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A new grazing incidence small angle x-ray scattering for the pore size determination of low-k films

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THE POSSIBILITIES ARE INFINITE

Contents

1. Introduction

Nano materials with nanoparticles or nanopores

●Fuel batteries: Pt nanoparticles ~3nm

●Disk media: PtFe nanoparticles 3~5nm

H.Kodama et al, Appl.Phys.Lett.83(2003)5253

●Porous low-k film: Nano-Clustering Silica

T.Nakamura and A.Nakashima, Proc. IITC2004(2004)175

Size distribution relates catalytic activities, magnetic properties or the mechanical rigidity of the films.

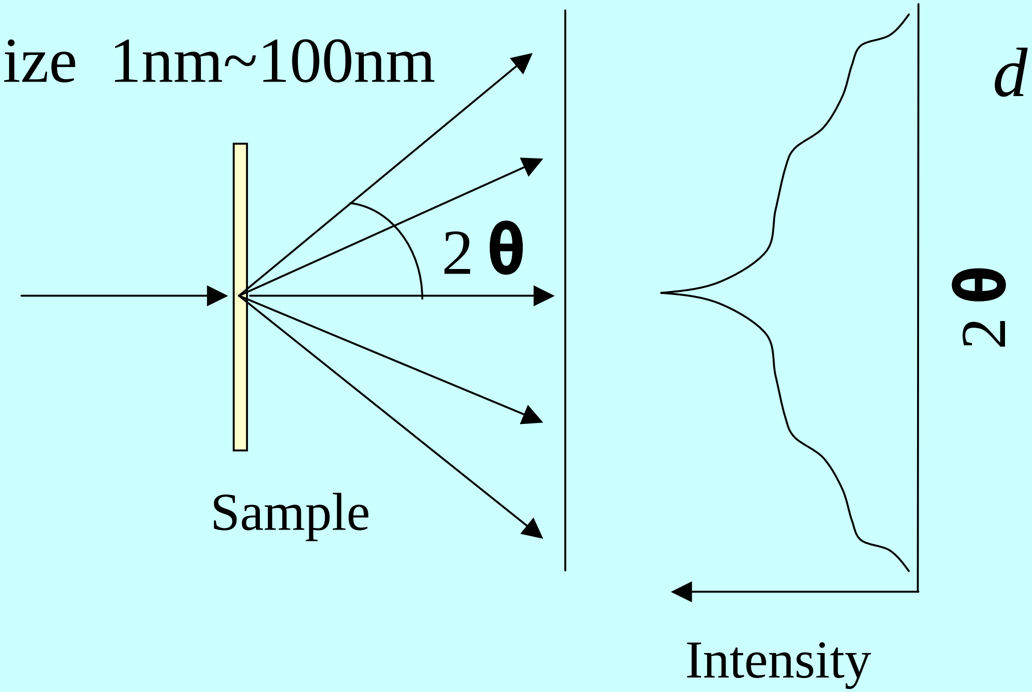
➡ Need the analysis method to determine its size distribution.

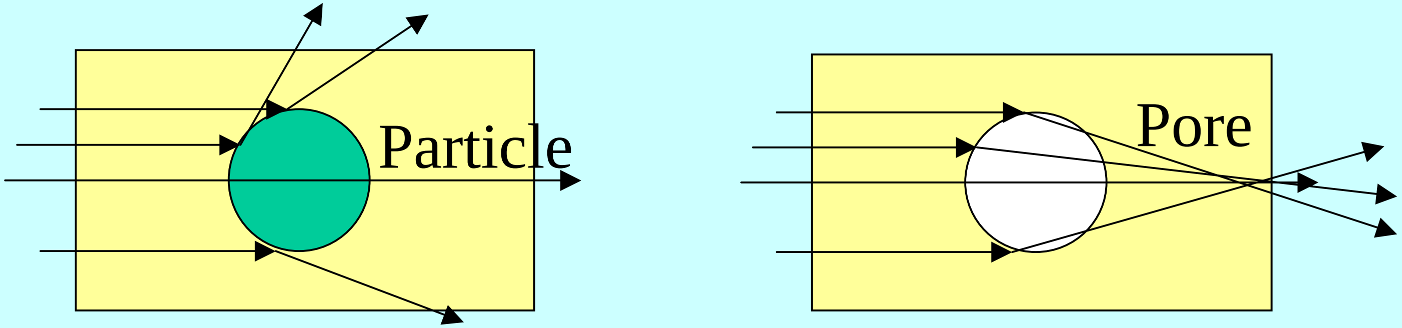
TEM, Gas adsorption, Positron annihiration

2. SAXS under transparent mode

SAXS: Size 1nm~100nm

$$d_{\min} \approx \pi / q_{\max}$$





$$I(\theta) \propto (\Delta\rho)^2 F(\theta)$$

Guinier Plot （Average Size）

$$q = 4\pi \cdot \sin\theta / \lambda$$

$$I(q) \approx e^{-R_G{}^2 q^2 / 3}$$

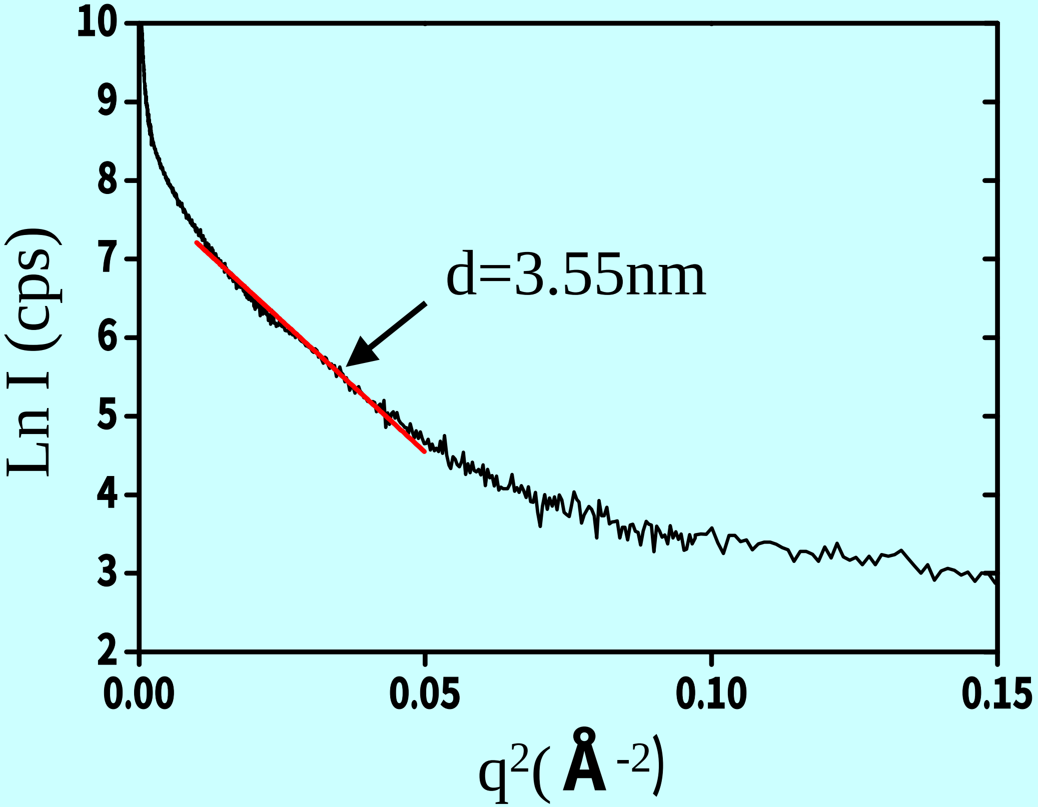
$$@\, q \leq 1/R$$

Sphere with radius R

$$R_G{}^2 = \frac{3}{5} R^2$$

d=2R

Pt nano particle; Transparent mode

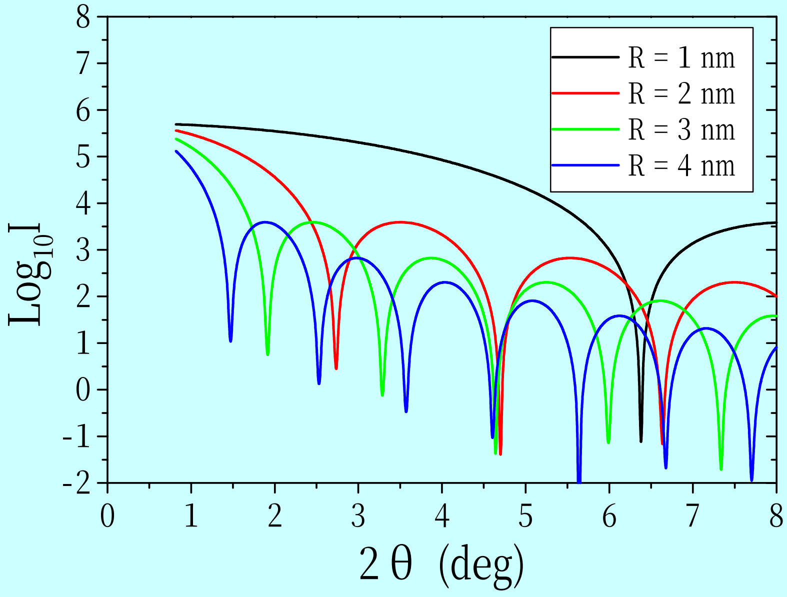


Model optimization (Size distribution)

(1) Particle/Pore shape

Spherical particle/pore

$$F(q,R) = 3V\Delta\rho \frac{(\sin(qR) - (qR)\cos(qR))}{(qR)^3}$$

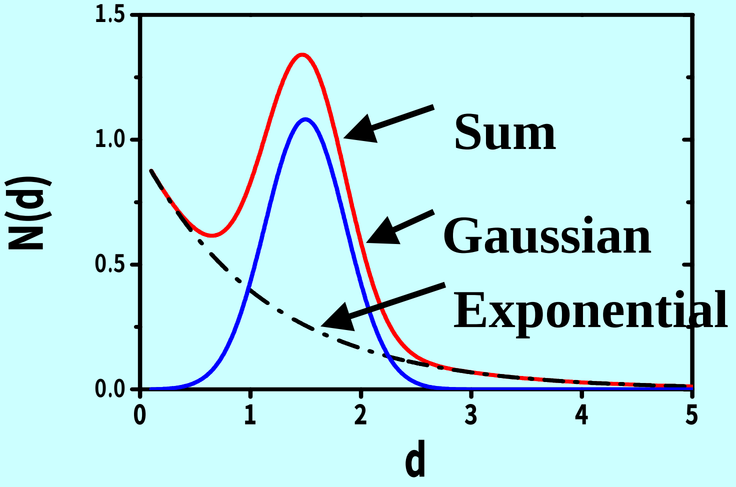


(2) Size distribution

Gauss-Exp model

$$N(R) = \frac{a_0}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}(\frac{R-R_0}{\sigma})^2} + \frac{a_1}{R_1} e^{-\frac{R}{R_1}}$$

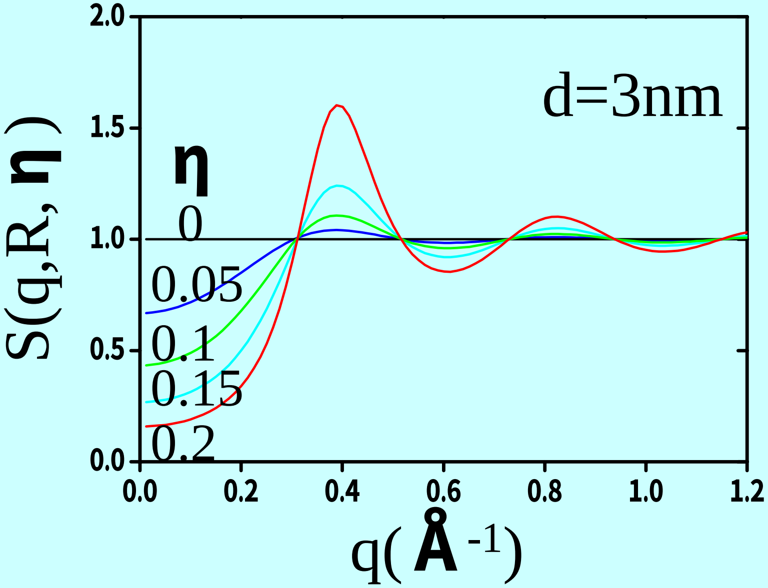
can be applied to the wide range of samples

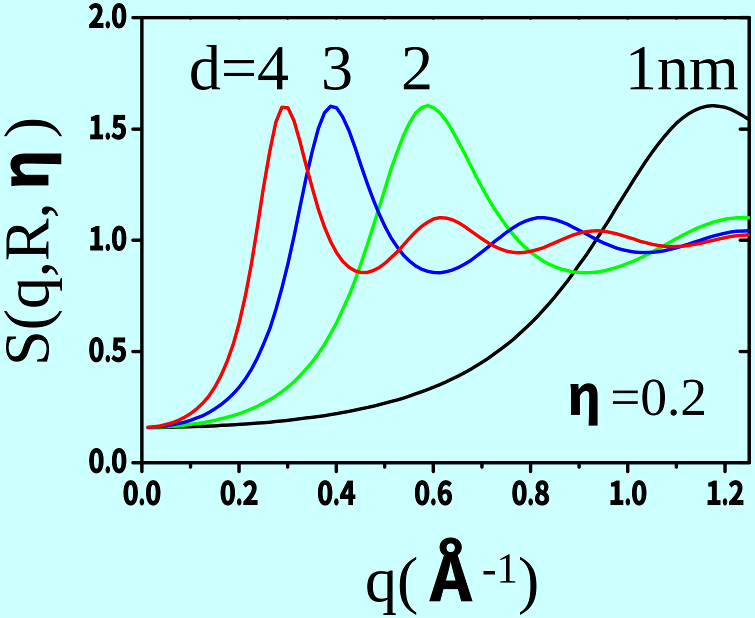


(3) Interference between particles/pores

Structure factor $S(q, R, \eta)$

Hard sphere model
J.S.Pedersen, J. Appl.Cryst,27(1994)595





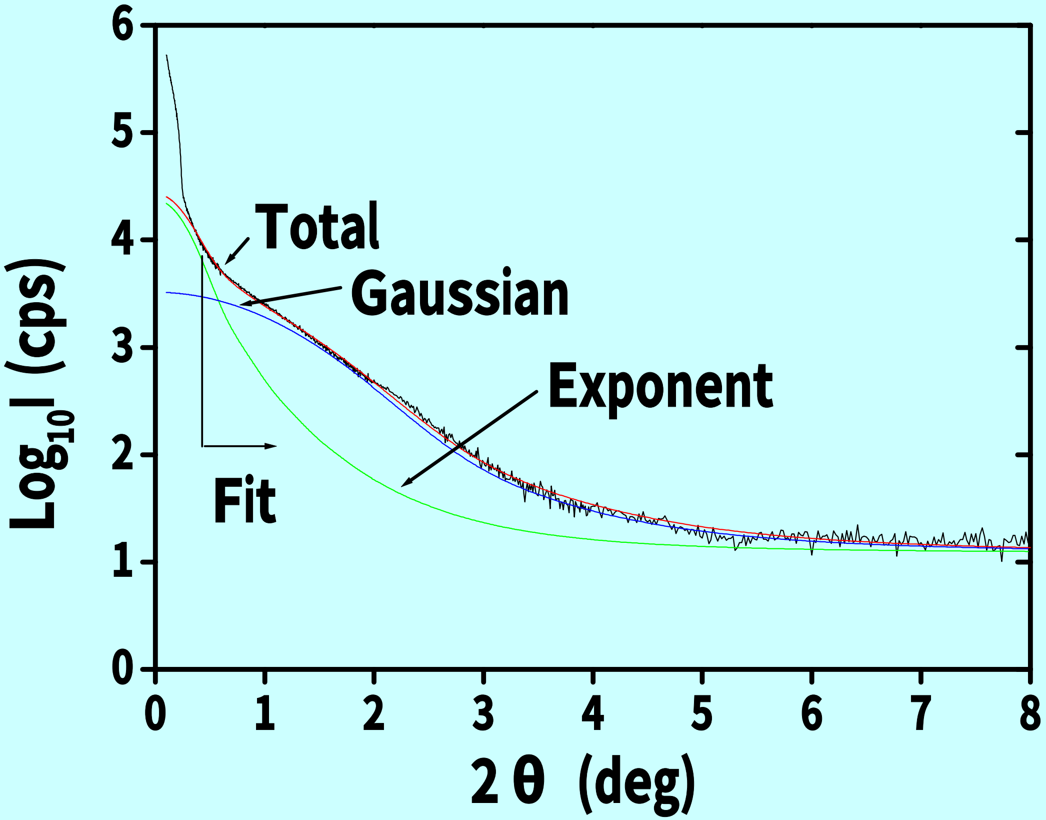
(4) SAXS intensity

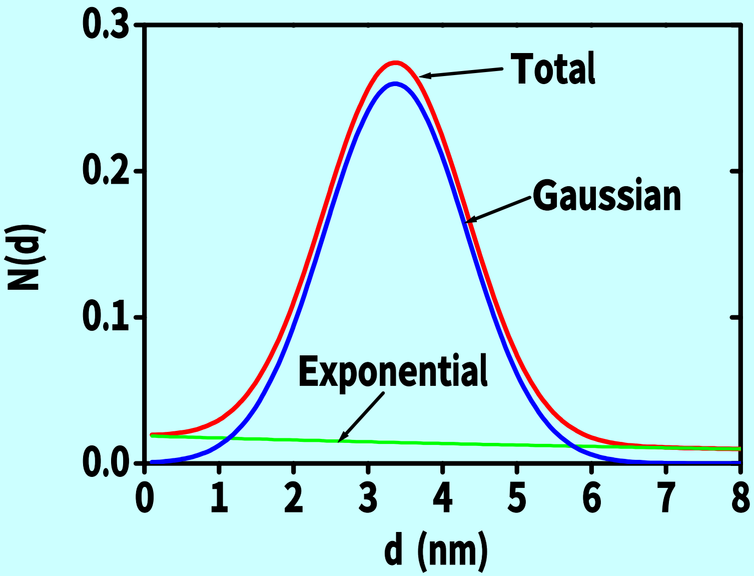
$$I(q) = \int_0^\infty N(R) \left| F(q,R) \right|^2 S(q,R,\eta) dR$$

Minimize

$$\chi^2 = \sum_{i=1}^{n} \left(I_{meas}(q_i) - I_{calc}(q_i) \right)^2 / \sigma_i^2$$

Pt nano particles - Transparent mode





d_{ave}=3.37nm

$$R_{ave} = \int_0^\infty R \cdot N(R)dR \Big/ \int_0^\infty N(R)dR$$

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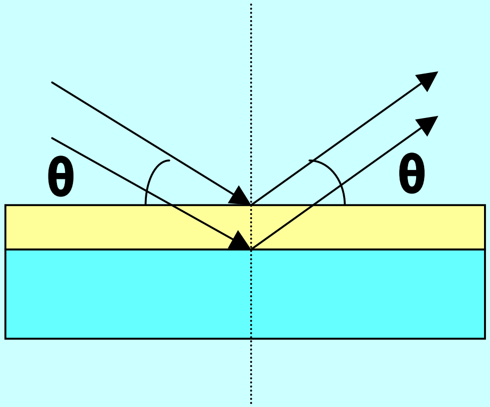
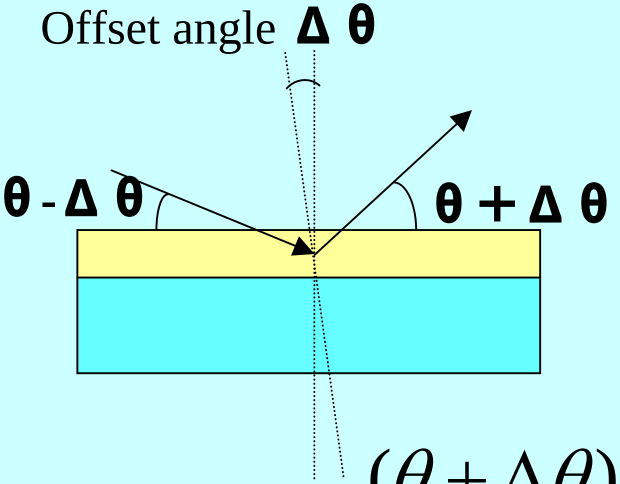
3. SAXS under reflection mode (Films on substrate)

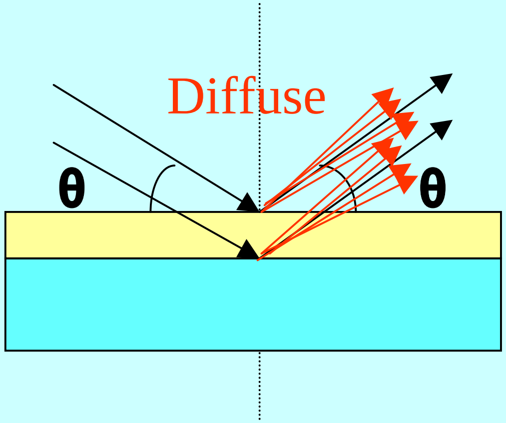
3-1 Offset scan (Rigaku)



Reflectivity



$$(\theta+\Delta\theta)/2\theta$$



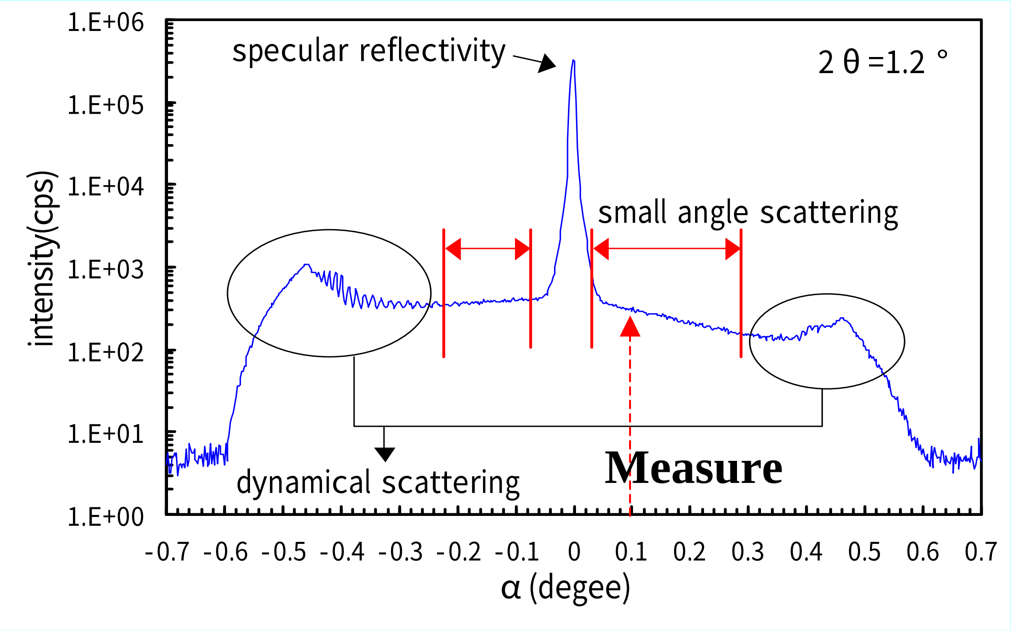
Scattering components

(a)SAXS

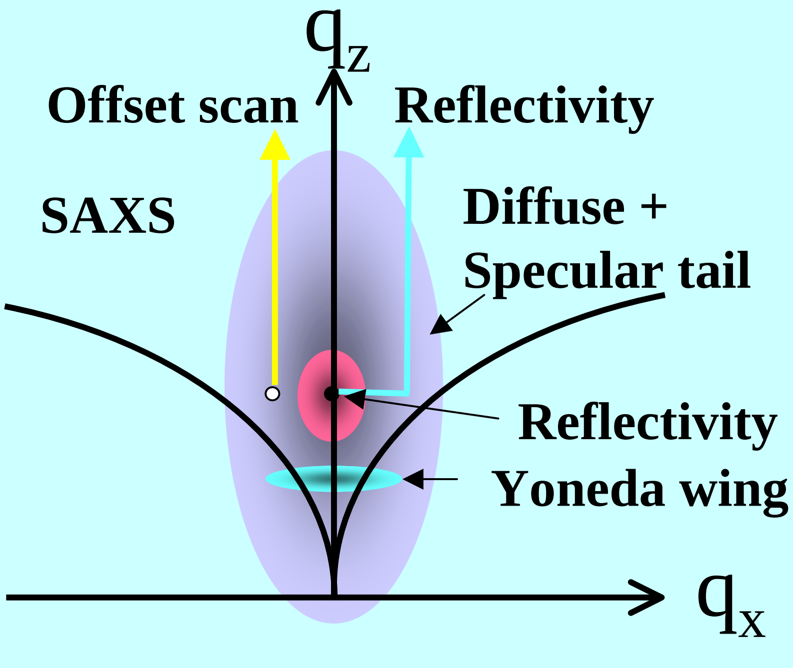
(b)Diffuse scattering by surface/interface roughness

(c)Tail of specular scattering

Offset scan $(\theta + \Delta\theta)/2\theta$



ω locking scan



q-space

Thick film (t> 1μm) : SAXS > diffuse, specular tail

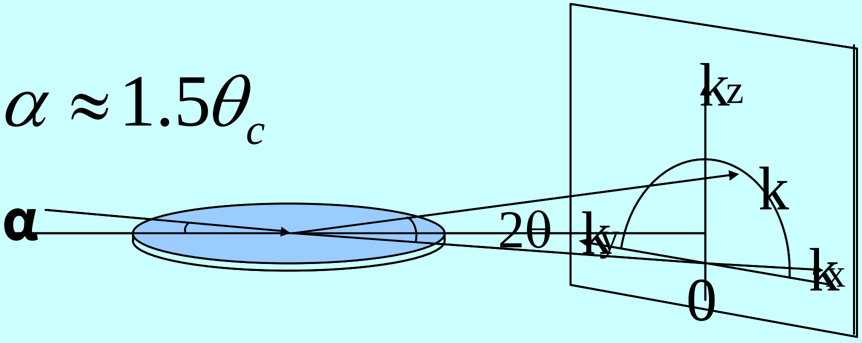
Thin film (t< 1μm) : SAXS < diffuse, specular tail

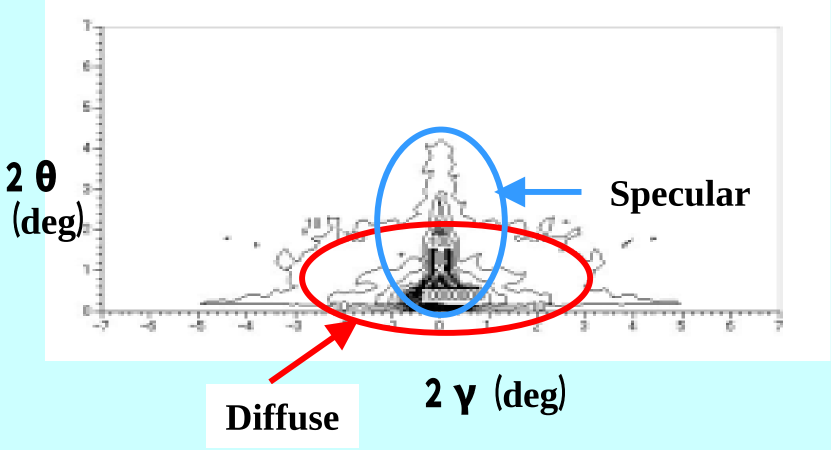
➡ Need decomposition of each contribution by complex analysis.

➡ Introduce uncertainty in results.

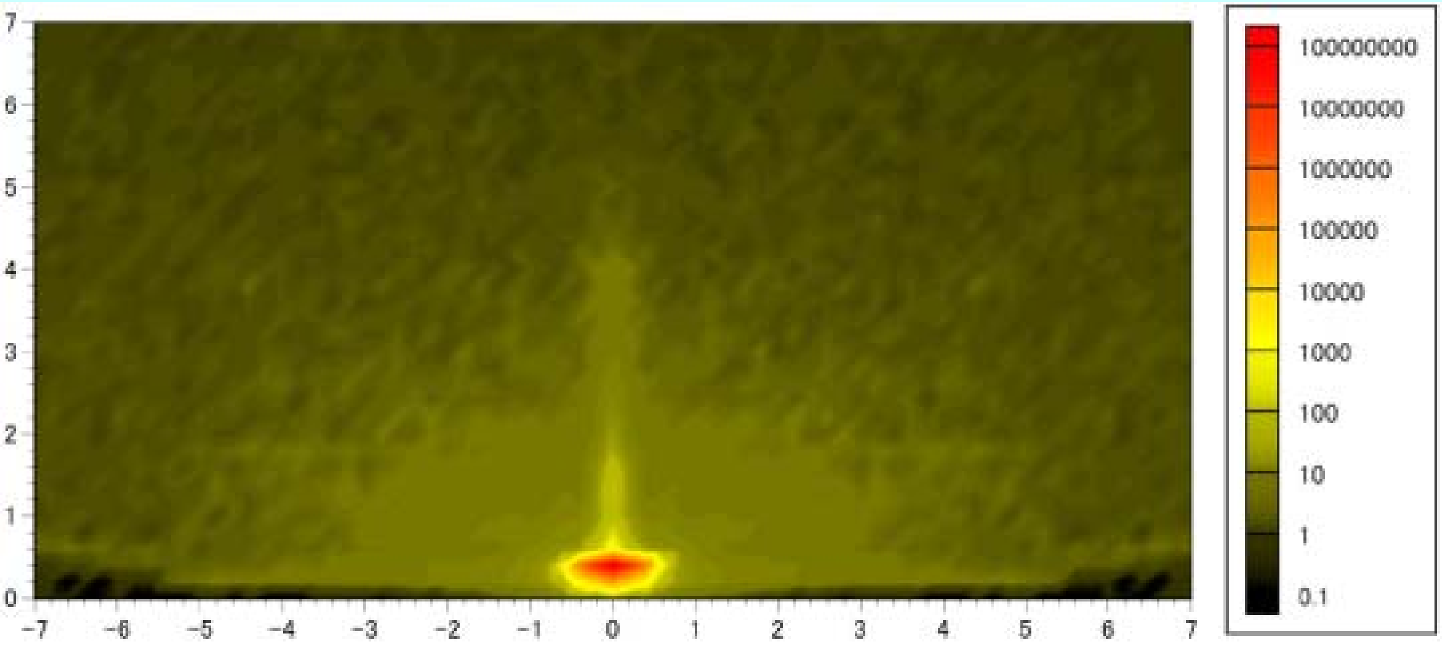
3-2. 2-dimensional GISAXS measurement

$\alpha \approx 1.5\theta_c$

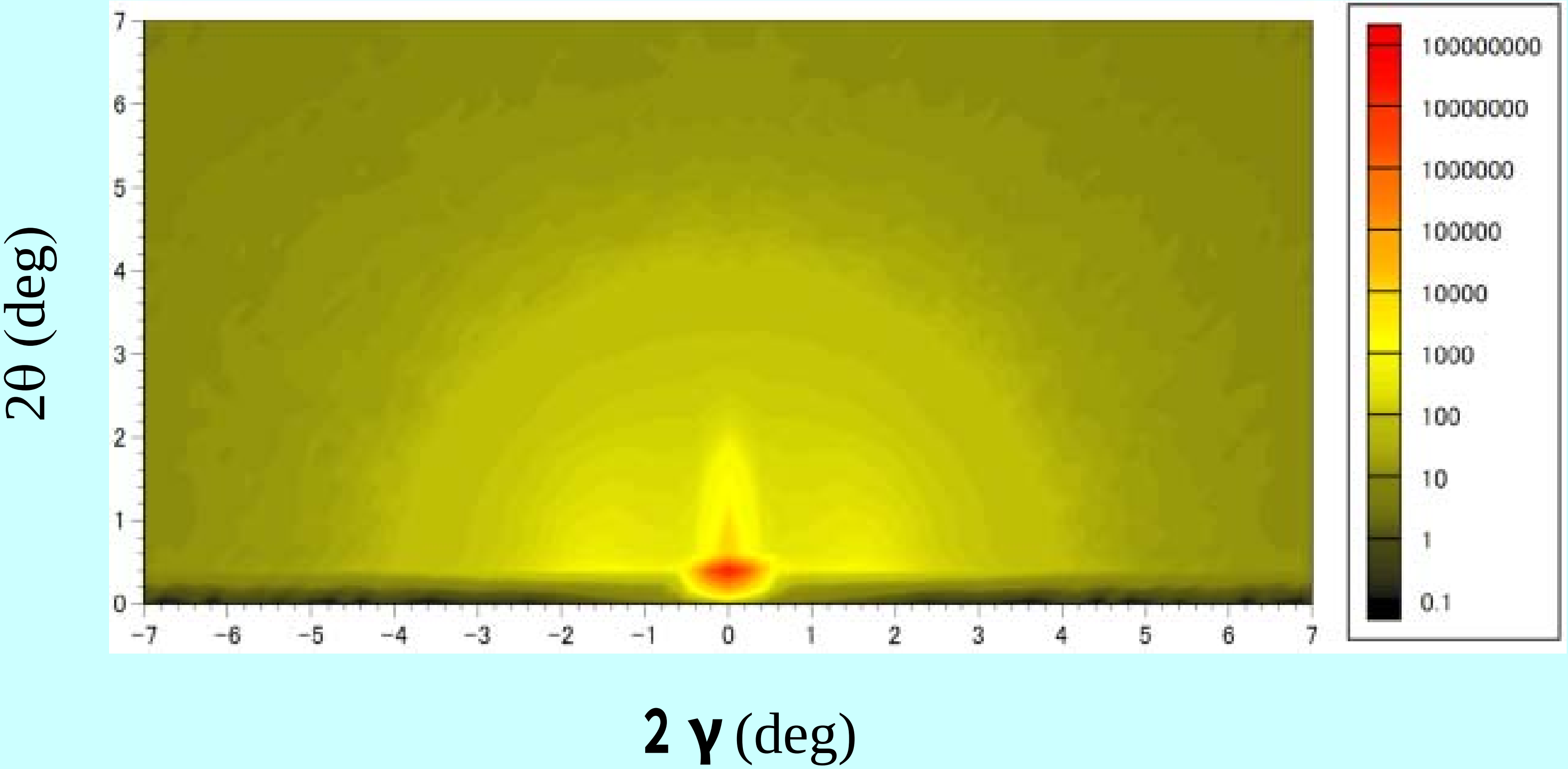




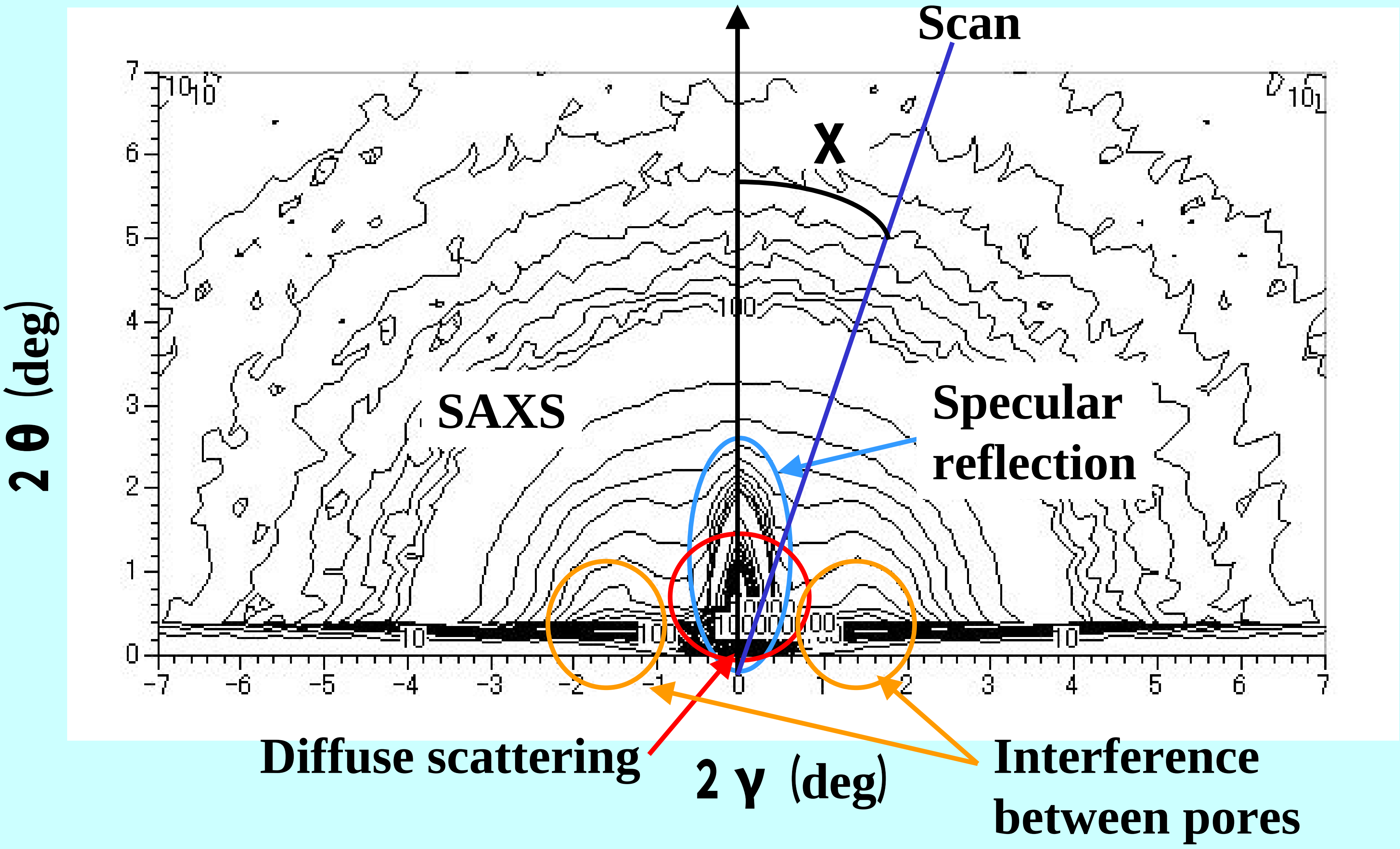
Si wafer



Low-k (NCS) film t=0.2 μm



$\lambda = 1.4 \text{Å} \qquad \alpha = 0.2^{\circ}$



Scan

SAXS

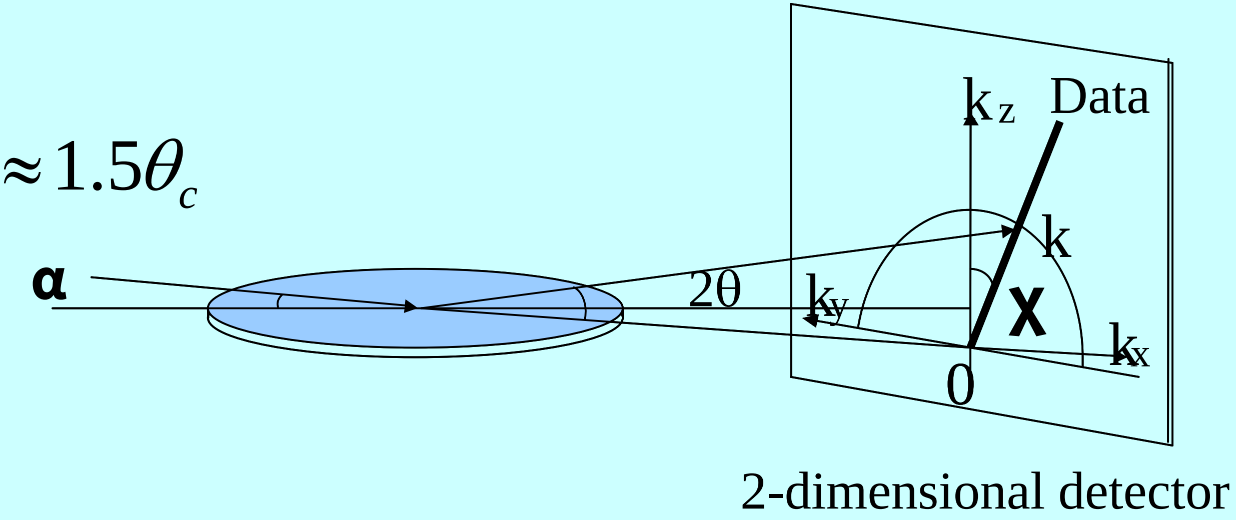
Specular reflection

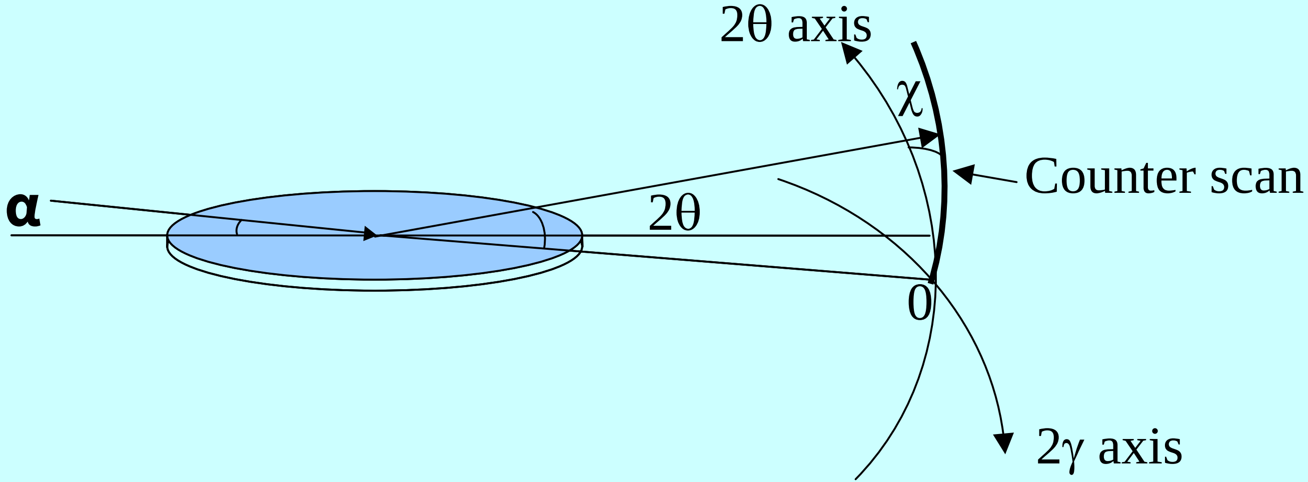
Diffuse scattering

Interference between pores

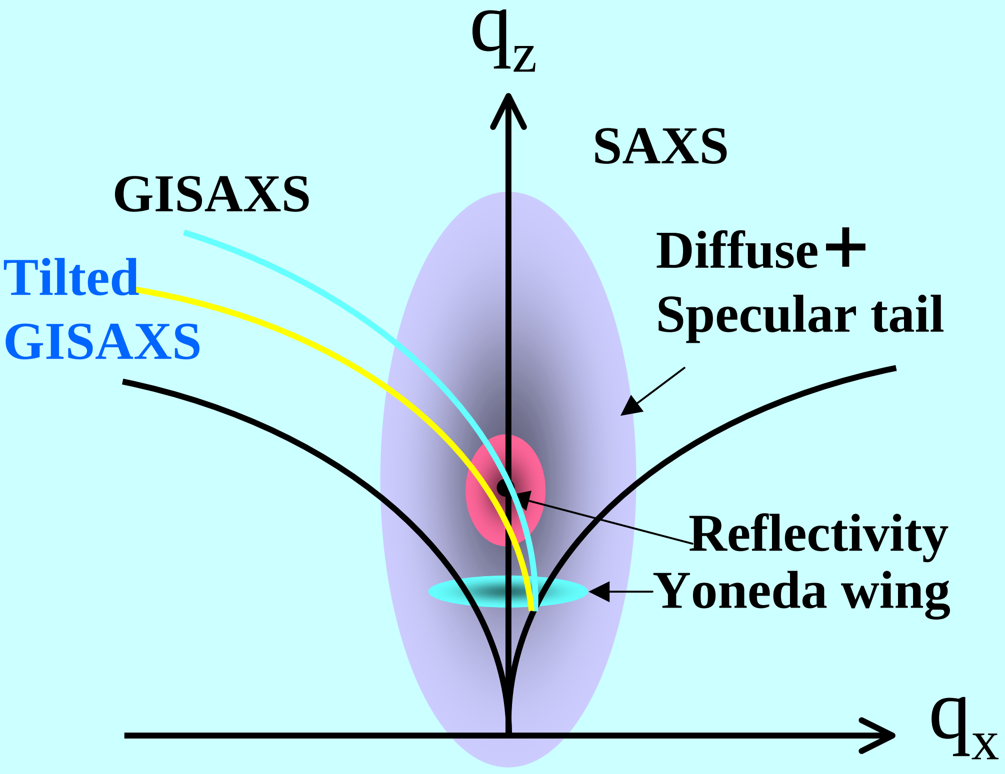
3-3. A new ‘Tilted GISAXS’ configuration

$$\alpha \approx 1.5\theta_c$$





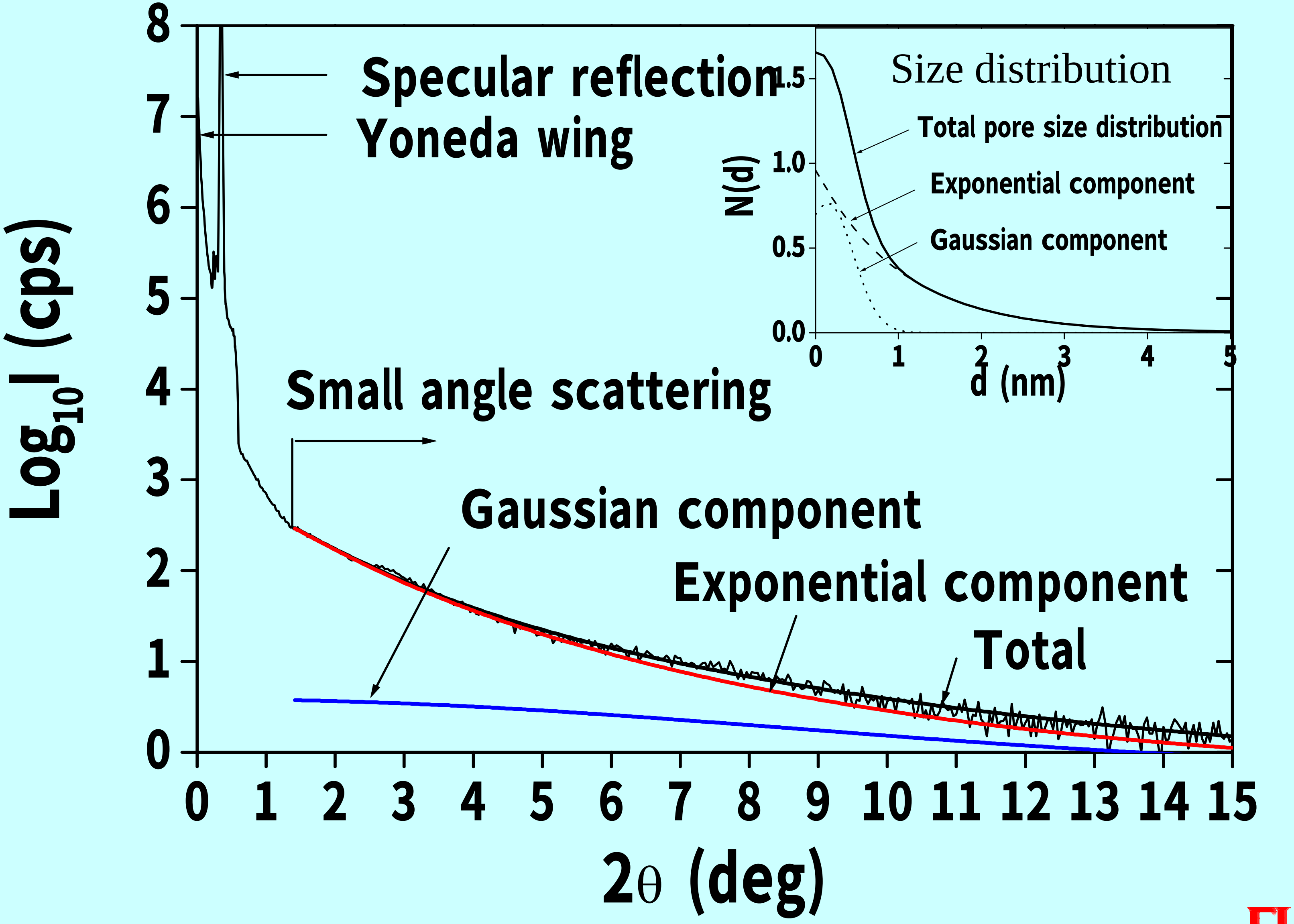
Tilted GISAXS



q-space

a. Fixed incidence angle
b. Avoid scan in vertical plane where non SAXS exists

Low-k NCS sample with χ=10 °



4. Conclusion

(1)Two component size distribution model
Gaussian + Exponential distribution

(2)New ‘Tilted GISAXS’ measurement
Avoid parasitic contribution of diffuse and specular scattering

(3) Thin low-k films (NCS) are successfully evaluated.
Average diameter 1.1nm with exponential-like
pore size distribution.