What Can be Measured by SANS and Reflectometry?

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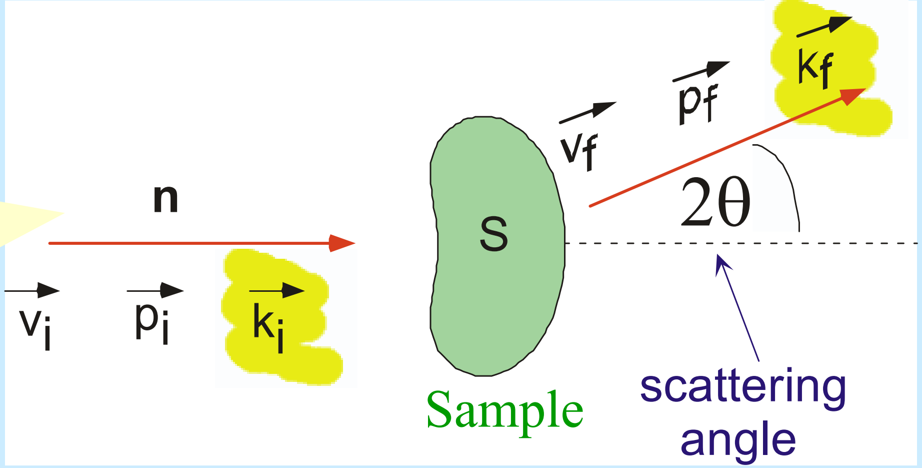
NIST Summer School on SANS and
Reflectometry from Submicron Structures

June 3-7, 2002

Concepts Common to SANS and NR

Collimated beam of monochromatic neutrons incident on sample, S

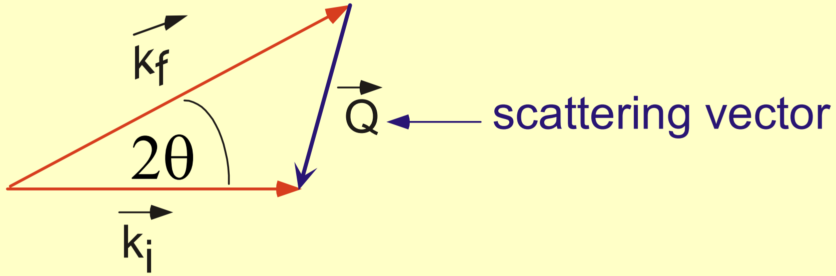
Incident neutron wave vector, $|\vec{k}_i| = \frac{2\pi}{\lambda_i}$



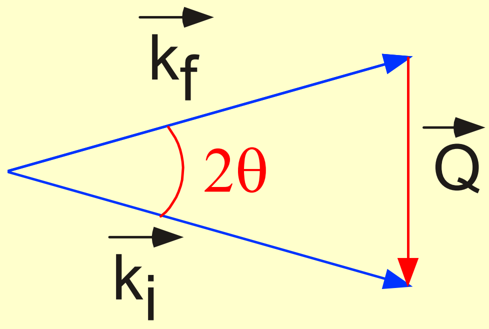
Scattered neutrons counted as a function of scattering angle, 2θ

Scattering Triangle

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



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



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

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

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

Recall Bragg's Law $\xrightarrow{\quad} \lambda = 2d\sin\theta$

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

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

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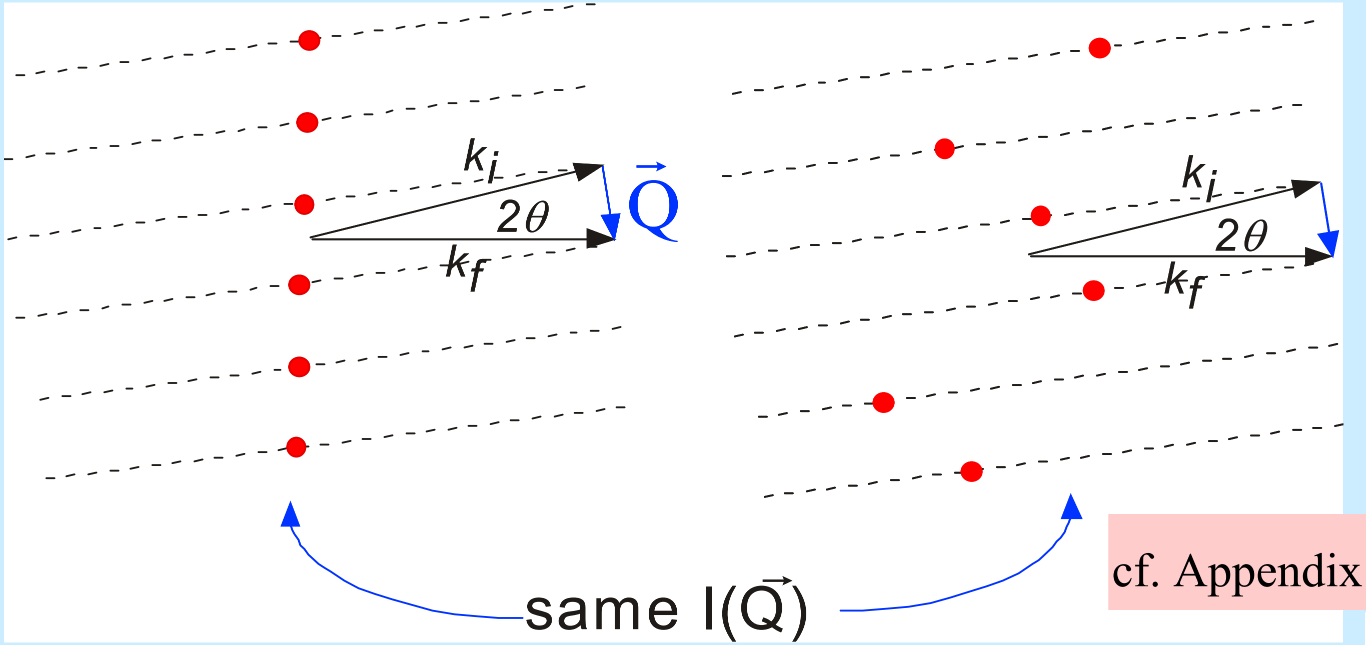
$$\boxed{d \approx \frac{2\pi}{Q}}, \quad \text{for small scattering angles, } d \approx \frac{\lambda}{2\theta}$$

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

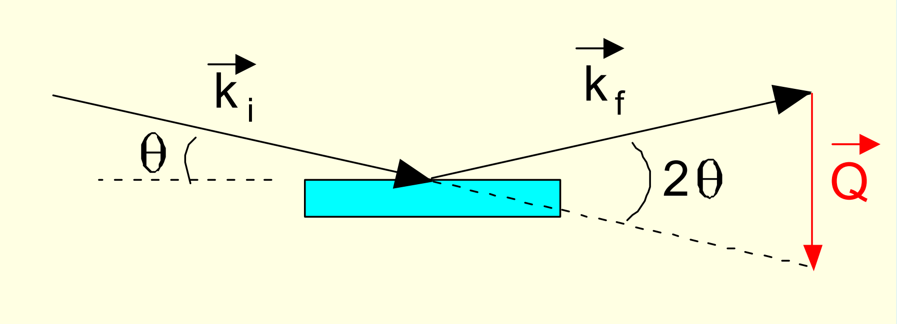


cf. Appendix A.

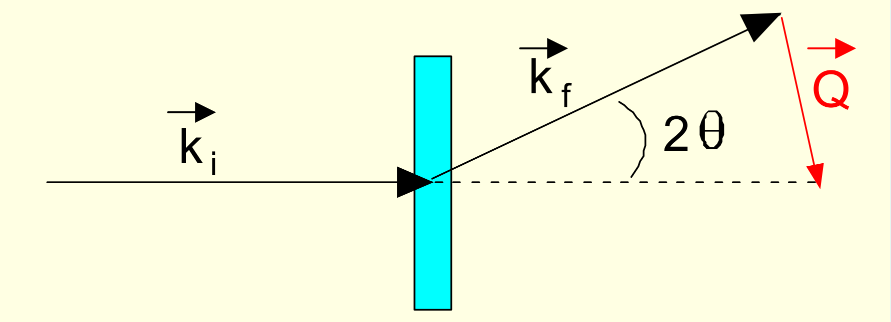
Diffraction Probes Structure in the Direction of $\vec{Q}$

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

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.*

Length Scales Probed by SANS and NR

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

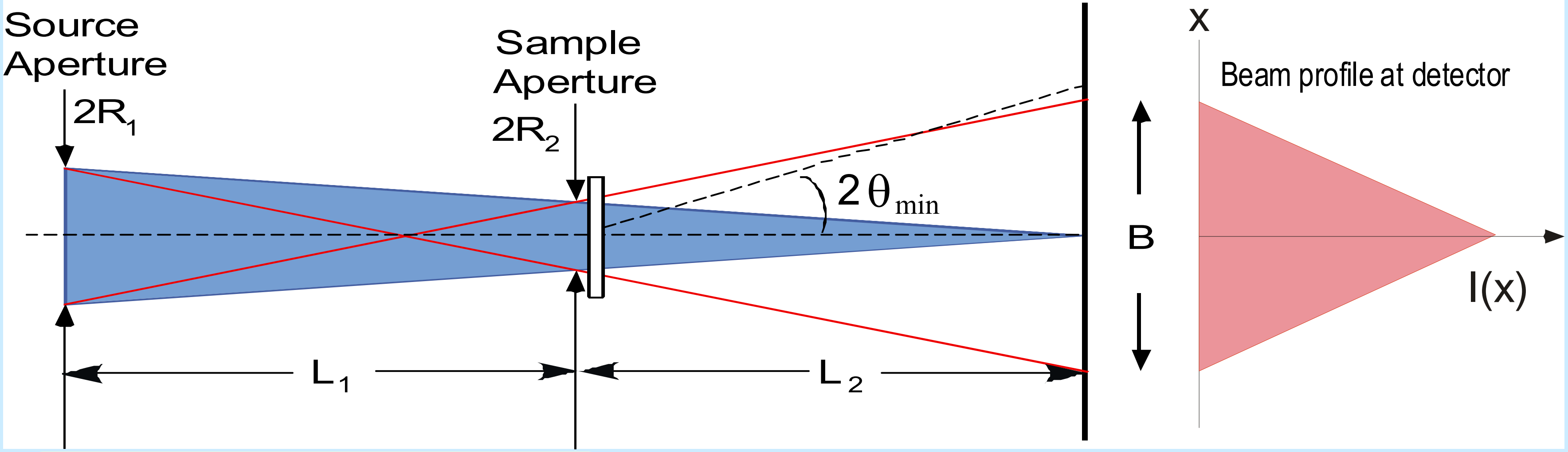
$$d \approx \frac{2\pi}{Q} \approx \frac{\lambda}{2\theta}$$ (wavelength) (scattering angle)

$0.5\ \text{nm} < 1 < 2\ \text{nm}$ (cold neutrons)

$0.1^\circ < 2\theta < 10^\circ$ (small angles)

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

SANS PINHOLE COLLIMATION GEOMETRY



$$I(2\theta_{\min}) \propto \left(\frac{R_1 R_2}{L_1 L_2}\right)^2 \propto (2\theta_{\min})^4$$

For ‘optimal’ geometry, where $L_1 = L_2$, $R_1 = 2R_2$

Length Scales Probed by SANS and NR

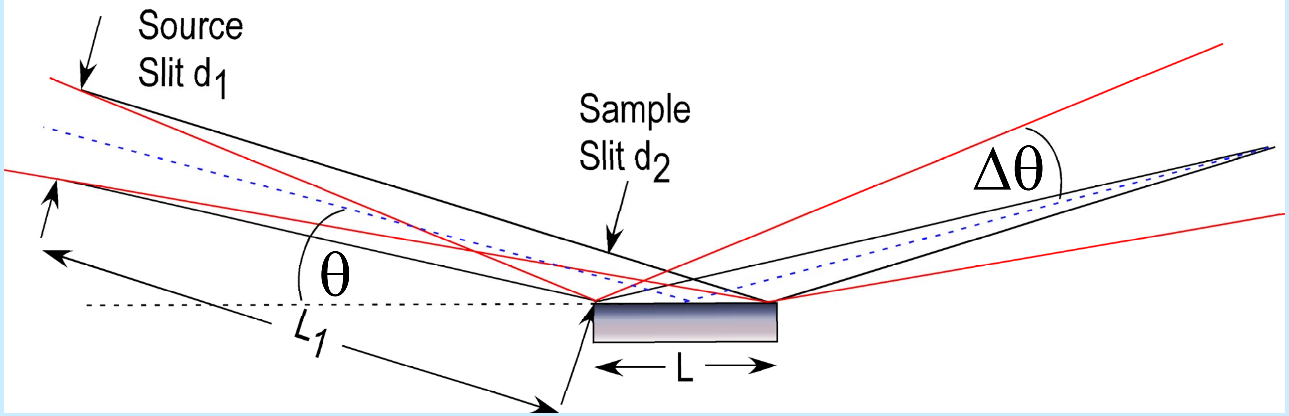
NR probes structure on a scale *d* , where

$d \approx \frac{2\pi}{Q} \approx \frac{\lambda}{2\theta}$ (wavelength) (reflection angle)

0.4 nm < λ < 0.6 nm

0.06° < θ < 20° (small angles)

0.5 nm < *d* < 500 nm



$$I(\theta) \propto \left(\frac{d_1 d_2}{L_1 L_2}\right) = \left(\frac{2L^2 \sin^2\theta}{L_1 L_2}\right), \quad \Delta\theta = \frac{3L\sin\theta}{2L_1}, \text{ for } d_1 = 2d_2 \longrightarrow d_{max} \approx \frac{\lambda}{\Delta\theta} = \frac{2\lambda L_1}{3L\sin\theta}$$

Length Scales Probed by SANS and NR

30-m SANS

NR

d_{max}

(limited by instrument resolution; in effect, source strength)

$$d_{max} \approx \frac{\lambda}{\Delta\theta_{min}} \approx 300\,\mathrm{nm}$$

$$d_{max} \approx \frac{\lambda}{\Delta\theta_{min}} \approx 500\,\mathrm{nm}$$

d_{min}

(limited by signal-to-noise)

$$I(0) = \phi V_p (\Delta\rho)^2 d_s T_s$$

ϕ= volume fraction

V_p= 'particle' volume

$\Delta\rho$ = scattering contrast

d_s = sample thickness

T_s = sample transmission

for $V_p = \frac{\pi}{6} d^3$ and 'good' contrast

particle diameter

for NCNR 30 m SANS instruments

$$\phi d^3 \geq 5 \times 10^{-4}\,\mathrm{nm}^3$$

d_{min}	ϕ
1 nm	0.05 %

$$R_{min} \approx 10^{-8} \approx \frac{(8\pi\Delta\rho)^2}{Q^4_{max}}$$

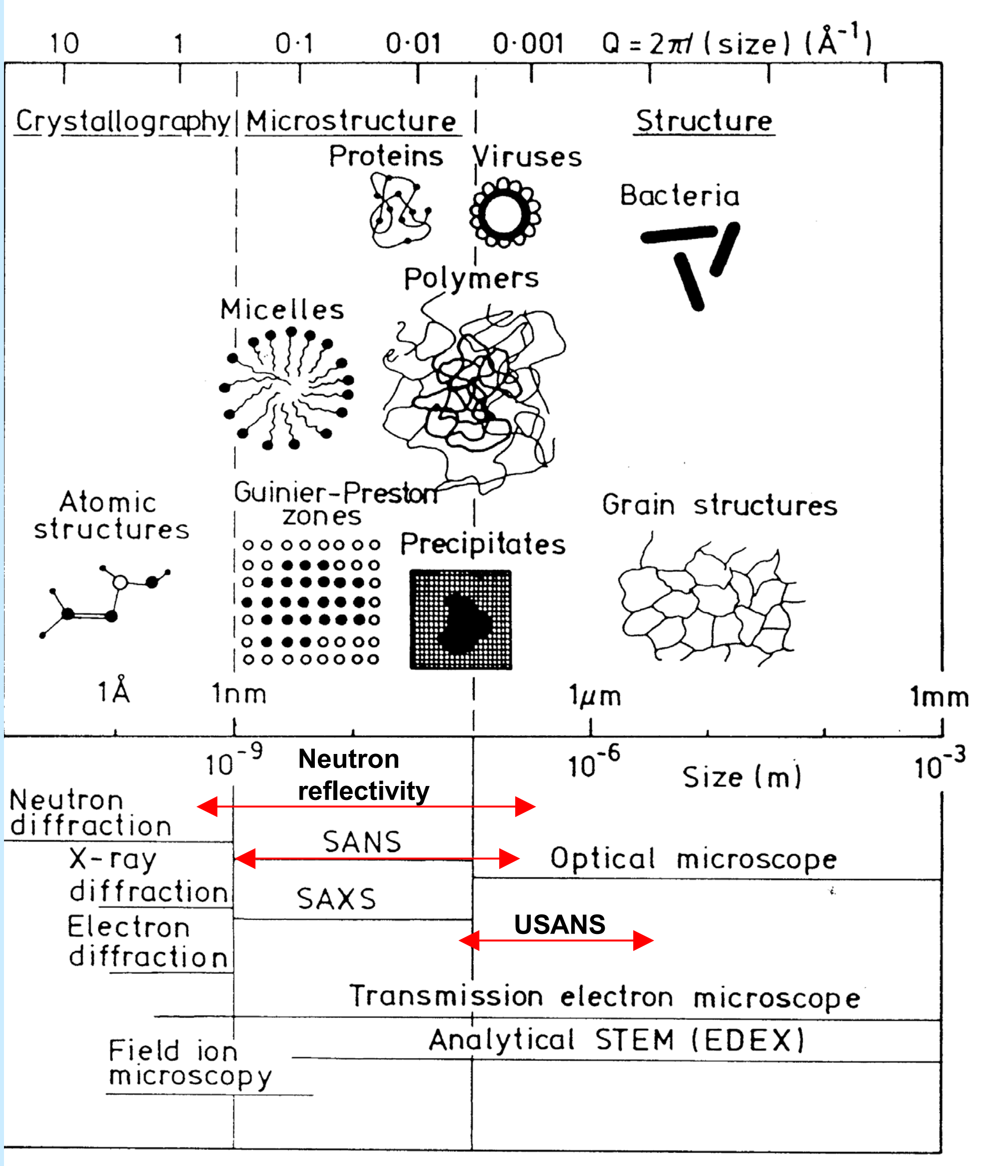
for NCNR instruments

for $\Delta\rho \approx 3 \times 10^{-6}$ A $^{-2}$ (good contrast)

Q_{max}~ 0.8 Å^{-1}

$$d_{min} \approx \frac{2\pi}{Q_{max}} \approx 0.8\,\mathrm{nm}$$

Techniques for the Measurement of Microstructure



Why Neutrons for SAS and Reflectometry?

- Unique Control of Scattering Contrast by Deuterium Labeling and H- and D-Solvent Mixtures

- Uniquely Powerful Probe of Magnetic Structure

Also,

- highly penetrating even at long wavelengths
- equally sensitive to light and heavy elements
- nondestructive

SANS APPLICATIONS

POLYMERS:

- Conformation of Polymer Molecules in Solution <u>and</u> 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:

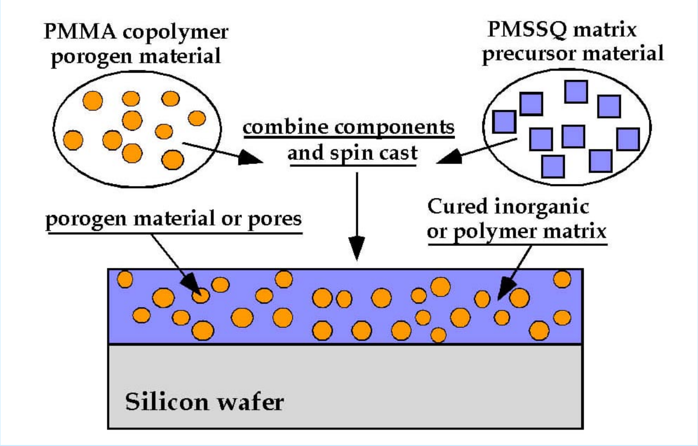
- Structure and Interactions in Colloidal Suspensions, Microemulsions, Surfactant Micelles, etc.
- Microporosity of Chemical Absorbents
- Mechanisms of Molecular Self-Assembly in Solutions and on Surfaces of Microporous Media

In Situ SANS Study of Evolution of Porosity in Low-K Films

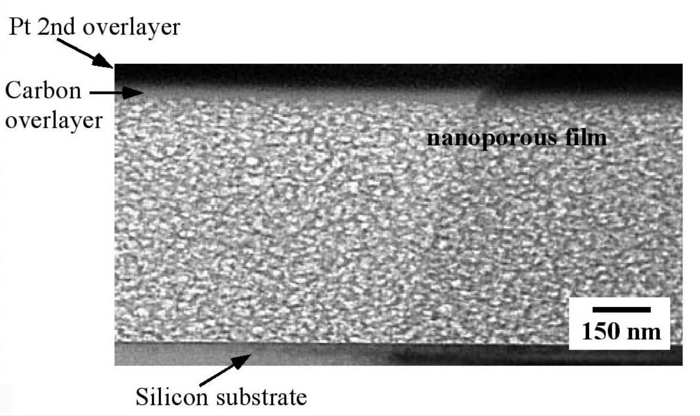
R.M. Briber and G.Y. Yang
University of Maryland

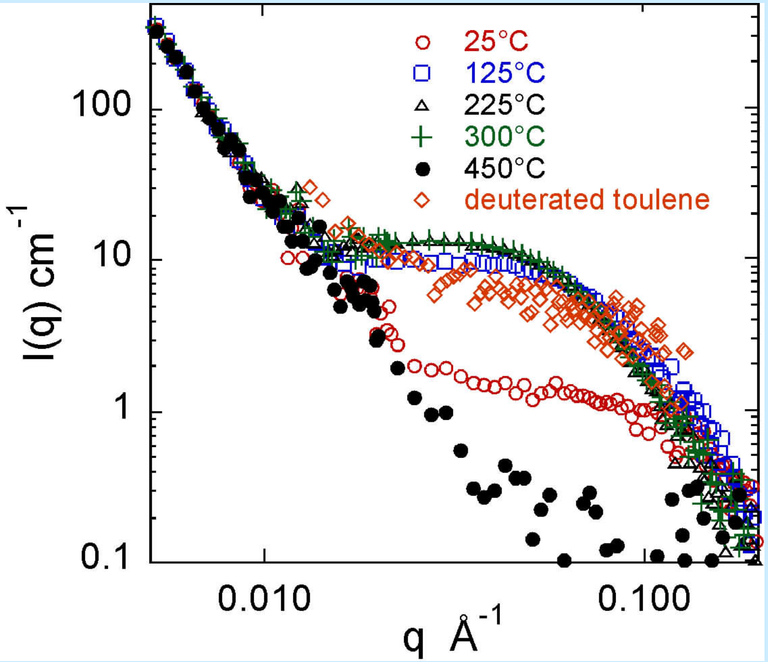
E. Huang, H.-C. Kim,
W. Volksen and R.D. Miller
IBM Almaden Res. Center

K. Shin
SUNY Stonybrook



- Use deuterated poragen to introduce contrast in as-spun films
- Follow evolution of poragen
- Backfill poragen-free final material with deuterated wetting fluid to compare pore with poragen structure





SANS APPLICATIONS

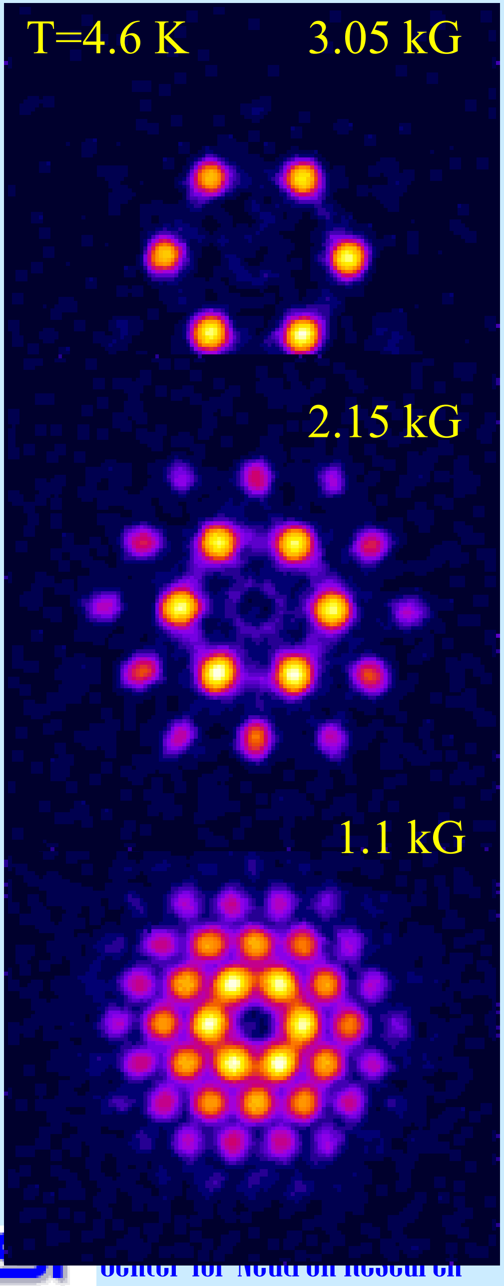
METALS AND CERAMICS:

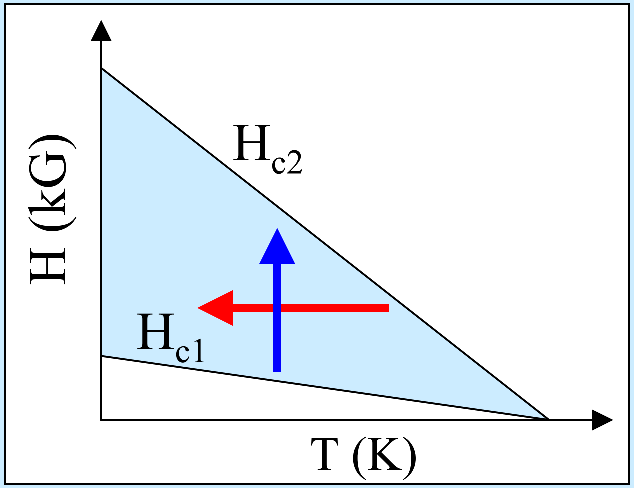
- Kinetics and Morphology of Precipitate Growth in Alloys and Glasses
- Defect Structures (e.g. microcracks, voids) Resulting from Creep, Fatigue or Radiation Damage
- Grain and Defect Structures in Nanocrystalline Metals and Ceramics

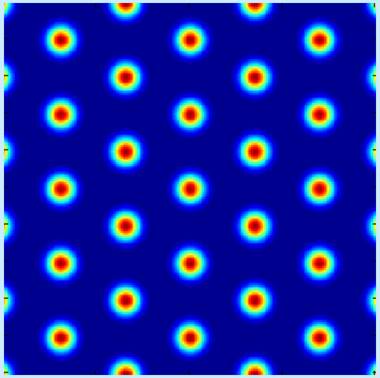
MAGNETISM:

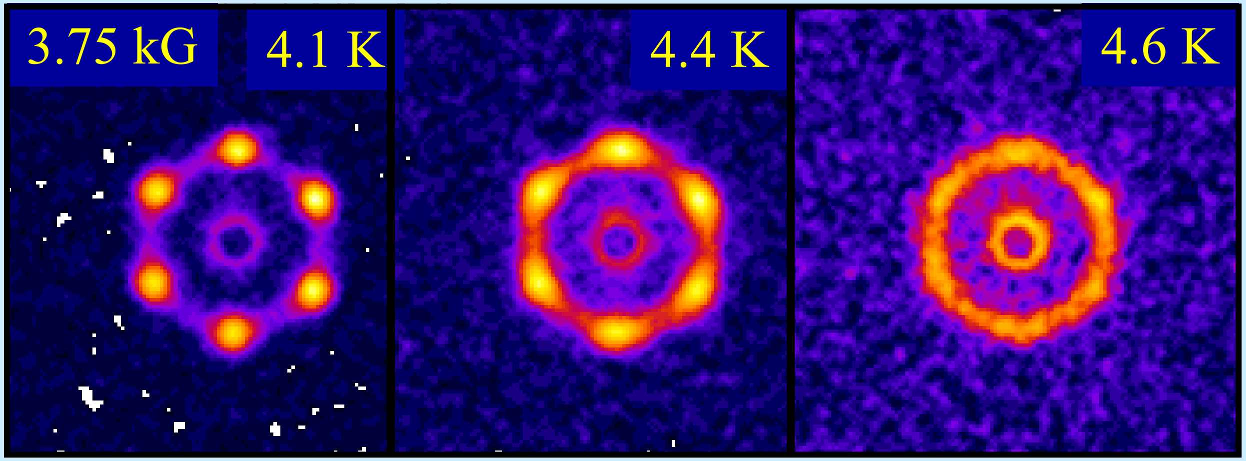
- Magnetic Ordering and Phase Transitions in Ferromagnets, Spin Glasses, Magnetic Superconductors, etc.
- Flux-Line Lattices in Superconductors

Vortex Matter in Superconductor Nb







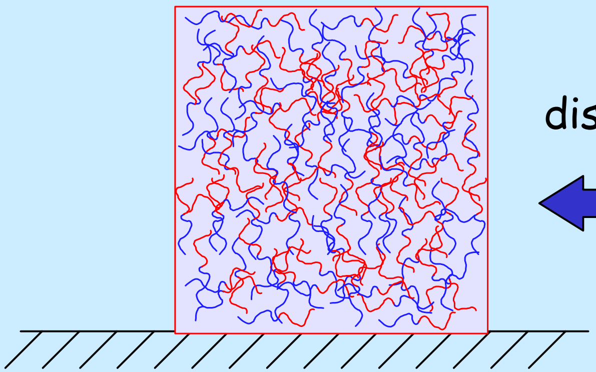


X. S. Ling and S.-R. Park (Brown University)
S.-M Choi, D. Dender and J. Lynn, (NCNR/NIST)

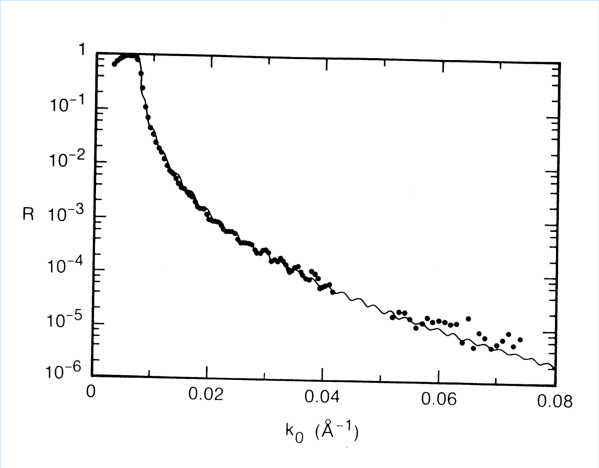
Neutron Reflectivity Application Areas

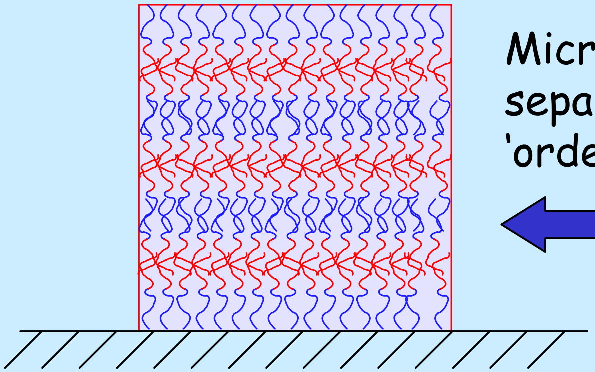
Polymers:

- polymer phase behavior in thin films
  - e.g. order-disorder phase transitions of block copolymers

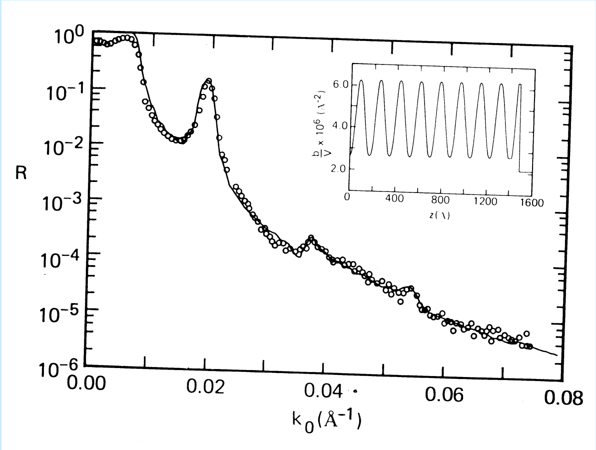


disordered





Microphase
separated
'ordered'



Neutron Reflectivity Application Areas

Polymers:

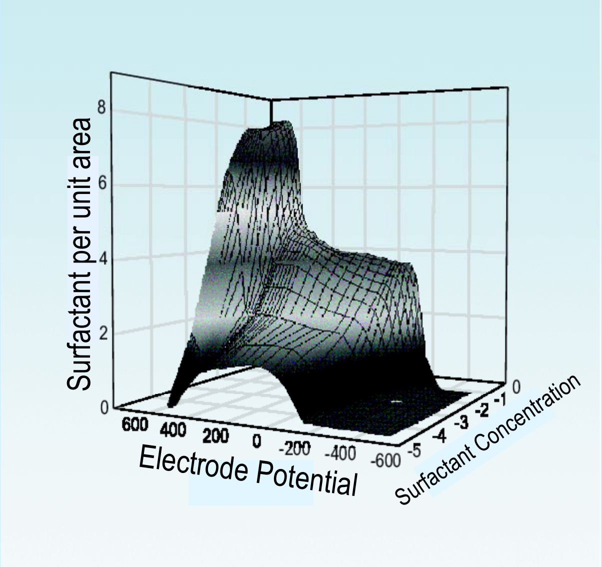
- Polymer Interdiffusion at Interfaces
- Factors Affecting Wetting and Dewetting
- Polymer conformation and concentration profiles at solid-liquid and liquid-air interfaces

Chemistry:

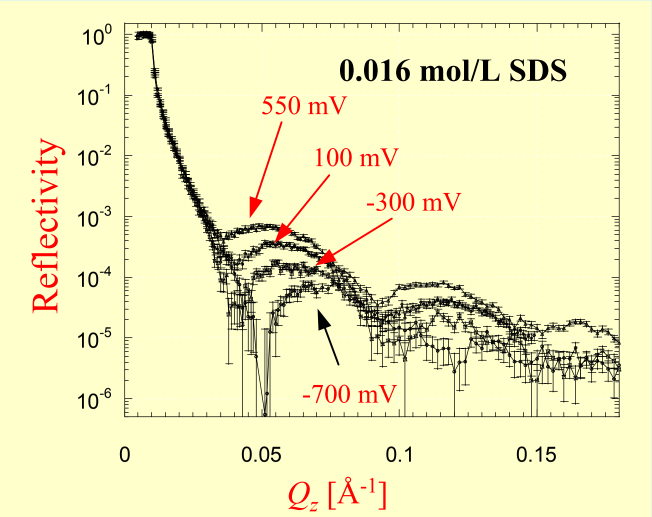
- Langmuir-Blodgett films
- Self-Assembled monolayers, bilayers, etc.
- Electrochemical reactions

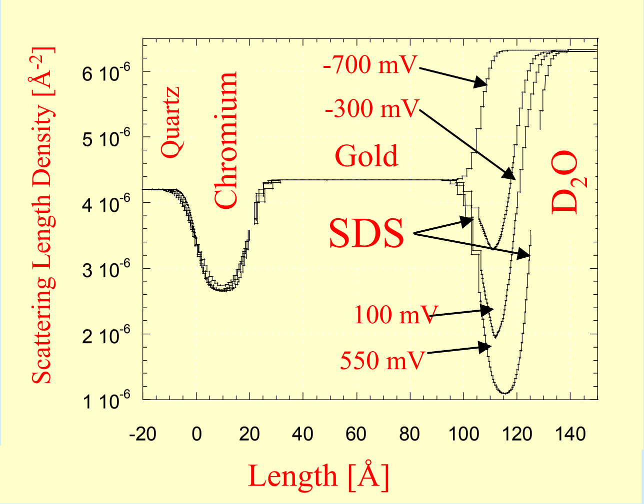
NR Study of Surfactants at Electrode Surfaces

I. Burgess, et al. (U. Guelph), J. Majewski & G. Smith (LANL), S. Satija & R. Ivkov (NCNR)

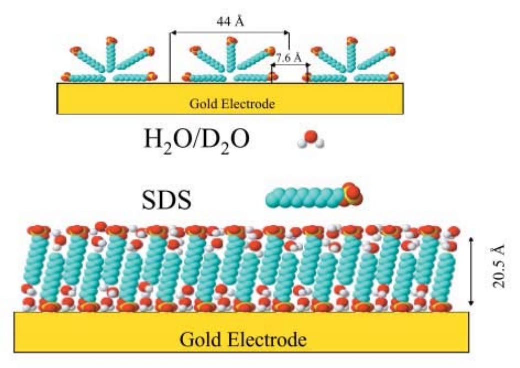


Electrical potential controls adsorption and desorbtion of surfactant





Neutron reflectivity combined with electrochemical studies and AFM yield picture below of adsorbed surfactant film structure



Neutron Reflectivity Application Areas

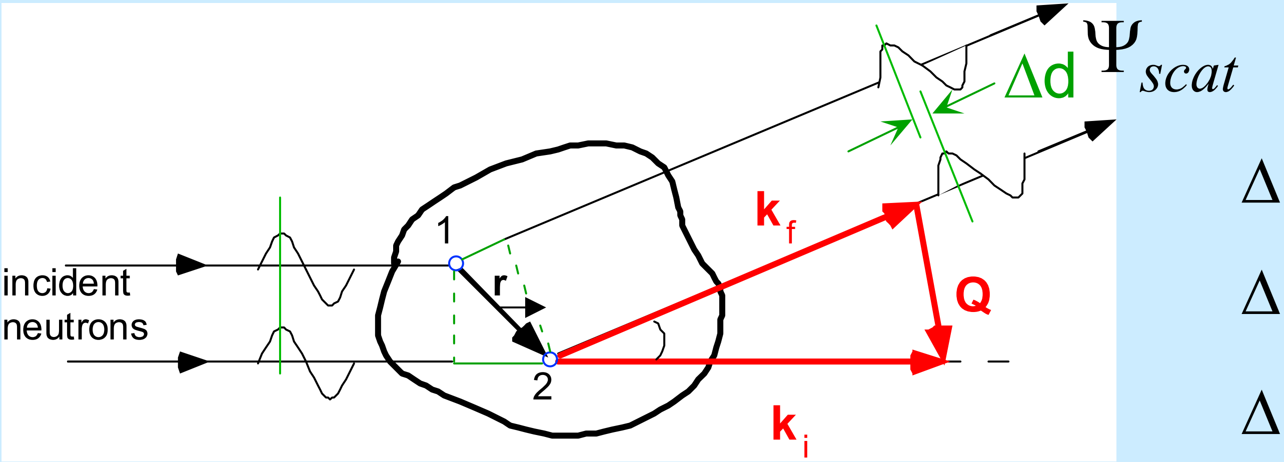
Biology:

- Location of Peptides in Biomimetic Single Bilayer Membranes
- Protein Adsorption/Desorption on Self-Assembled Monolayers
- Vectorially-Oriented Protein Monolayers

Magnetism:

- Magnetic Structure and Interlayer Coupling in GMR Multilayer Thin Films
- Magnetic Coupling and Ordering across Non-Magnetic Layers
- Spin Structures Associated with Exchange-Biased Magnetic Thin Films

Appendix A. Scattering from Two Nuclei



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

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

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

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

$$\Psi_{scat} = -\frac{\mathrm{b}_1}{\mathrm{R}} e^{ikR} - \frac{\mathrm{b}_2}{\mathrm{R}} e^{i(kR+\Delta\phi)} \longleftarrow$$

Scattered wave function

for N nuclei

SAS of X rays - Guinier (1955), Ch.1

Polymers and Neutron Scattering, Higgins & Benoît (1994), p.11

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

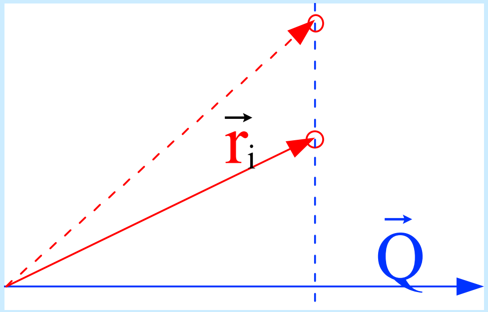
Appendix A. Scattering from N Nuclei

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

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*!!