Neutron scattering presentation series

(2) Small angle neutron scattering and neutron reflectometry

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Outline

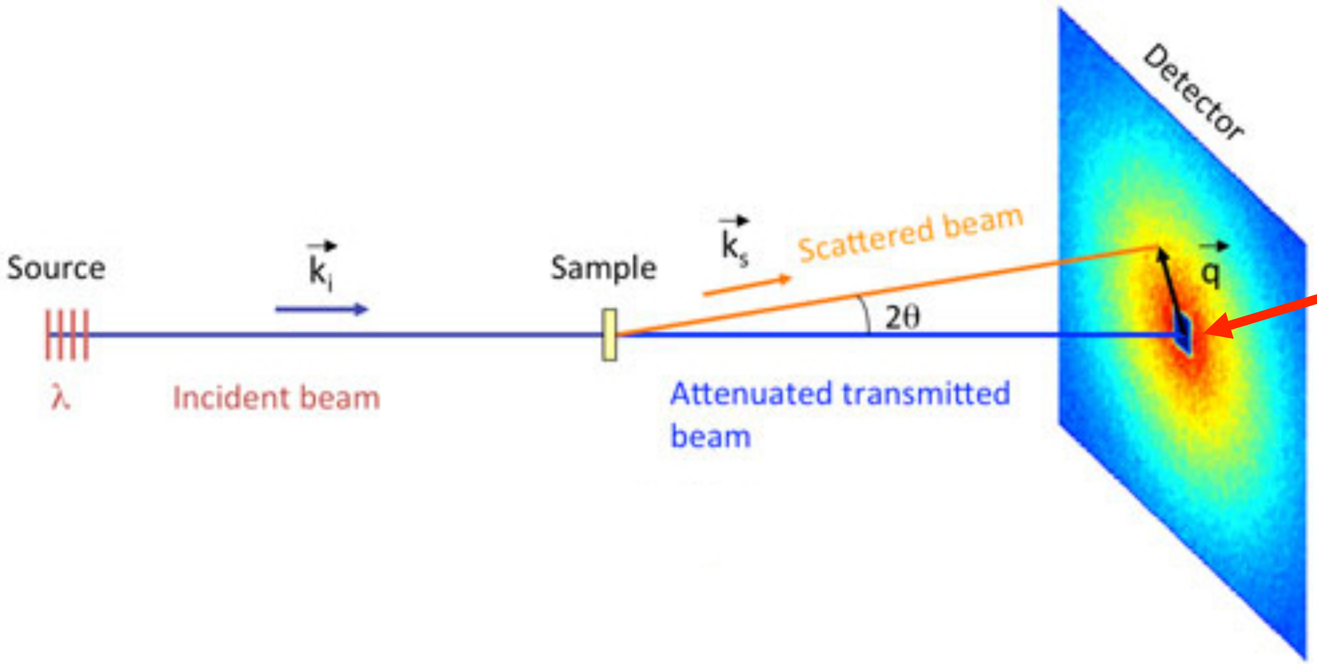
Small angle neutron scattering:

1. Experiment setup
2. Data reduction
3. Instrument resolution function
4. Standard plots
5. Contrast variation

Neutron reflectometry:

1. Surface reflection
2. Reflection of thin film
3. Surface roughness

SANS Experiment Setup

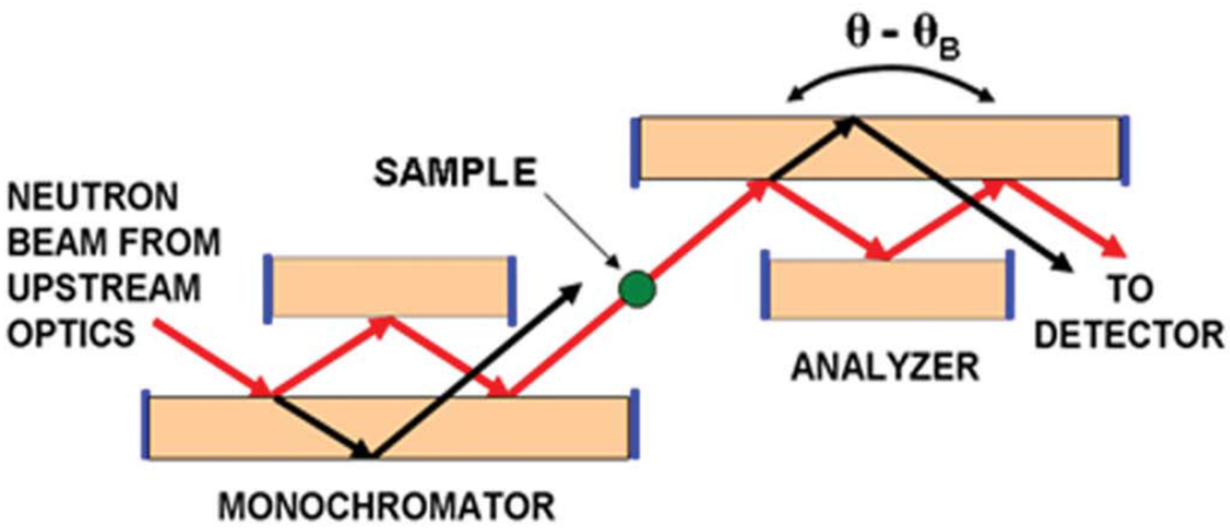


beamstop

$2\theta \sim (0.5°, 5°)$

$Q \sim (0.001 Å^{-1}, 0.5 Å^{-1})$

$r \sim (1 nm, 500 nm)$



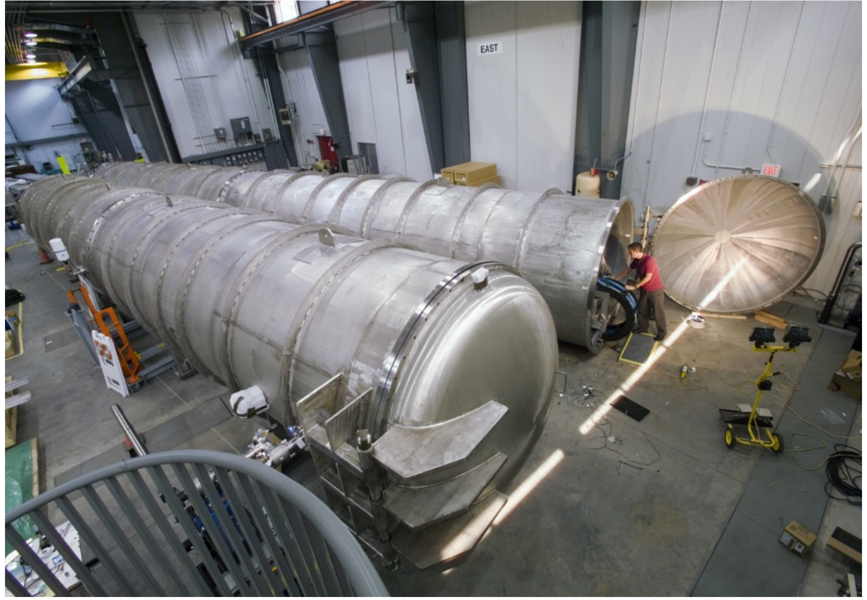
Ultra-Small Angle Neutron Scattering (USANS)

$Q \sim (5 \times 10^{-6} Å^{-1}, 0.005 Å^{-1})$

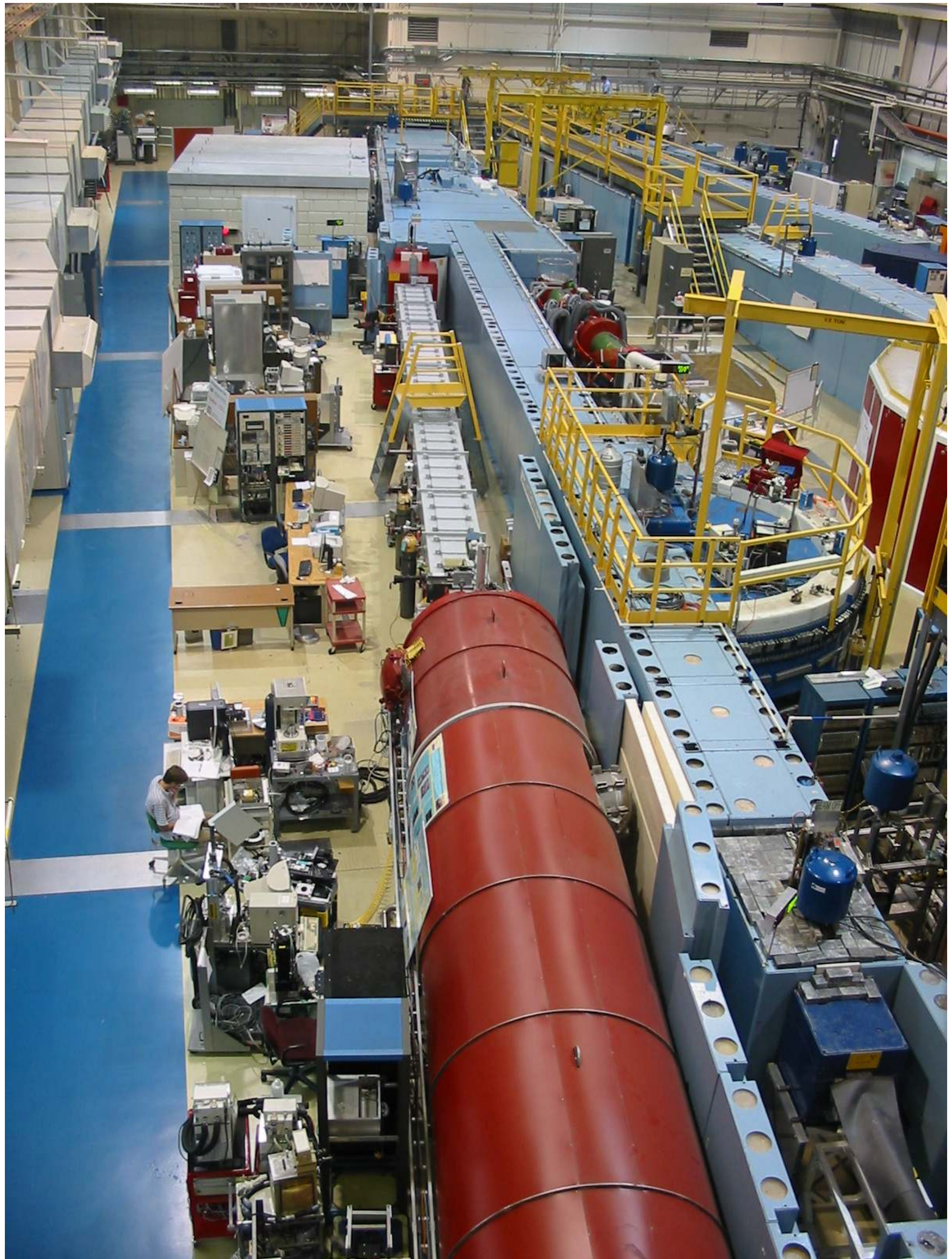
$r \sim (100 nm, 100 \mu m)$

low flux!

CG2/CG3 ORNL

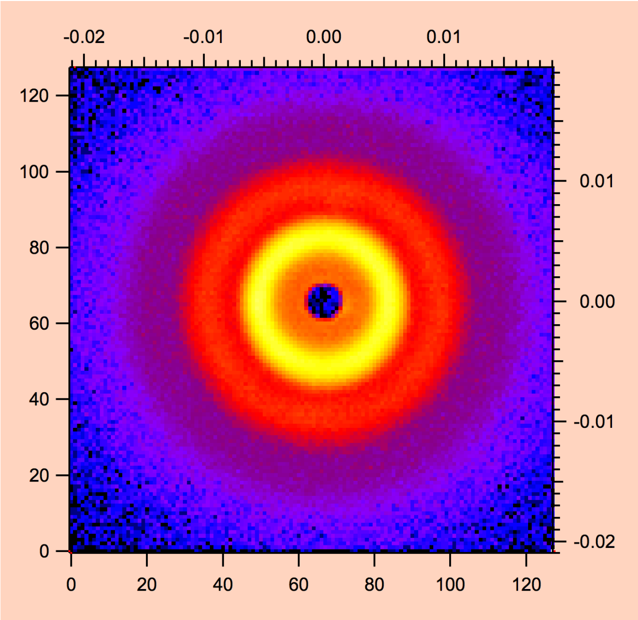


NG7 NIST

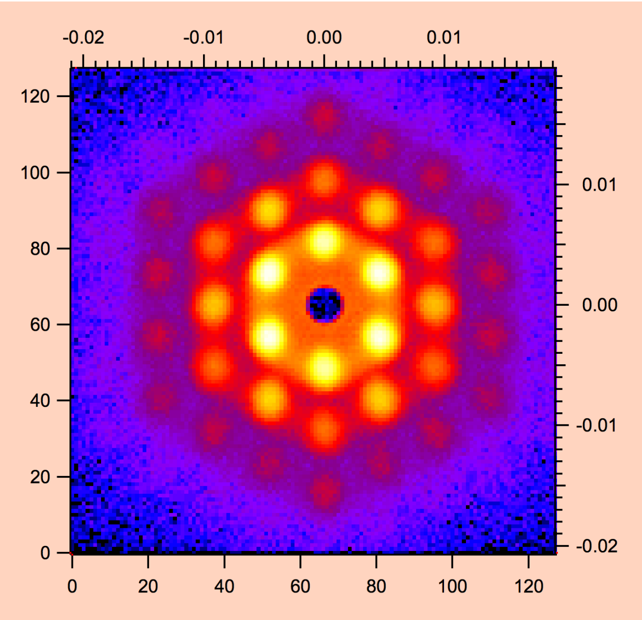


EQSANS ORNL

Data Reduction



Isotropic scattering



Anisotropic scattering

Sample transmission T_{sample}
Sample scattering S_{sample}
Background (empty cell) transmission T_{cell}
Background (empty cell) scattering S_{cell}
Direct open beam intensity I_{open}
Blocked beam (room background) I_{block}

$$I_{abs} = S_{sample} - I_{block} / T_{sample} - S_{cell} - I_{block}$$

Data Reduction (cont'd)

$$I_{abs}(Q) = \frac{S_{sample} - I_{block}}{T_{sample}} - \frac{S_{cell} - I_{block}}{T_{cell}} = \frac{I_{scattered}(2\theta,\phi)}{I_{incident}\, T_{mate}}$$

$$I_{abs}(Q) = \frac{d\Sigma}{d\Omega}(Q) = \frac{d}{d\Omega}(Q) \sum_{i} n_i \sigma_i$$

σ_i : microscopic cross section [L^2] (cm^2)

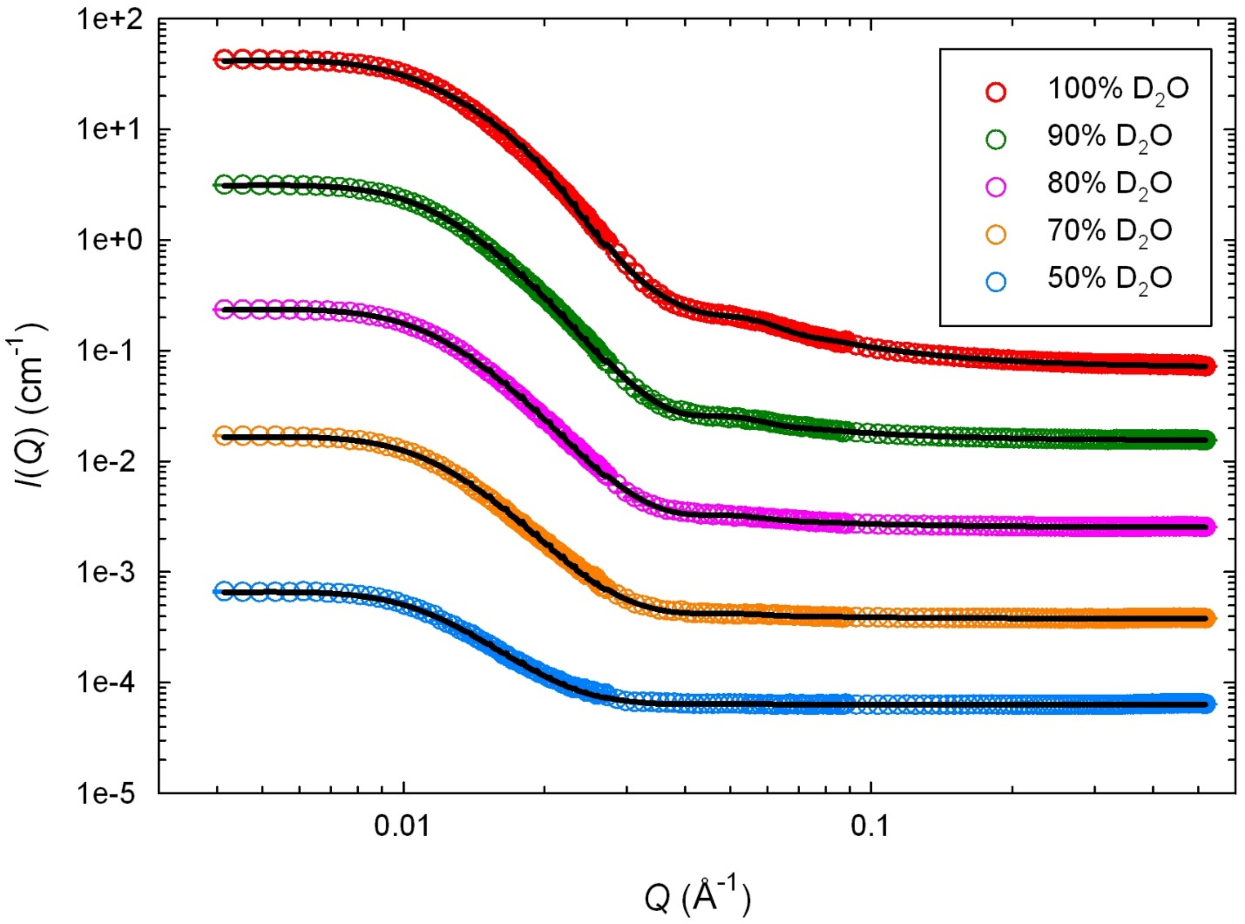
n_i : number density [L^{-3}] (cm^{-3})

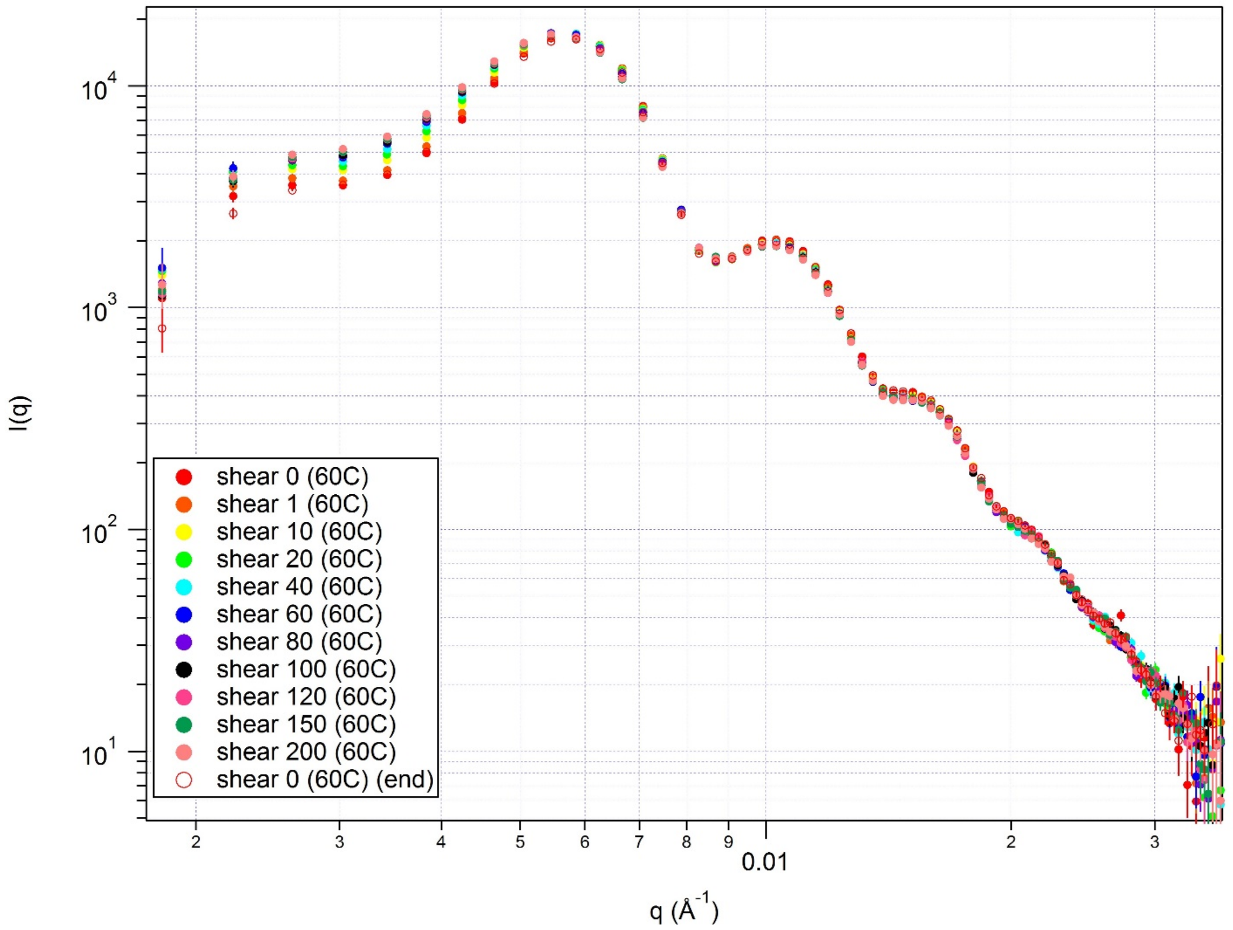
$\Sigma = \sum_{i} n_i \sigma_i$: macroscopic cross section [L^{-1}]

(cm^{-1})

I_{abs} : absolute intensity

Data Reduction (cont'd)





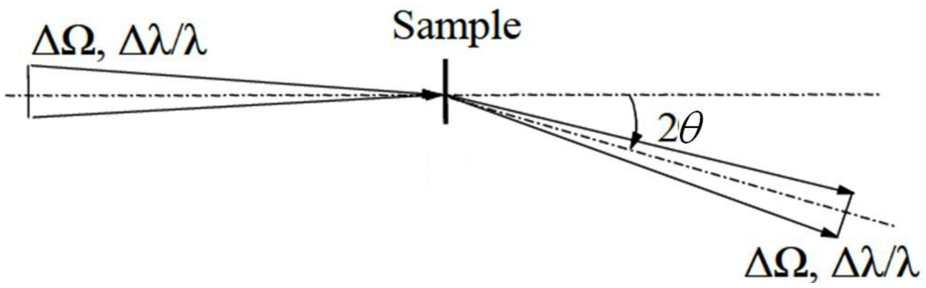
Peaks, bumps, oscillation: size, distance, interface sharpness

Amplitudes: concentration, contrast, coherent/incoherent scattering

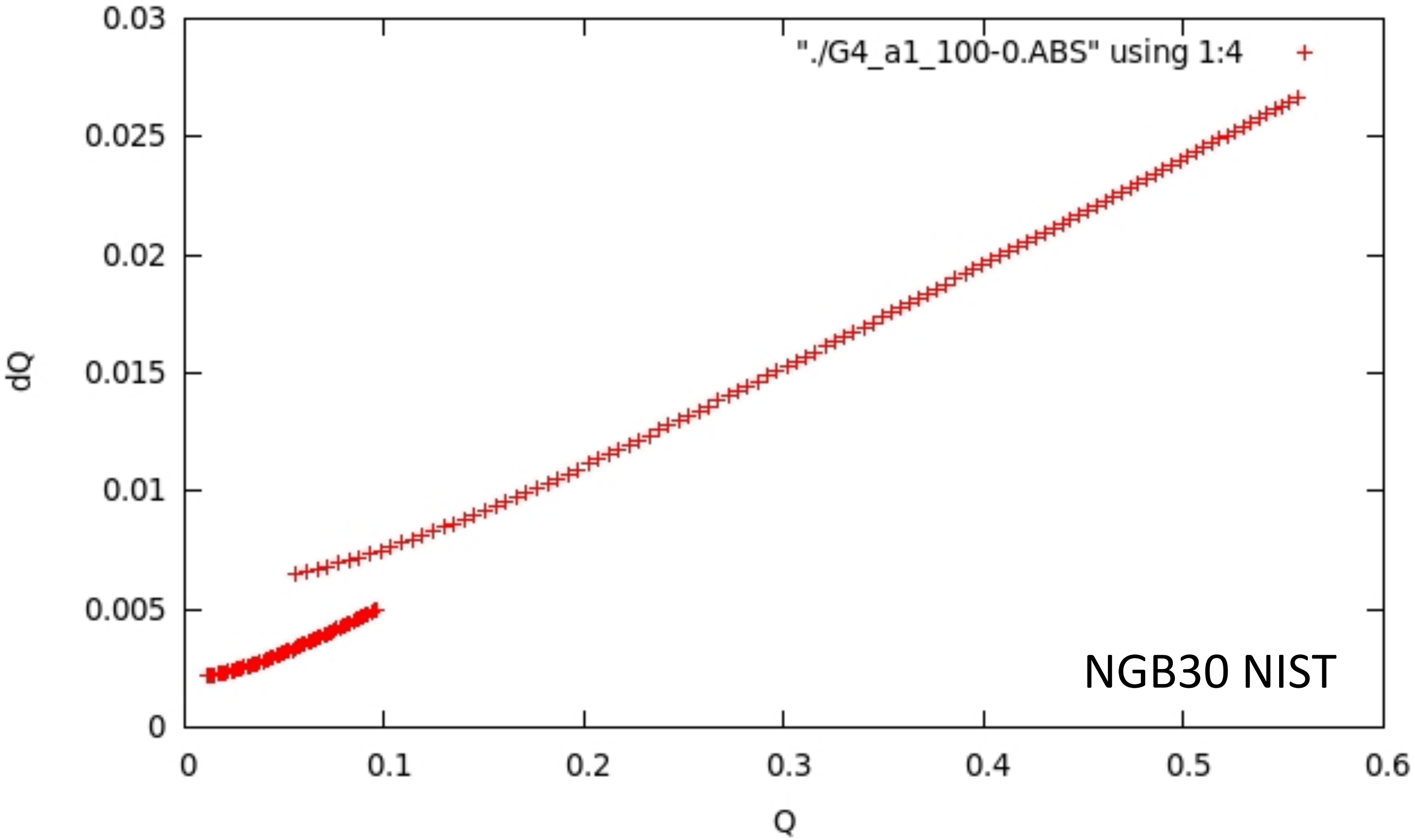
Instrument resolution

Instrument resolution function

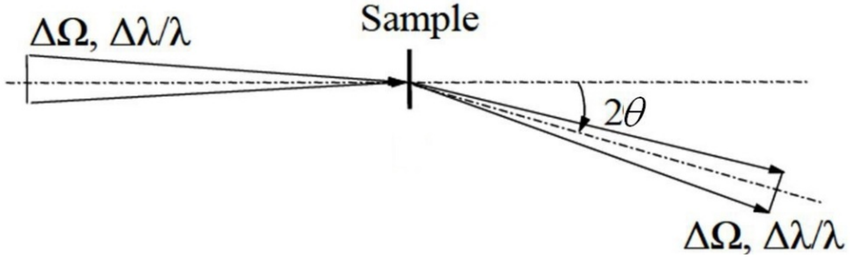
$$(\Delta Q/Q)^2 = (\Delta\lambda/\lambda)^2 + (\cos^2\theta)(\Delta\theta/\sin^2\theta)^2 = (\delta(Q)/Q)^2$$



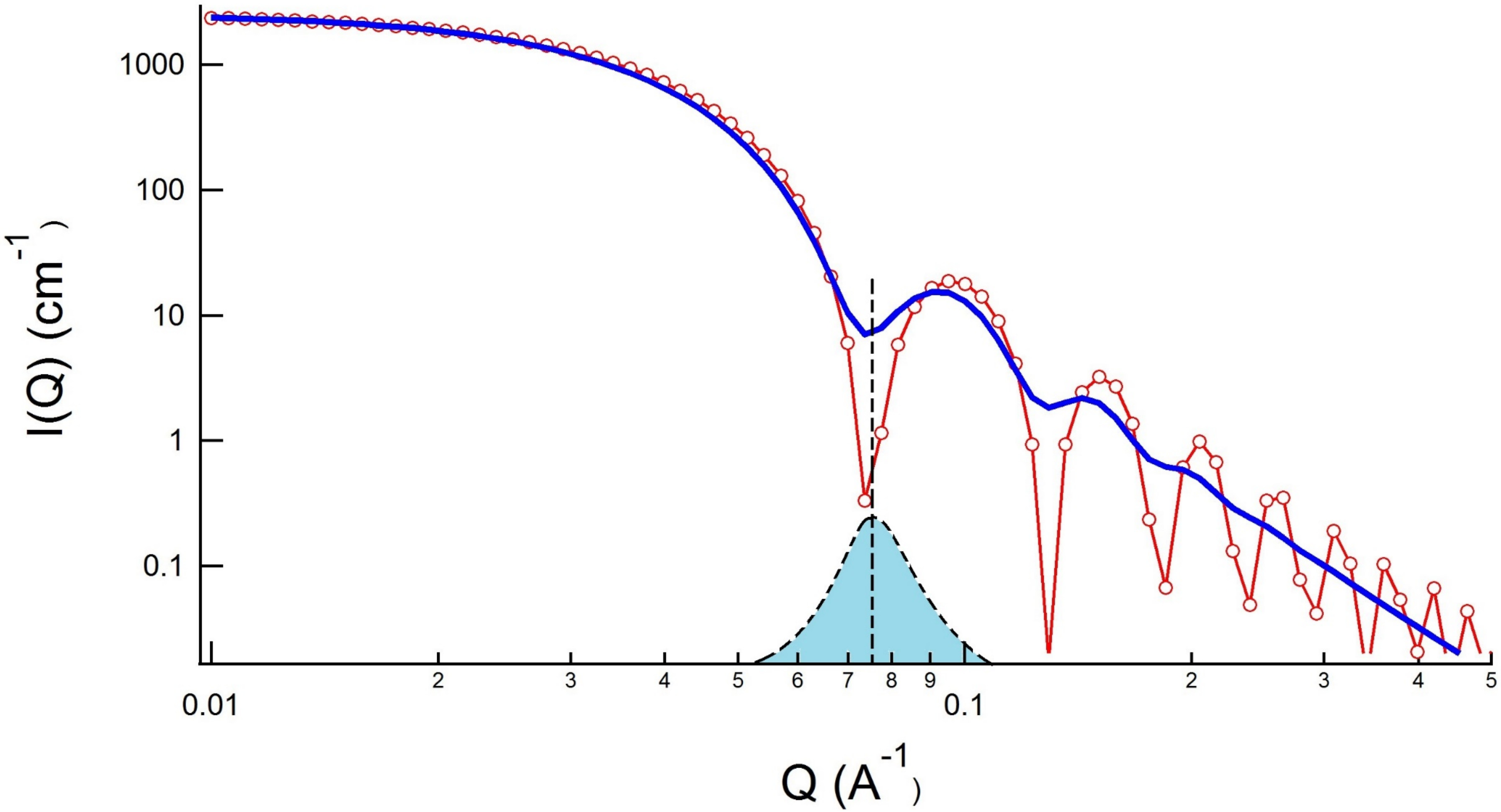
$$Q = 4\pi/\lambda \sin\theta$$



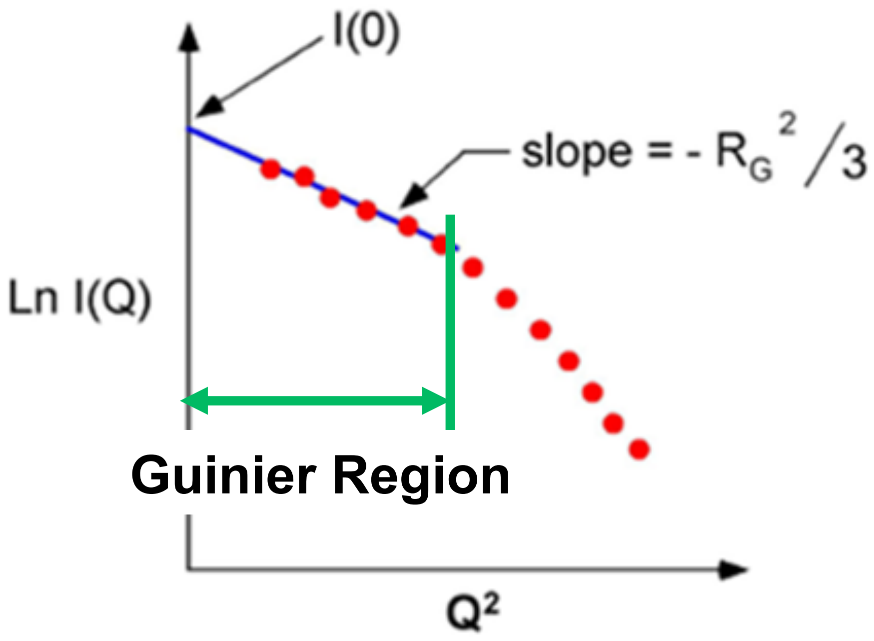
Instrument resolution (cont'd)



$$I_{measured}(Q)=\int_0^{\infty} I_{theoretical}(Q')/\sqrt{2\pi}\,\delta(Q)\; e^{-(Q-}$$



Standard Plots (1) – Guinier Plot



3D:

$ln(I(Q))$ vs. Q^2 → $I(Q=0)=n\Delta\rho^2 V_p^2$, $R_G=\sqrt{0.6}\,R$

$$I(Q)\approx I(Q=0)e^{-Q^2 R_G^2/3} \quad (QR_G \ll 1)$$

Generalization (modified Guinier plots):

1D:

$$I(Q)\approx I_c(Q=0)/Q\, e^{-Q^2 R_c^2/2} \quad (QR_c \ll 0.8)$$

$ln[QI(Q)]$ vs. Q^2 $\quad R=\sqrt{2}\,R_c$

2D:

$$I(Q)\approx I_t(Q=0)/Q^2\, e^{-Q^2 R_t^2} \quad (QR_t \ll 0.8)$$

$ln[Q^2 I(Q)]$ vs. Q^2 $\quad R=\sqrt{12}\,R_t$

1. Only valid for dilute solution.
2. R_G and R_c does not have shape information.

Guinier Plot - Examples

pH dependent self assembly of β -amyloid(10-35) and β-amyloid(10-35)-PEG3000

P Thiyagarajan [a*] T.S. Burkoth [b] V. Urban [ac] S. Seifert [d] T.L.S. Benzinger [e] D.M. Morgan [b] D. Gordon [e] S.C. Meredith [e] and D.G. Lynn [b]

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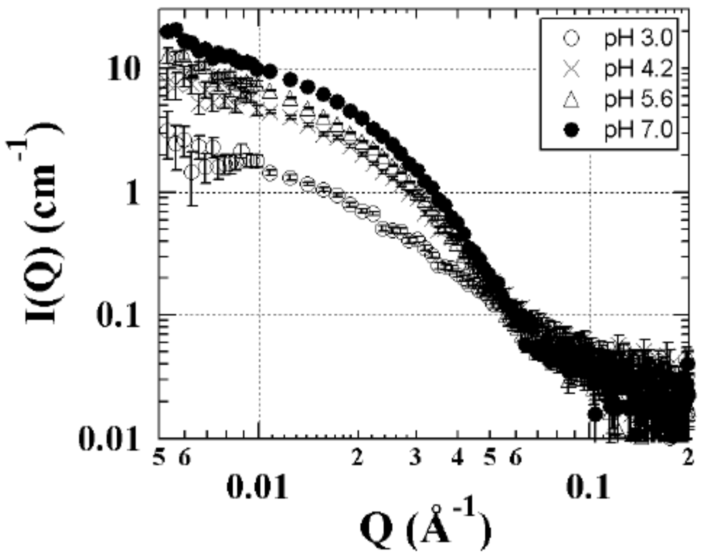
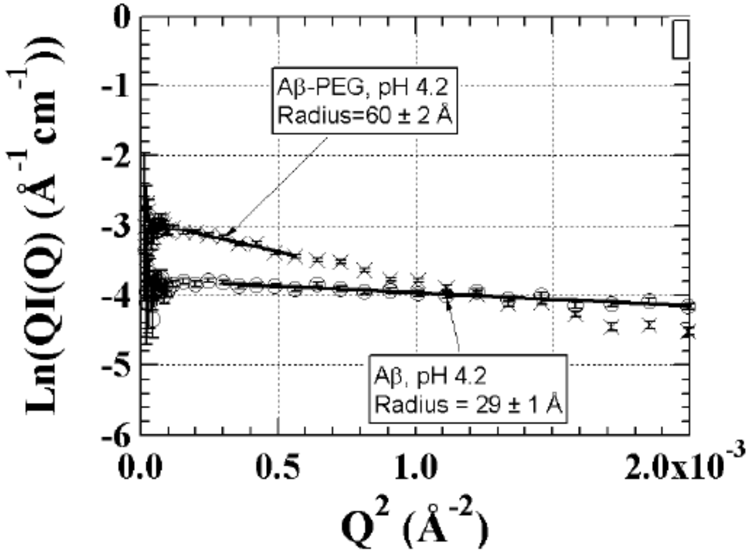
[c]*European Synchrotron Radiation Facility, Grenoble, France*
[d]*Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne 60439, USA*
[e]*Department of Pathology, University of Chicago, Chicago, IL 60637, USA*
Email:thiyaga@anl.gov

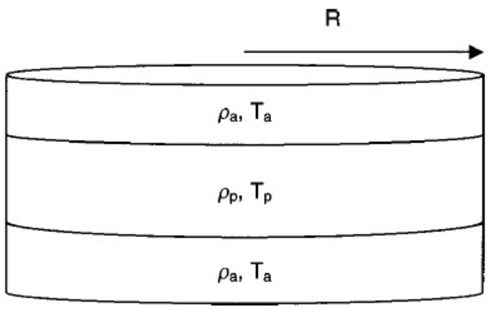


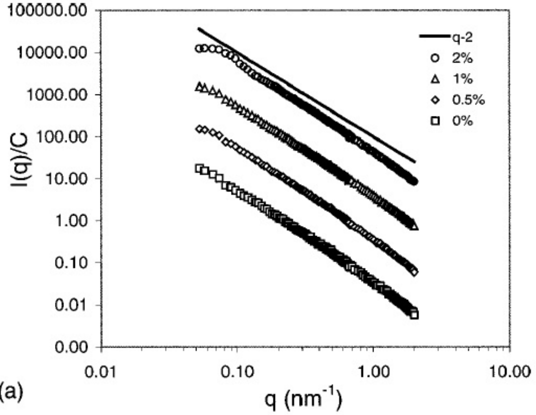


PHYSICAL REVIEW E, VOLUME 64, 021401

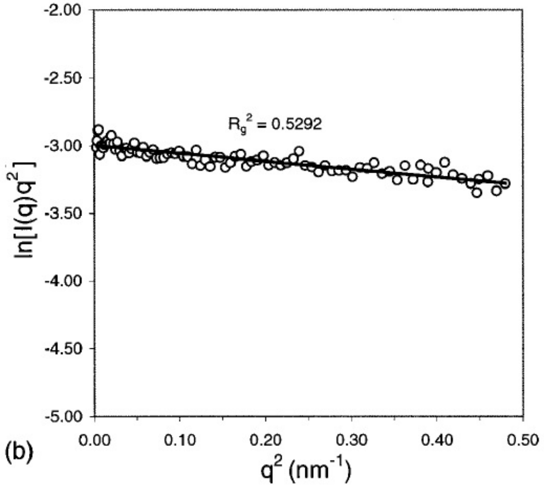
Interpretation of small-angle x-ray scattering data from dilute montmorillonite suspensions using a modified Guinier approximation

C. Shang and J. A. Rice*
Department of Chemistry and Biochemistry, South Dakota State University, Brookings, South Dakota 57007-0896
(Received 17 January 2001; published 18 July 2001)





(a)



(b)

Standard Plots (2) – Porod Plot

At high Q limit: $(QR \gg 1)$

Mass fractal (3D): $I(Q) \propto Q^{-d_f}$

Surface fractal (2D): $I(Q) \propto Q^{d_f - 6}$

$I(Q) \propto Q^{-1} \Rightarrow cylinder$

$I(Q) \propto Q^{-5/3} \Rightarrow polymer\ in\ good\ solvent$

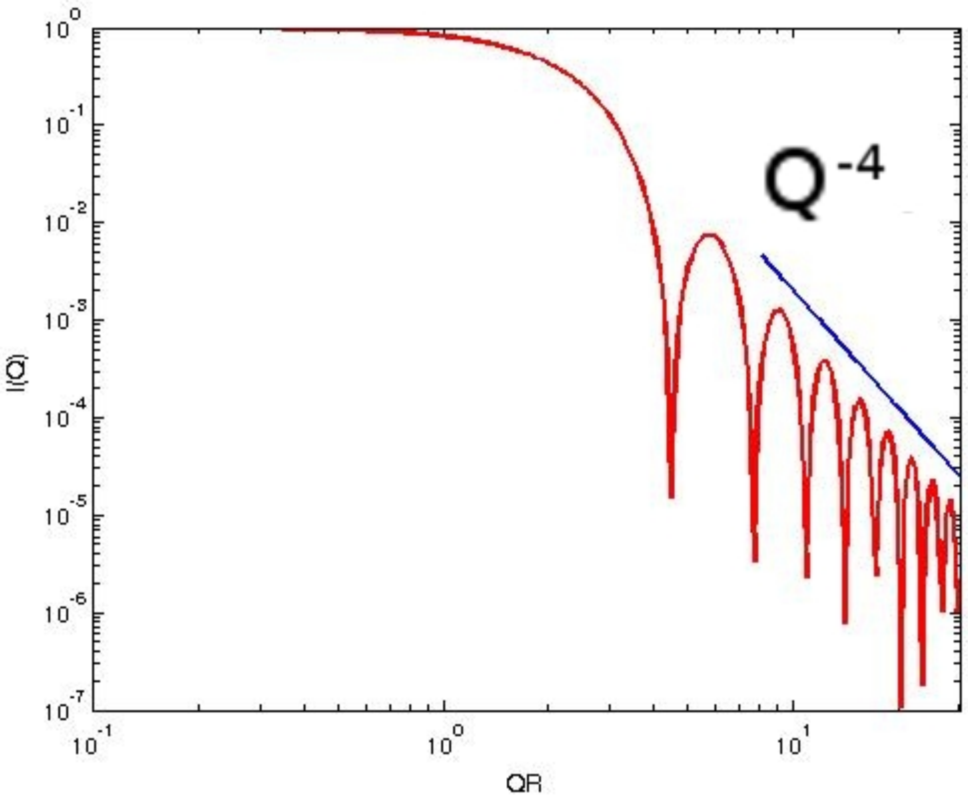
$I(Q) \propto Q^{-2} \Rightarrow polymer\ in\ \theta\text{-}solvent$ $I(Q) \propto Q^{-3} \Rightarrow polymer\ in\ poor\ solvent$

$I(Q) \propto Q^{-2} \Rightarrow disk$

$I(Q) \propto Q^{-2 \sim -3} \Rightarrow mass\ fractal$

$I(Q) \propto Q^{-3 \sim -4} \Rightarrow rough\ interface$

$I(Q) \propto Q^{-4} \Rightarrow perfect\ surface$



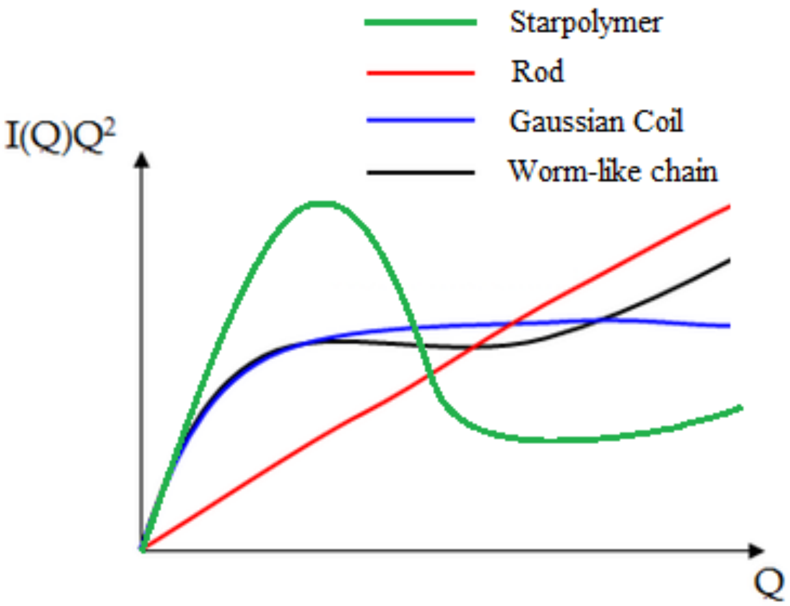
$I(Q) \approx 2\pi A / Q^4$

A: surface area of the spheres

Standard Plots (3) – Kratky Plot

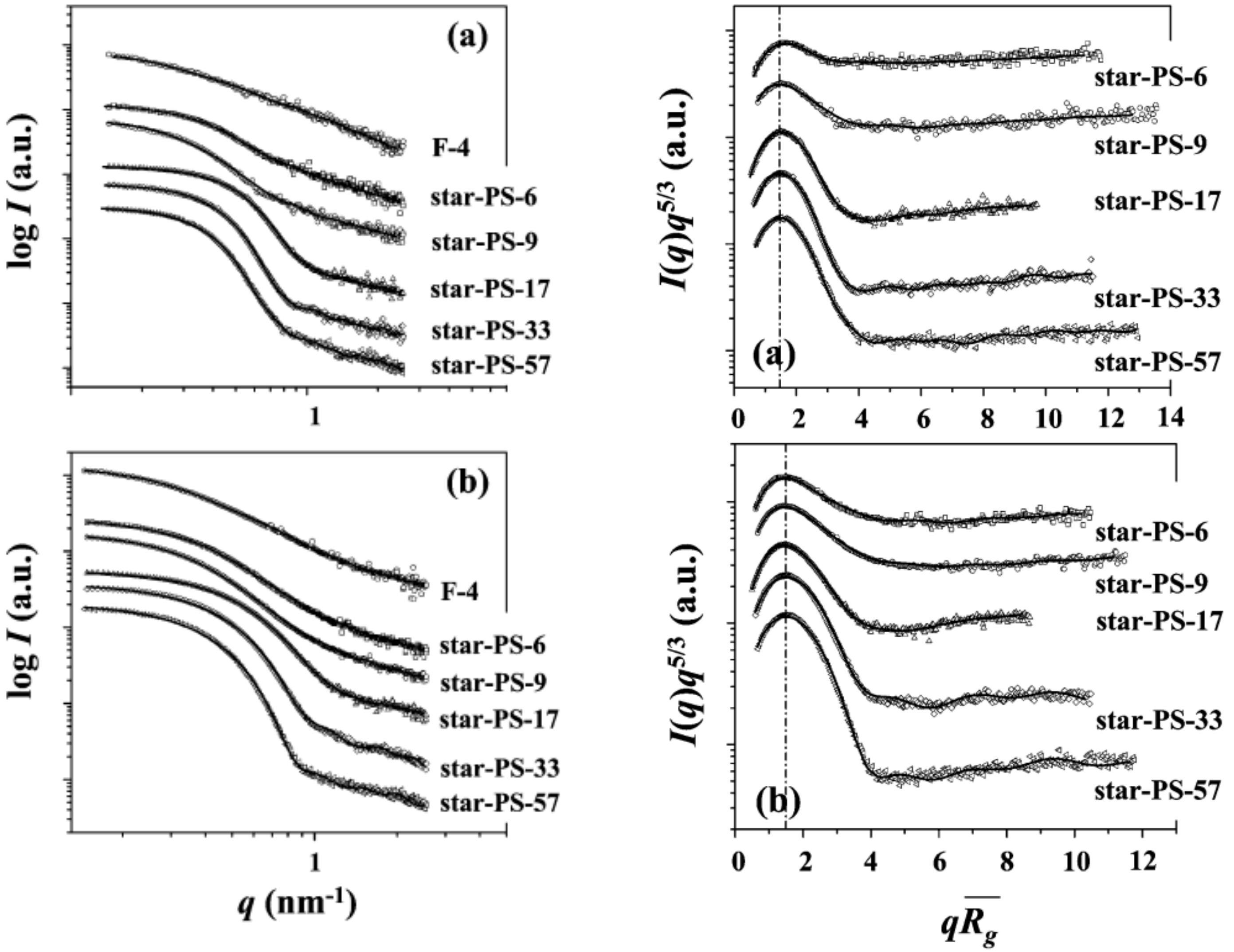
$I(Q)Q^{2}$ vs. Q

- Cylinder
- Linear polymer chain
- Globular structure



Generalized Kratky plot

$I(Q)Q^{d_f}$ vs. Q



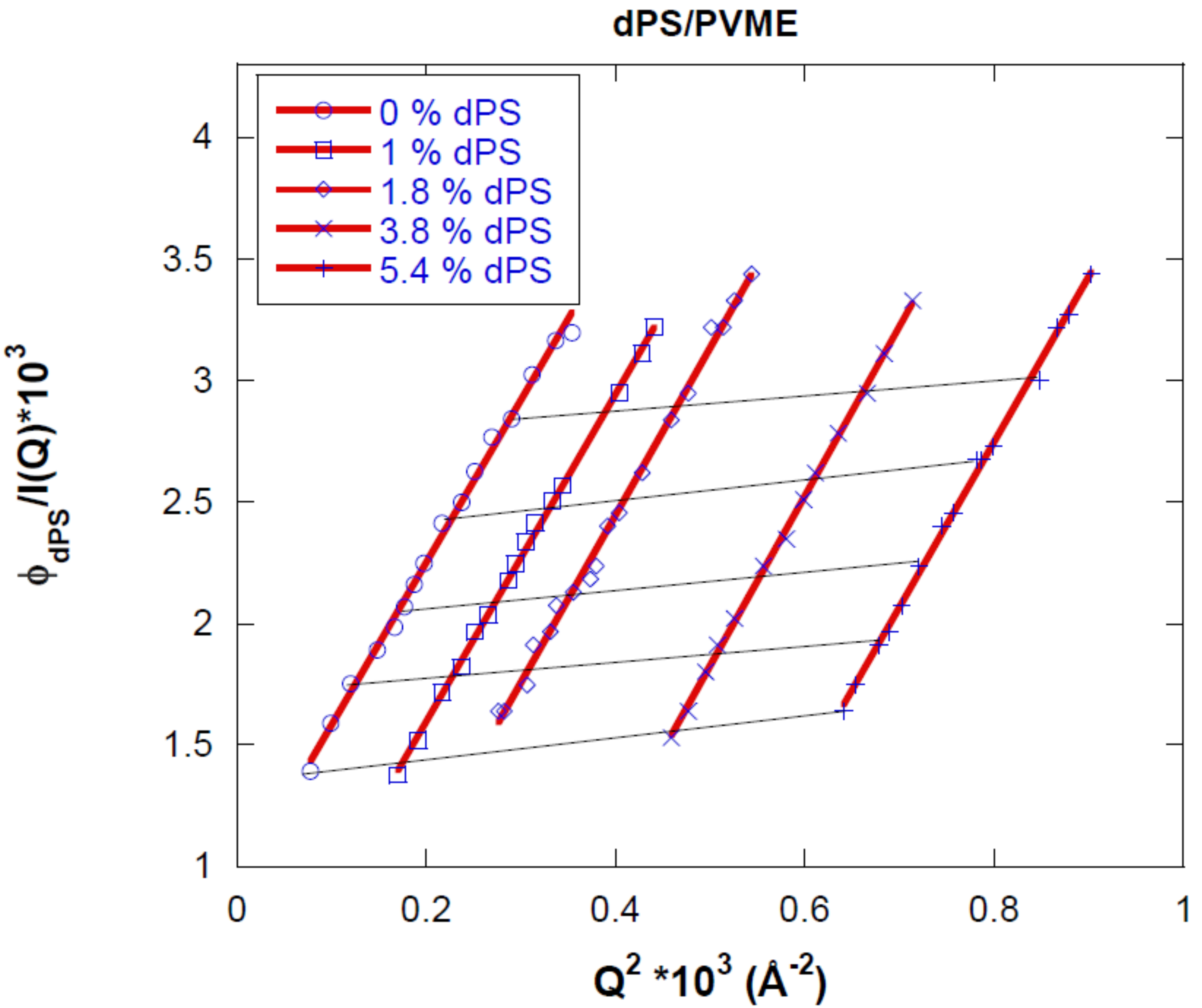
Ree et al., *J. Chem. Phys. B* 2010, 114, 6247-6257

Standard Plots (4) – Zimm Plot

$$1/I(Q) \ \ vs. \ Q^2$$

$$Kc/I(Q) \approx 1/M_w \ (1+Q^2 R_G^2/3) + 2A_2 c$$

- Molecular weight
- Radius of gyration (size)
- Second virial coefficient (interaction)

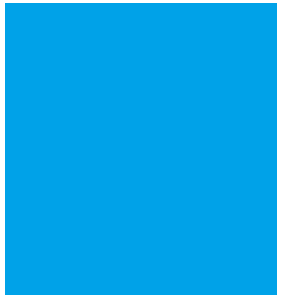


Contrast Variation

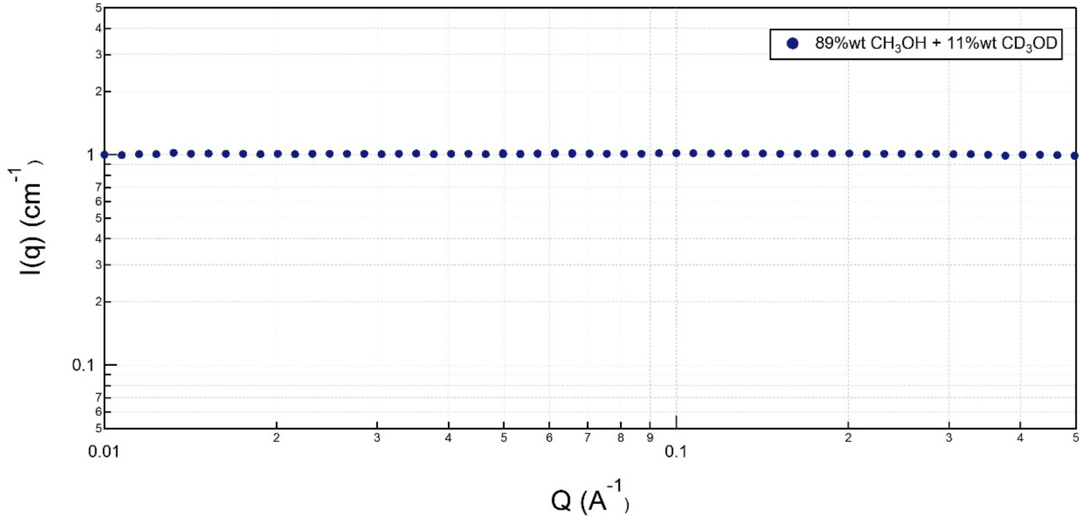
Coherent scattering signal

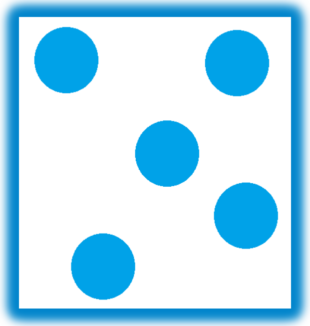
vs.

incoherent scattering background

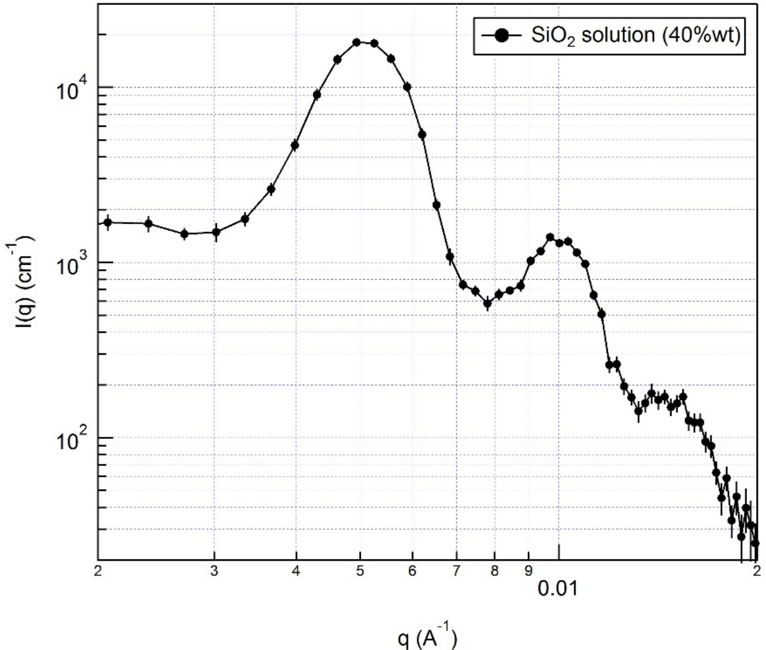


$\rho(r)=\rho\downarrow solvent$

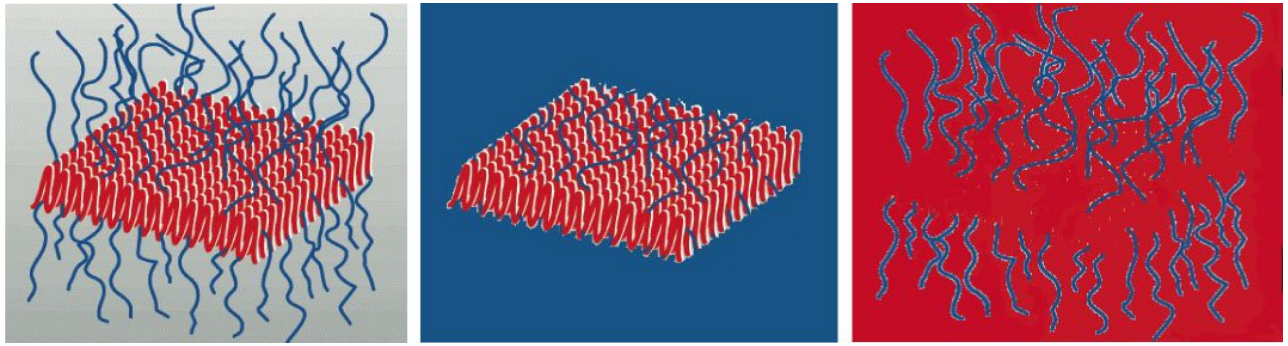


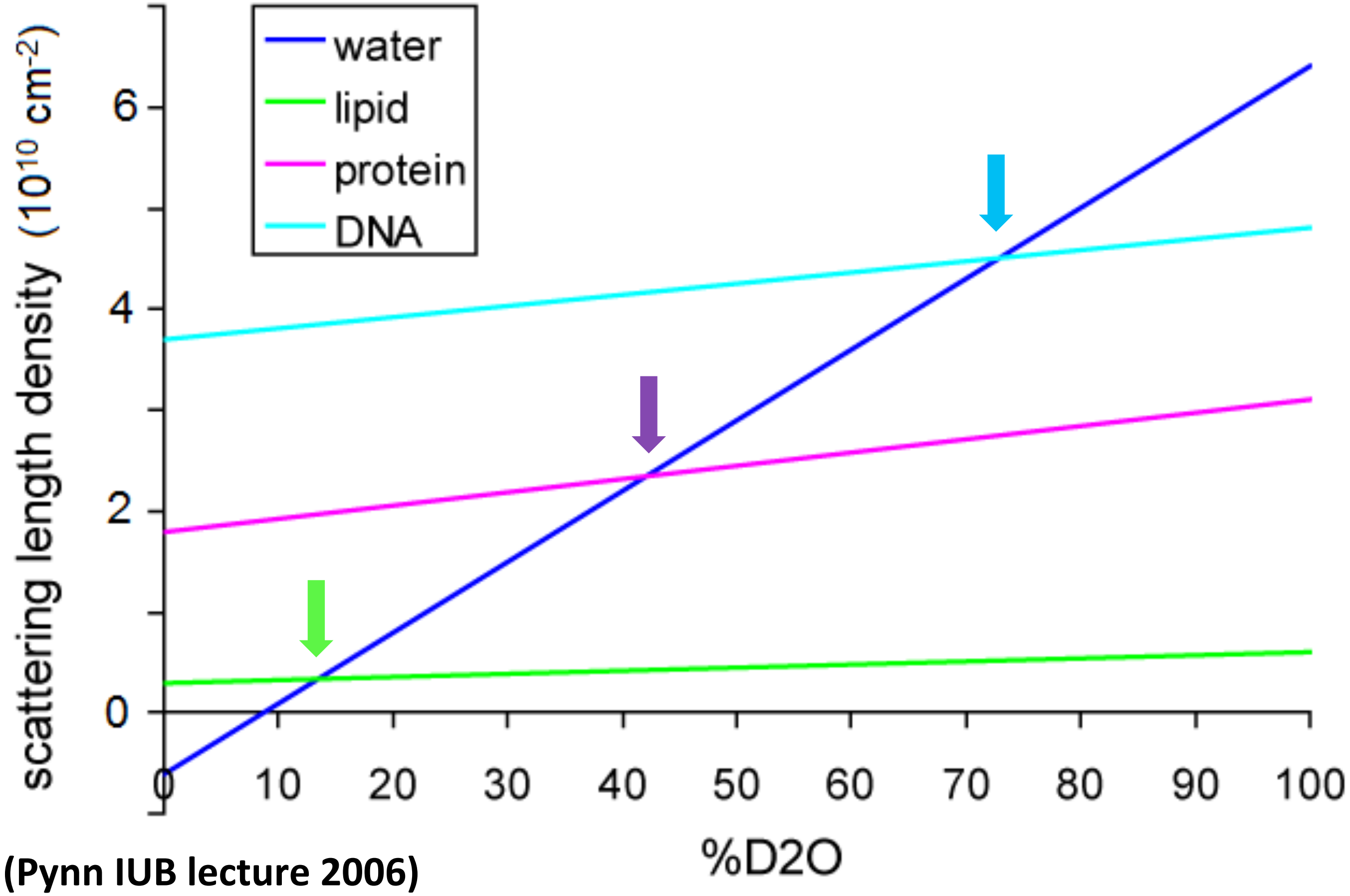


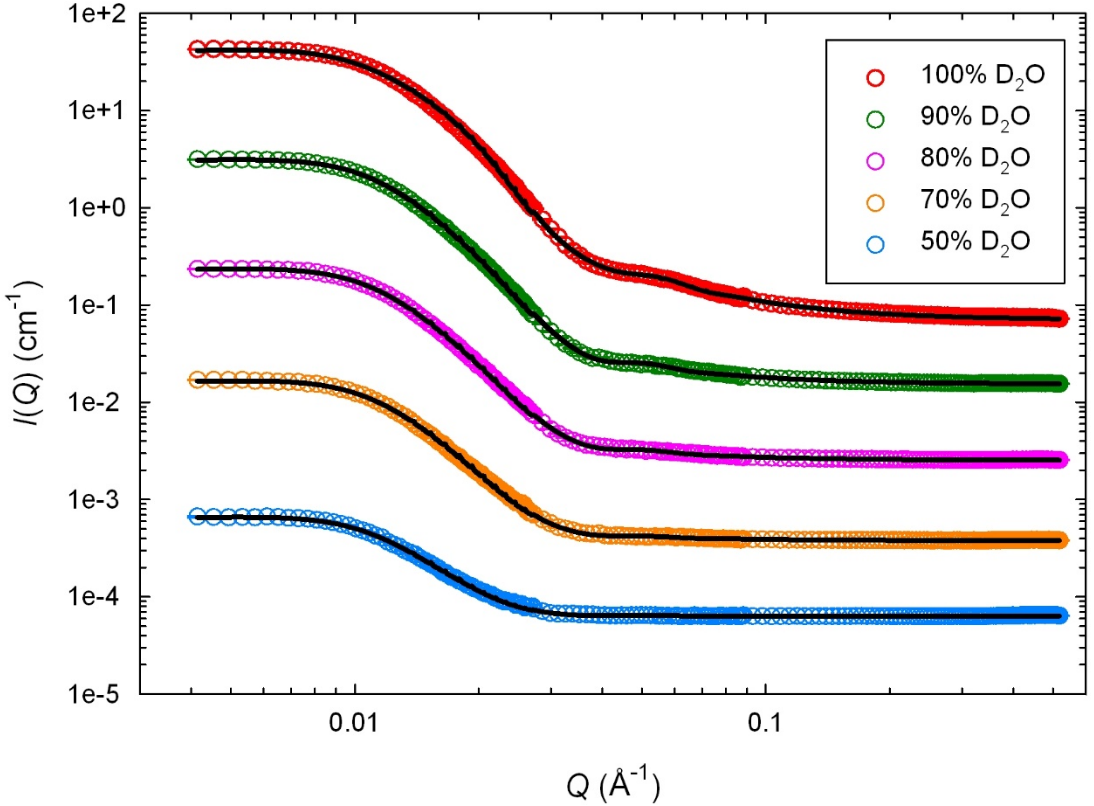
$\rho(r)=■\Delta\rho$ (particle) @0 (solve



Contrast Variation (cont'd)







(Pynn IUB lecture 2006)

Contrast Variation - Example

EUROPHYSICS LETTERS 1 October 1988

Europhys. Lett., 7 (3), pp. 243-248 (1988)

Direct Measurement of Partial Structure Factors in Micellar Solutions by Small-Angle Neutron Scattering.

P.-J. DÉRIAN, L. BELLONI and M. DRIFFORD

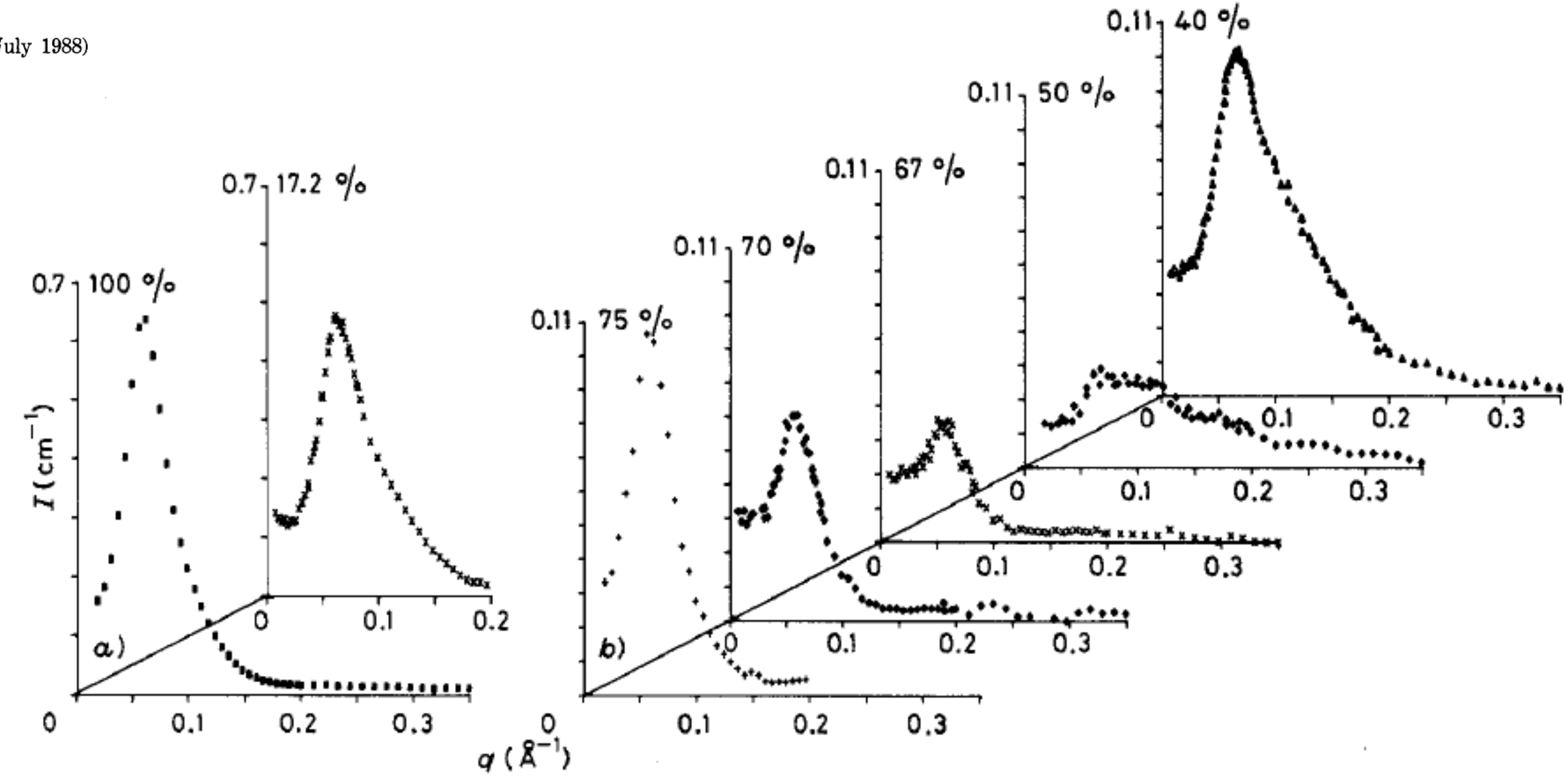
CEA-IRDI-DESICP, Département de Physico-Chimie
CEN-Saclay - 91191 Gif-sur-Yvette Cedex, France

(received 4 February 1988; accepted in final form 21 July 1988)

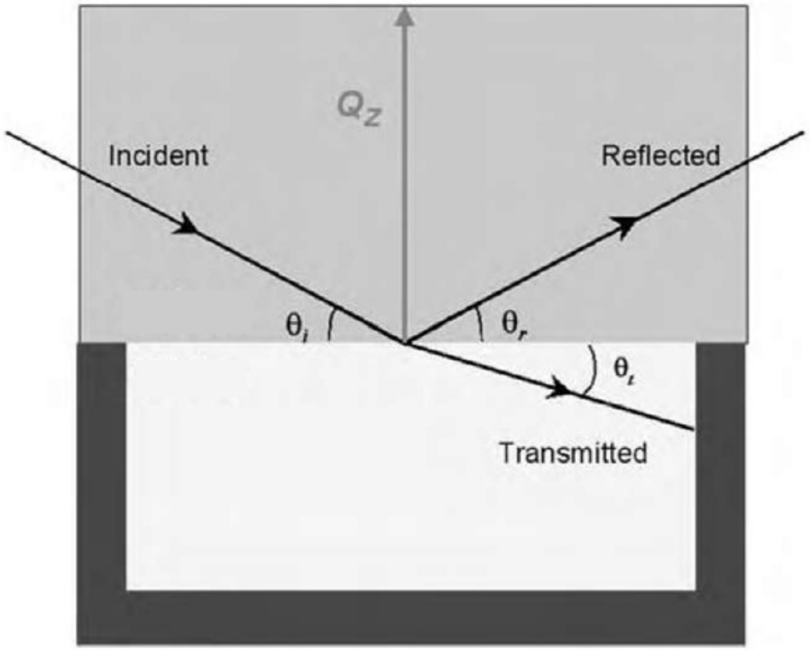
PACS. 61.12 – Neutron determination of structures.
PACS. 82.70 – Disperse systems.
PACS. 65.50 – Thermodynamic properties and entropy.

$$I = \Delta\rho_c^2 I_{cc} + 2\,\Delta\rho_c\,\Delta\rho_p\,I_{pc} + \Delta\rho_p^2 I_{pp}$$

$$I_{ij}(q) = \sqrt{c_i c_j}\,V_i V_j f_i(q)\,S_{ij}(q)$$



Surface Reflection



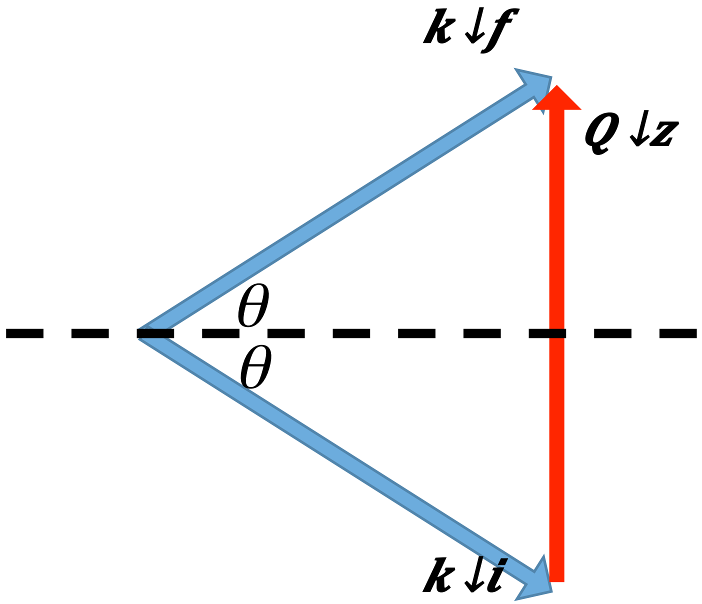
$$\Psi_0 = e^{ik_0 z} + re^{-ik_0 z}$$

$$\Psi_1 = te^{ik_1 z}$$

$$\Psi_0 |_{z=0} = \Psi_1 |_{z=0}$$

$$\partial\Psi_0 / \partial z |_{z=0} = \partial\Psi_1 / \partial z |_{z=0}$$

Scattering triangle



$$Q_z = |Q_z| = 2|k_i| \sin\theta = 4\pi/\lambda \sin\theta$$

Surface Reflection (cont'd)

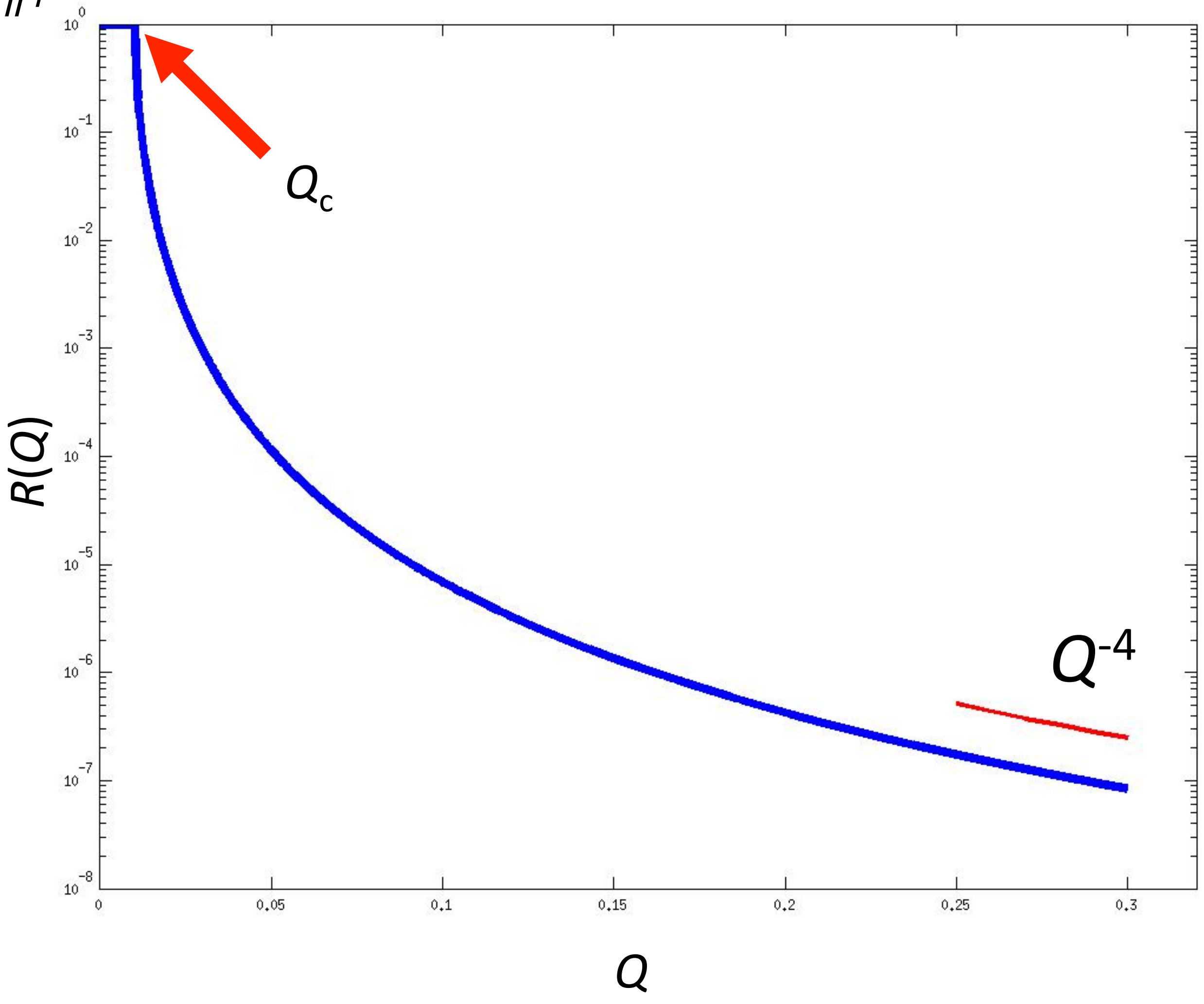
$$R = |r|^2 = \left|\frac{1-\sqrt{1-16\pi\rho/Q_z^2}}{1+\sqrt{1-16\pi\rho/Q_z^2}}\right|^2$$

ρ: scattering length density of the substrate

Critical edge: $Q_c = 4\sqrt{\pi\rho}$

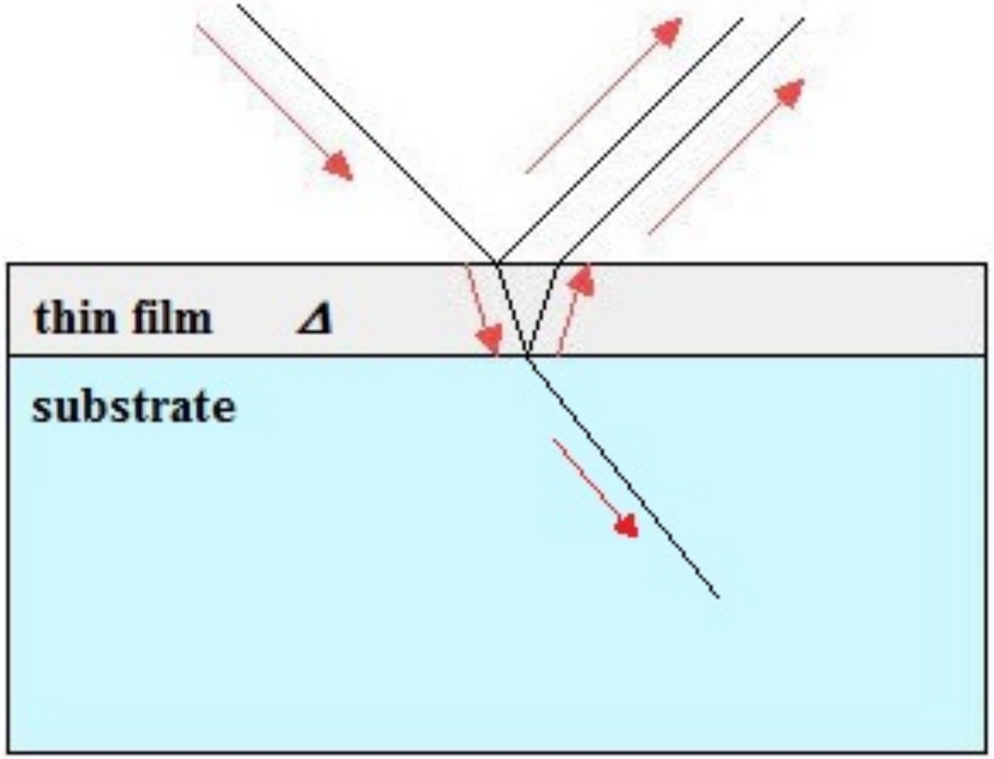
Example: Si substrate

$\rho = 2.07\times10^{-6}$ Å-2, $Q_c = 0.0103$ Å^{-1}



(Fresnel decay)

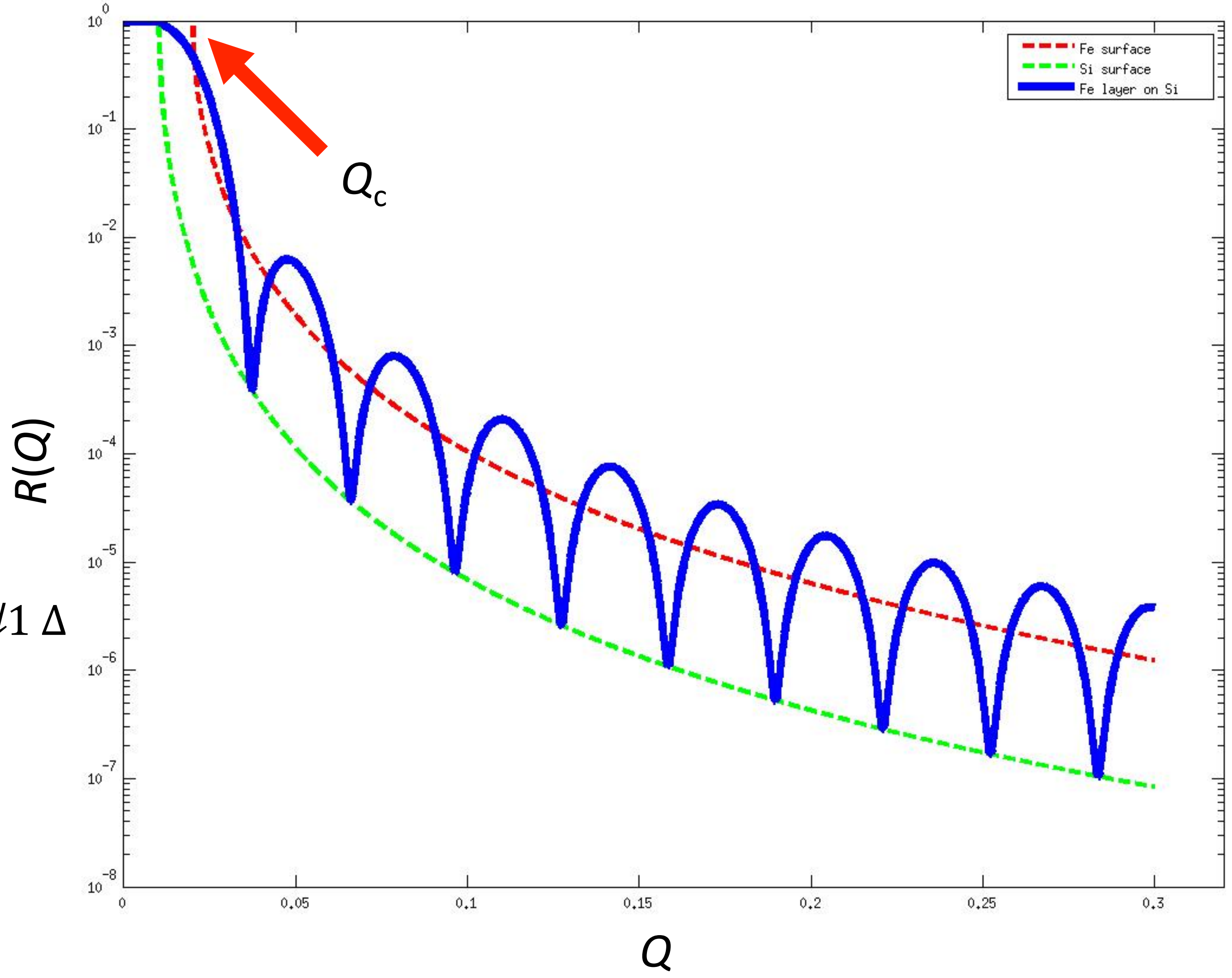
Reflection of Thin Film



$$R=\|r\|^{2}=\left\|\frac{r_{01}+r_{12}e^{i2k_1\Delta}}{1+r_{01}r_{12}e^{i2k_1\Delta}}\right\|$$

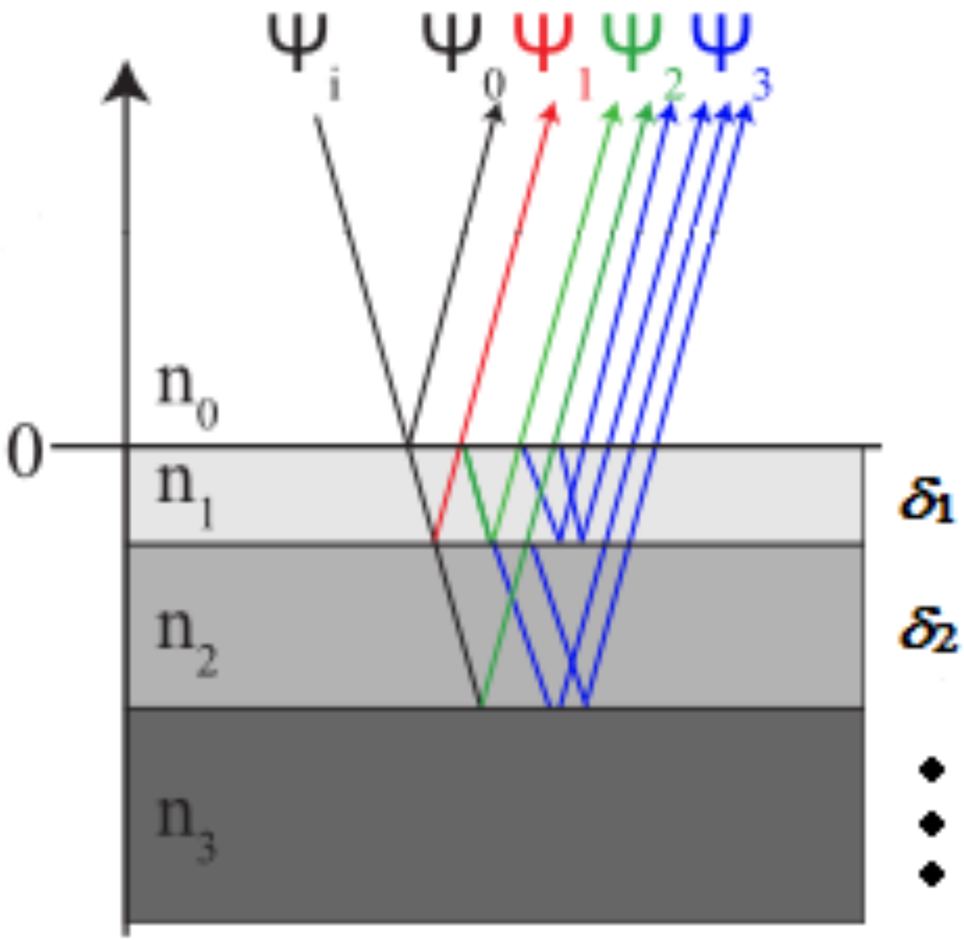
r_{01}, r_{12}: functions of the scattering length densities of the film and substrate

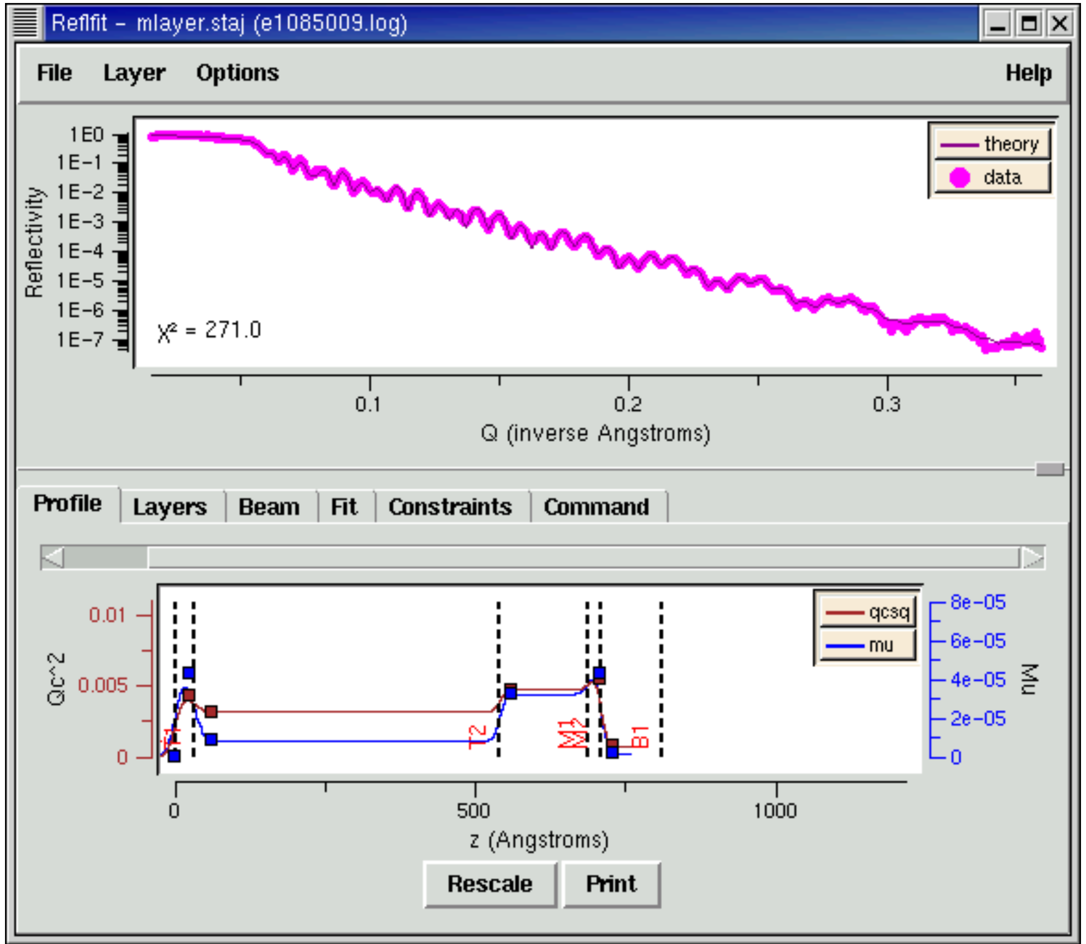
Oscillation period $=2\pi/\Delta$



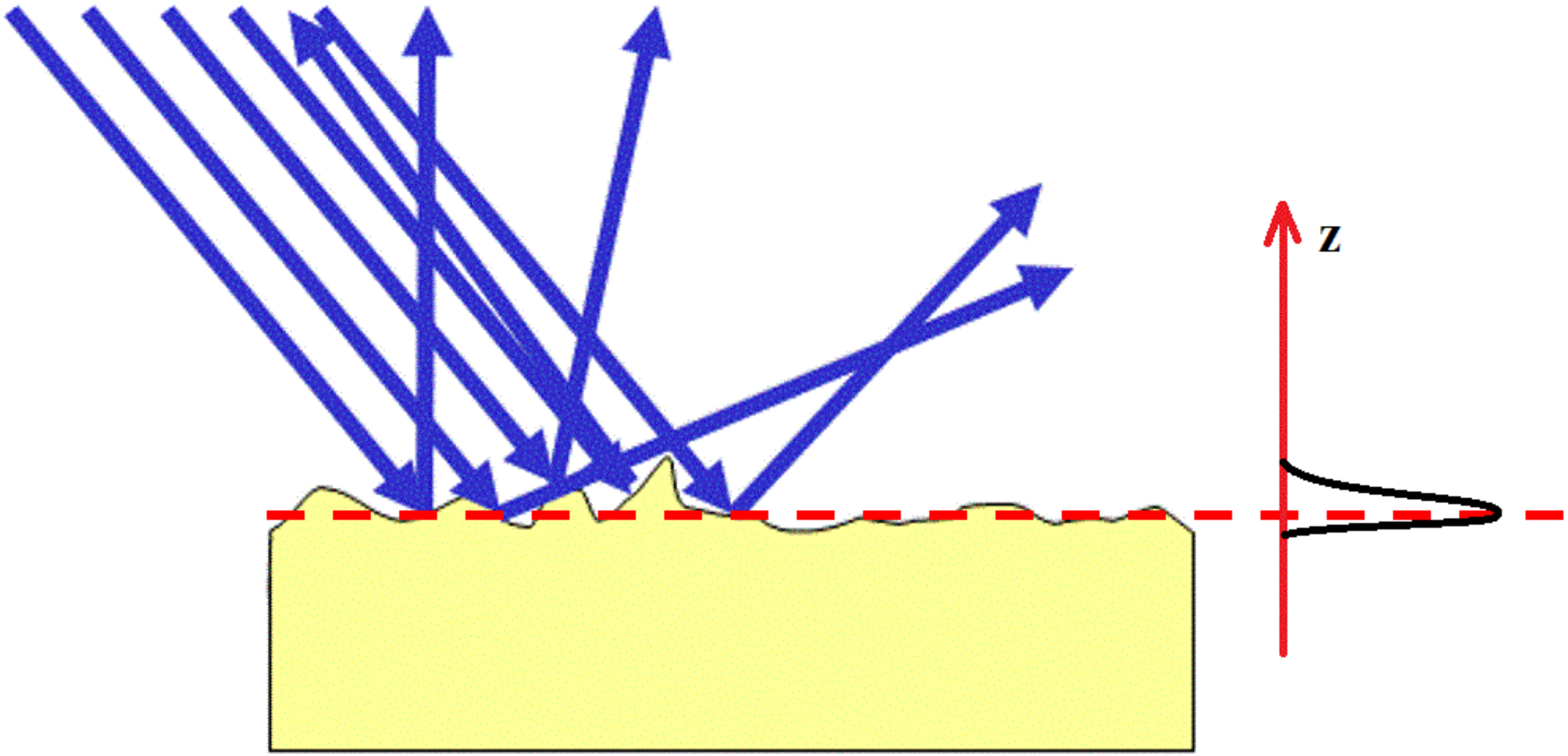
Reflection of Thin Film (cont'd)

$$\prod_{j=n-1}^{0} \begin{pmatrix} \cos(k_j \delta_j) & \frac{1}{k_j}\sin(k_j \delta_j) \\ k_j \sin(k_j \delta_j) & \cos(k_j \delta_j) \end{pmatrix} \begin{pmatrix} 1+r \\ ik_0 (1-r) \end{pmatrix} = \begin{pmatrix} t \\ ik \end{pmatrix}$$





Effect of Surface Roughness



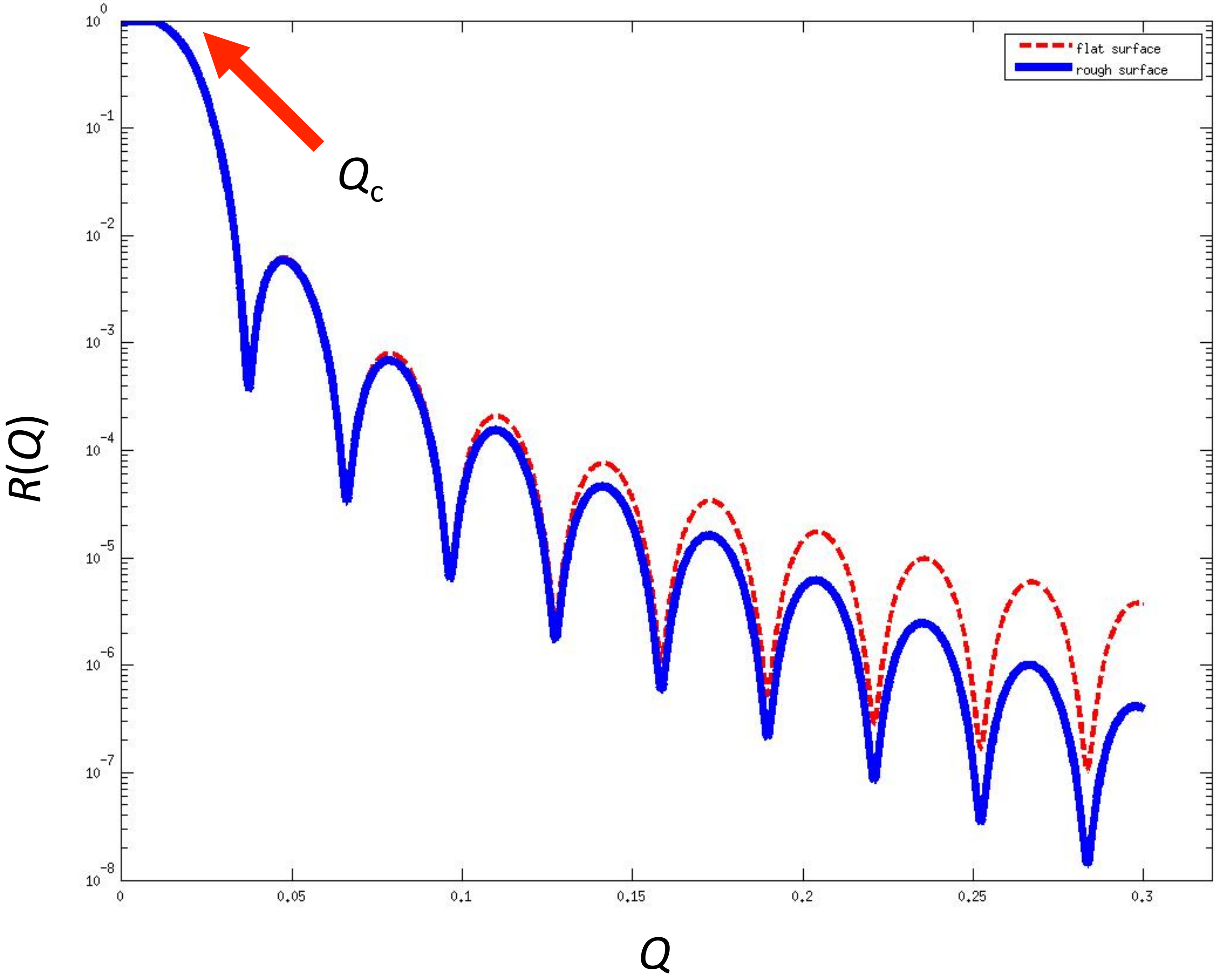
Method 1: treat as multiple discrete steps and solve the reflection numerically

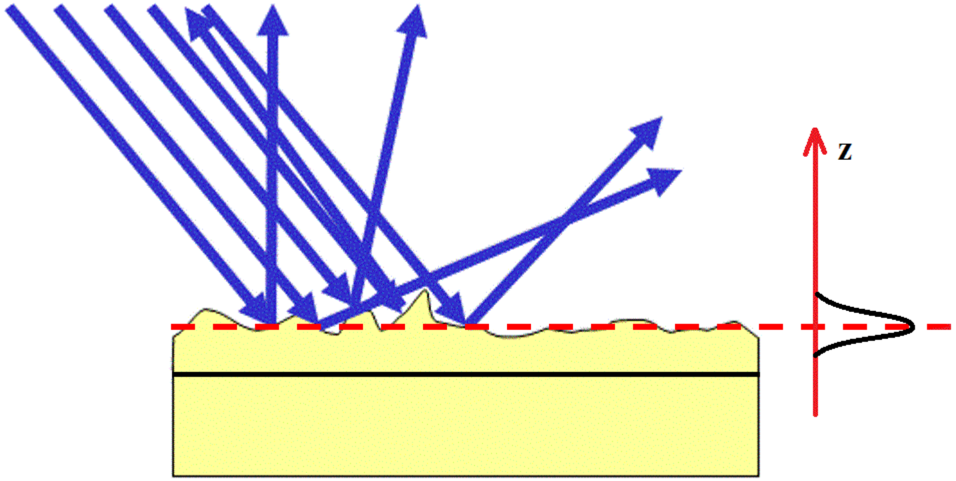
Method 2: assume the roughness as a Gaussian distribution $\mathcal{N}(0,\sigma)$

$$R = R_{flat}\, e^{-Q_{\perp} Q_{\perp}^{t} \sigma^{2}} \approx R_{flat}\, e^{-Q_{\perp}^{2} \sigma^{2}}$$

Effect of Surface Roughness (cont'd)

$$R = R_{flat}\, e^{-Q_\perp Q_\perp^t \sigma^2} \approx R_{flat}\, e^{-Q_\perp^2 \sigma^2}$$





Example: Thin Film with Deuterated Layers

Langmuir
Article
pubs.acs.org/Langmuir

Spin-Assisted Layer-by-Layer Assembly: Variation of Stratification as Studied with Neutron Reflectivity[†]

Eugenia Kharlampieva,[‡] Veronika Kozlovskaya,[‡] Jennifer Chan,[‡] John F. Ankner,[§] and Vladimir V. Tsukruk*,[‡]

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