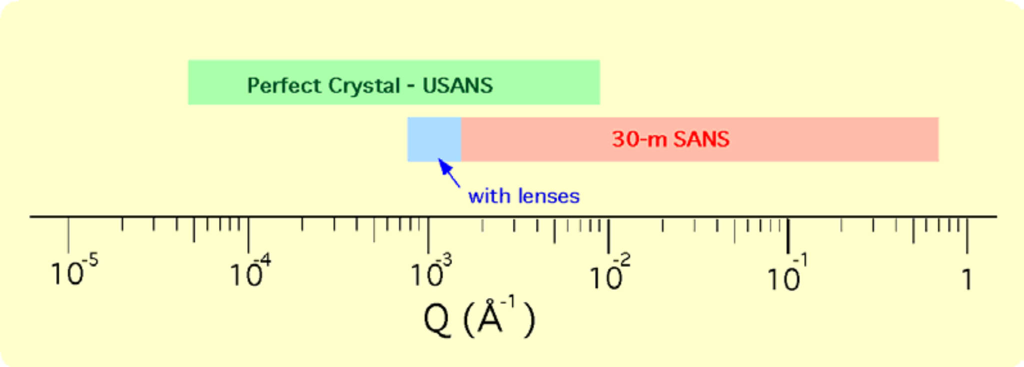
NIST / ExxonMobil 30-m SANS

$0.008 \text{ nm}^{-1} < Q < 7 \text{ nm}^{-1}$

SANS Instruments at the NCNR

John Barker at Perfect-Crystal USANS Instrument

NIST/NSF 30-m SANS



SANS APPLICATIONS

POLYMERS:

- Conformation of Polymer Molecules in Solution and in the bulk
- Structure of Microphase-Separated Block Copolymers
- Factors Affecting Miscibility of Polymer Blends

BIOLOGY:

- Organization of Biomolecular Complexes in Solution
- Conformation Changes Affecting Function of Proteins, Enzymes, DNA/Protein complexes, Membranes, etc.
- Mechanisms and Pathways for Protein Folding and DNA Supercoiling

CHEMISTRY:

- Structure and Interactions in Colloidal Suspensions, Microemulsions, Surfactant Micelles, etc.
- Microporosity of Chemical Absorbents
- Mechanisms of Molecular Self-Assembly in Solutions and on Surfaces of Microporous Media

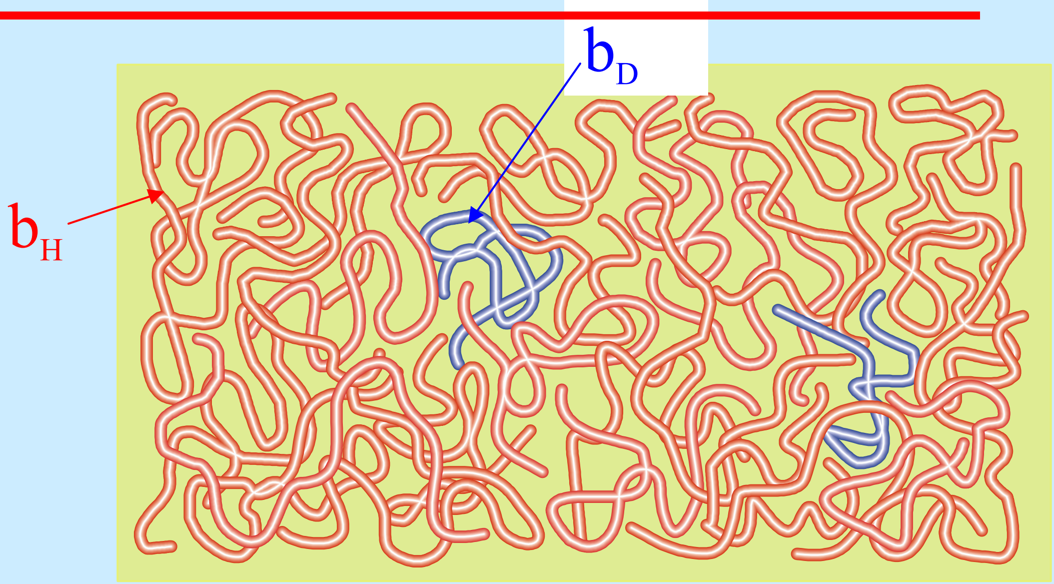
Using Deuterium Labeling to Reveal Polymer Chain Conformation

$$\mathrm{I(Q)} \propto \mathrm{c}\left(\mathrm{b_H} - \mathrm{b_D}\right)^2\ P(\mathrm{Q})$$

$P(\mathrm{Q})$ < - - Single Chain

"Form Factor"

$$P(\mathrm{Q}) = \frac{1}{z^2}\sum_{i}^{N}\sum_{j}^{z}\left\langle e^{i\vec{q}\cdot\vec{r}_{i,j}}\right\rangle$$



High Concentration Labeling

- if labeled chains are randomly dispersed

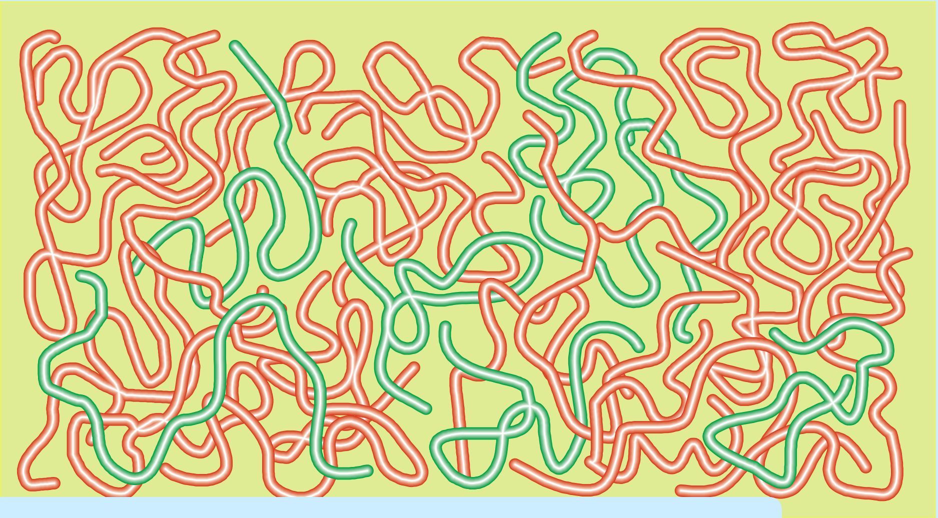
$$\mathrm{I(Q)} \propto \mathrm{x\ (1 - x)\ (b_H - b_D)^2}\ P(\mathrm{Q})$$

homopolymer

blend

$$\mathrm{I(Q)} \propto \mathrm{(x\ b_D + (1 - x) b_H)^2\ S_T(Q)} +$$

$$\mathrm{x\ (1 - x)\ (b_H - b_D)^2}\ P(\mathrm{Q})$$



Can determine S_T and P(Q) from 2 measurements, with different fractions (x) of labeled chains

SANS APPLICATIONS

METALS AND CERAMICS:

- Kinetics and Morphology of Precipitate Growth in Alloys and Glasses
- Defect Structures (e.g. microcracks, voids) Resulting from Creep, Fatigue or Radiation Damage
- Grain and Defect Structures in Nanocrystalline Metals and Ceramics

MAGNETISM:

- Magnetic Ordering and Phase Transitions in Ferromagnets, Spin Glasses, Magnetic Superconductors, etc.
- Flux-Line Lattices in Superconductors

General References: SANS and SAXS

Methods of X-Ray and Neutron Scattering in Polymer Science By R.-J. Roe, Oxford University Press (2000).

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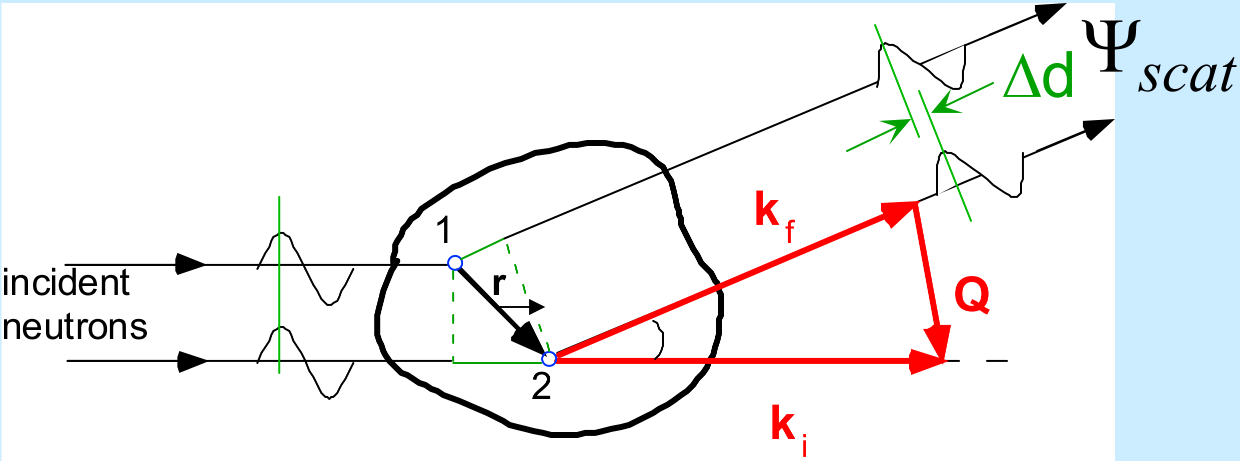
Polymers and Neutron Scattering, J.S. Higgins and H.C. Benoit, Clarendon Press-Oxford (1994).

Small Angle X-Ray Scattering, O. Glatter and O. Kratky, Academic Press (1982).

Appendix A. Scattering from Two Nuclei



$$\Delta\phi = 2\pi\frac{\Delta d}{\lambda}$$

$$\Delta\phi = \vec{r}\cdot\vec{k}_i - \vec{r}\cdot\vec{k}_f$$

$$\Delta\phi = \vec{r}\cdot(\vec{k}_i - \cdot\vec{k}_f)$$

$$\Delta\phi = \vec{r}\cdot\vec{Q}$$

$$\Psi_{scat} = -\frac{b_1}{R}e^{ikR} - \frac{b_2}{R}e^{i(kR+\Delta\phi)} \longleftarrow$$ Scattered wave function

for N nuclei

<u>SAS of X rays</u> - Guinier (1955), Ch.1

<u>Polymers and Neutron Scattering</u>,
Higgins & Benoît (1994), p.11

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

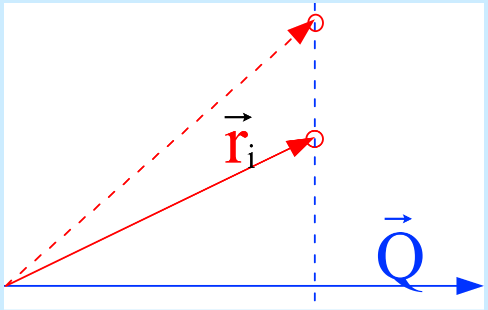
Appendix A. Scattering from N Nuclei

$$\frac{d\sigma}{d\Omega} = \frac{1}{N}\left|\sum_{1}^{N} b_i \; e^{i\vec{Q}\cdot\vec{r}_i}\right|^2$$

Scattering cross section: # neutrons scattering in direction corresponding to Q, divided by # incident per unit area

$$\vec{r}_i = \vec{r}_{//} + \vec{r}_{\perp}$$

$$\vec{Q}\cdot\vec{r}_i = Q\,r_{//}$$



Only components of r_i parallel to Q contribute to summation

Therefore, diffraction probes structure in the direction of Q *only*!!