N-8 Neutron Reflectometry

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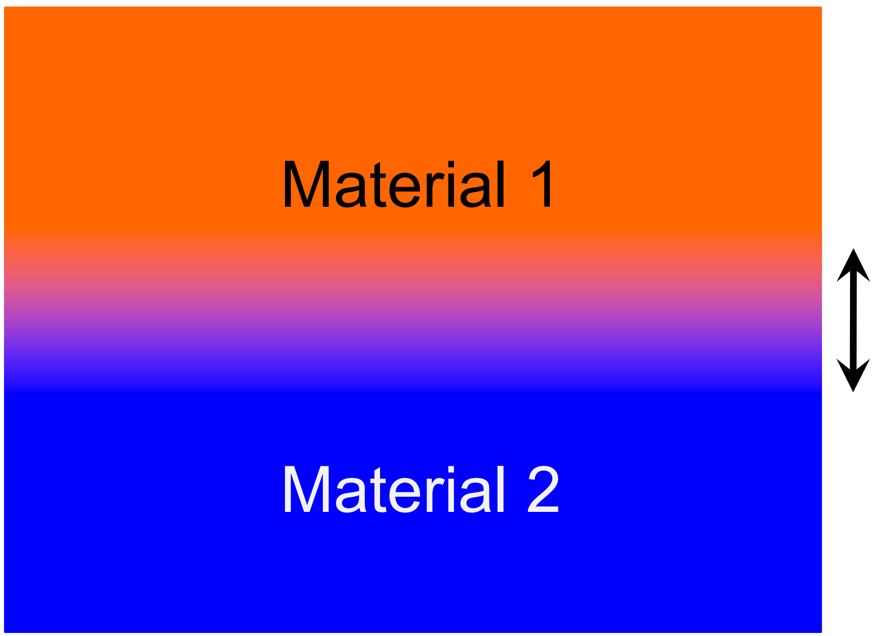
Contents

Material interface (surface)

Material 1/Material 2
solid/solid
gas/solid
liquid/solid
gas/liquid
liquid/liquid



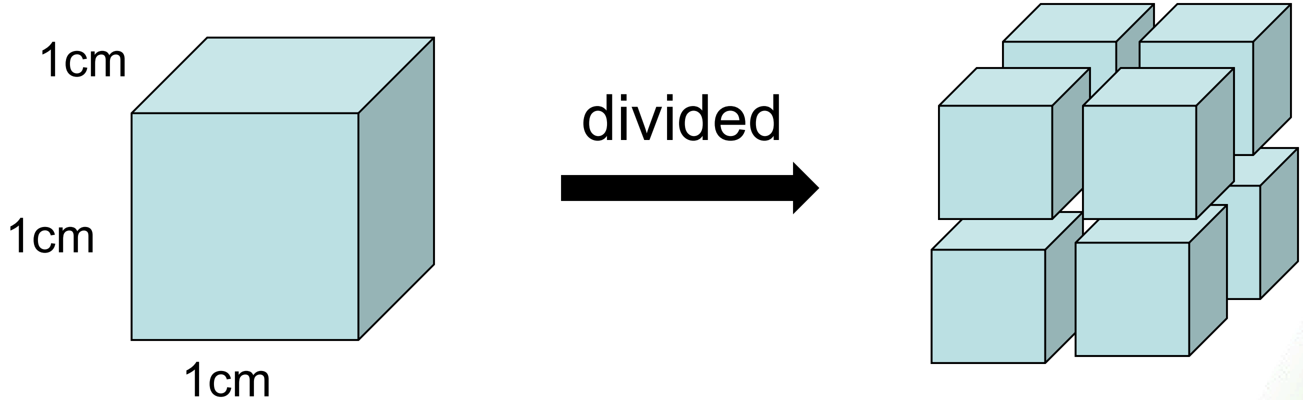
thickness:
a few Å ~ a few nm

extremely-thin boundary region between materials

appearance of peculiar properties
because different materials contact in a very narrow space

Nanometer space

a cubic (1cm each side) eight cibics (0.5cm each side)



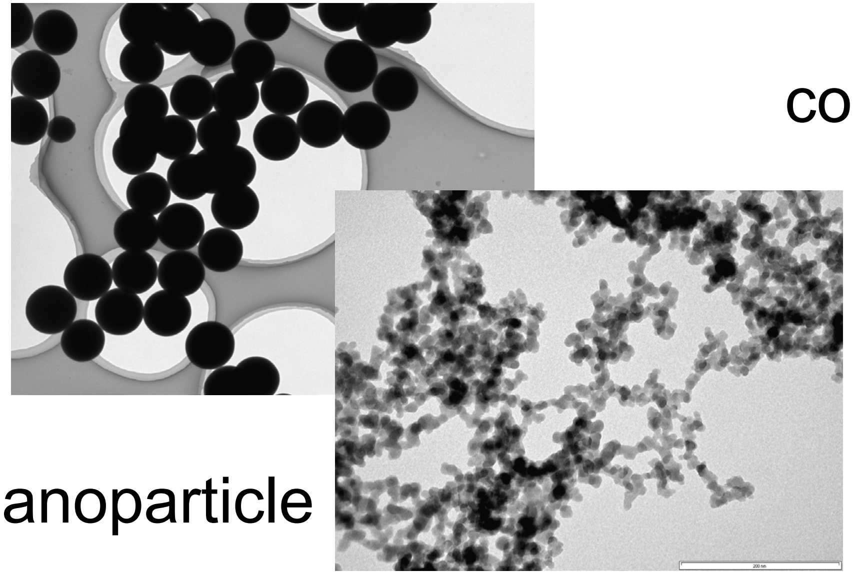
surface area= [ ] cm^2 [ ] cm^2

divided into tiny cubics (1μm each side)
surface area= [ ] cm^2

further 1nm each side？ [ ] cm^2 (= [ ] m^2)

"Colloid Size"

Requirement for material development



nanoparticle

composite material

combination of different materials

polymer nanocomposite

Interface between
and matrix polymer

thin film material

monomolecular, a few 100nm thickness

adhesion, paint, coating, ...

Interface between material and

control of interface

important for material development

Difficulties in structural observation of interface

Interface

the volume occupied by interface is extremely small
interfacial thickness ~a few nm at most
weak signal from interface

deeply-buried inside materials
liquid, non-transparent material, special environment
(high pressure, humidity, etc.)

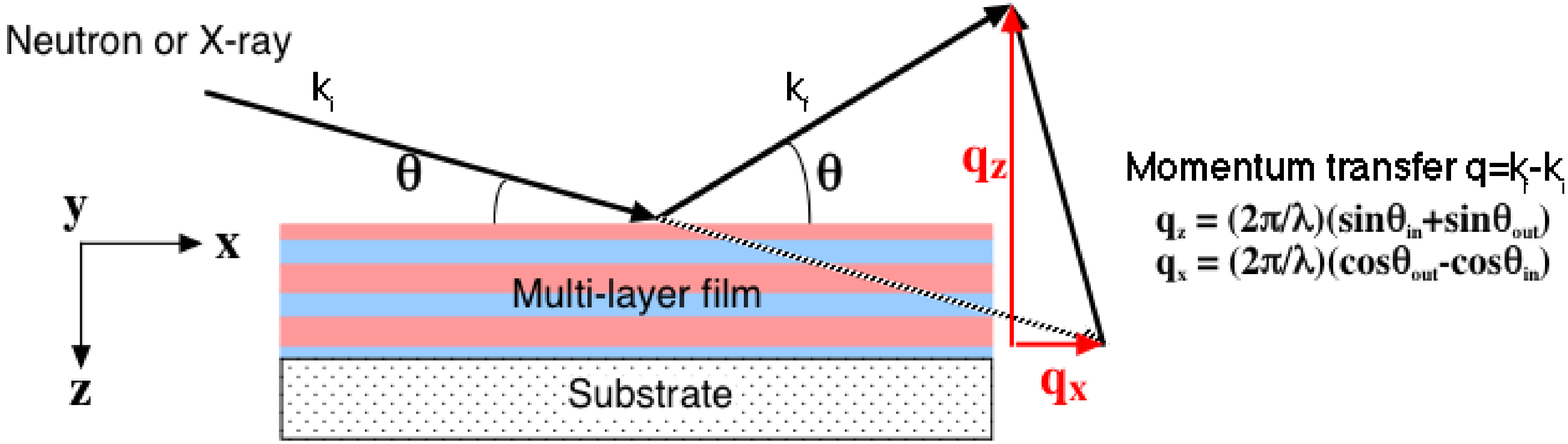
Contents

Reflectivity measurement

Essential for studies on material interfaces and thin films

High ▭ resolution with a sub-*nm* scale

Deeply-buried interfaces, Free interface, Non-destructive, Density fluctuations, Temporal structural changes



Specular reflection : ▭

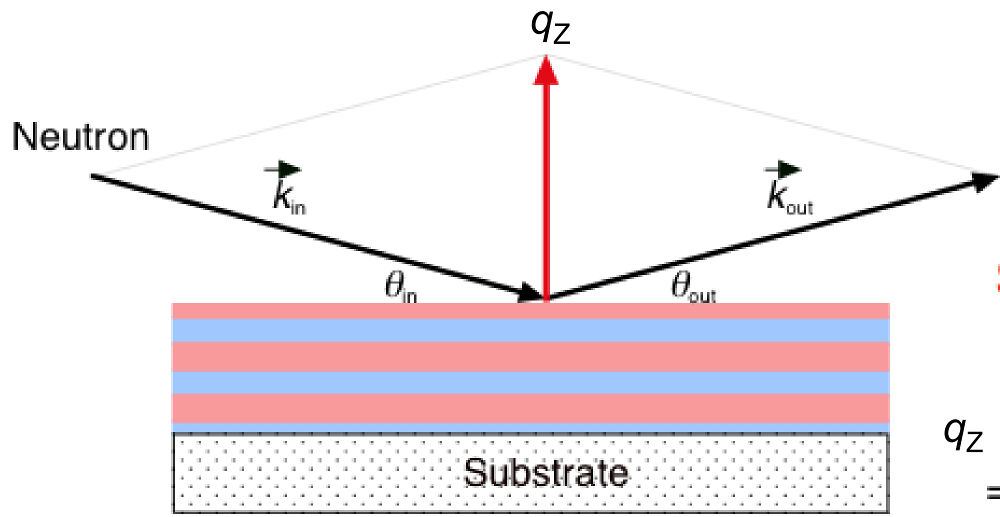
○Averaging structures in the x-y plane

○Sensitive for structural changes along the z-direction

Off-specular reflection : $\theta_{in} \neq \theta_{out}$

○Sensitive for structures in the x-y plane

Specular reflectivity measurement



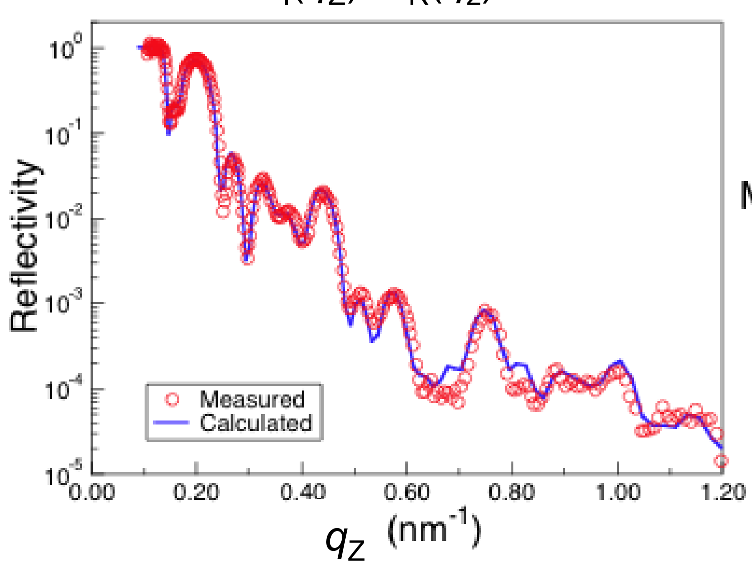
Elastic scattering

Specular reflection

$$\theta_{in} = \theta_{out} \equiv \theta$$

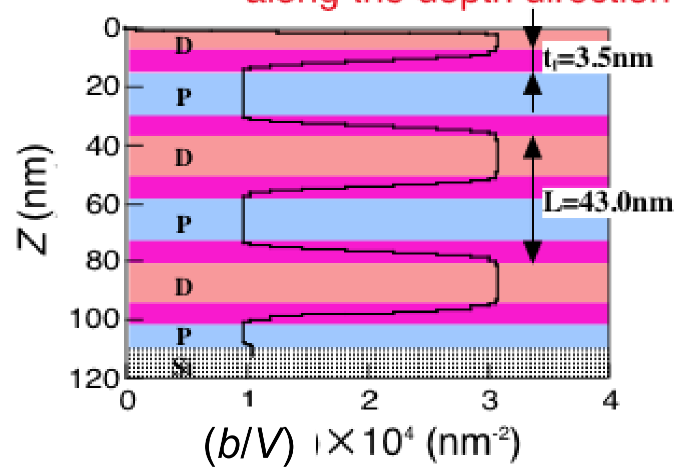
$$q_Z = |\vec{k}_{out} - \vec{k}_{in}| = (2\pi/\lambda)(\sin\theta_{in} + \sin\theta_{out})$$
$$= (4\pi/\lambda)\sin\theta$$

$R = I_I(q_Z) / I_R(q_z)$



Model fitting

Precise density profile
along the depth direction



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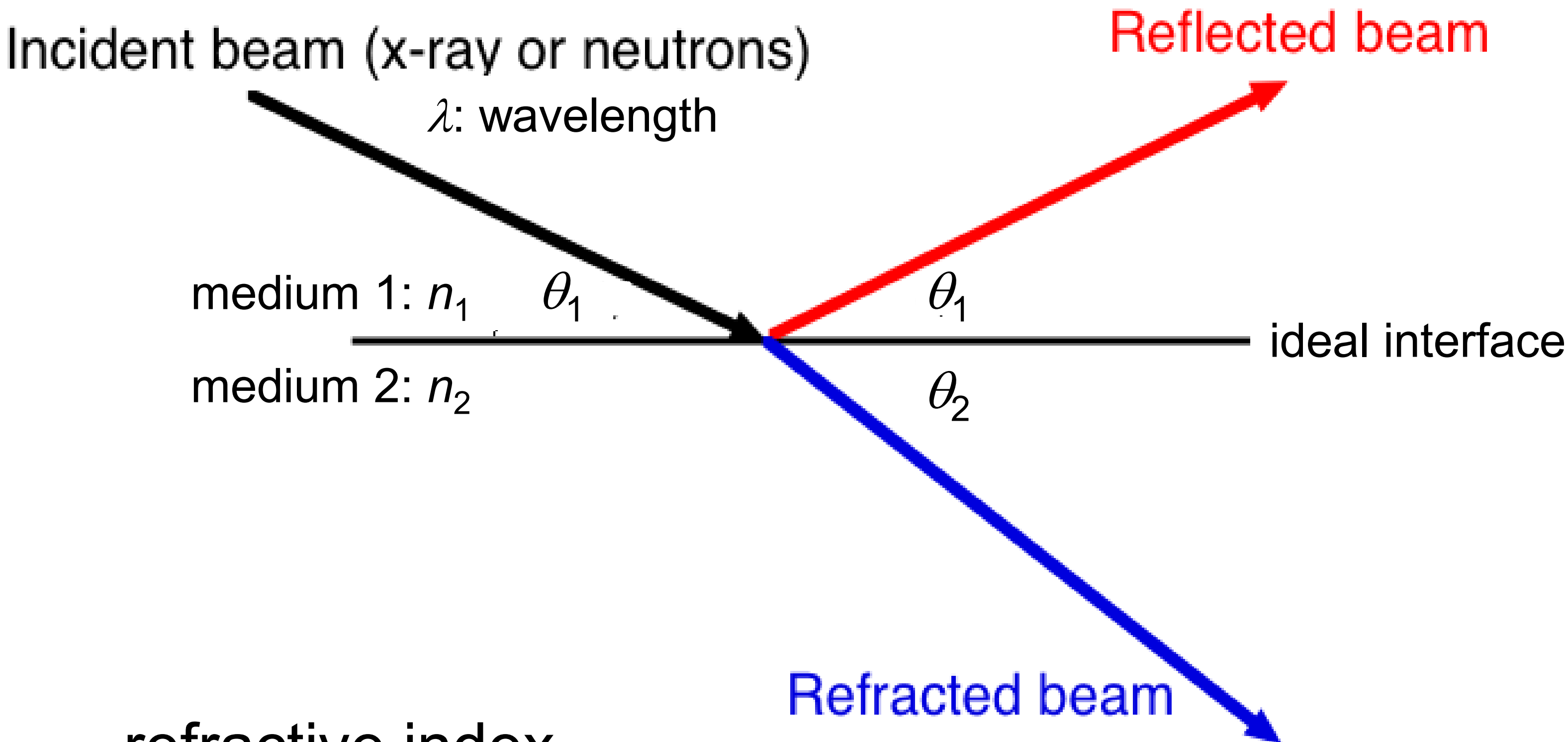
Reflection



refractive index

$$n = 1-(\lambda^2/2\pi)r_0\rho_{e,i}+i(\mu_i\lambda/4\pi) \quad \text{for X-ray}$$
$$= 1-(\lambda^2/2\pi)n_i\{b_i \pm p_i+i(\sigma_{a,i}/4\pi)^{1/2}\} \text{ for neutron}$$

$\rho_{e,i}$: electron number density
b_i: coherent scattering length
p_i: magnetic scattering length

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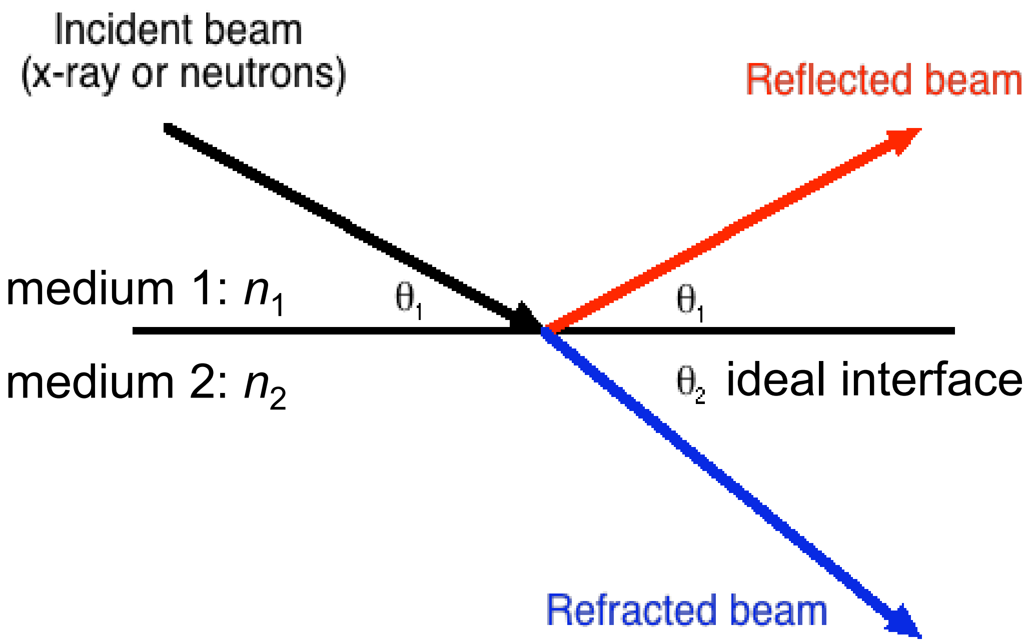


$n_1\cos\theta_1 = n_2\cos\theta_2$

medium 1: air (n_1=1)

$$\cos\theta_2 = \cos\theta_1/n_2$$

1) $\cos\theta_1 > n_2\cos\theta_2 > 1$

2) $\cos\theta_1 = n_2$

critical angle for total reflection

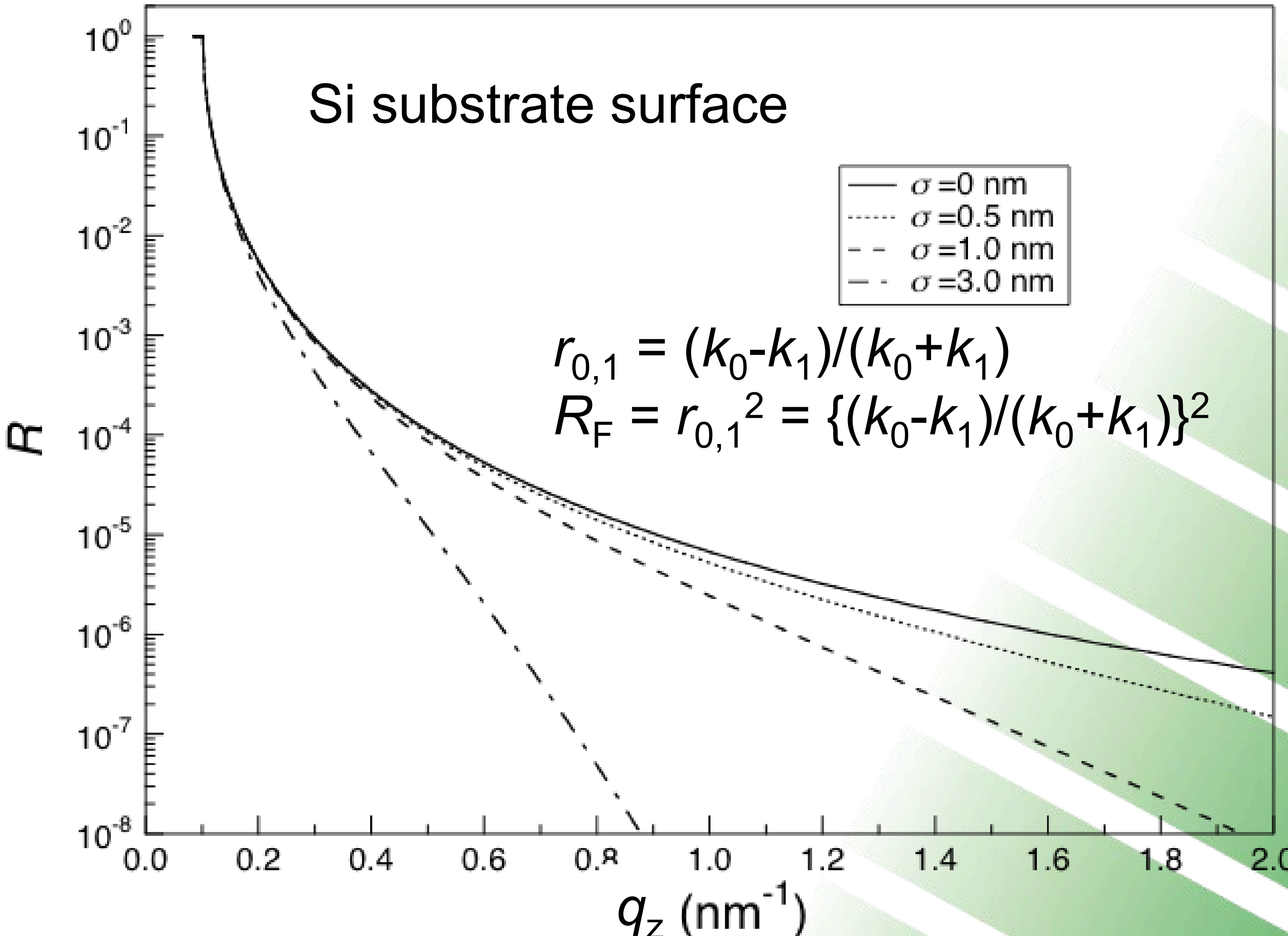
$\theta_c=\{2(1-n_2)\}^{1/2}$

X-ray: $\theta_c=\lambda(\rho_e r_0/\pi)^{1/2}$

neutron: $\theta_c=\lambda\{(b/V)/\pi\}^{1/2}$

3) $\cos\theta_1 < n_2\cos\theta_2 < 1$

Reflection from a single interface



$r_{0,1} = (k_0 - k_1)/(k_0 + k_1)$

$R_F = r_{0,1}^2 = \{(k_0 - k_1)/(k_0 + k_1)\}^2$

$R(q_z) = R_F(q_z)\exp(-q_z^2\sigma^2)$

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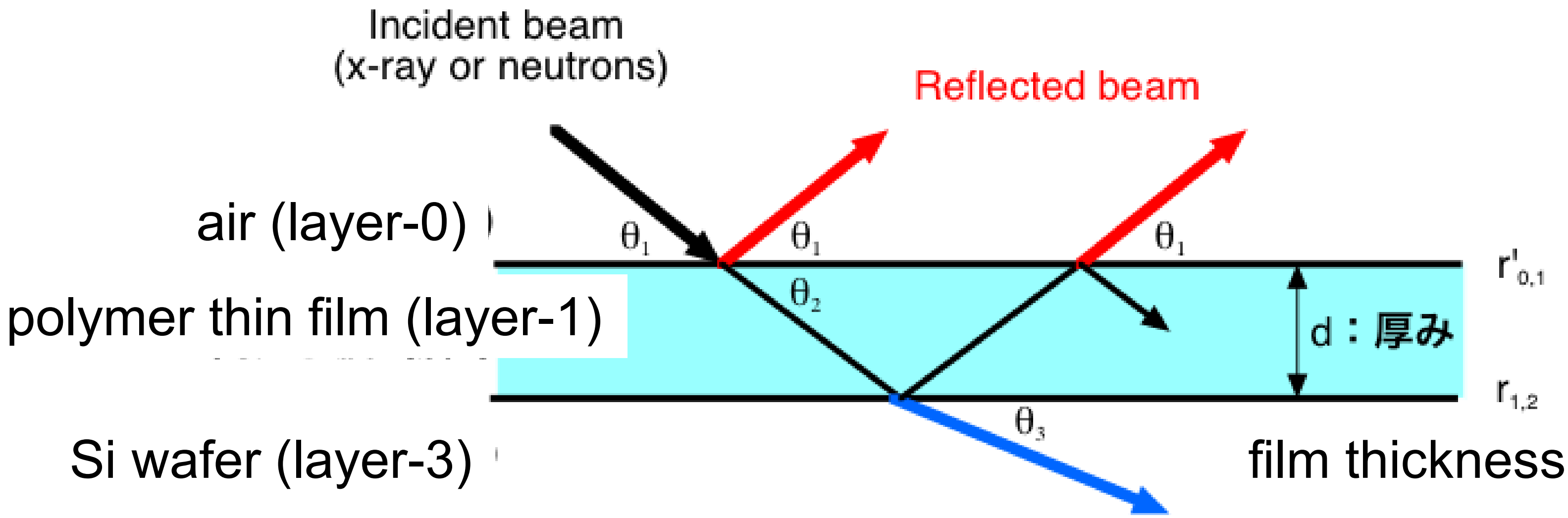
Reflection from a monolayer on a substrate



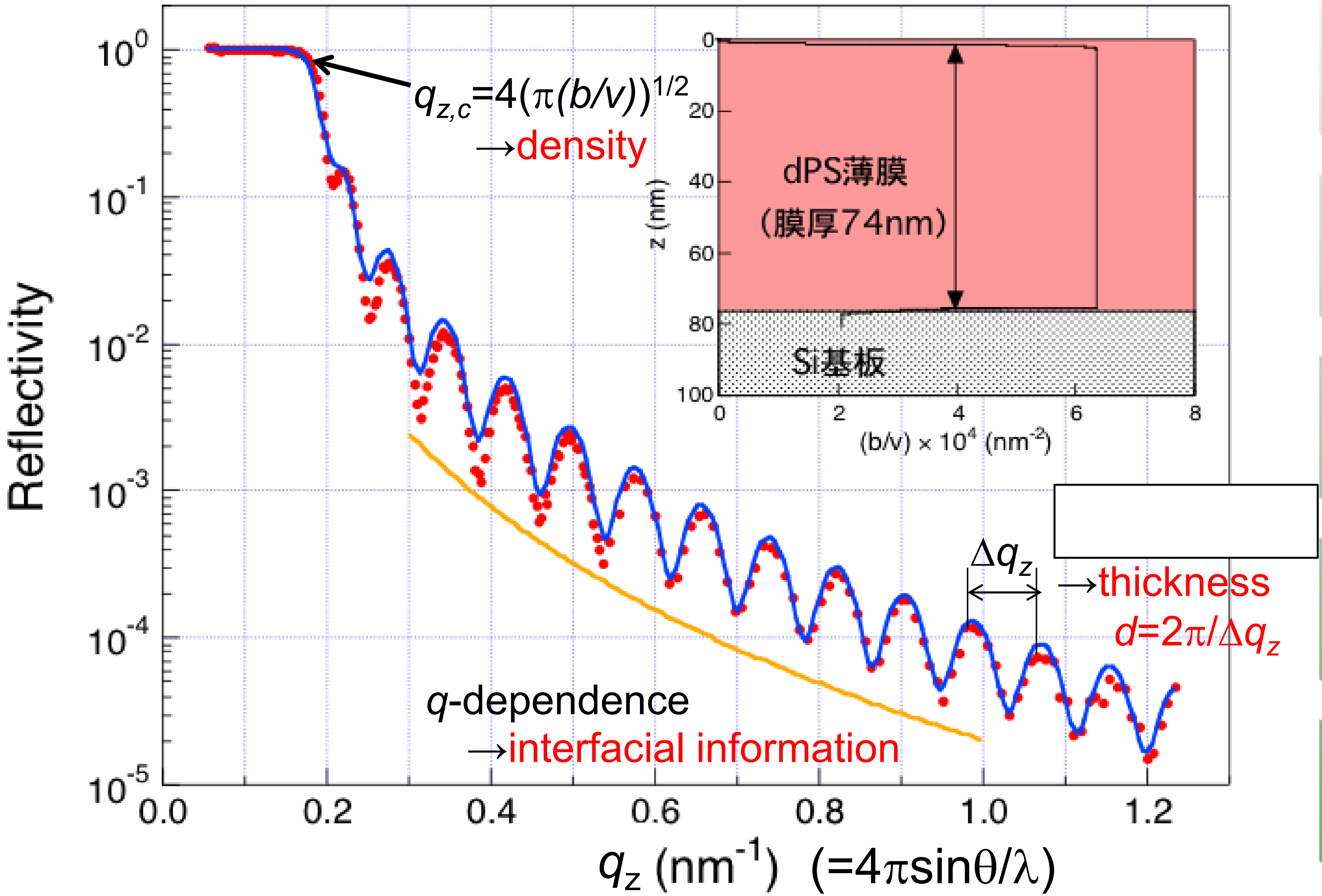
reflection coefficient $r'_{0,1} = \dfrac{r_{0,1} + r_{1,2}\exp(iq_{z,1}d)}{1 + r_{0,1}r_{1,2}\exp(iq_{z,1}d)}$

reflectivity $R = r'_{0,1}\, r'^{*}_{0,1} = \dfrac{r_{0,1}^{2} + r_{1,2}^{2} + 2r_{0,1}r_{1,2}\cos(q_{z,1}d)}{1 + r_{0,1}^{2}r_{1,2}^{2} + 2r_{0,1}r_{1,2}\cos(q_{z,1}d)}$

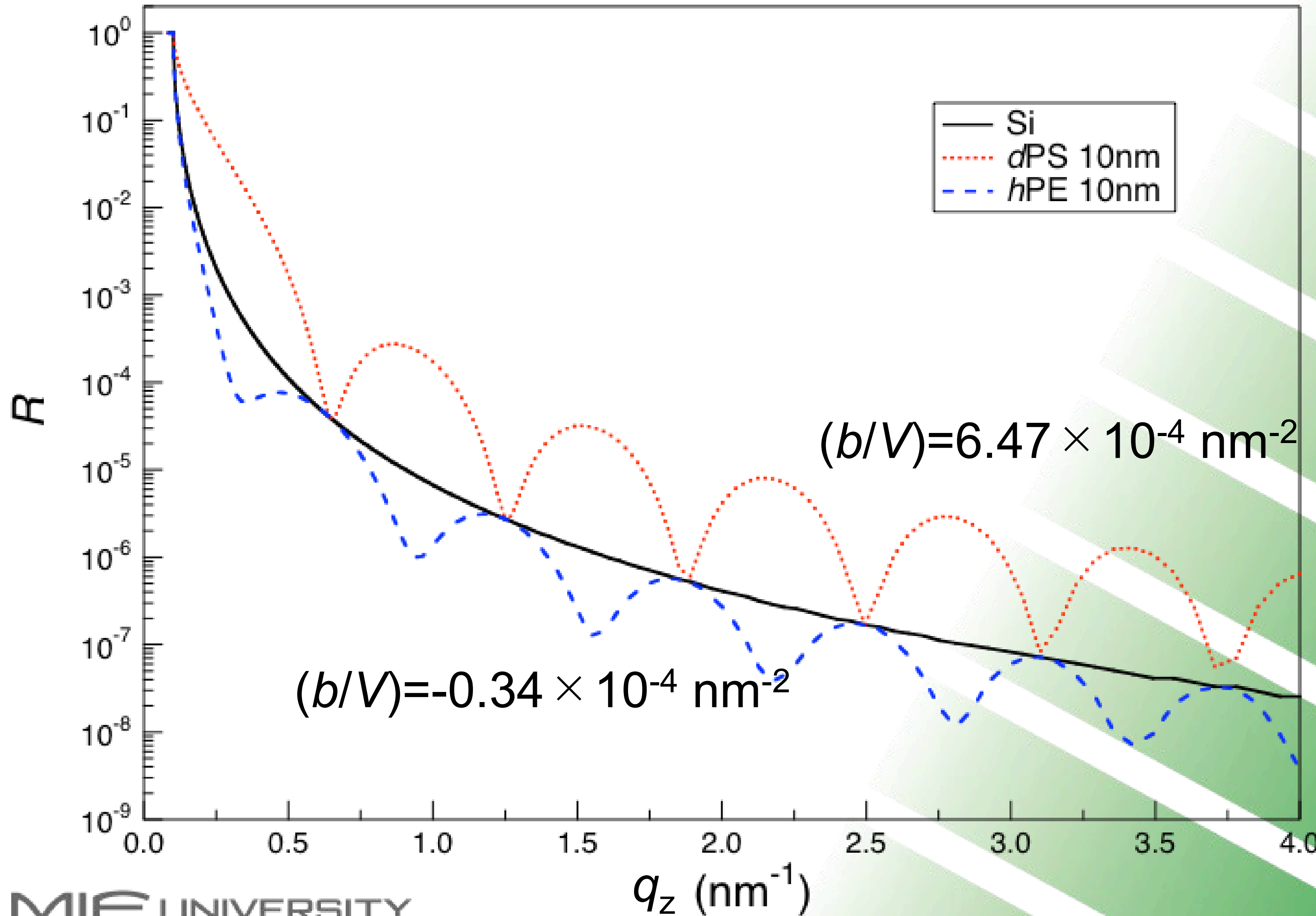
$r_{j-1,j}$: Fresnel reflection coefficient $r_{j-1,j}=(q_{j-1}-q_j)/(q_{j-1}+q_j)$

q_j: neutron momentum transfer in j-th layer $q_j=2\{(q_z^2/4))-4\pi(b/V)_j\}^{1/2}$

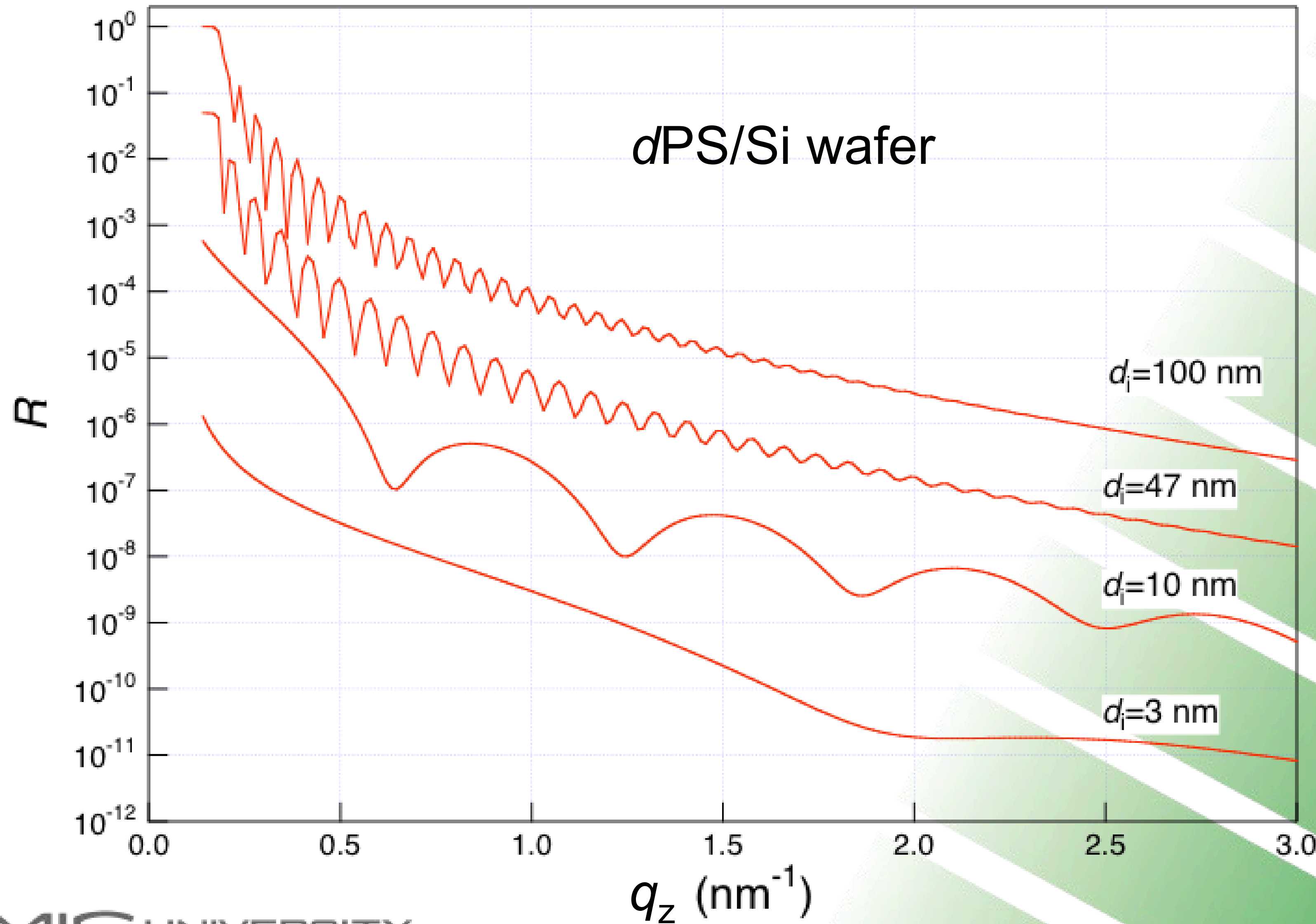
NR profile for a d-polystyrene thin film



Thin films with different (b/V)



Thin films with different thickness



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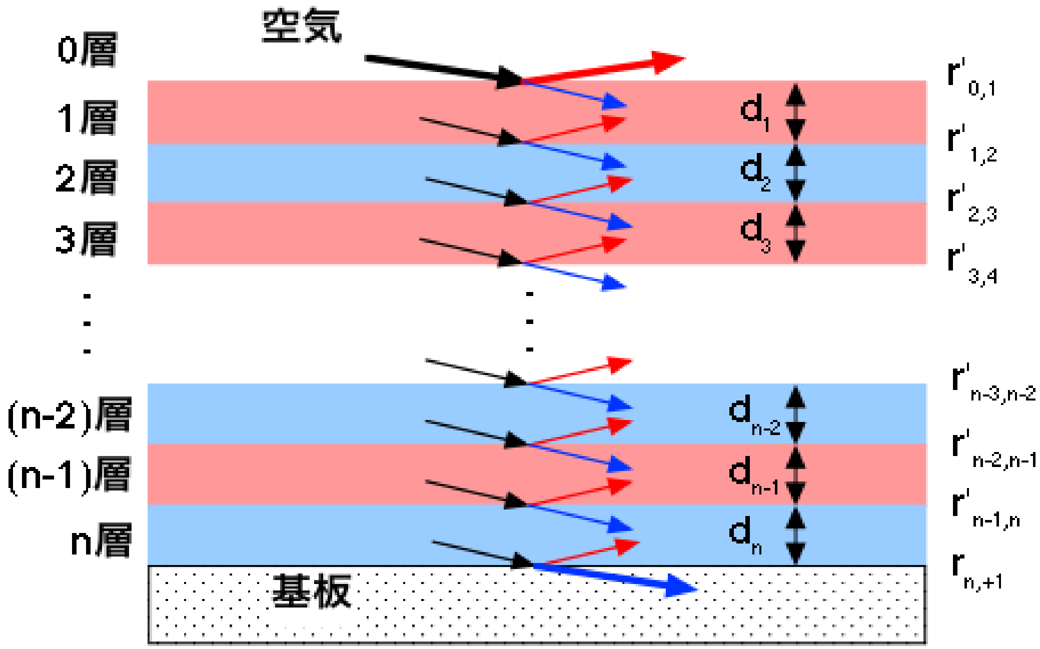
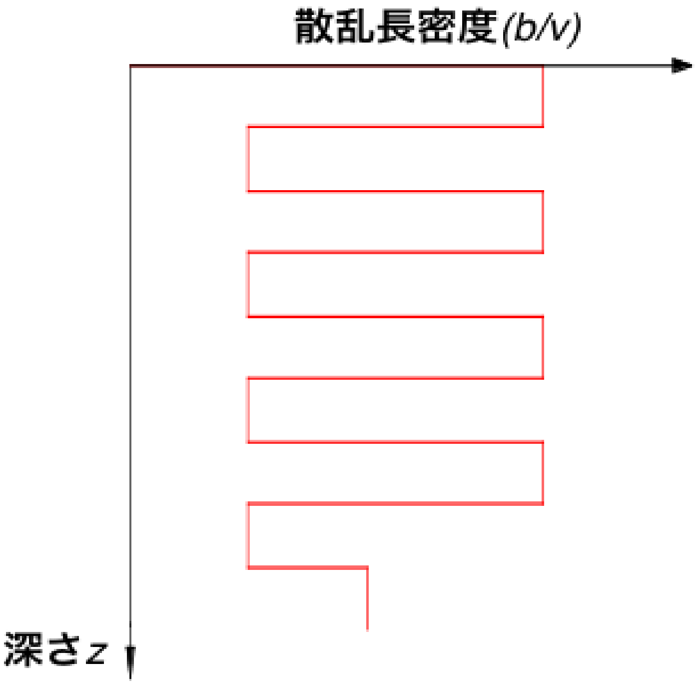
Reflection from a multilayer





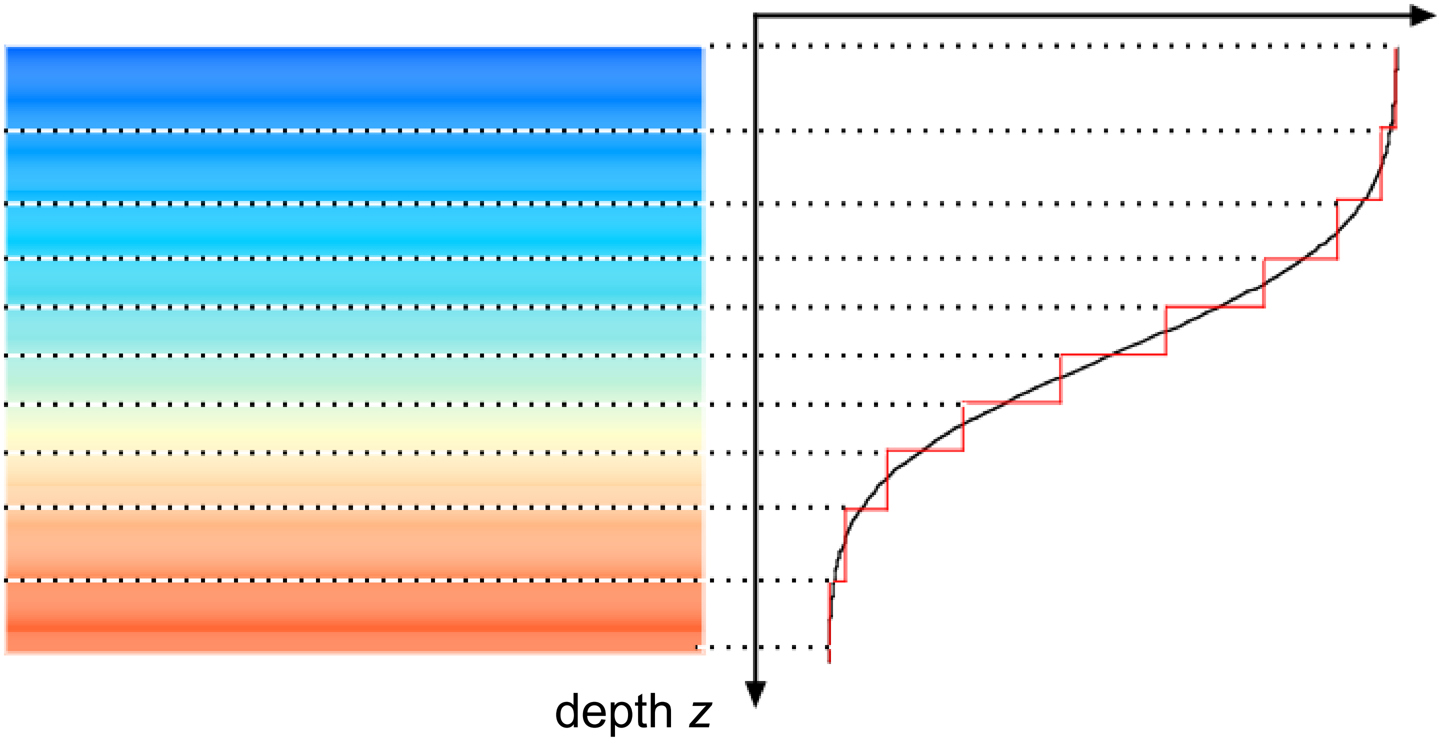
reflection coefficient between each interface $r'_{i-1,i} = \dfrac{r_{i-1,i} + r'_{i,i+1}\exp(iq_i d_i)}{1 + r_{i-1,i}\, r'_{i,i+1}\exp(iq_i d_i)}$

Fresnel reflection coefficient $r_{i-1,i} = \dfrac{q_{i-1} - q_i}{q_{i-1} + q_i}$

反射率$R = r'_{0,1} \cdot r'^{*}_{0,1}$

q_j: neutron momentum transfer in j-th layer $q_j = 2\{(q_z^2/4)) - 4\pi(b/V)_j\}^{1/2}$

Smoothly-varied structure



approximate as **multilayer structure** with ideal interfaces

(*b*/*V*) profile = **step function**

Reflectivity Simulation and Analysis Software

1) Parratt32
Hahn-Meitner Institute (HMI)
Windows
neutron & X-ray

2) Reflfit
National Institute of Standards and Technology (NIST)
IRIX, OS X, Windows, Linux
neutron

3) Motofit
Australian Nuclear Science and Technology Organization (ANSTO)
Igor
neutron & X-ray

Features of reflectometry

High resolution with a scale

→ structural analysis of surface and interface

Average structure over a wide plane

↔ secondary-ion mass spectroscopy (SIMS)

Measurable for density fluctuation

( )

↔ atomic force microscopy (AFM)

In-situ measurement for structural evolution in time

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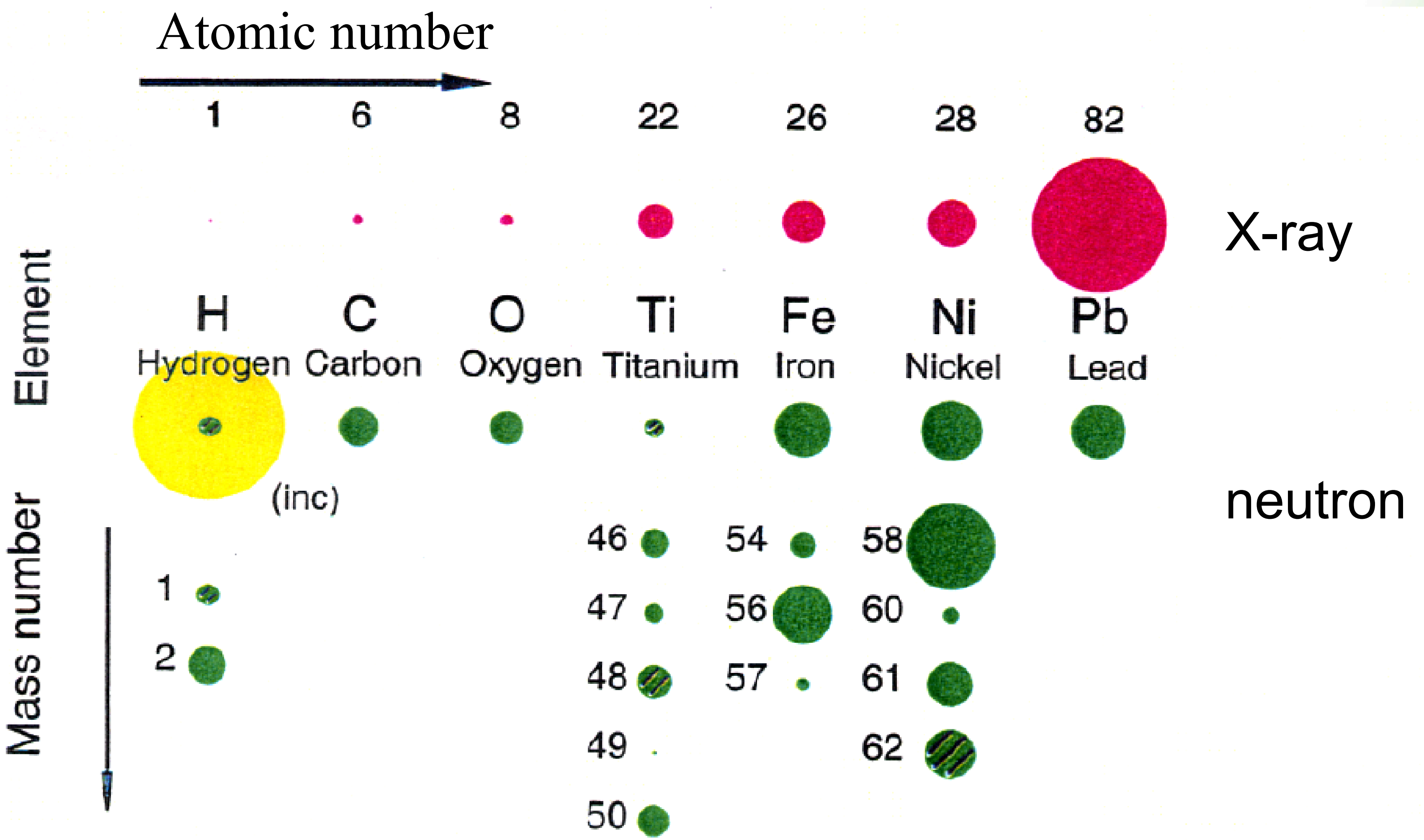
Scattering cross-section for X-ray and neutron



Merits for soft matter research

1) different scattering contrast among isotopes

(selective labeling for specific part, ,
)

scattering length *b*

H : -3.74×10^{-15} m, D : $+6.67 \times 10^{-15}$ m

→useful for soft matter research

complementary information to X-ray

2) high transmissivity

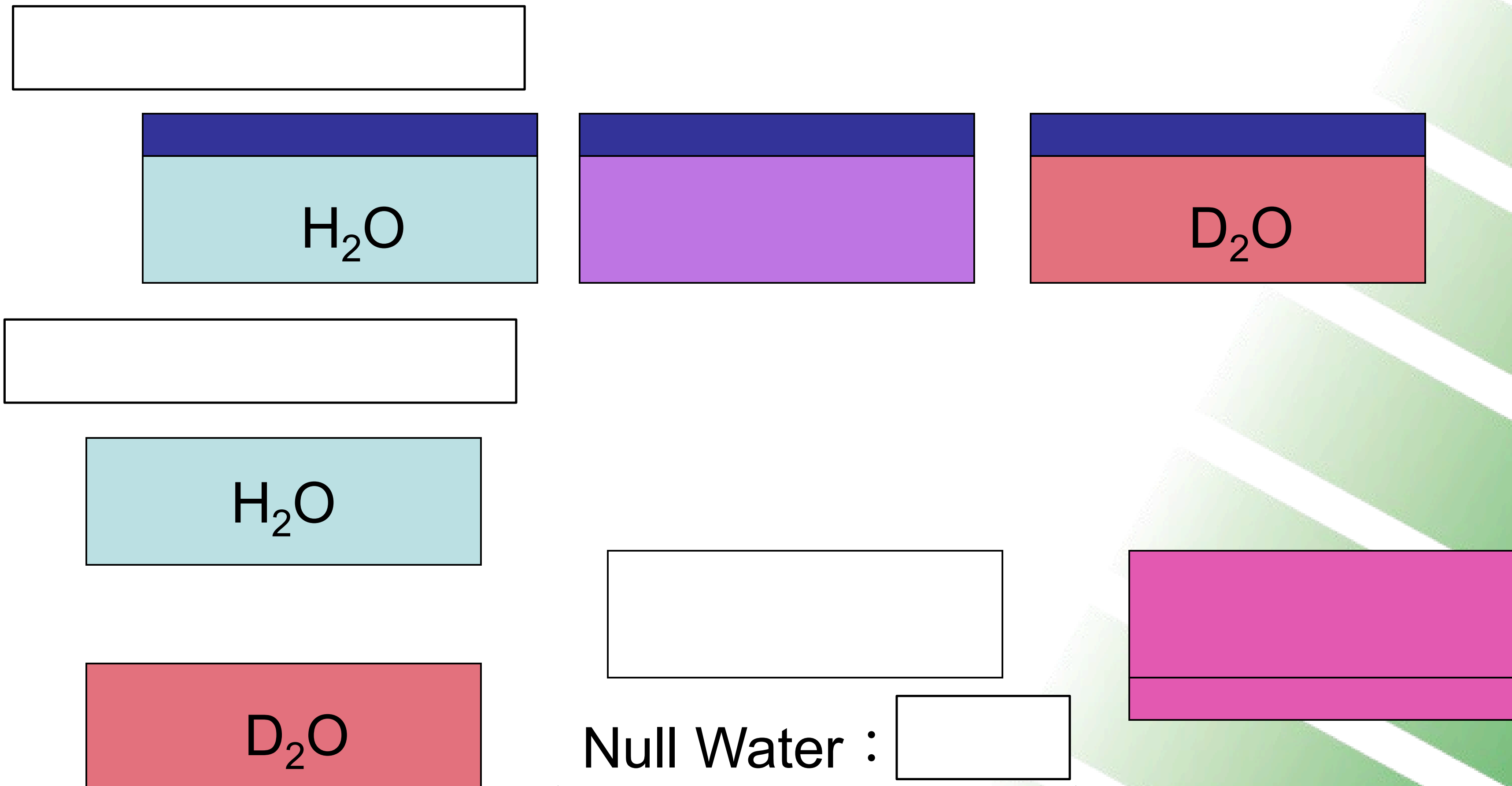
for deeply-buried interface

ease in combination with special sample environment

Contrast Adjustment for Water

scattering length density

H_2O : -5.61×10^{-7} Å^{-2} D_2O : $+6.35 \times 10^{-6}$ Å^{-2}



Null Water :

(H_2O:D_2O= about 9:1)

Contents

1) Material interface and interfacial science

2) Principles and merits of reflectivity measurement

3) Constant lambda vs time-of-flight (TOF)

4) Some examples

5) Summary

Classification of Neutron Reflectometer

1) Vertical or Horizontal Sample Geometry

Vertical: solid, solid/liquid interface
Horizontal: all kinds of interfaces including free interfaces
(But, downward beam is required.)

2) Constant-lambda or Time-of-Flight (TOF)

Constant-lambda: reactor source with monochromator
Time-of-Flight (TOF): reactor source with choppers or
spallation neutron source

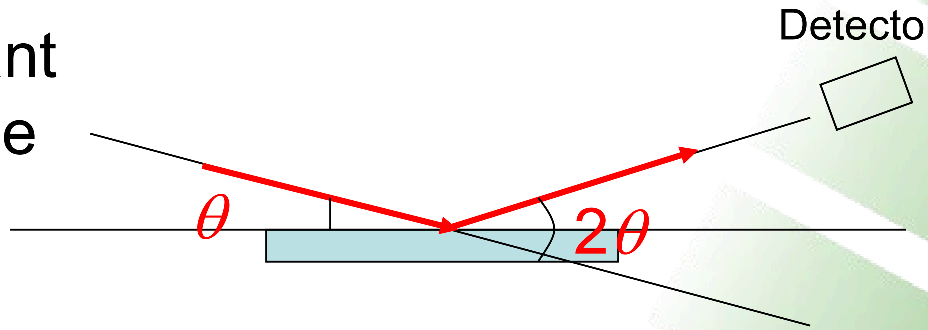
Specular reflectivity measurement

Constant-lambda

$q_Z=(4\pi/\lambda)\sin\theta$

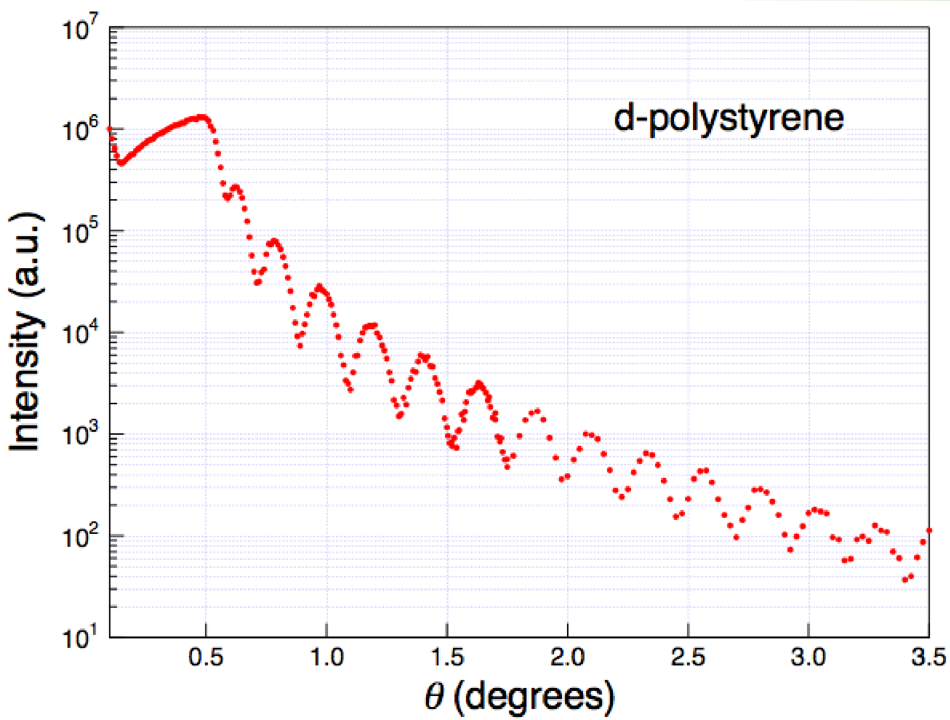
λ : constant

θ : variable



step by step

commercial X-ray reflectometer (CuKα)



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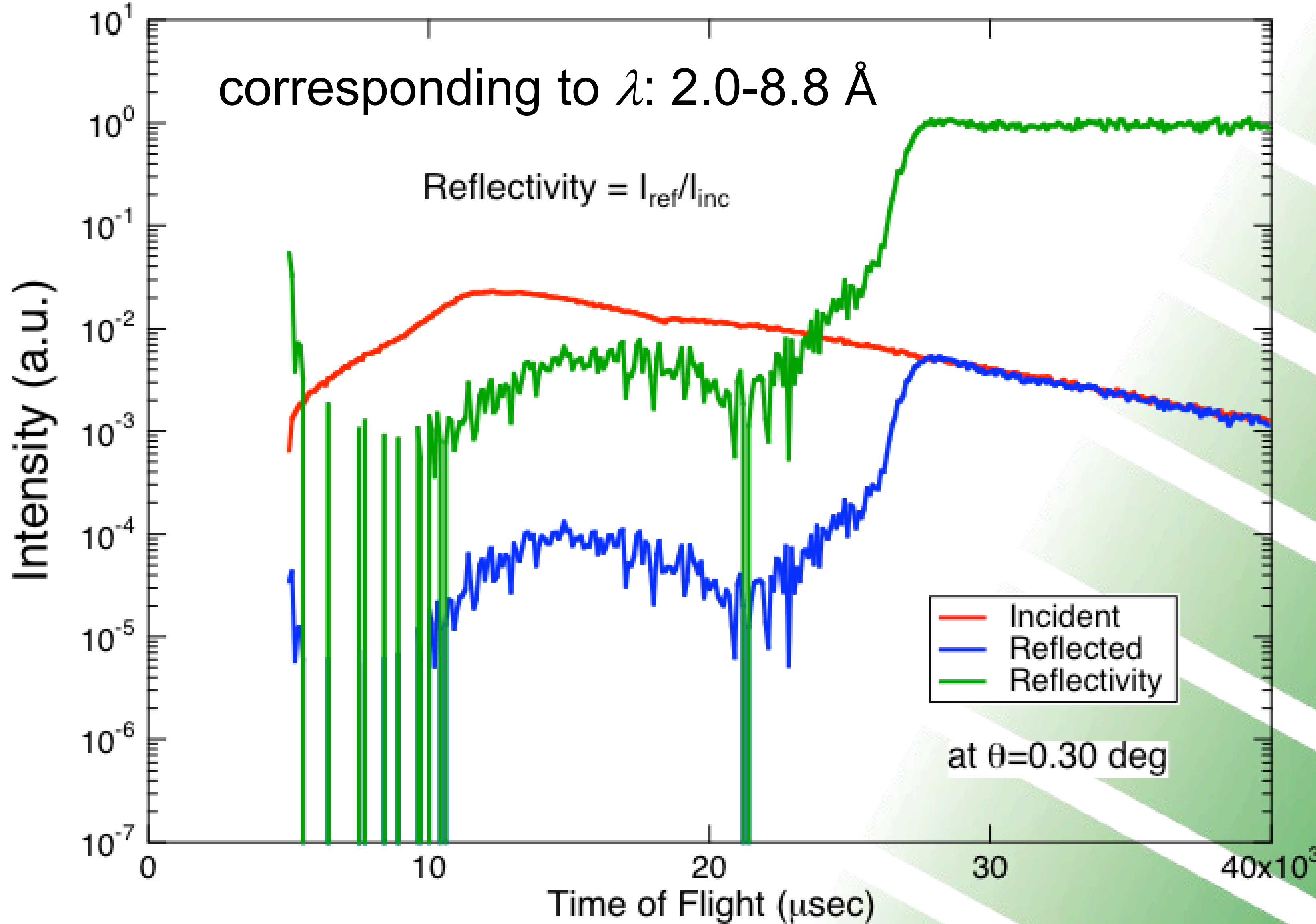
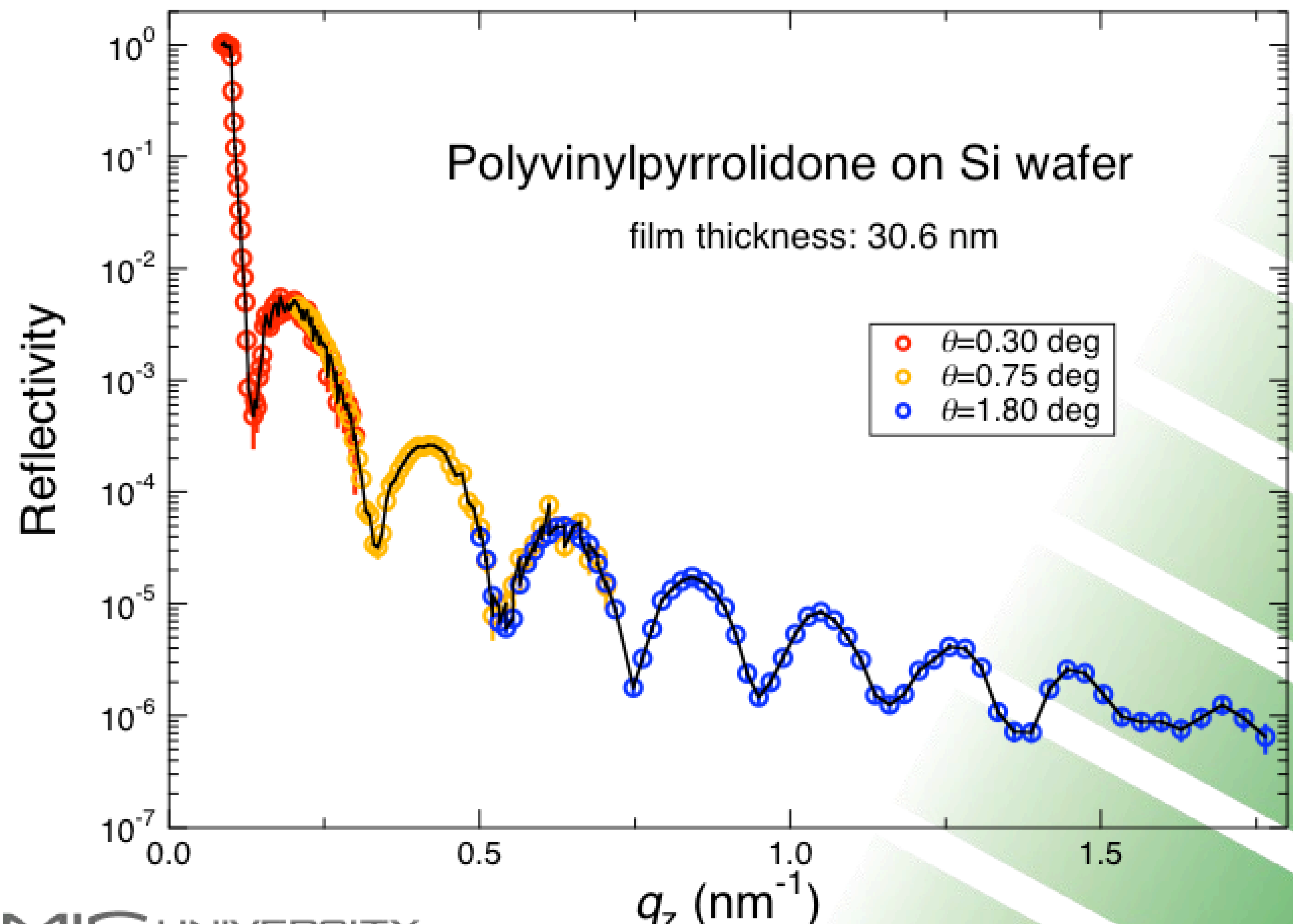
Time-of-Flight (TOF)

spallation neutron source
white beam (λ: wide band)
time-of-flight (TOF) analysis
wide qz coverage at one angle

$q_Z=(4\pi/\lambda)\sin\theta$ λ : variable
θ : constant

combination with horizontal geometry
→applicable to almost all material
interfaces including free interface
suitable for time-resolved (enough flux of incident beam)


corresponding to λ: 2.0-8.8 Å
Reflectivity = I_ref/I_inc
Intensity (a.u.)
Time of Flight (μsec)
Incident
Reflected
Reflectivity
at θ=0.30 deg
10^1
10^0
10^-1
10^-2
10^-3
10^-4
10^-5
10^-6
10^-7
0
10
20
30
40x10^3



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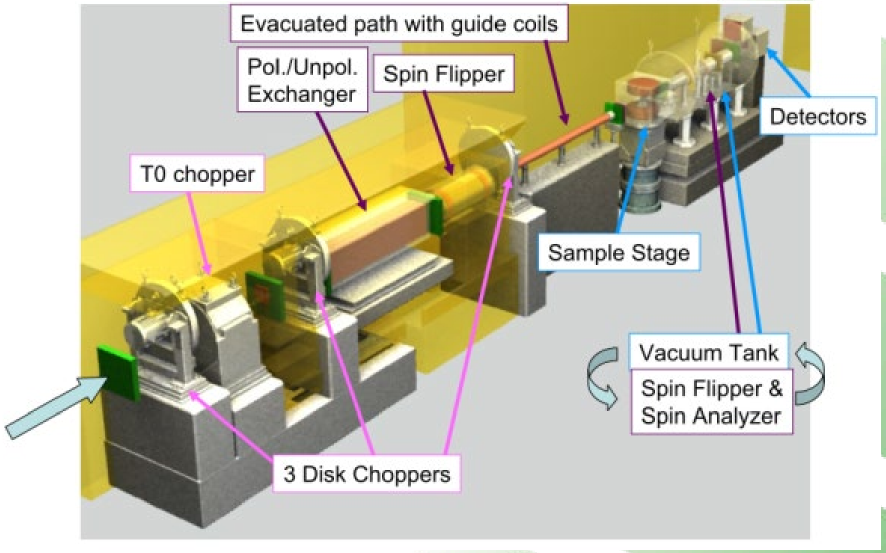
Reflectometers in Japan (J-PARC)

SOFIA(horizontal/non polarized)

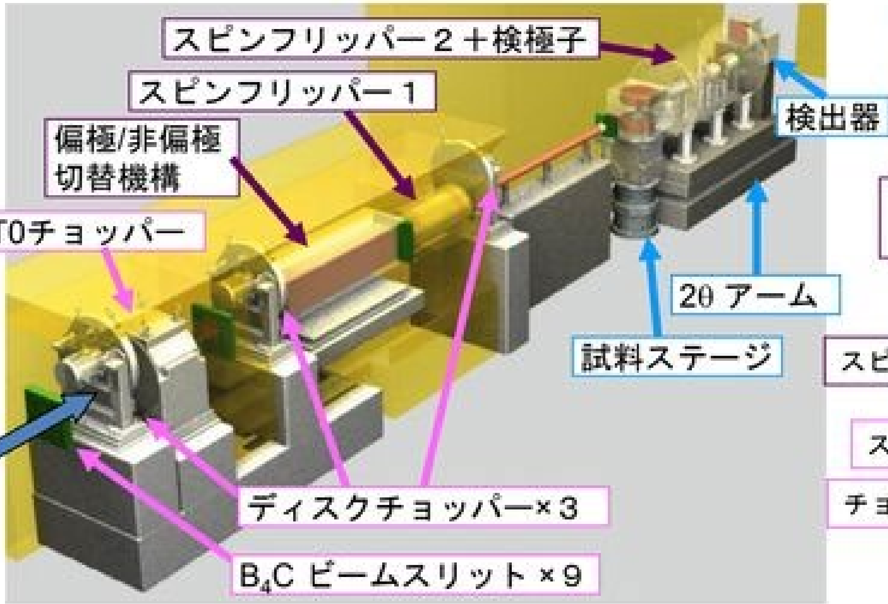
SHARAKU(vertical/polarized)



Both the reflectometers adopt wavelength dispersive scan.

偏極中性子反射率計「写楽」

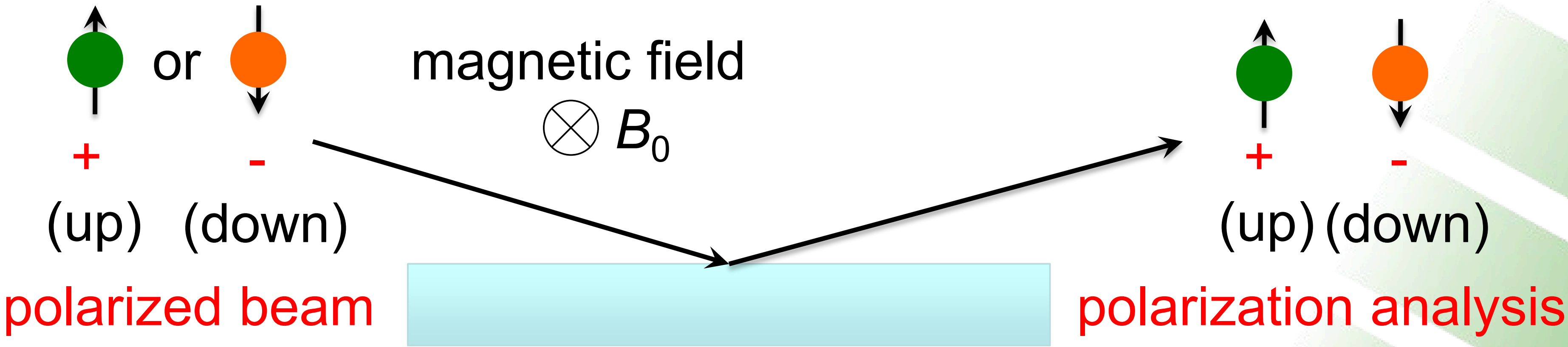
SHARAKU
BL17@MLFJ-PARC



モデレータ種類	結合型モデレータ
中性子波長	λ=0.2～0.84 nm（偏極モード） λ=0.1 ～ 0.88 nm（非偏極モード）
散乱角	2θ = 0 ～23°
測定可能なq領域*	$q=0.1 \sim 12 nm^{-1}$（偏極モード） $q=0.05 \sim 25 nm^{-1}$（非偏極モード） $*q=(4\pi/\lambda)\sin(2\theta/2)$ $(0<2\theta<23.0°)$
中性子源から試料中心までの距離	15.5m 試料中心から検出器までの距離：2.5m 中性子源から検出器までの距離：18m
検出器	0次元^{3}Heガス中性子検出器

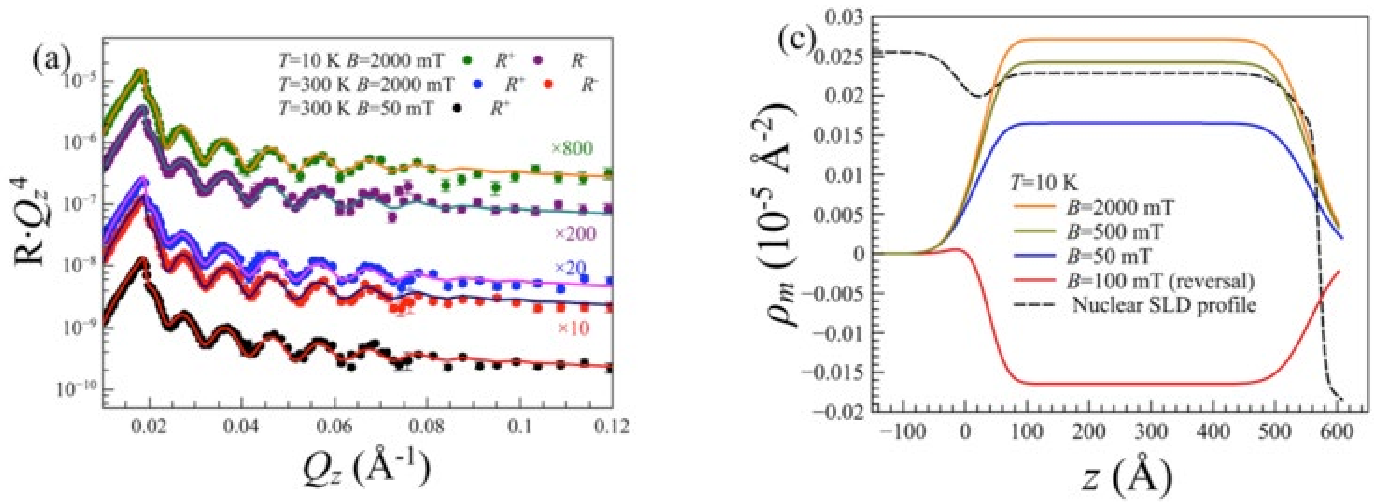
・試料垂直型（反射面は水平面）
・多様な試料環境
・磁性膜を含む多様な試料
　固体表面界面
　固液界面への吸着層
　試料サイズ 15x15 mm^2 ～
・大強度パルス中性子ビーム(TOF)
・イベントレコーディング
・面内構造解析（近年中）

Polarized neutron reflection



Four data set: R^{++}, R^{--}, R^{+-}, R^{-+}

magnitude, orientation, depth distribution, and lateral arrangements of magnetization vectors in thin films

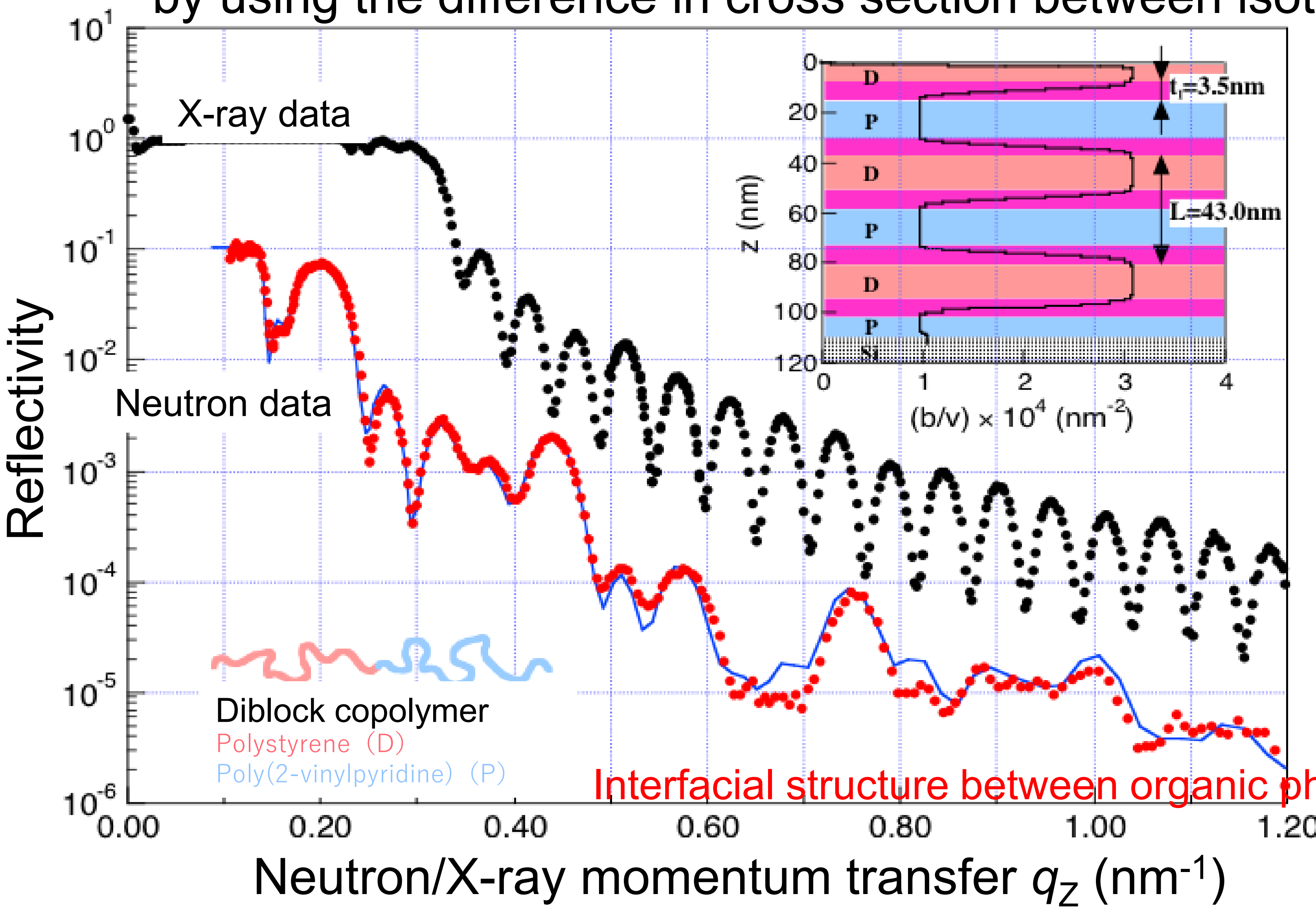


V. Ukleev et al., *Sci. Rep.* **2018**, *8*, 8741.

Contents

Application to organic thin films

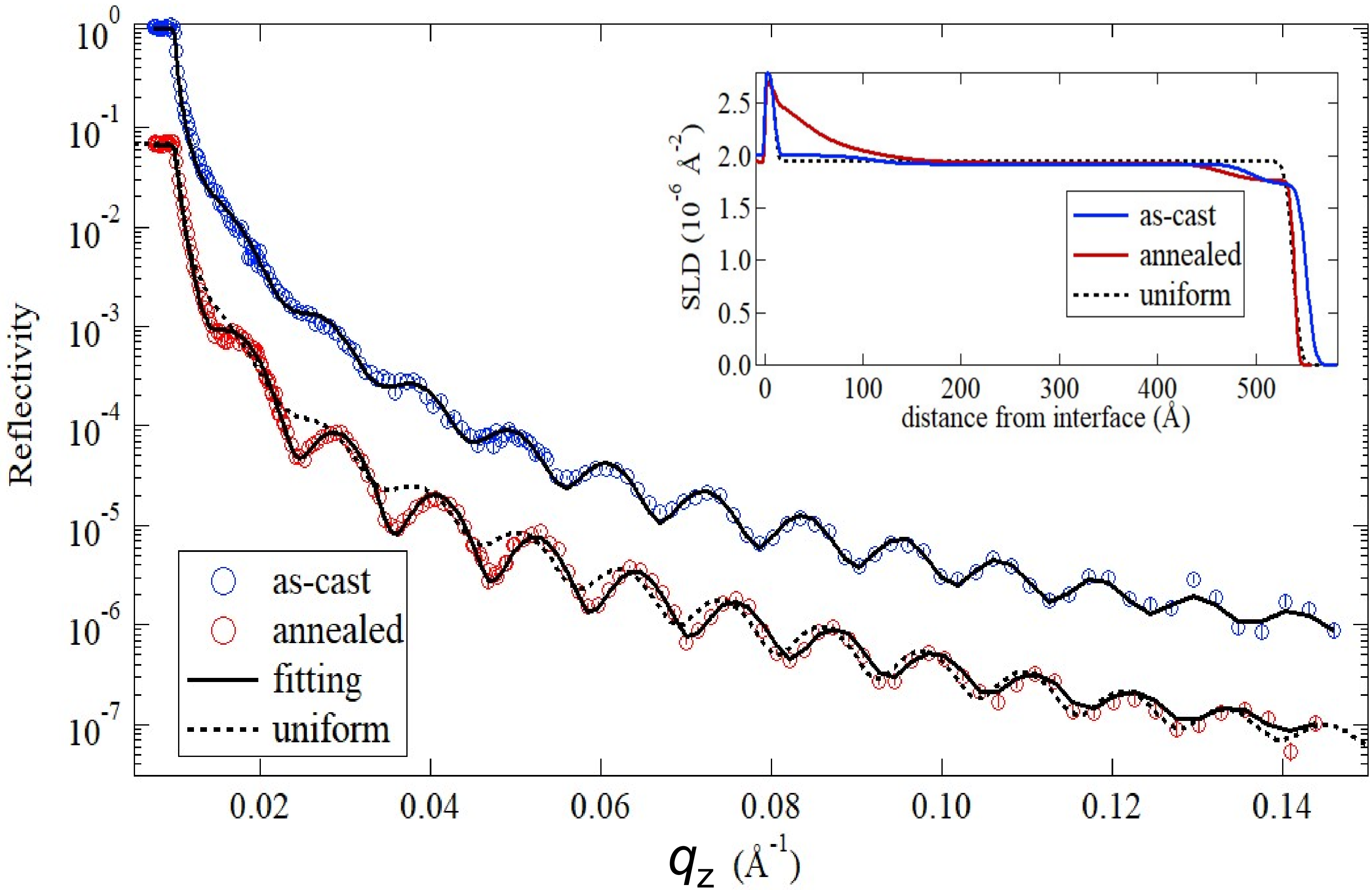
by using the difference in cross section between isotopes



Interfacial structure between organic phases

ave. SLD
as-cast: 1.94
annealed: 1.95

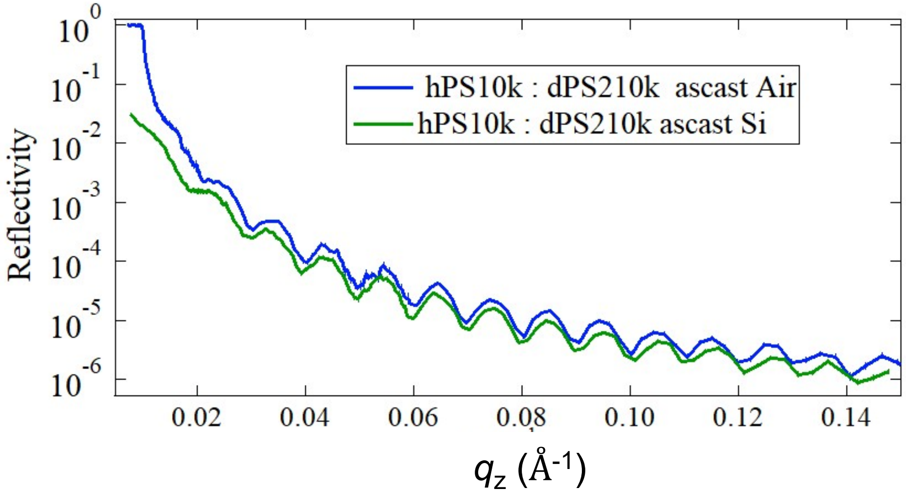
dPS210k 12.5wt% blend acid-treated

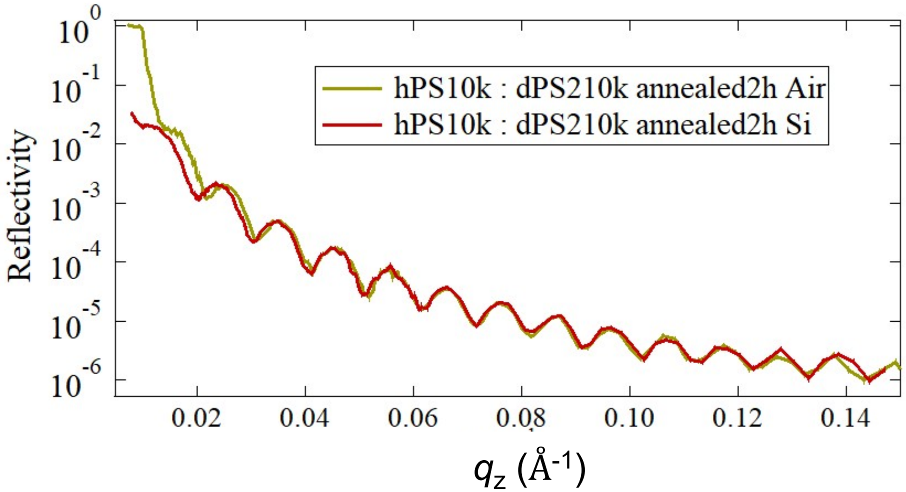


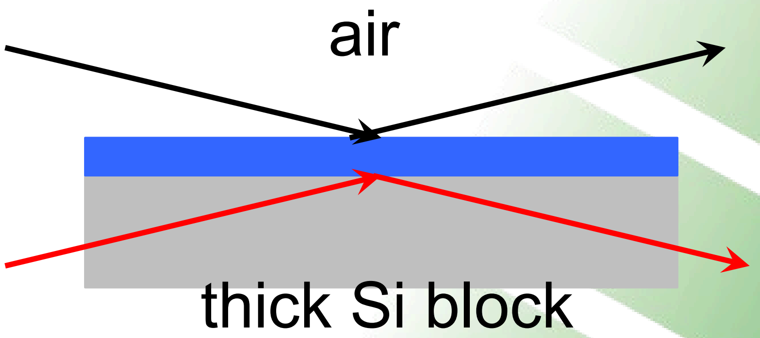
Twin reflecitivity using thick silicon block

a binary polystyrene blend thin film

hPS10k : dPS210k







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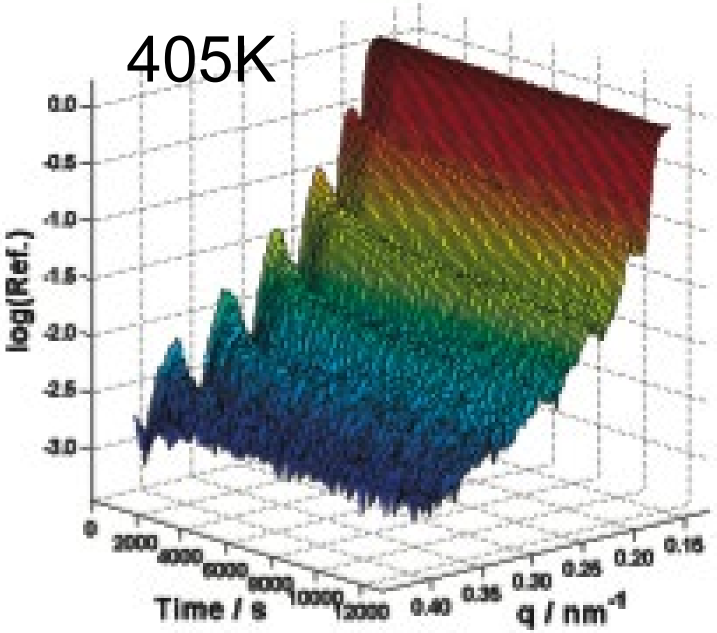
Time-resolved measurement

a polystyrene bilayer thin film

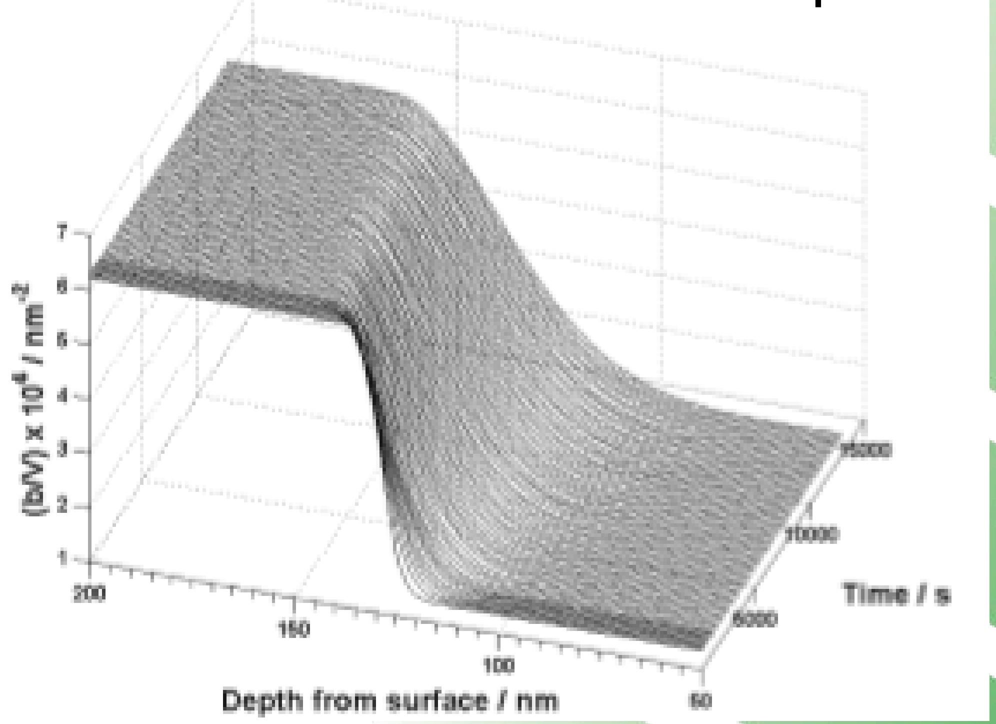
specular reflectivity profile

405K



every 3 minitues

time evolution of interfacial profile

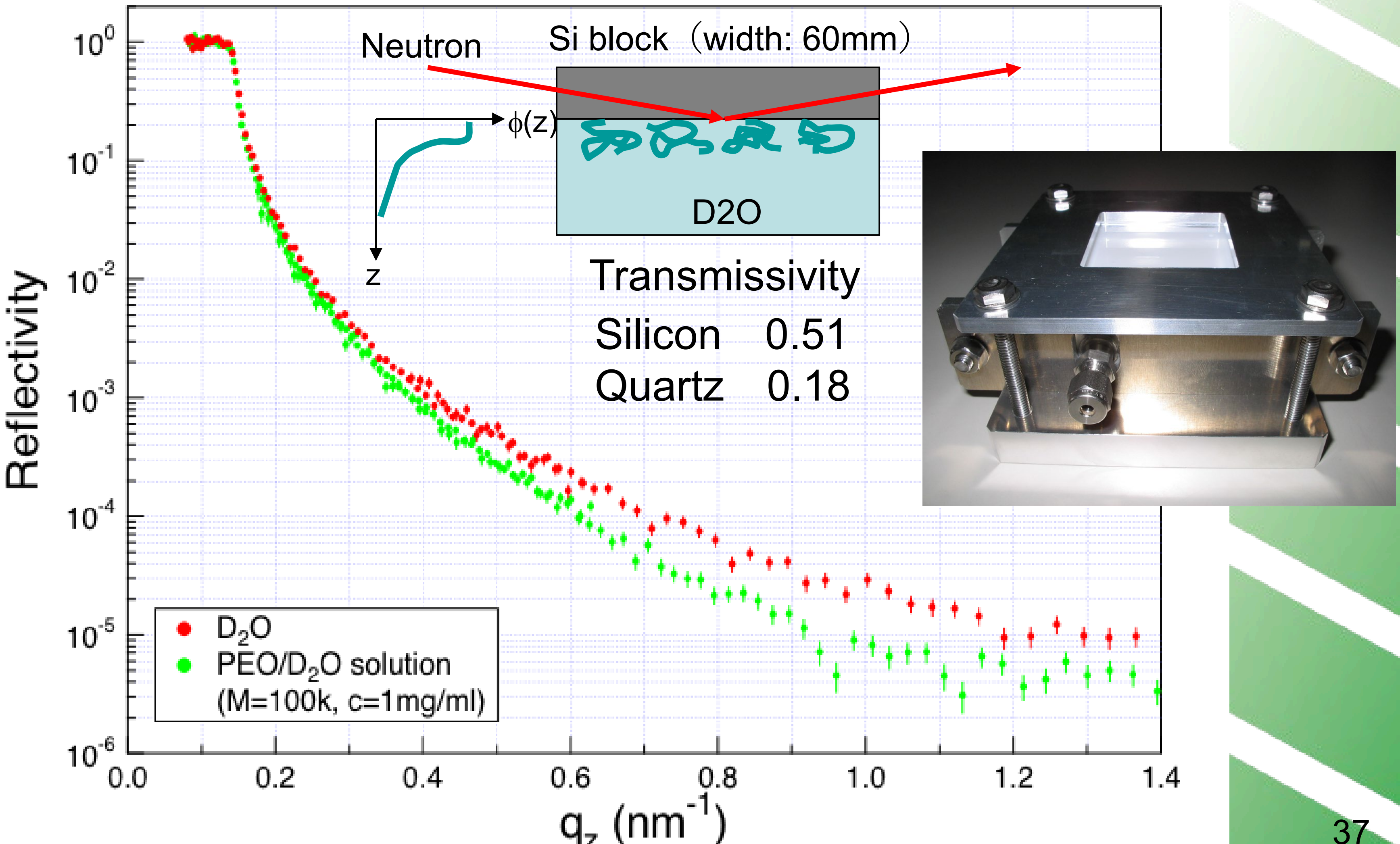


Kawaguchi et al., *Macromolecules.* **2011**, *44*, 9424.

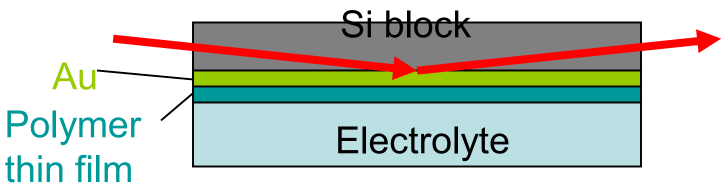
Application to solid/liquid interface

by high transmission to materials

Adsorption behavior and conformation of polymer on a solid substrate



Application to electrochemical interface



Conducting polymer thin film
on Au electrode

Changes in polymer film thickness and water composition with applied potential along a voltanmetric cycle

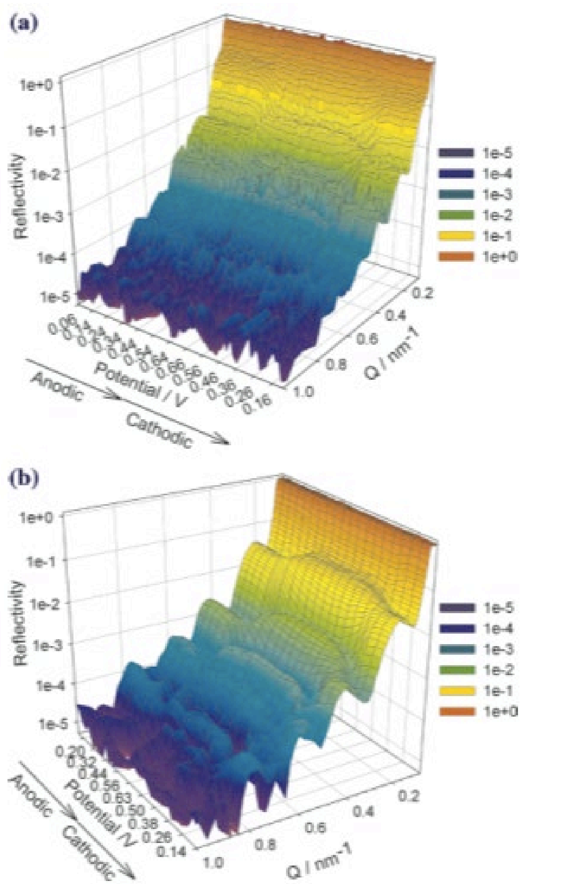


Figure 1. Dynamic NR profiles as functions of Q and E during redox cycling of PVF films exposed to 0.1 M $NaClO_4/D_2O$: (a) Γ = 27 nmol cm^{-2}, υ = 10 mV s^{-1}; (b) Γ = 18 nmol cm^{-2}, υ = 1 mV s^{-1}.

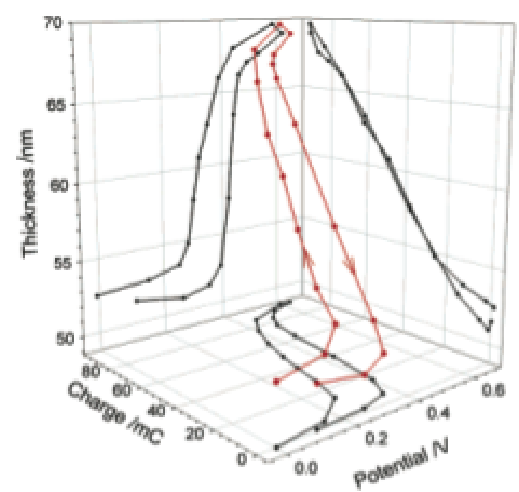


Figure 2. Film thickness and charge as functions of applied potential for the experiment of Figure 1a. Projections: black traces. 3D vector: red trace.

Cooper et al., *J. Am. Chem. Soc.*, **2004**, *126*, 15362.
CRISP@ISIS and D-17@ILL

Summary

Neutron reflectometry

Specular reflectivity measurement
with high depth resolution of a sub-nm scale

Deutreium labeling

Non-destructive ex) solid/liquid interface

Time-resolved measurement for temporal change

Powerful tool for structural observation of material interface and thin film