Small Angle X-ray Scattering and Applications in Structural Analysis

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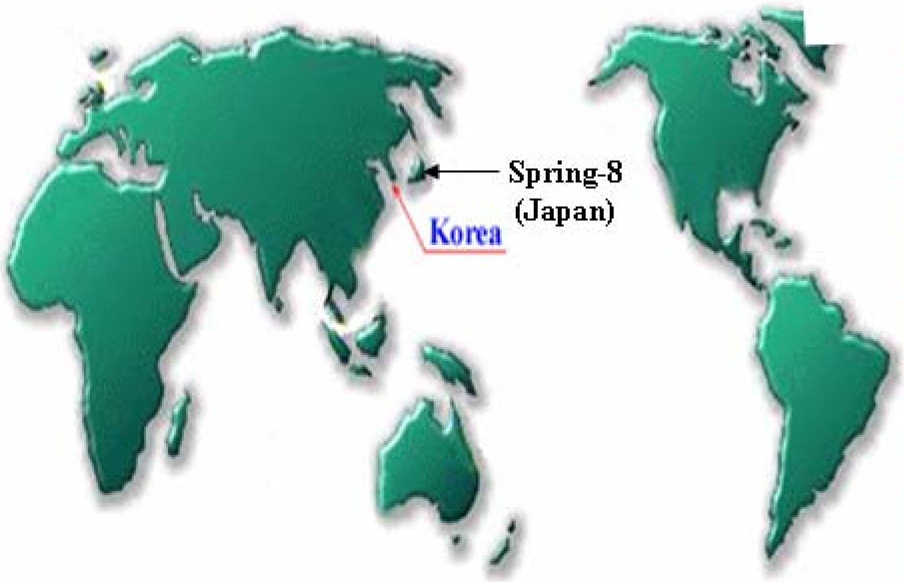
Outline

1. Introduction – POSTECH & Pohang Light Source
2. Optics, Beamlines and Equipments of SAXS
3. Data Collection and Samples
4. Fundamentals of SAXS
5. Fundamentals of Conventional, Transmission SAXS (TSAXS)
    (1) Single Molecule (or Particle)
    (2) Multiple Molecules (or Particles) and Their Assemblies
6. Fundamentals of Grazing Incidence SAXS (GISAXS)
    (1) Static GISAXS
    (2) In-Situ GISAXS
1. Conclusions – I, II
2. References
3. Introduction – M. Ree's Group at Postech
4. Acknowledgments


Spring-8
(Japan)
Korea

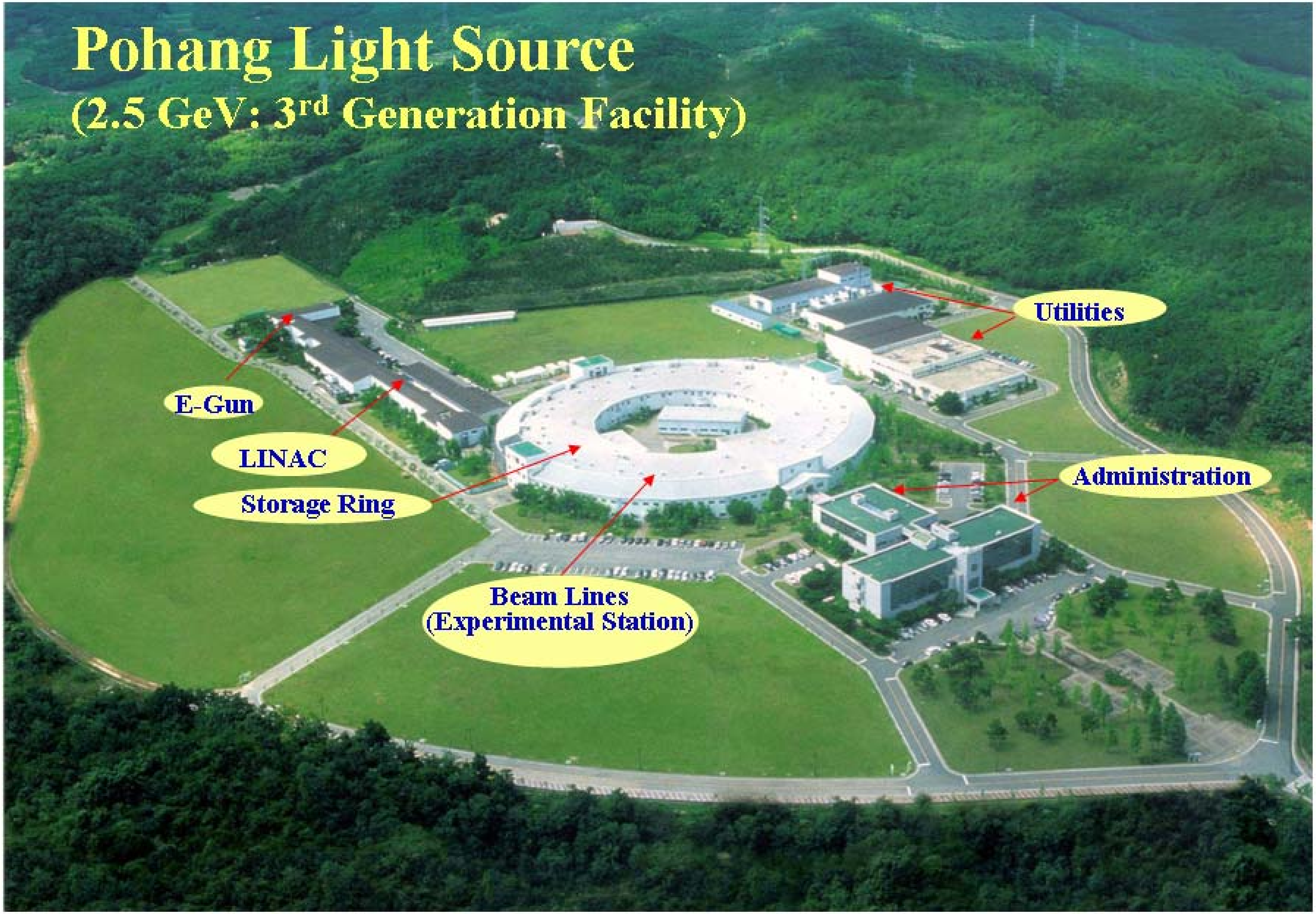

Kimpo International Airport
Seoul
Seoul Station
Express bus Station
Pohang
Pusan
Kimhae International Airport
Cheju Island


Korea
Seoul
Daejeon
Pohang
Gwangju
Busan


Pohang Light Source
POSTECH
Campus

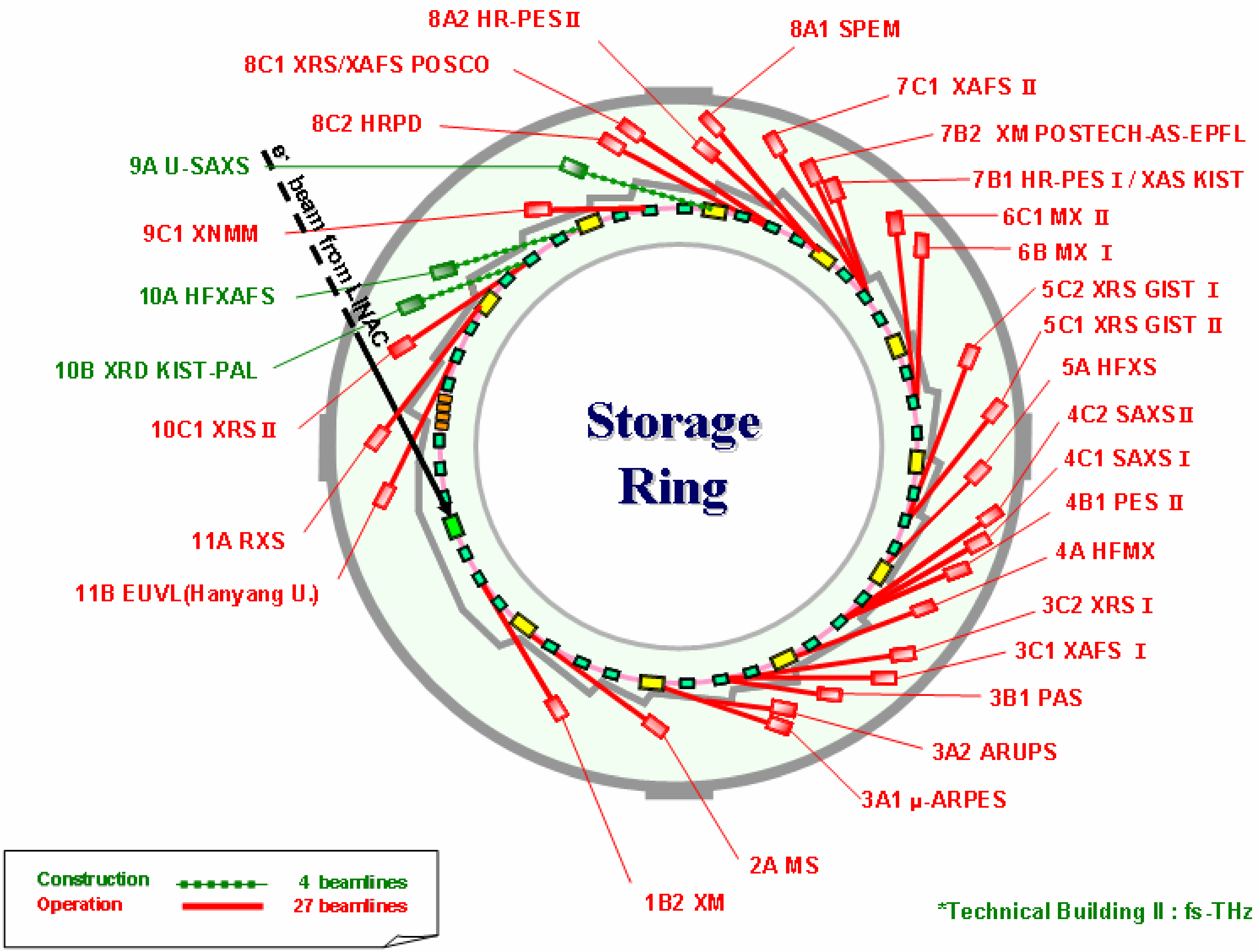
Pohang Light Source

(2.5 GeV: 3rd Generation Facility)



SEPTEMBER 2007

PLS Beamline Status



*Technical Building II : fs-THz

M. Ree et al., *Phys. High Tech.*(Korea), 14(3-4), 2-7 (2005)

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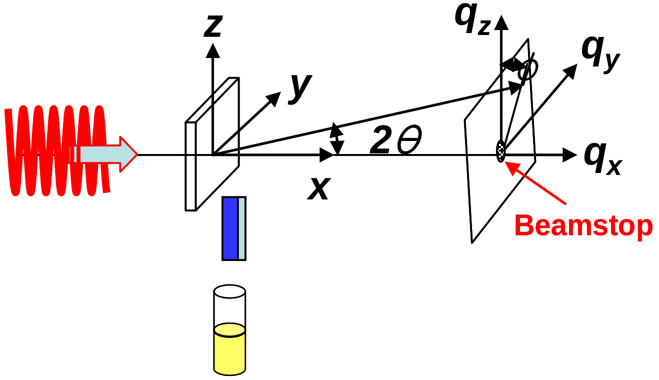
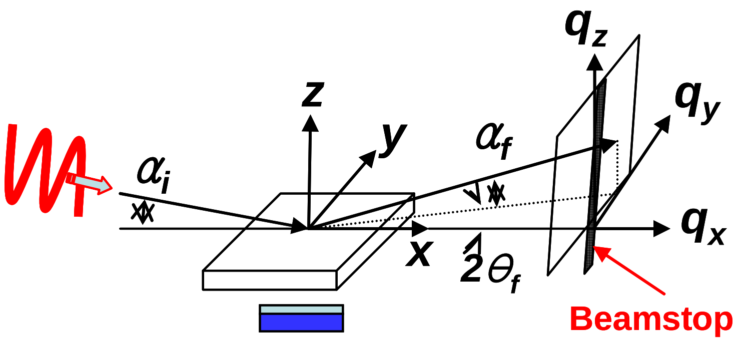
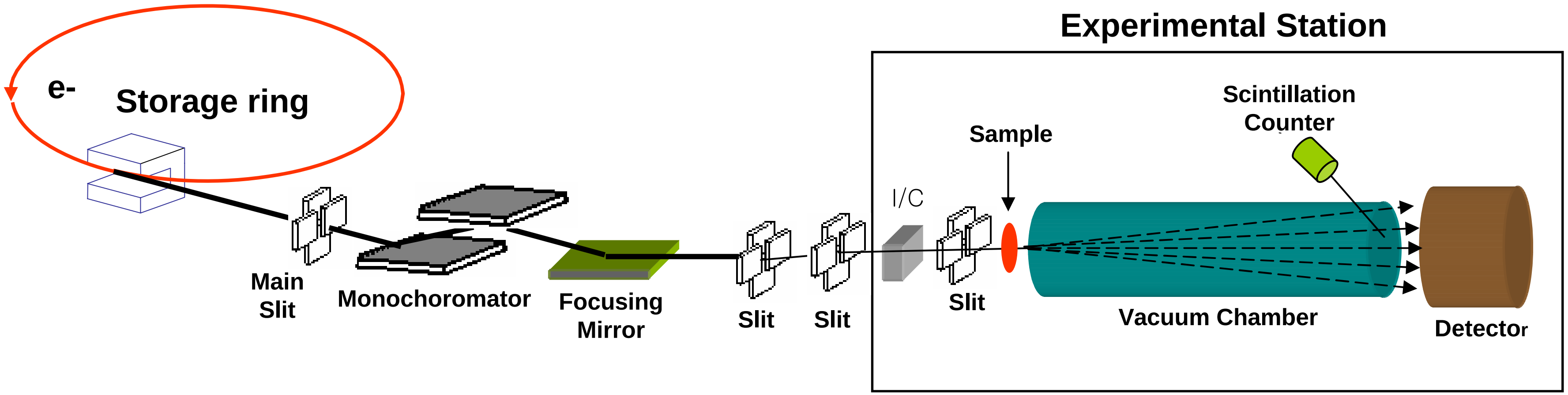
Optics of
Small Angle X-ray Scattering (SAXS)





SAXS Beamlines



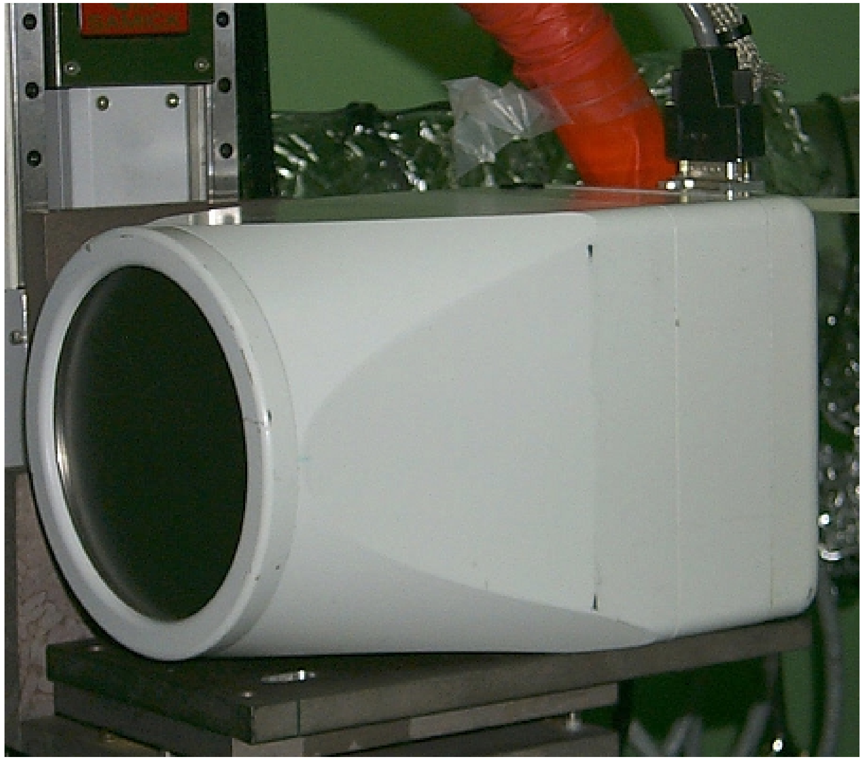
X-rays at the sample

- Photon flux (monochoromatic, focusing) :

  $10^{11} – 10^{18}$ photons/sec/mm^2 at 8 keV

- Beam size : < 0.8 × 0.8 mm^2

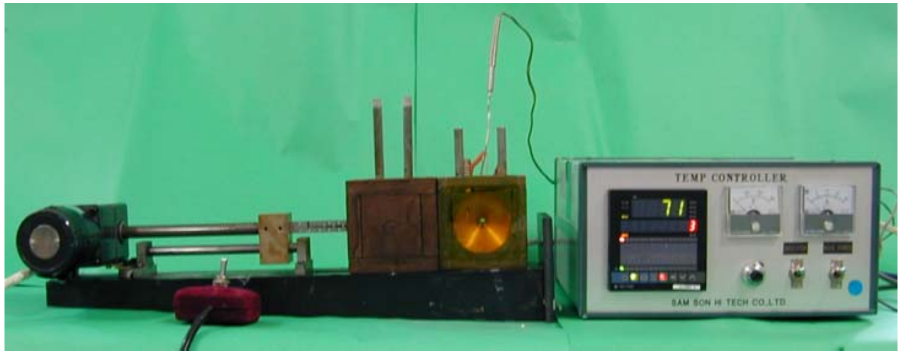
2-D CCD X-Ray Detector

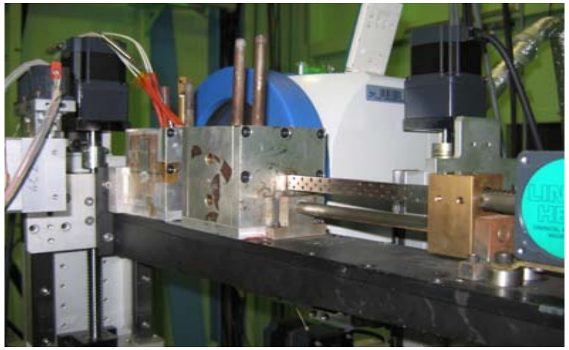


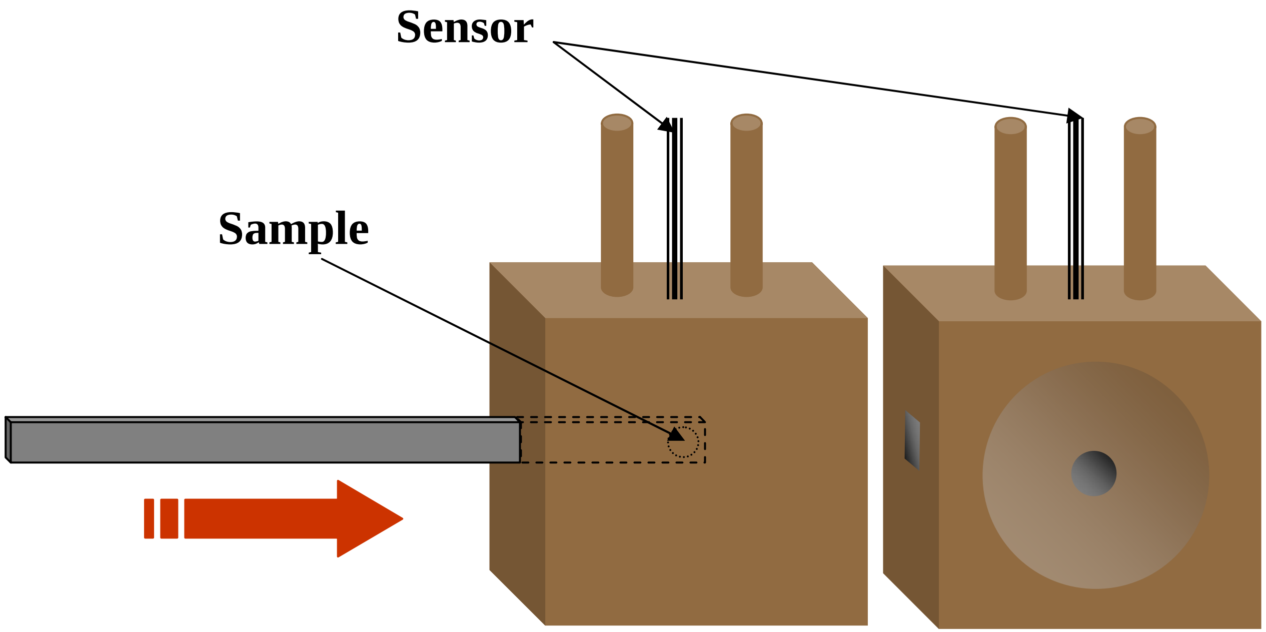
Roper Scientific

MAR research

Device for Temperature Jumping







Sensor

Sample

Temperature A

Temperature B

Other Devices for Samples

1. **Mechanical Tester**
2. **Rheometer**
3. **DSC**
4. **Liquid Cell**
5. **Liquid Flow Cell**
6. **Fiber Spinner**
7. **Magnets**
8. **Many Other Devices**
   depending on what you want

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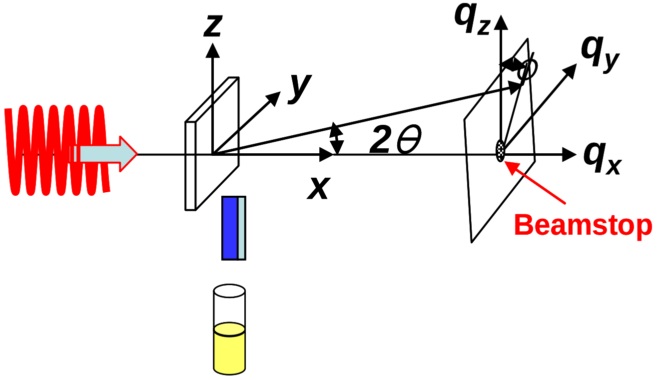
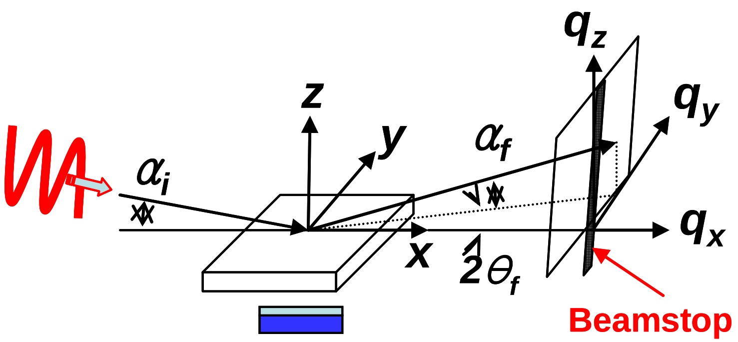
Data Collection Time and Sample Thickness (Volume) in SAXS Measurements





Optimization of Collection Time (Error Analysis)

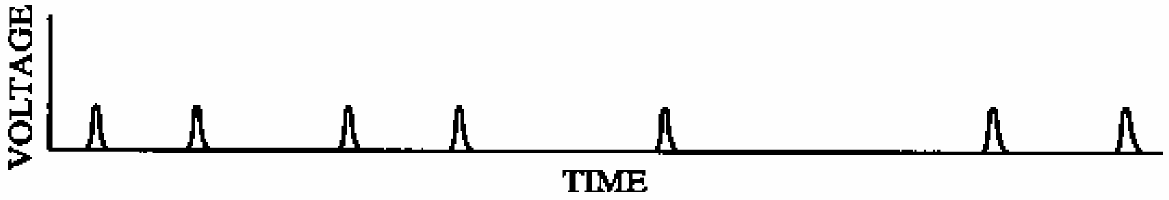


Figure 6-12 Randomly spaced voltage pulses produced by a detector.

Poisson distribution

$$P(N) = \frac{(nt)^N e^{-nt}}{N!}$$

nt: average value

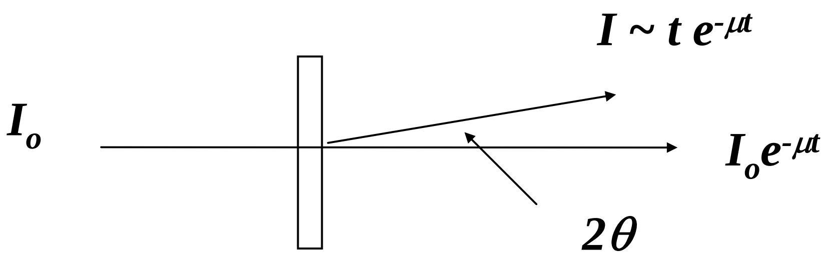
P(N) ; probability of having N count in a given time t

$$\pm\frac{\sqrt{N}}{N}$$

Relative error possessed in the count N

number of pulses counted	standard deviation (%)	collection time (sec)
1,000	3.2	1
10,000	1.0	10
100,000	0.3	100

Optimum Sample Thickness (transmission geometry)



t, μ : Thickness, Linear Absorption Coefficient

$$I_{obs}(s) \sim t \cdot e^{-\mu t}$$

$$t_{opt} = \frac{1}{\mu}$$

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Fundamentals of
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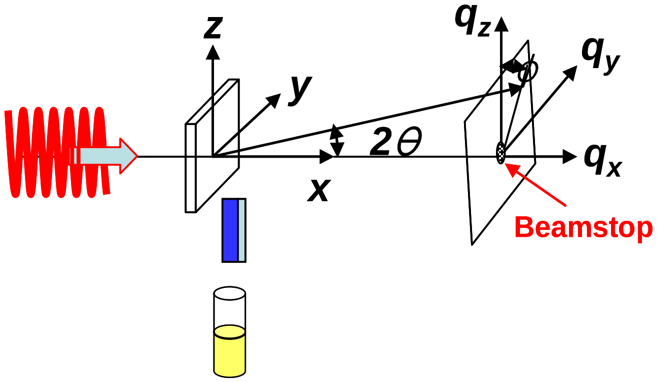

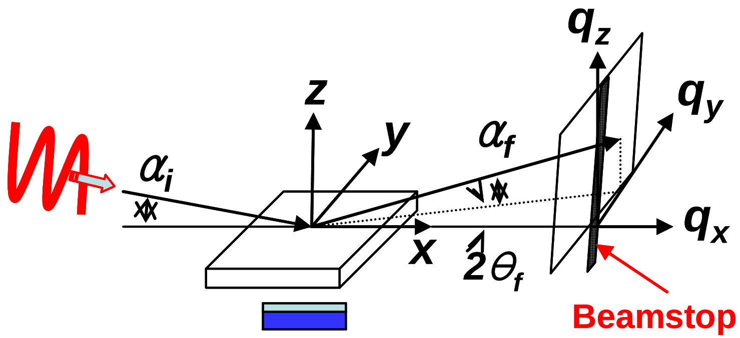

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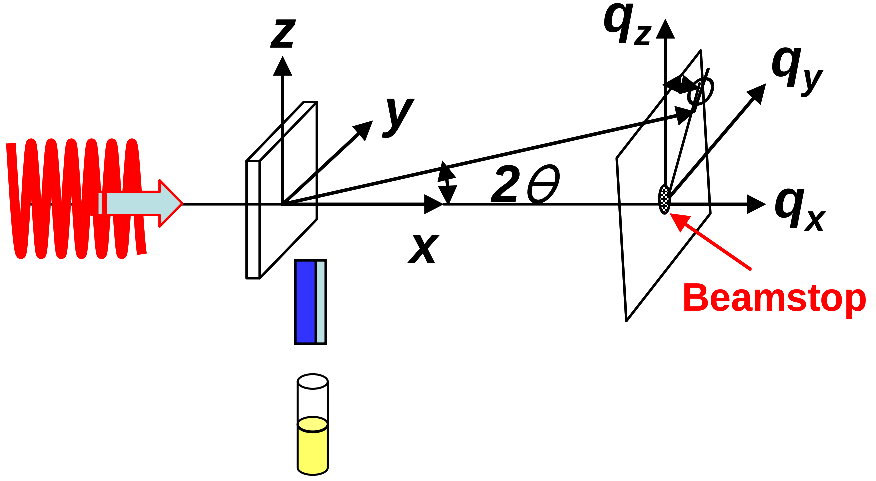
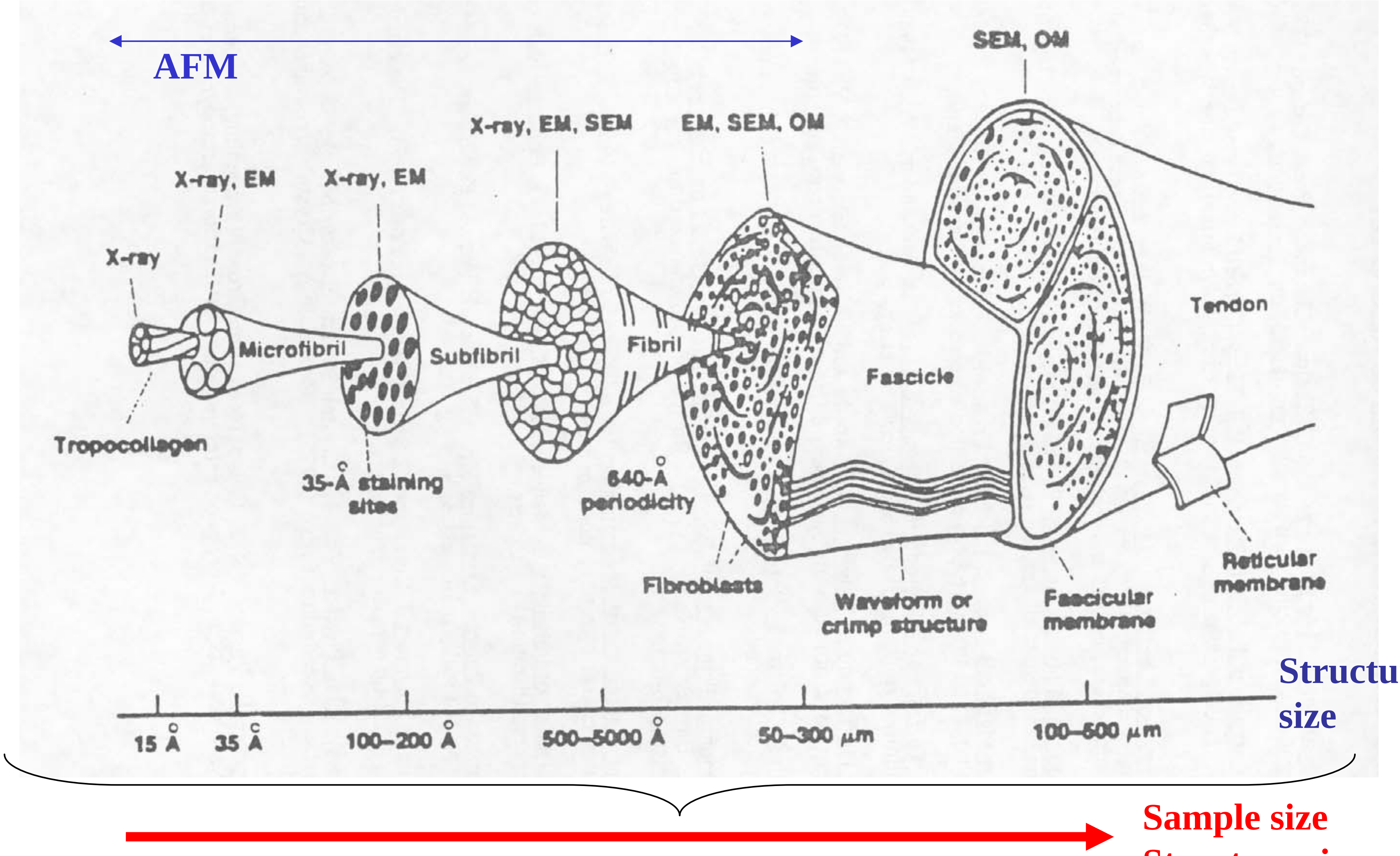
Fundamentals:

Conventional
Small Angle X-ray Scattering (SAXS)

Transmission Small Angle X-ray Scattering (TSAXS)



Length Scales in Structure

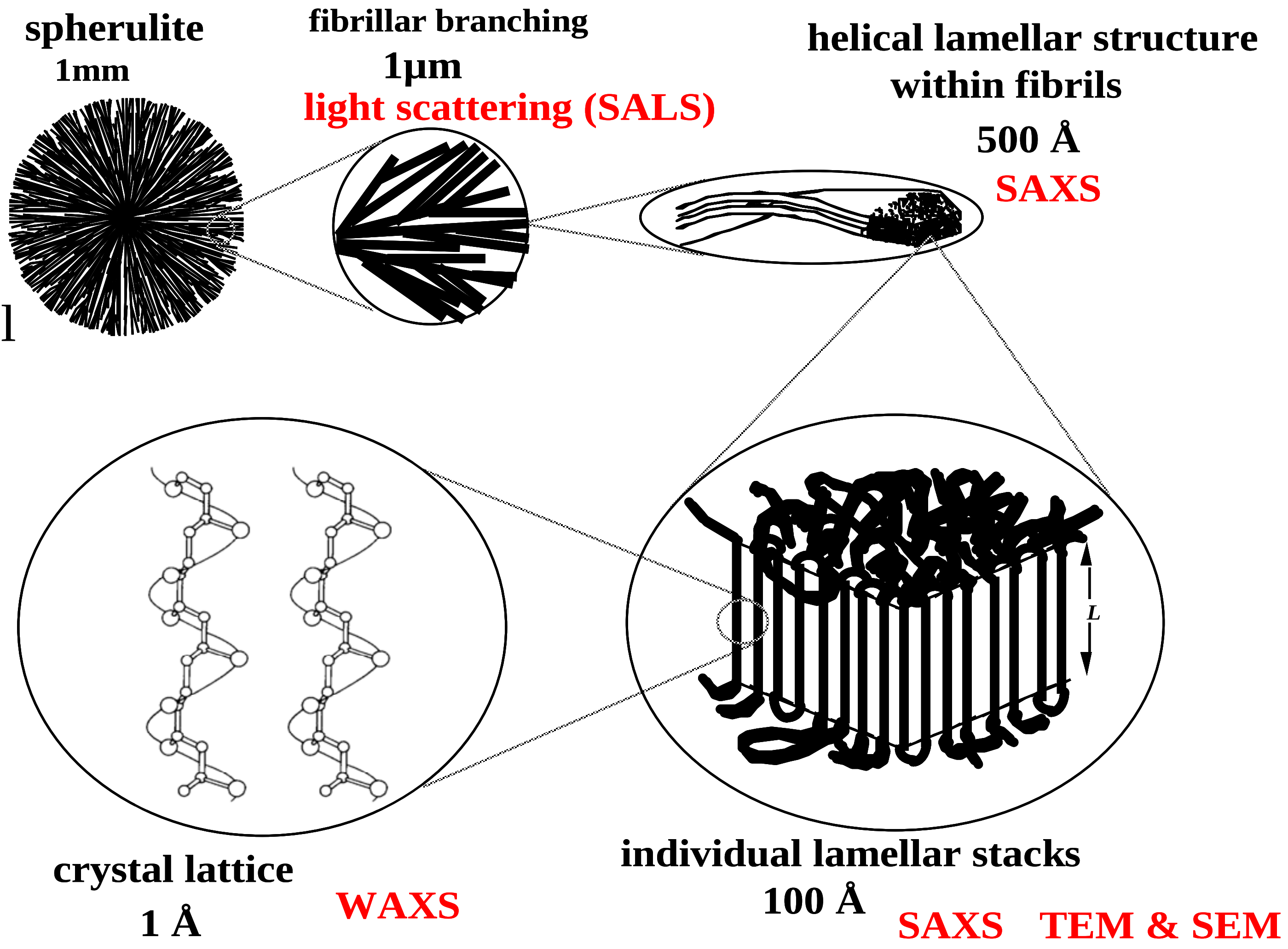


AFM

Structure size

Sample size
Structure size

Hierarchical Structure of Polymer Crystals



spherulite
1mm

optical microscopy (OM)

fibrillar branching
1μm
light scattering (SALS)

helical lamellar structure within fibrils
500 Å
SAXS

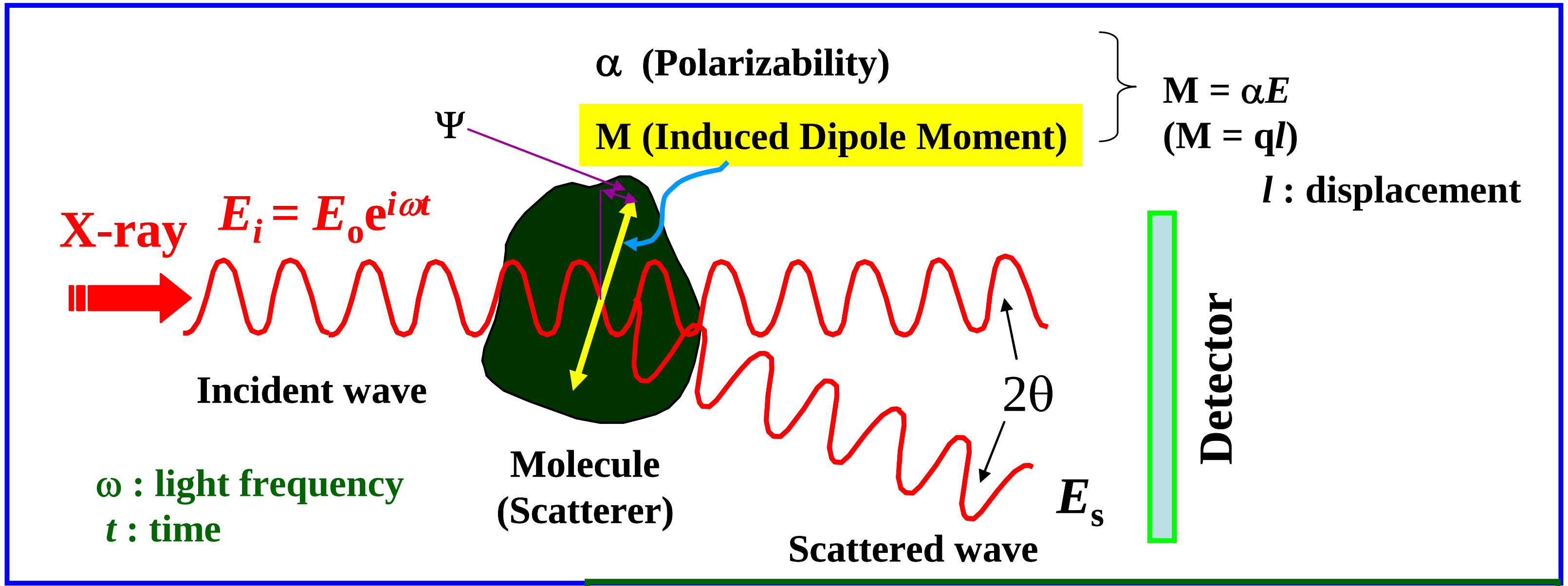
crystal lattice
1 Å
WAXS

individual lamellar stacks
100 Å
SAXS TEM & SEM

Experimental techniques for the length scales involved are indicated in Red

X-Ray Scattering from Single Molecule (or Particle)

X-Ray Scattering from One Molecule (Particle)



M = α*E*
(M = q*l*)
l : displacement

ω : light frequency
t : time

$$E_s = \frac{(\partial^2 \mathbf{M}/\partial t^2)}{c^2 r}\cos\Psi$$

$$\mathbf{M} = \alpha E = \alpha E_o e^{i\omega t}$$

$$(\partial^2 \mathbf{M}/\partial t^2) = -\alpha\omega^2 E_o e^{i\omega t}$$

$$E_s = \frac{-\alpha\omega^2 E_o e^{i\omega t}}{c^2 r}\cos\Psi$$

$I_s = E_s \cdot E_s^*$ (scattered wave intensity)

$I_o = E_o \cdot E_o^* = E_o^2$ (incident wave intensity)

c : light speed
r : sample-to-detector distance

LOW FREQUENCY (Rayleigh) CASE, $\omega << \omega_o$ → **Light scattering**

$$\alpha = e^2 / k$$

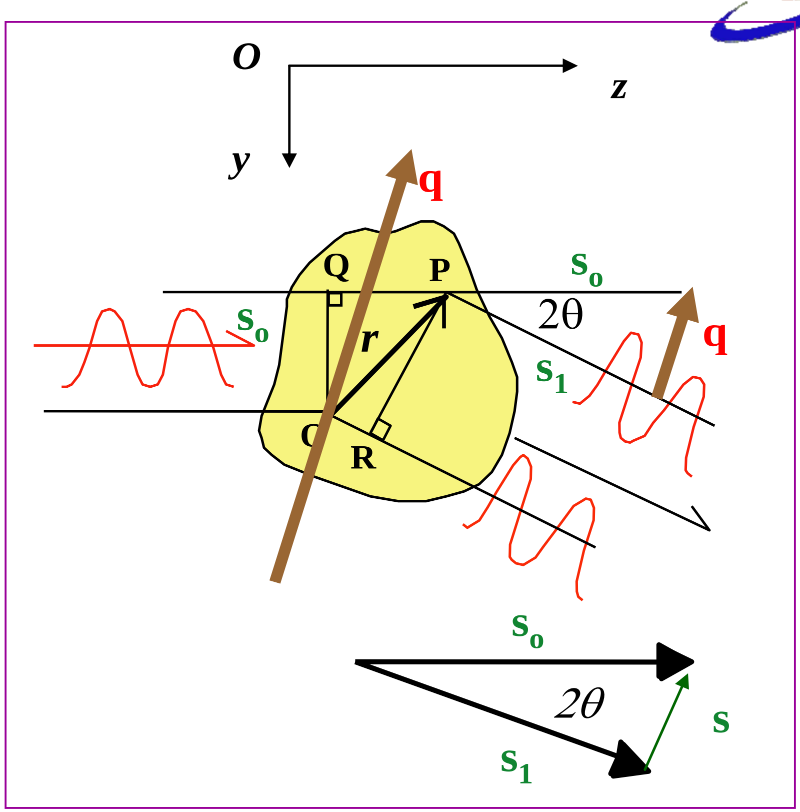
HIGH FREQUENCY (Thomson) CASE, $\omega >> \omega_o$ → **X-Ray Scattering**

$$\alpha = e^2 / m\omega^2$$

It is independent of k and decreases with ω. **(because ω is very high.)**

e : charge of an electron
k : force constant
m : mass of an electron

Scattering vector



Scattering vector

$$\mathbf{s}_o = \mathbf{e}_z, \qquad \mathbf{s}_1 = \mathbf{e}_y \sin 2\theta + \mathbf{e}_z \cos 2\theta$$

$$\mathbf{s} = \mathbf{s}_o - \mathbf{s}_1 = \left[\mathbf{e}_z(1-\cos 2\theta) - \mathbf{e}_y \sin 2\theta\right]$$

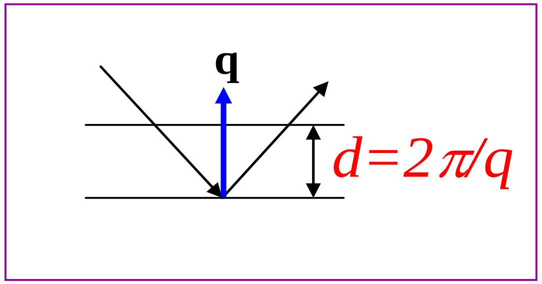
$k = 2\pi/\lambda$ **Wave number (modulus of wave vector)**

$$s = |\mathbf{s}| = \left[(1-\cos 2\theta)^2 + \sin^2 2\theta\right]^{1/2} = 2\sin\theta$$

$$\mathbf{q} = k\,\mathbf{s} \qquad q = k\,s = \frac{4\pi}{\lambda}\sin\theta$$

Bragg's eq.: lattice spacing d

$$2d\sin\theta = n\lambda(n = 1,2,3\ldots) \Rightarrow d = \frac{n\lambda}{2\sin\theta} = \frac{2\pi}{q}\,(n=1)$$



The phase difference δ, from O and P is equal to the inner vector product, q.r.

$$\delta = \frac{2\pi}{\lambda}(\mathrm{QP} - \mathrm{OR}) = \frac{2\pi}{\lambda}(\mathbf{s}_o\cdot\mathbf{r} - \mathbf{s}_1\cdot\mathbf{r}) = \mathbf{q}\cdot\mathbf{r}$$

Phase Factor $\delta =$ $\mathbf{q}\cdot\mathbf{r}$

$$E_s = \frac{-\alpha\omega^2 E_o e^{i\omega t}}{c^2 r}\cos\Psi$$

$$E_s = \frac{-\omega^2 E_o e^{i\omega t}}{c^2 r}\cos\Psi \sum_i \alpha_i e^{-ikx_i}$$

$$F = \sum_i \rho_i e^{-ikx_i}$$

$$F(\mathbf{r}_i) = \sum_i \rho_i e^{-i(\mathbf{q}\cdot\mathbf{r}_i)}$$

F : **Form Factor**

$$E_s = K_s F(\mathbf{r}_i)$$

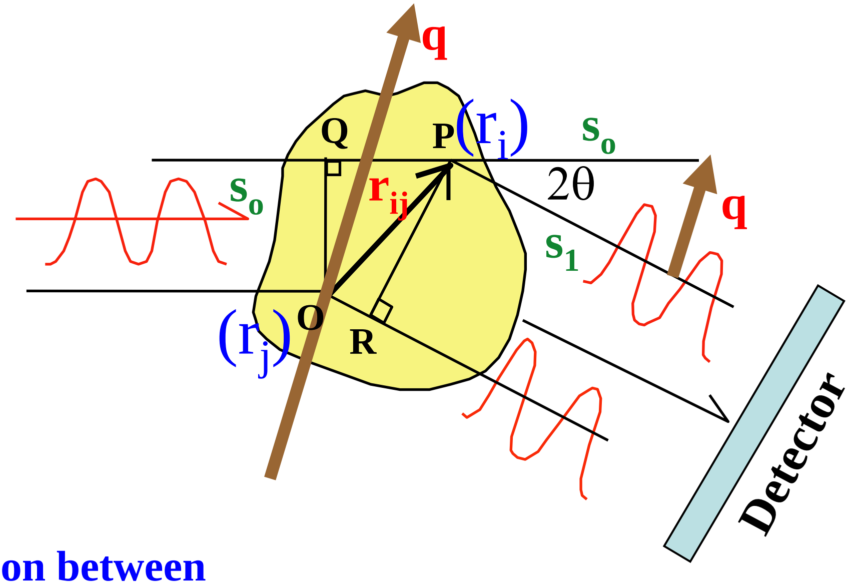
$$K_s = \frac{-\omega^2 E_o e^{i\omega t}}{c^2 r}\cos\Psi$$

$$I_s = E_s \cdot E_s^*$$

$$I_s = K_s\{F(\mathbf{r}_i)\cdot F^*(\mathbf{r}_i)\}$$

I_s : **Scattering Intensity**

$$\left.\begin{aligned} F(\mathbf{r}_i) &= \sum_i \rho_i(\mathbf{r}_i) e^{-i(\mathbf{q}\cdot\mathbf{r}_i)} \\ F(\mathbf{r}_j) &= \sum_j \rho_j(\mathbf{r}_j) e^{-i(\mathbf{q}\cdot\mathbf{r}_j)} \end{aligned}\right\} \quad \begin{aligned} \rho(\mathbf{r}_i) &= \rho_o + \Delta\rho_i \\ \rho(\mathbf{r}_j) &= \rho_o + \Delta\rho_j \end{aligned}$$



$$I_s = K_s\{F(\mathbf{r}_i)\cdot F^*(\mathbf{r}_i)\}$$

$$= K_s \sum_i \rho_i e^{-i(\mathbf{q}\cdot\mathbf{r}_i)} \sum_j \rho_j e^{i(\mathbf{q}\cdot\mathbf{r}_j)}$$

(no correlation between the fluctuation of a volume element and its distance away from another)

$$= K_s \sum_i \sum_j \{\underbrace{\cancel{\rho_o^2 e^{-i(\mathbf{q}\cdot\mathbf{r}_{ij})}}}_{0} + \underbrace{\cancel{\rho_o \Delta\rho_i e^{-i(\mathbf{q}\cdot\mathbf{r}_{ij})}}}_{0} + \underbrace{\cancel{\rho_o \Delta\rho_j e^{-i(\mathbf{q}\cdot\mathbf{r}_{ij})}}}_{0} + \Delta\rho_i \Delta\rho_j e^{-i(\mathbf{q}\cdot\mathbf{r}_{ij})}\}$$

(homogeneous)

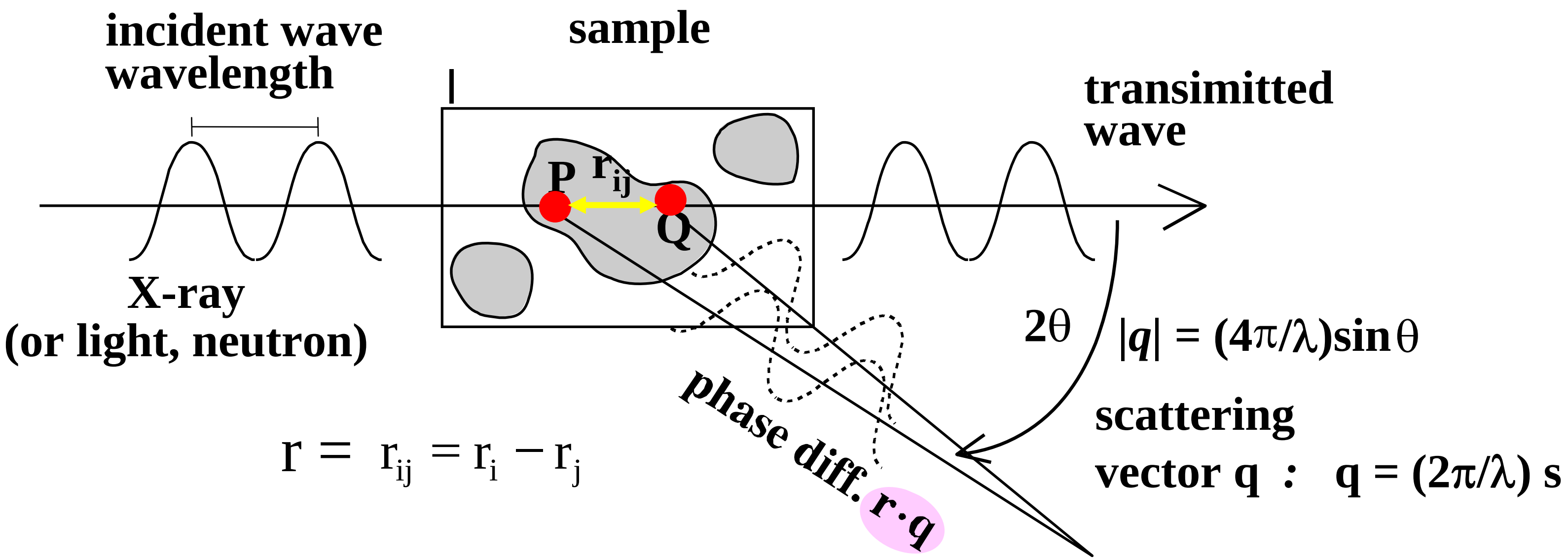
$$I_s = K_s \sum_i \sum_j \Delta\rho_i \Delta\rho_j e^{-i(\mathbf{q}\cdot\mathbf{r}_{ij})}$$

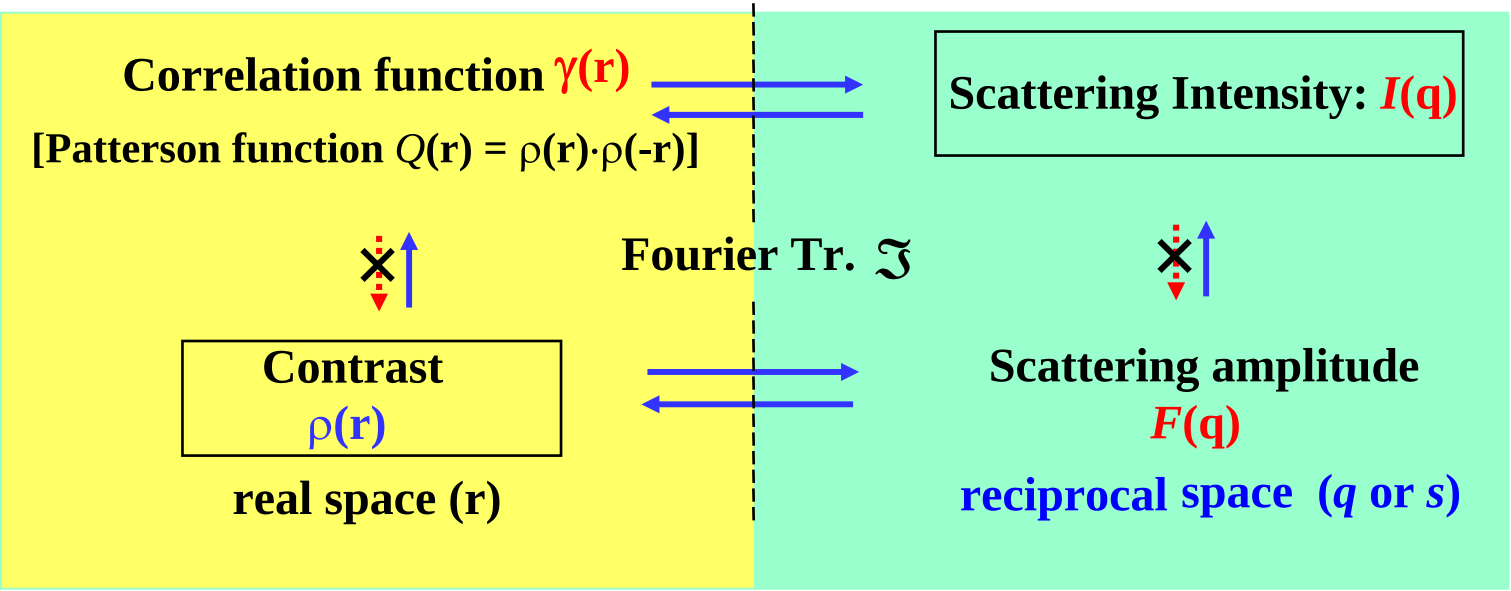
$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ **(interdistance of a pair of scatters)**

$$\boxed{I_s(\mathbf{q}) = K_s \sum_i \sum_j \Delta\rho_i(\mathbf{r}) \Delta\rho_j(\mathbf{r}) e^{-i(\mathbf{q}\cdot\mathbf{r})}}$$

(a generalized scattering equation)

Structure analysis by Scattering and Concept of Real and Reciprocal Spaces





Correlation function $\gamma(r)$

[Patterson function $Q(r) = \rho(r) \cdot \rho(-r)$**]**

Scattering Intensity: $I(q)$

Fourier Tr. $\mathfrak{F}$

Contrast
$\rho(r)$

real space (r)

Scattering amplitude
$F(q)$

reciprocal space (*q* or *s*)

How to find Scattering Amplitude [*F*(r)] from Scattered Intensity?

$$I_s(\mathbf{q}) = K_s \sum_i \sum_j \Delta\rho_i(\mathbf{r})\Delta\rho_j(\mathbf{r}) e^{-i(\mathbf{q}\cdot\mathbf{r})}$$

$$I(\mathbf{q}) = K_s\,[F(\mathbf{r})\cdot F^*(\mathbf{r}')]$$

Correlation function

$\gamma(\mathbf{r})$

(1) Correlation Function Approach

- Correlation function $\gamma(\mathbf{r})$

(2) Fine Structural Model Approach

- sphere
- Gaussian sphere
- core/shell sphere
- rod
- cylinder
- disc

etc

(1) Correlation function Approach

Auto-Correlation Function $\gamma(r)$ (Patterson Function)

$$\gamma(\mathbf{r}) = \frac{\Delta\rho(\mathbf{r}) * \Delta\rho(-\mathbf{r})}{\int_0^\infty [\Delta\rho(\mathbf{r})]^2 \, d\mathbf{r}} = \frac{\int_0^\infty \Delta\rho(\mathbf{u})\Delta\rho(\mathbf{r}+\mathbf{u})\,d\mathbf{u}}{\int_0^\infty \Delta\rho(\mathbf{u})\Delta\rho(\mathbf{u})\,d\mathbf{u}}$$

$$\gamma(\mathbf{r}) = \Im^{-1}\{I_{obs}(\mathbf{q})\} \cdot \frac{1}{\langle(\Delta\rho)^2\rangle V}$$

$$\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0$$

For an isotropic system $|\mathbf{q}| = q,\ |\mathbf{r}| = r$

$$\gamma(r) = \Im^{-1}\{I_{obs}(q)\} \frac{1}{\langle\{\Delta\rho(u)\}^2\rangle V} = \frac{\int q^2 I_{obs}(q) \frac{\sin qr}{qr} dq}{\int q^2 I_{obs}(q) dq}$$

Pair Distance Distribution Function (PDDF) $p(r) = r^2 \gamma(r)$

Correlation function *versus* Scattering intensity

Density distribution

$$\rho(\mathrm{r}) \longrightarrow \gamma(\mathbf{r})$$

Correlation of paired scatters

Correlation function

$$\gamma(\mathbf{r}) = \underbrace{\int \rho(\mathbf{r}')\rho(\mathbf{r}-\mathbf{r}')d\mathbf{r}'}\,/\underbrace{\int \rho^2(\mathbf{r}')d\mathbf{r}'}$$

Scattering intensity $\updownarrow$ **Fourier transform**

$$I(q) = \frac{K}{V}\int \gamma(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}$$

$\mathbf{r} = \mathbf{r} - \mathbf{r}'$

Patterson Function

$$\begin{tikzcd}
\substack{\gamma(\mathbf{r})\\ Q(\mathbf{r})} \arrow[r, leftrightarrow, "\Im"] \arrow[d, shift right, "\times"'] & I(\mathbf{q}) \arrow[d, shift left, "\times"] \\
\rho(\mathbf{r}) \arrow[u, shift right] \arrow[r, leftrightarrow, "\Im"'] & F(\mathbf{q}) \arrow[u, shift left]
\end{tikzcd}$$

$$I(\mathbf{q}) = \Im\{Q(\mathbf{q})\} \qquad Q(\mathbf{r}) = \Im^{-1}\{I(\mathbf{q})\}$$

$$Q(\mathbf{r}) = \rho(\mathbf{r}) * \rho(-\mathbf{r}) = \int \rho(\mathbf{u})\rho(\mathbf{r}+\mathbf{u})\,d\mathbf{u}$$

$$Q(\mathbf{r}) = \int_0^\infty (\Delta\rho(\mathbf{u}) + \rho_0)(\Delta\rho(\mathbf{r}+\mathbf{u}) + \rho_0)\,d\mathbf{u}$$
$$= \int \Delta\rho(\mathbf{u})\Delta\rho(\mathbf{r}+\mathbf{u})\,d\mathbf{u} + C$$

$$\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0$$

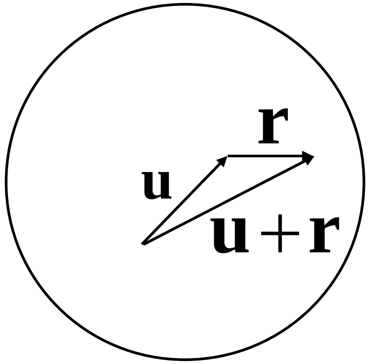
$$I(\mathbf{q}) = \Im\{\Delta\rho(\mathbf{r}) * \Delta\rho(-\mathbf{r})\} + \Im\{C\}$$

$$I_{obs}(\mathbf{q}) = \Im\{\Delta\rho(\mathbf{r}) * \Delta\rho(-\mathbf{r})\}$$

$$I_{obs}(\mathbf{q}) = \Im\left[Q_{\Delta\rho}(\mathbf{r})\right] \Leftrightarrow Q_{\Delta\rho}(\mathbf{r}) = \Im^{-1}\{I_{obs}(\mathbf{q})\}$$

Meaning of Correlation Function

$$\frac{\int_0^\infty \Delta\rho(\mathbf{u})\Delta\rho(\mathbf{r}+\mathbf{u})d\mathbf{u}}{\int_0^\infty \Delta\rho(\mathbf{u})\Delta\rho(\mathbf{u})d\mathbf{u}}$$



$$\rho(r)=\begin{Bmatrix}\rho & inside\\ 0 & outside\end{Bmatrix}$$

u *and* **r + u** ***(inside the particle):*** $\gamma(\mathbf{r})=1$

r + u ***(outside the particle):*** $\gamma(\mathbf{r})=0$

γ depending on particle shape and size,
representing the probability of finding of a point u + r within the particle

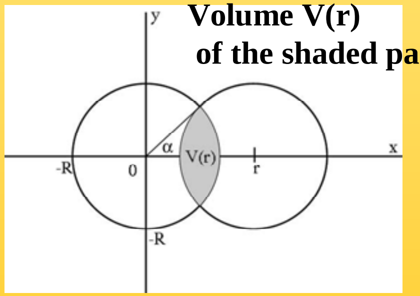
Correlation function of sphere of radius R

$$\gamma(r)=0 \qquad r>2R$$

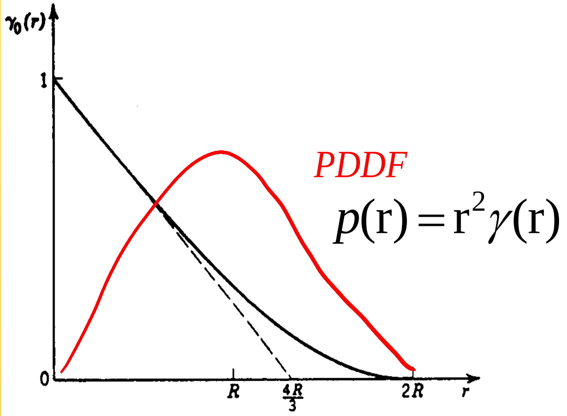
$$\gamma(r)=1-\frac{3}{4}\frac{r}{R}+\frac{1}{16}(\frac{r}{R})^3$$

$$\gamma(r)\equiv\frac{V(r)}{4\pi R^3/3}=\frac{1}{2}\left(1-\frac{r}{2R}\right)^2\left(2+\frac{r}{2R}\right)$$

$$=1-\frac{3}{4}\left(\frac{r}{R}\right)+\frac{1}{16}\left(\frac{r}{R}\right)^3$$



Volume V(r)
of the shaded part

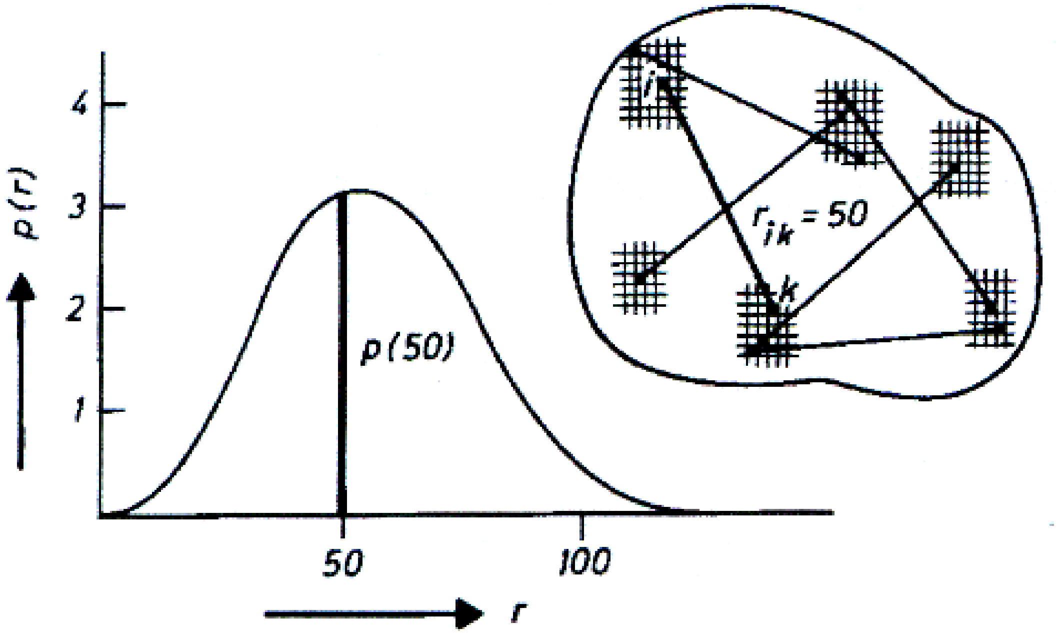


$p(\mathrm{r})=\mathrm{r}^2\gamma(\mathrm{r})$

Pair Distance Distribution Function (PDDF) and Correlation Function

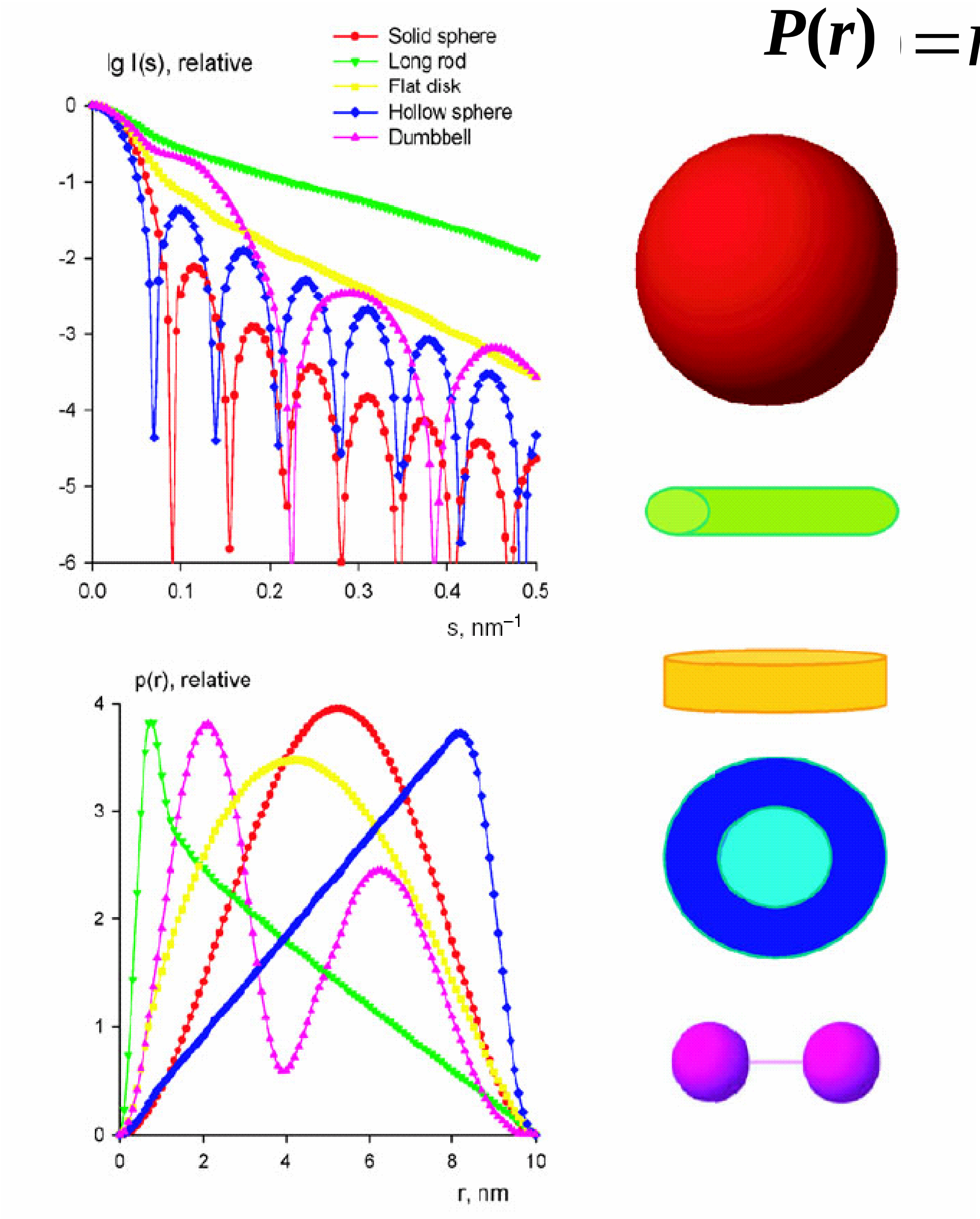
$$p(r) = r^2\gamma(r)$$

Probability finding scattering elements separated by r



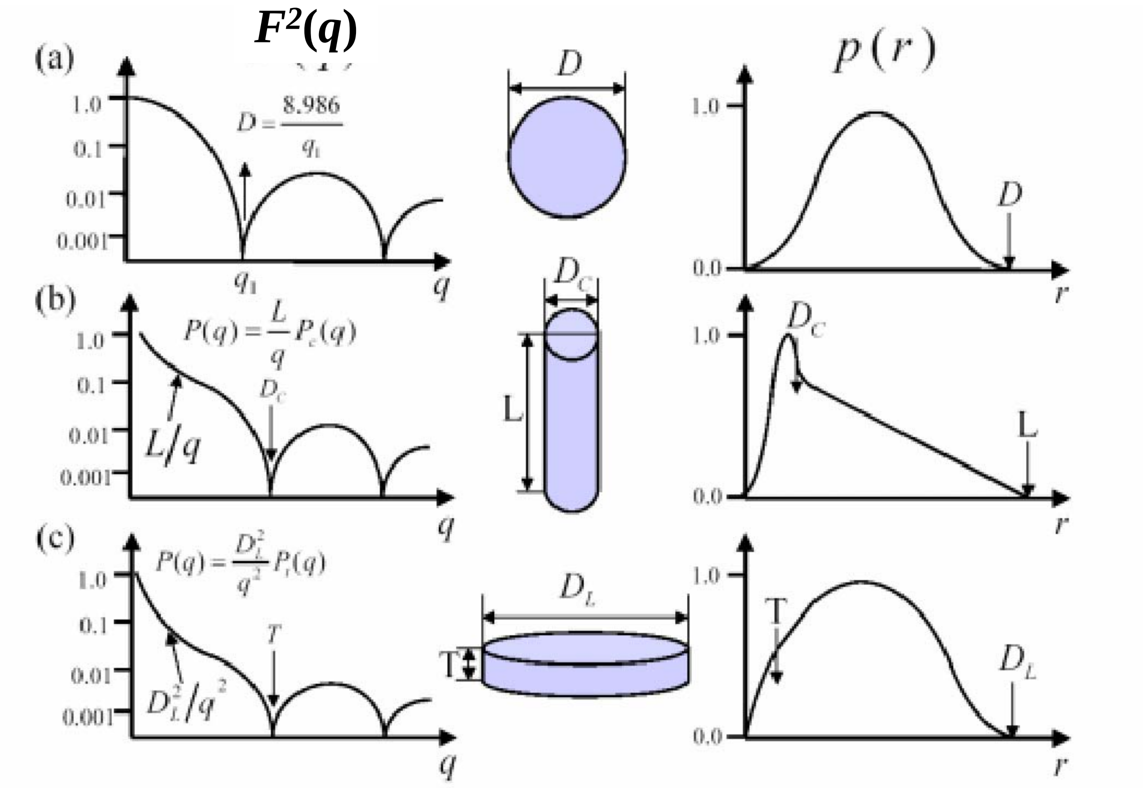
Pair Distance Distribution Function *P*(r)

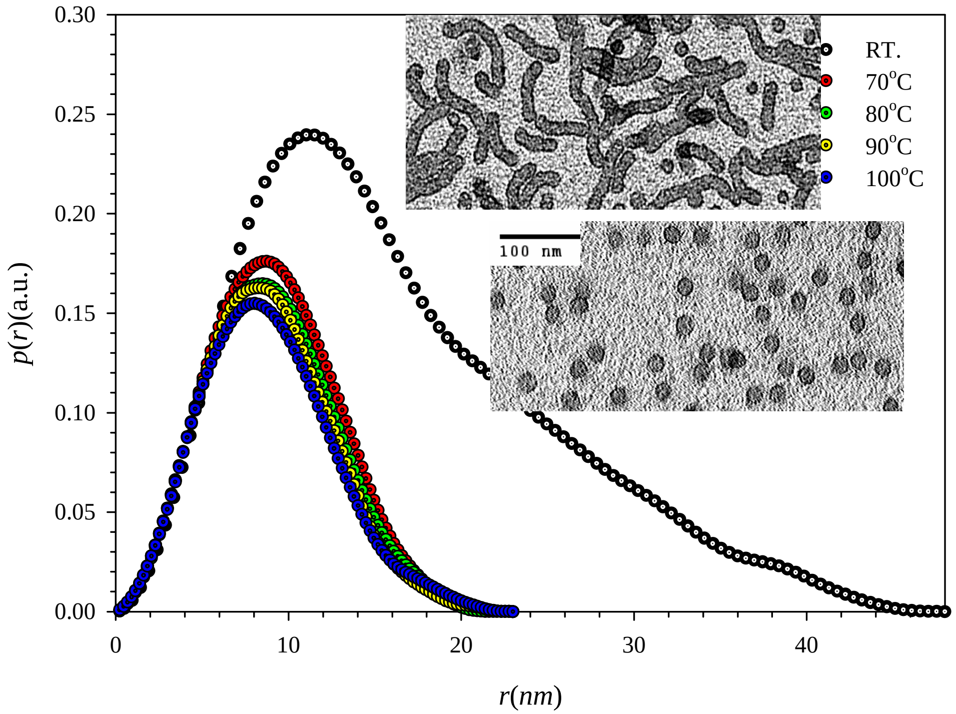
$$\boldsymbol{P(r)} = r^2\gamma(r) = r^2 \cdot \int \Delta\rho(u)\,\Delta\rho(r+u)\,du$$

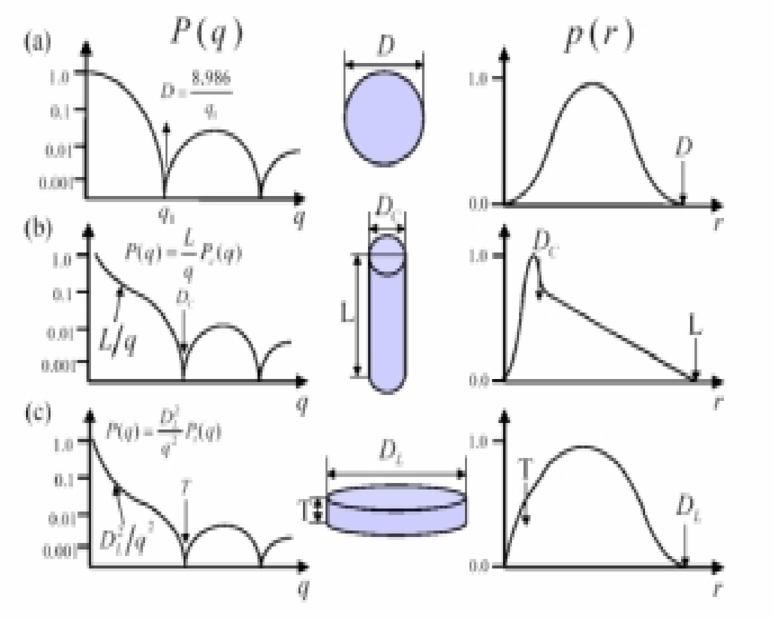


- ✓ Distribution of distances of atoms from centroid
- ✓ 1-D: Only distance, not direction
- ✓ 20:1 ratio $q_{min}(\pi/d_{max}):q_{max}$ usually ok
- ✓ p (r) gives an alternative measure of Rg and also “longest cord”

Particle Scattering Pattern and PDDF







S.-Y. Park et al., *Macromolecules*, 40, 3757-3764 (2007)

(2) Fine Structural Model Approach

Scattering amplitude (i.e., Scattering Function = Structure Function); Scattering intensity

Density distribution

$$\rho(\mathrm{r})$$

Fourier TF = summation with phase difference

$$F(\mathbf{q}) = \frac{K_s}{V}\int \rho(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}$$

Scatt. amplitude

Scattering intensity

$$I(q) = \frac{K}{V}\iint \rho_{\mathrm{i}}(\mathbf{r})\rho_{\mathrm{j}}(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}$$

$\mathbf{r} = \mathbf{r} - \mathbf{r}'$

- X-ray scattering from the electron density distribution in sample
- Small angle scattering for the large distance

$$F(\mathbf{q}) = \int_{V_r} \rho(\mathbf{q}) e^{i(\mathbf{q}\cdot\mathbf{r})} d\mathbf{r}$$

$$I(\mathbf{q}) = F(\mathbf{q}) \cdot F^*(\mathbf{q})$$

$$I(\mathbf{q}) = \left|\Im\{\rho(x)\}\right|^2$$

$$|\mathbf{s}| = \frac{2\sin\theta}{\lambda} = \frac{1}{d} \qquad |\mathbf{q}| = \frac{4\pi\sin\theta}{\lambda}$$

$$\begin{tikzcd}
\begin{matrix}\gamma(\mathbf{r})\\ Q(\mathbf{r})\end{matrix} \arrow[rr, leftrightarrow, "\Im"] \arrow[d, shift right=2, "\times" marking] & & I(\mathbf{q}) \arrow[d, shift left=2, "\times" marking] \\
\rho(\mathbf{r}) \arrow[u, shift right=2] \arrow[rr, leftrightarrow, "\Im"'] & & F(\mathbf{q}) \arrow[u, shift left=2]
\end{tikzcd}$$

$$I(\mathbf{q}) = \Im\{Q(\mathbf{r})\}$$

$$Q(\mathbf{r}) = \Im^{-1}\{I(\mathbf{q})\}$$

$F(\mathbf{r})$: **Amplitude of scattered X-ray**

$I(\mathbf{q})$: **Scattered Intensity**

$\rho(\mathbf{r})$: **Electron density function**

$\mathbf{Q}(\vec{\mathbf{r}})$: **Patterson function** $(\rho(\mathbf{r}) * \rho(-\mathbf{r}))$

$\Im$: **Fourier transform**

Example of FFT

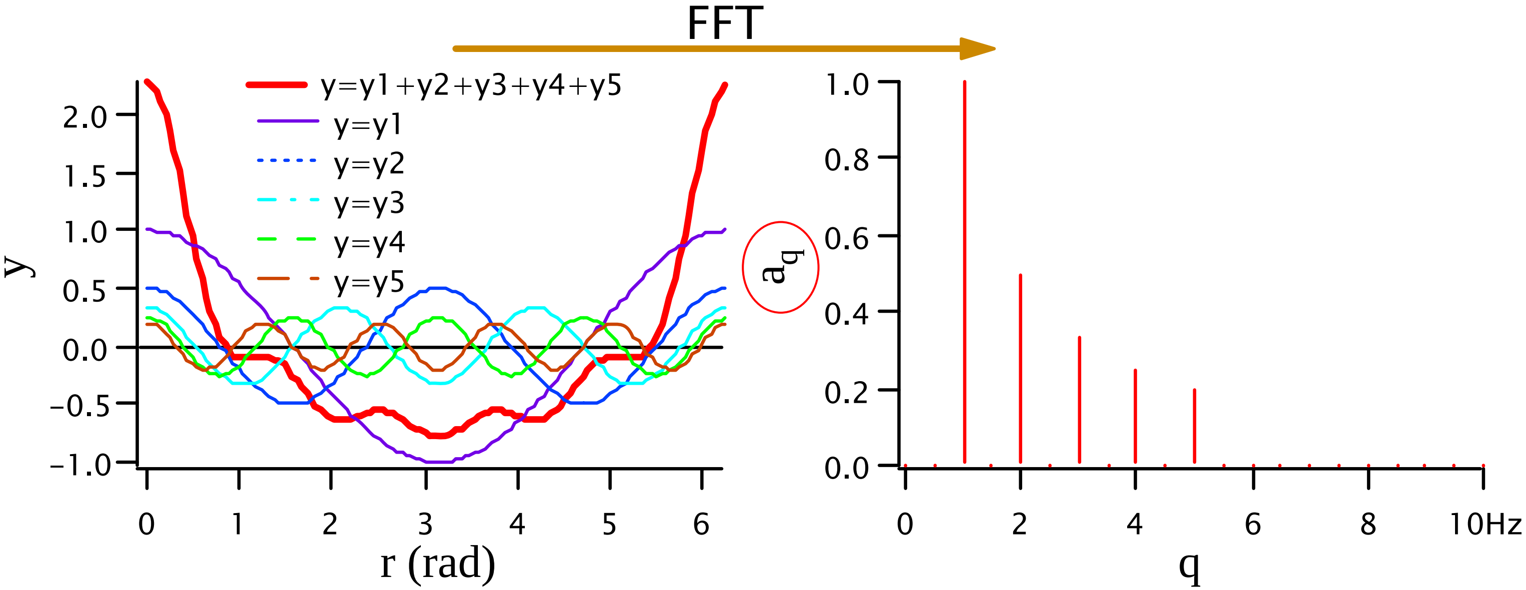
$$y = y_1 + y_2 + y_3 + y_4 + y_5$$

$$y_1 = \cos r, \quad y_2 = \frac{1}{2}\cos 2r, \quad y_3 = \frac{1}{3}\cos 3r,$$

$$y_4 = \frac{1}{4}\cos 4r, \quad y_5 = \frac{1}{5}\cos 5r, \quad y_{q'} = a_{q'}\cos(q'r)$$

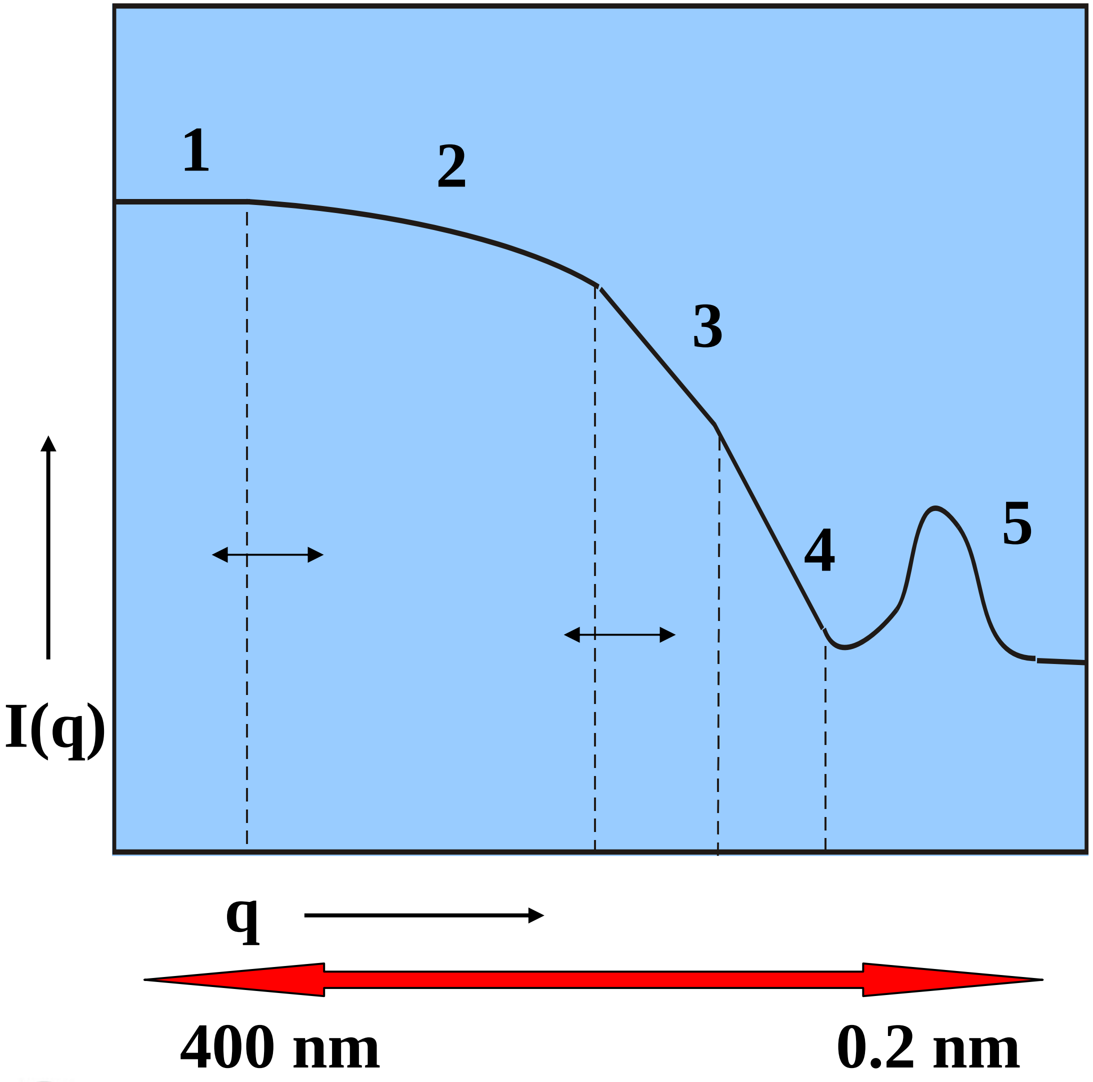
$$Y(q) = a_q = \frac{1}{2\pi}\int_0^{2\pi} y\exp(iqr)dr = \frac{1}{\pi}\int_0^{\pi} y\cos(qr)dr$$

1. **FT of even functions are Fourier cosine transform.**
2. **FT of a cosine function is a delta function.**
3. **The amplitude of each function gives a spectrum.**



Real space **Fourier space**

Scattering Angle Region versus Length Scale in Structural Information



1 limit q → 0
electron density contrast
density fluctuations
molecular weights

2 Guinier range
particle size

3 particle shape
large scale structures

4 Porod range
particle surface
Surface/volume

5 Intermolecular
ordering

Scattering at Low Angles

Inhomogeneous Density Distribution over Large Distance (nm scale)

$s = 1/d$ (or $q = 2\pi / d$) ($Å^{-1}$)
$s = 0.001 - 0.1$ $Å^{-1}$ d (10~ 1000 Å)
$2\theta = 0.008\text{-}8$, $\lambda = 1.542$ Å

$$s = |\mathbf{s}| = \frac{2\sin\theta}{\lambda} \qquad q = |\mathbf{q}| = 2\pi s$$

- **Morphological information of multiphase system:**
  Domain (Particle) Size, Distribution,
  Surface Area, Interface Thickness
- **Density Fluctuation**
- **Supramolecular Ordered Structure**

Various types of plots

Methods to analyze I(q)

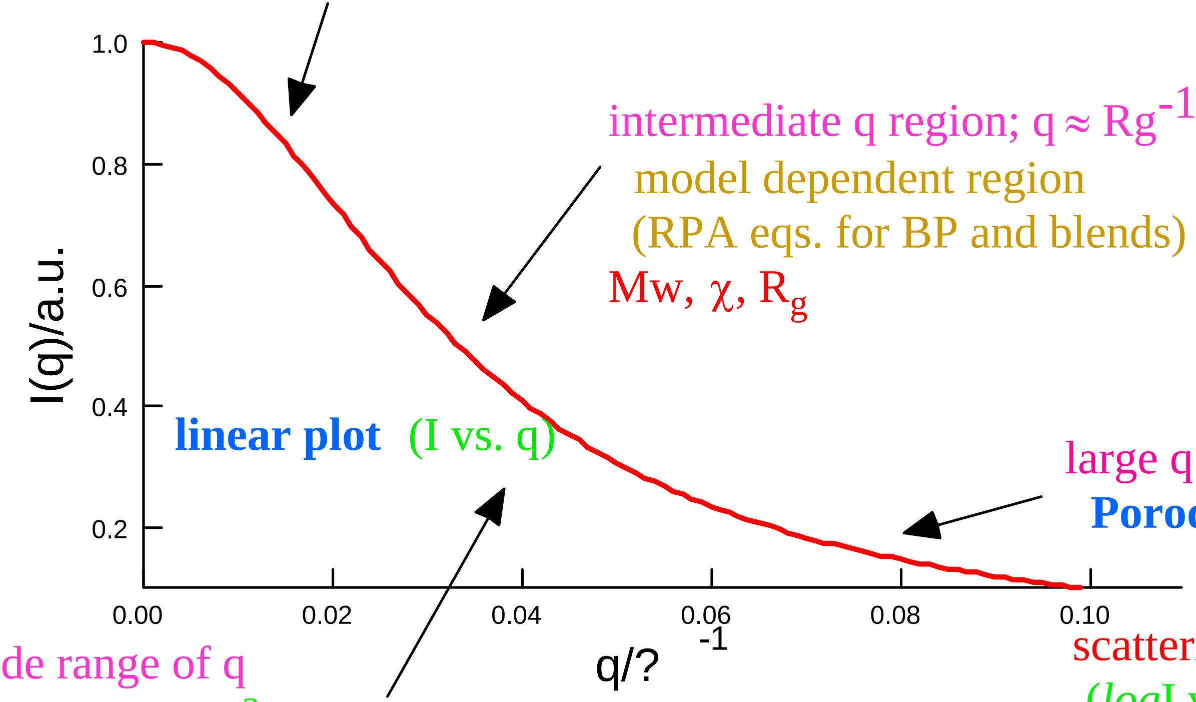
low q region; $q < Rg^{-1}$

Guinier plot ... R_g (*log*I vs. q^2) $I(q) \sim exp[-R_g^2 q^2/3]$

Zimm plot ... R_g, A_2, Mw (I^{-1} vs. q^2) $KC/I(q) = M^{-1}[1 + R_g^2 q^2/3 + ..] + 2A_2C$

Ornstein-Zernike plot ... ξ (I^{-1} vs. q^2) $I(q) = I(0)/[1 + \xi^2 q^2]$

Debye-Bueche plot (two phase) ($I^{-1/2}$ vs. q^2) ... chord length $I(q) = I(0)/[1 + a^2 q^2]^2$



linear plot (I vs. q)

intermediate q region; $q \approx Rg^{-1}$

model dependent region

(RPA eqs. for BP and blends)

Mw, χ, R_g

large q region; $q > Rg^{-1}$

Porod law (two phase)

$I(q) \sim q^{-4}$

scattering exponent

(*log*I vs. *log*q)

$I(q) \sim q^{-1/\nu}$

wide range of q

Kratky plot (q^2I vs. q)... segment length, a

$q^2 I(q) \sim \frac{z}{q^4 R_g^4}\{exp[-R_g^2 q^2] - 1\} - \frac{1}{a^2}$ (Debye fun.)

Invariant

Integration of Intensity

$$\int_0^{\infty} I_{obs}(\mathbf{s})d\mathbf{s} = \int_0^{\infty} I_{obs}(\mathbf{s})e^{2\pi i\mathbf{s}\cdot\mathbf{r}}d\mathbf{s}$$

$$\Im^{-1}\left[I_{obs}(\mathbf{s})\right]$$

$$\left\langle(\Delta\rho)^2\right\rangle V\cdot\gamma(0) = \left\langle(\Delta\rho)^2\right\rangle V, \qquad r = 0$$

Integration of intensity =
average density difference * scattering volume

Outline

1. Introduction – POSTECH & Pohang Light Source
2. Optics, Beamlines and Equipments of SAXS
3. Data Collection and Samples
4. Fundamentals of SAXS
5. **Fundamentals of Conventional, Transmission SAXS (TSAXS)**
   (1) Single Molecule (or Particle)
   (2) Multiple Molecules (or Particles) and Their Assemblies
6. Fundamentals of Grazing Incidence SAXS (GISAXS)
   (1) Static GISAXS
   (2) In-Situ GISAXS
1. Conclusions – I, II
2. References
3. Introduction – M. Ree's Group at Postech
4. Acknowledgments

X-Ray Scattering from Multiple Molecules (or Particles)

Molecules (or Particles) and Their Assemblies

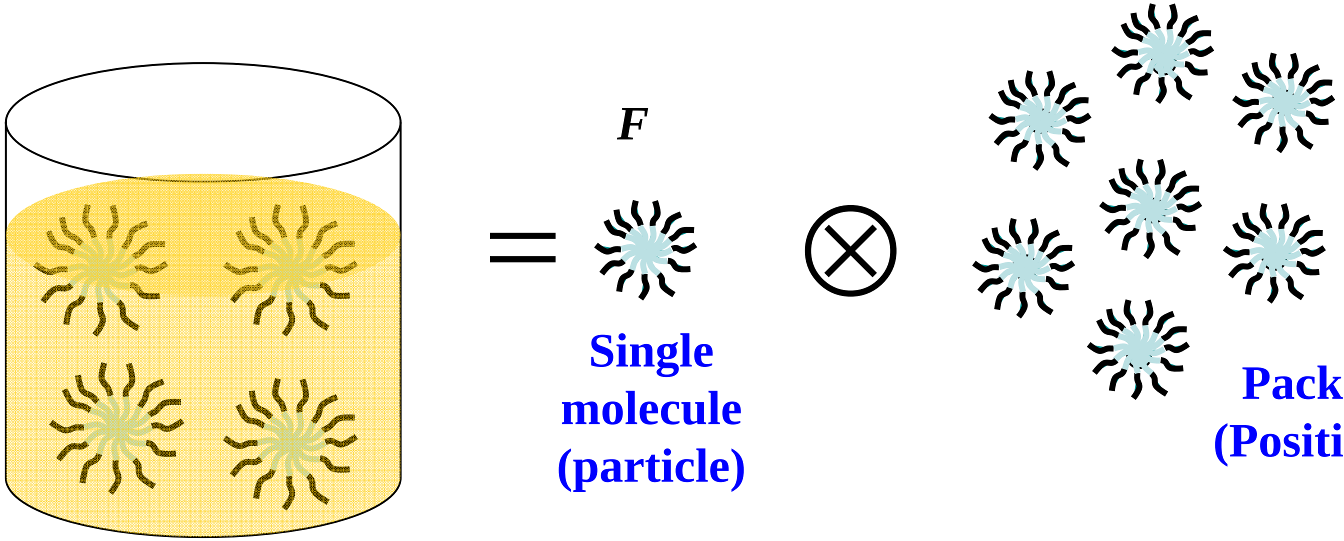
X-Ray Scattering from Multiple Molecules (Particles)

Convolution

$$\{F * S\}(\mathbf{r}) \equiv \int_{-\infty}^{\infty} F(\mathbf{u})S(\mathbf{r}-\mathbf{u})\,d\mathbf{u}$$

$$\{F * S\}(-\mathbf{r}) \equiv \int_{-\infty}^{\infty} F(\mathbf{u})S(\mathbf{r}+\mathbf{u})\,d\mathbf{u}$$

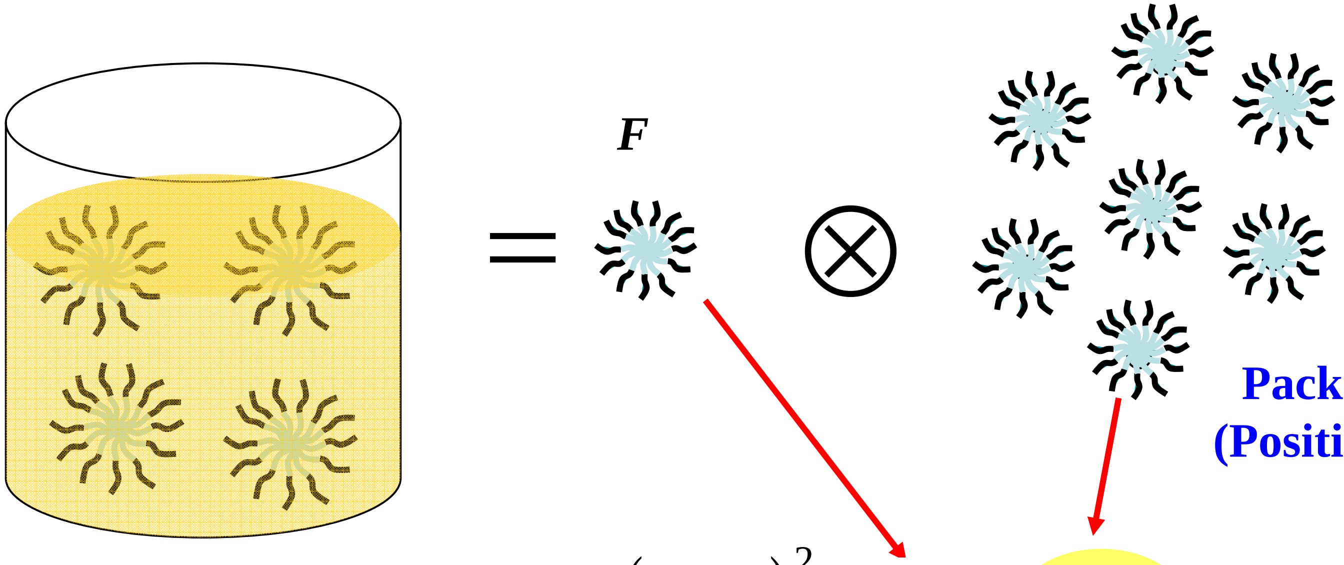
$$\Im\{F * S\} = \Im\{F\}\cdot\Im\{S\}$$



Single molecule (particle)

**Packing order ?
(Positional order?)**

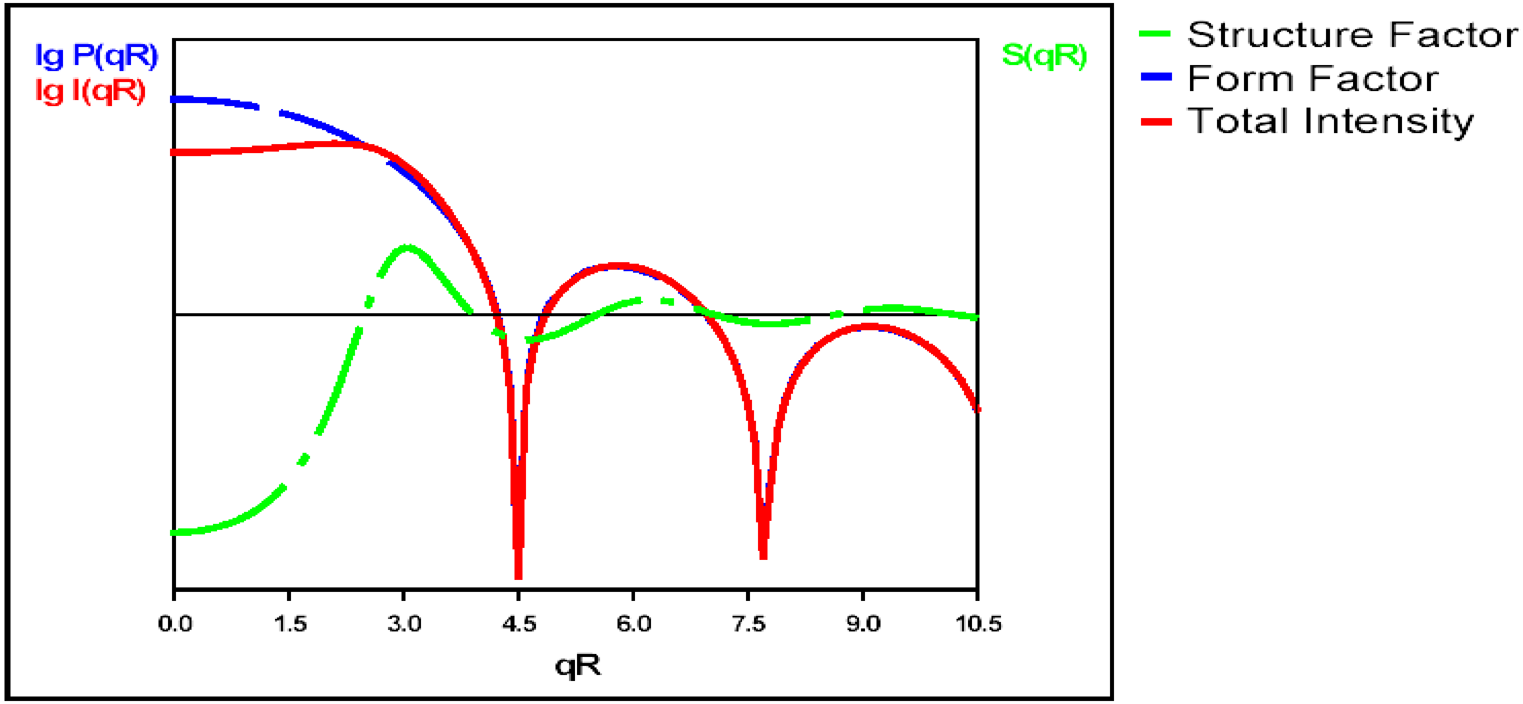
X-Ray Scattering from Multiple Molecules (Particles)



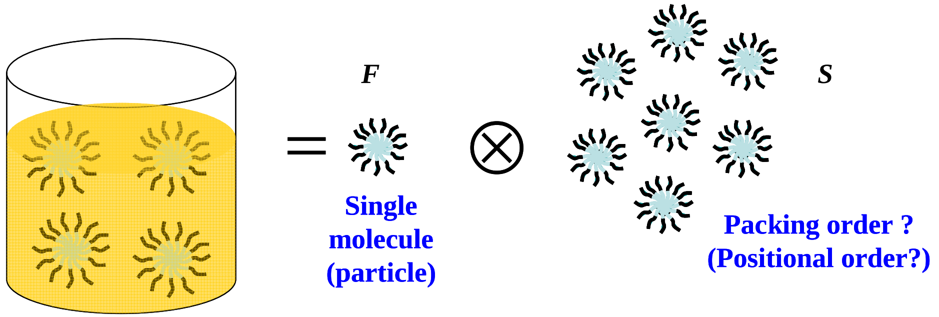
Packing order ?
(Positional order?)

$$I = N_p \left(\Delta\rho_p\right)^2 \underbrace{F^2(q)}_{\text{Form Factor}} \underbrace{S^2(q)}_{\text{Structure Factor}}$$

$$S(q) \approx 1 \text{ for dilute solution}$$



$$I = N_p\left(\Delta\rho_p\right)^2 \underbrace{F^2(q)}_{\substack{\text{Form}\\ \text{Factor}}}\underbrace{S^2(q)}_{\substack{\text{Structure}\\ \text{Factor}}}$$



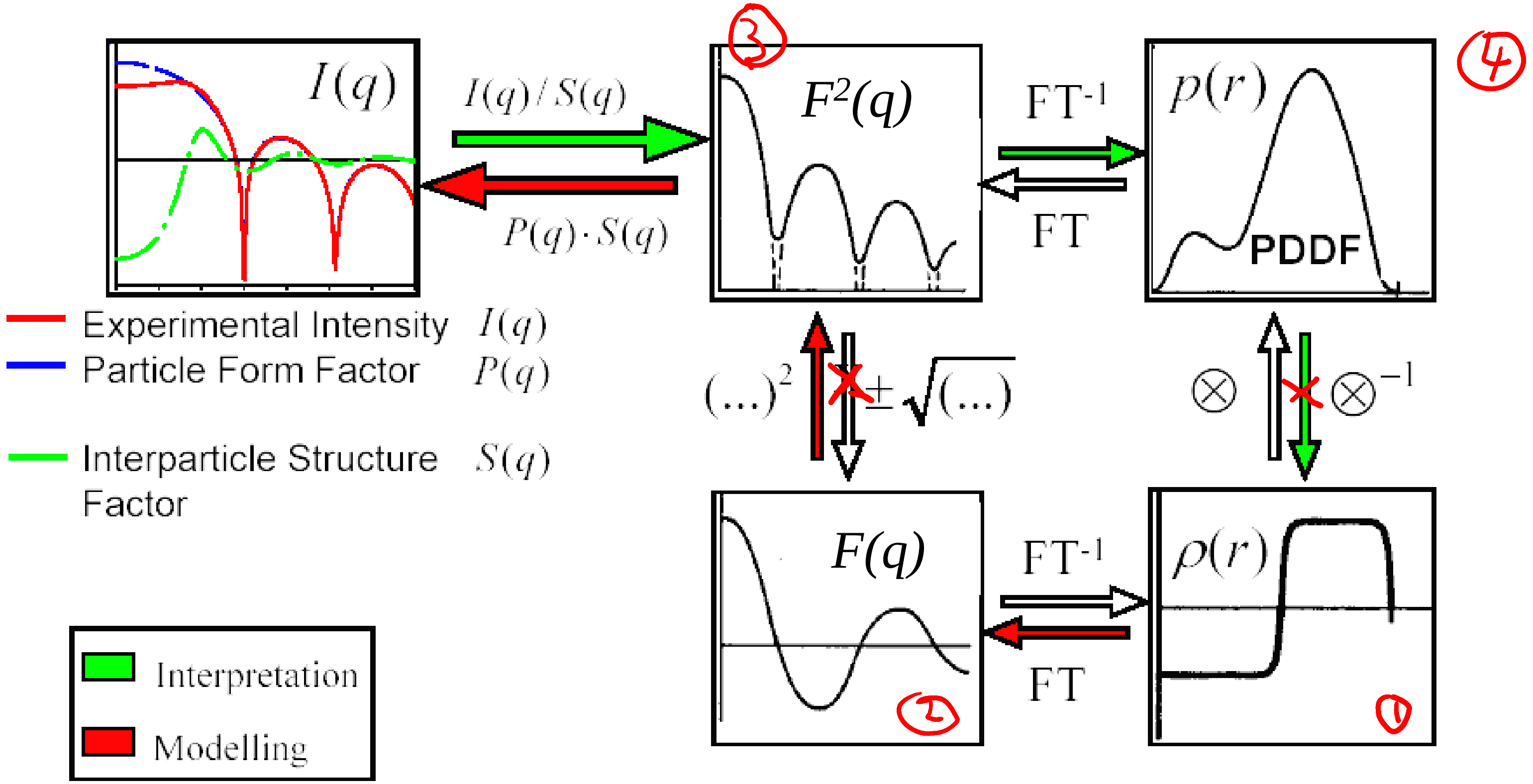
Single molecule (particle)

Packing order ? (Positional order?)

$$\begin{tikzcd} \text{④}\ \gamma(\mathbf{r}),\ Q(\mathbf{r}) \arrow[r, leftrightarrow, "\Im"] \arrow[d, shift right, "\times"'] & I(\mathbf{q})\ \text{③} \arrow[d, shift left, "\times"] \\ \text{①}\ \rho(\mathbf{r}) \arrow[u, shift right] \arrow[r, leftrightarrow, "\Im"'] & F(\mathbf{q})\ \text{②} \arrow[u, shift left] \end{tikzcd}$$

Dense system

Dilute system



Experimental Intensity $I(q)$
Particle Form Factor $P(q)$

Interparticle Structure Factor $S(q)$

🟩 Interpretation
🟥 Modelling

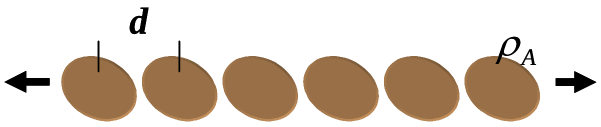
Various Shapes of Molecules (Particles) and Their Packing

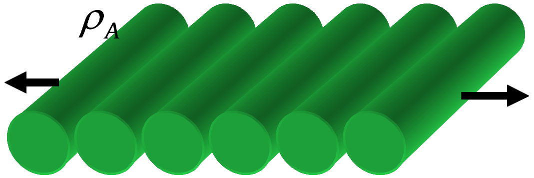
$$I(s) = \left|\Im\{\rho(x)\}\right|^2$$

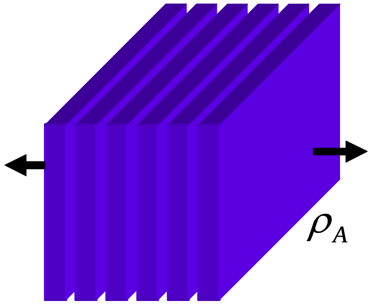
$$s = \frac{2\pi \sin\theta}{\lambda} = \frac{1}{d}$$

$$\rho(x) = \rho_A(x) * S(x)$$
$$\Im\{\rho(x)\} = \Im\{\rho_A(x) * S(x)\}$$
$$= \Im\{\rho_A(x)\}\ \Im\{S(x)\}$$
$$= F(s)\ \ S(s)$$

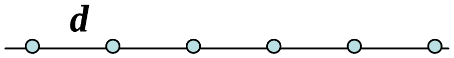
$$\Im\{F * S\} = \Im\{F\}\cdot\Im\{S\}$$

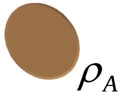


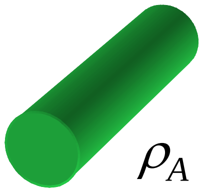


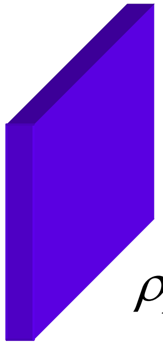


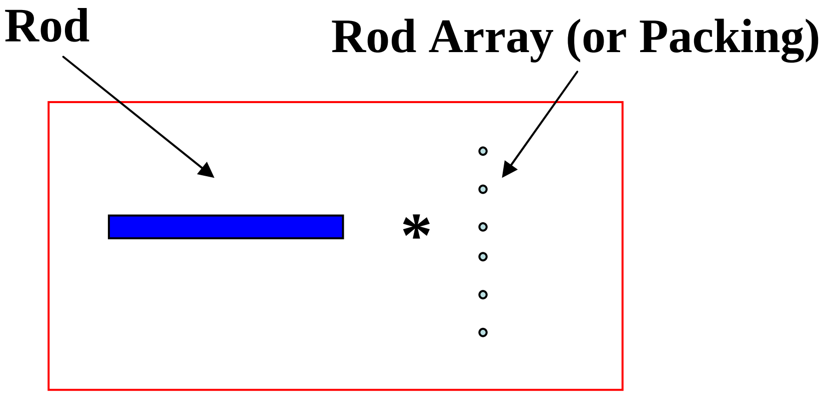
$$S(x) \equiv \sum_{n=-\infty}^{+\infty} \delta(x - nd)$$



$\rho(x) = S(x) *$  ρ_A

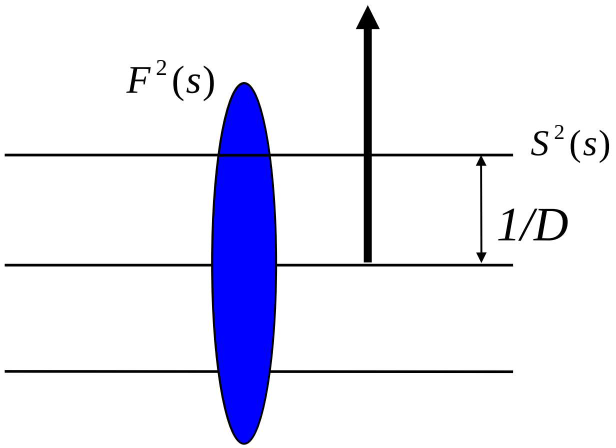
$S(x) *$  ρ_A

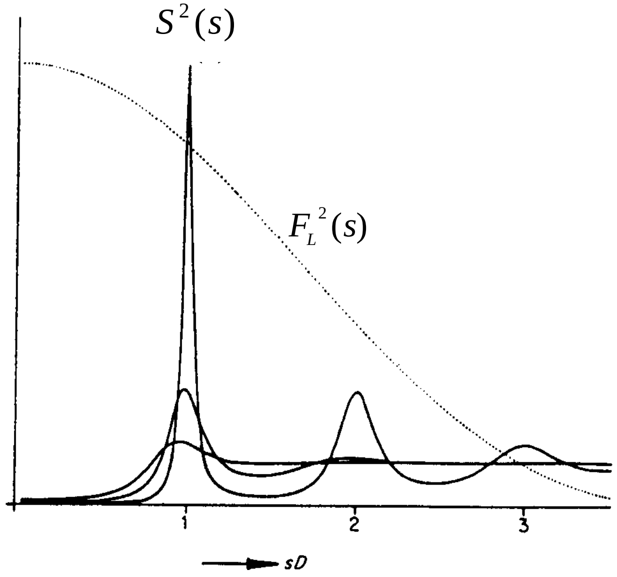
$S(x) *$  ρ_A

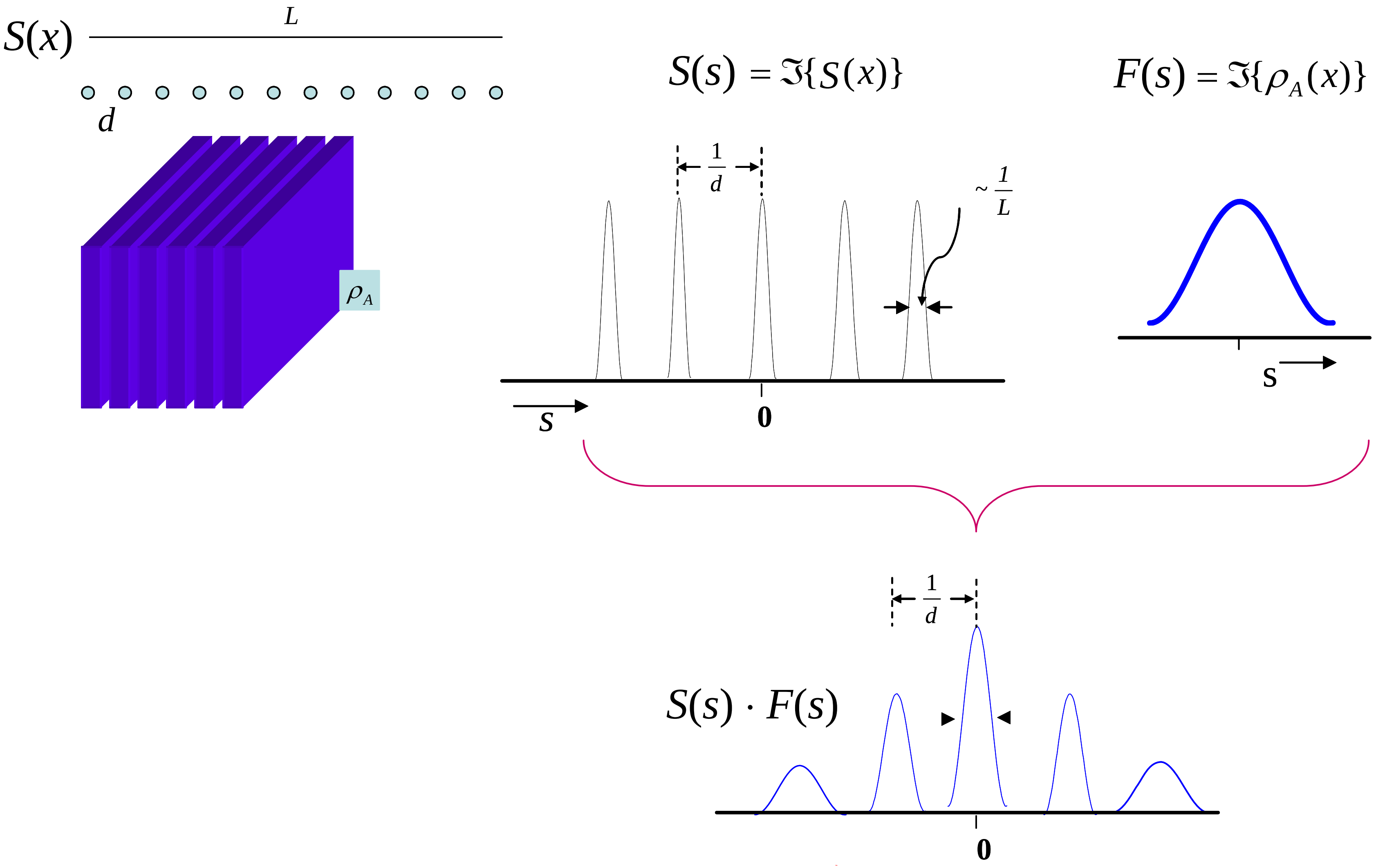


$$
\begin{aligned}
&\rho(x) = \rho_A(x) * S(x) \\
&\Im\{\rho(x)\} = \Im\{\rho_A(x) * S(x)\} \\
&= \Im\{\rho_A(x)\}\ \Im\{S(x)\} \\
&= F(s)\ S(s)
\end{aligned}
$$

$$I_{obs}(s) = \left(F^2(s) \cdot S^2(s)\right)$$





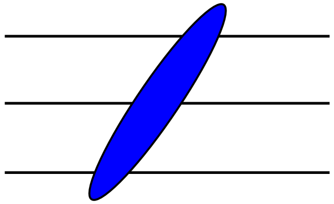


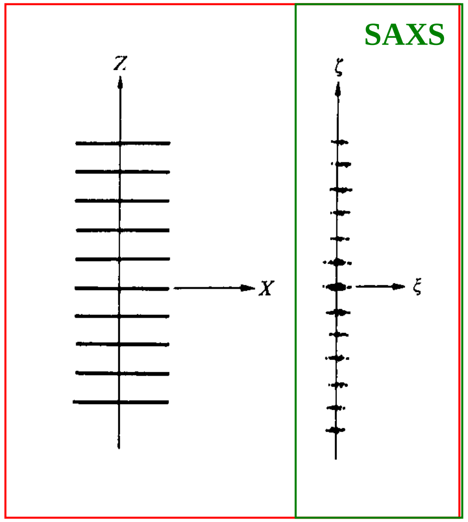
$S(x)$

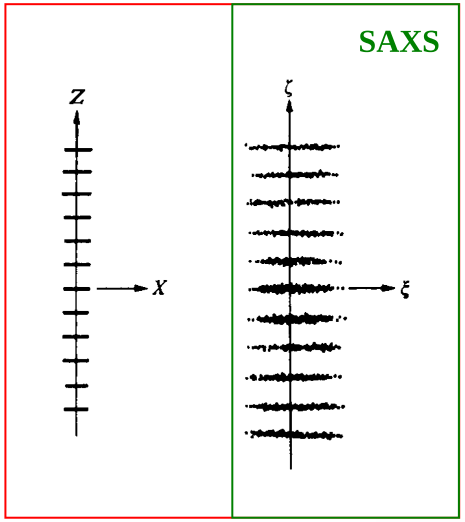
$$S(s) = \Im\{S(x)\}$$

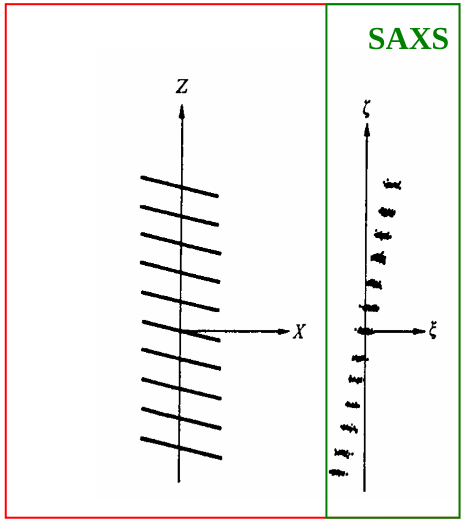
$$F(s) = \Im\{\rho_A(x)\}$$

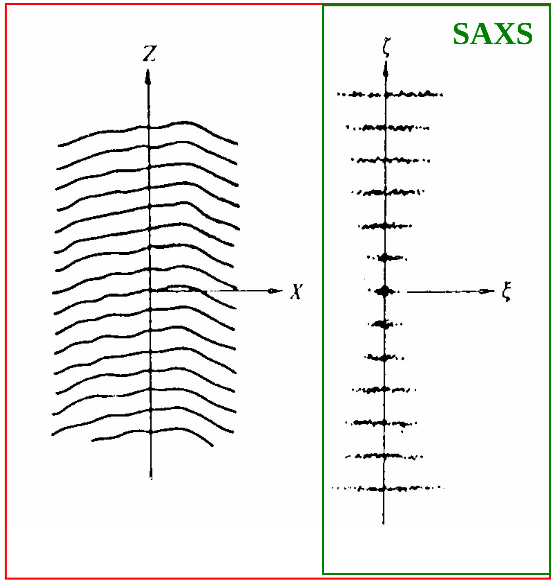
$$S(s) \cdot F(s)$$

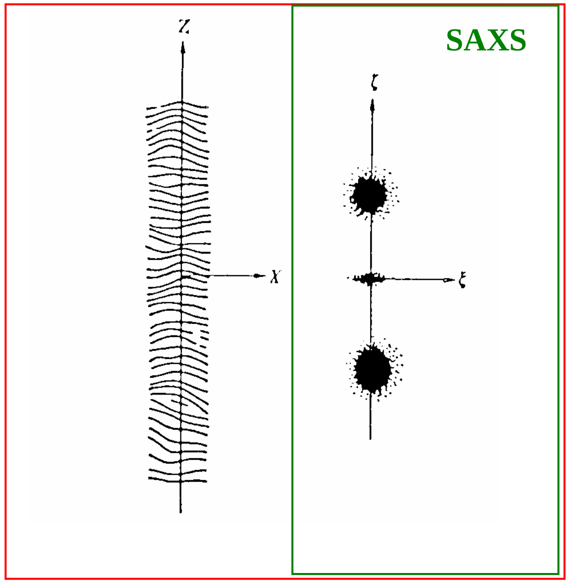


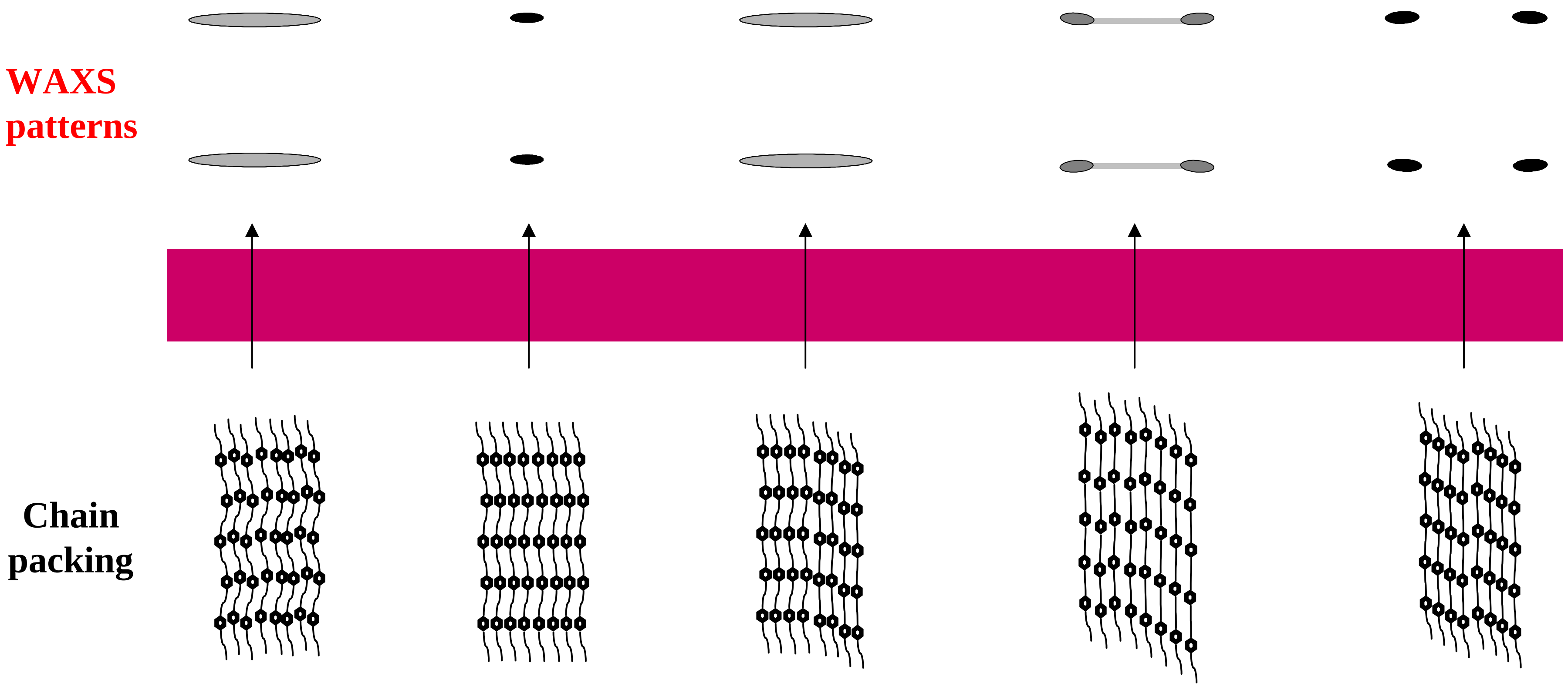

SAXS
z
x
ζ
ξ


SAXS
z
x
ζ
ξ


SAXS
z
x
ζ
ξ


SAXS
z
x
ζ
ξ


SAXS
z
x
ζ
ξ

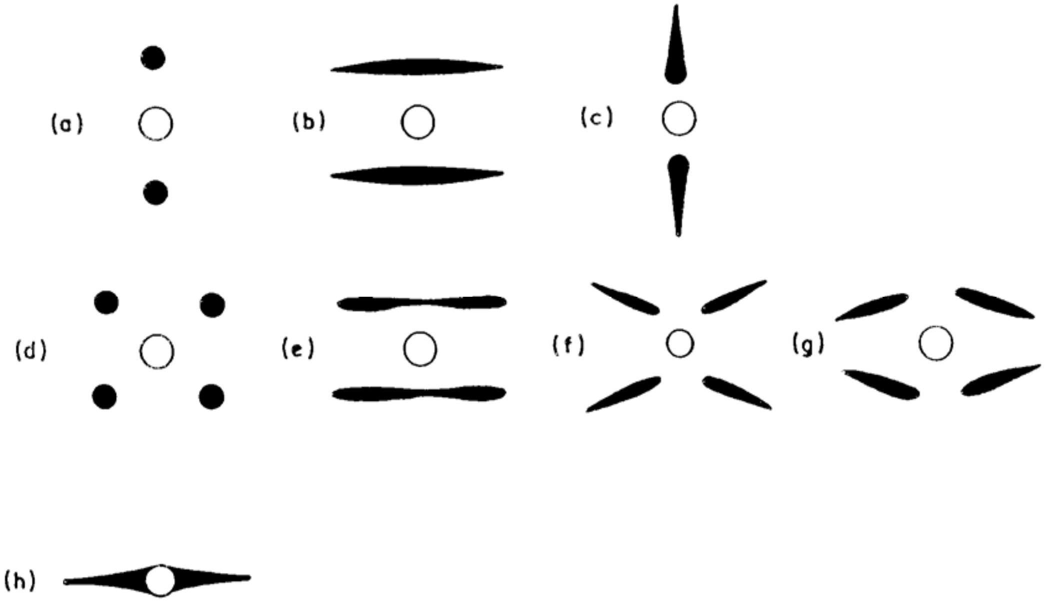


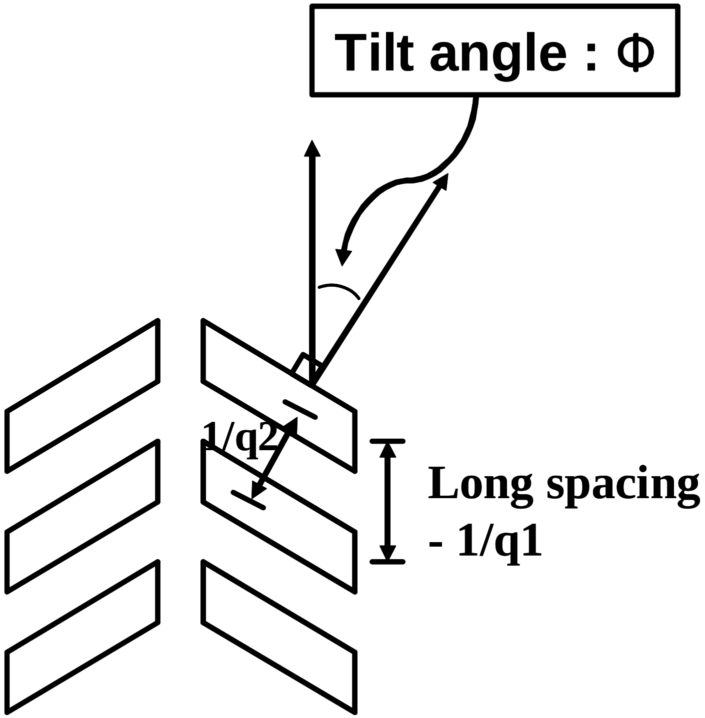
WAXS patterns

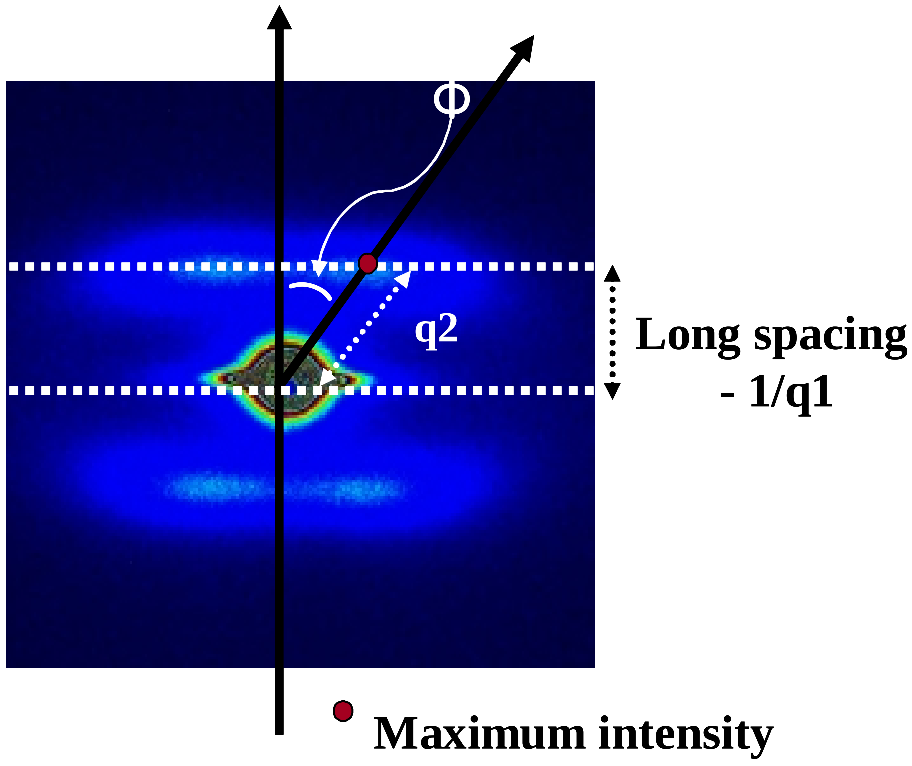
Chain packing

H.H. Song et al., *Macromolecules*, 36, 9873 (2003)

Oriented Lamellar Patterns (WAXS)

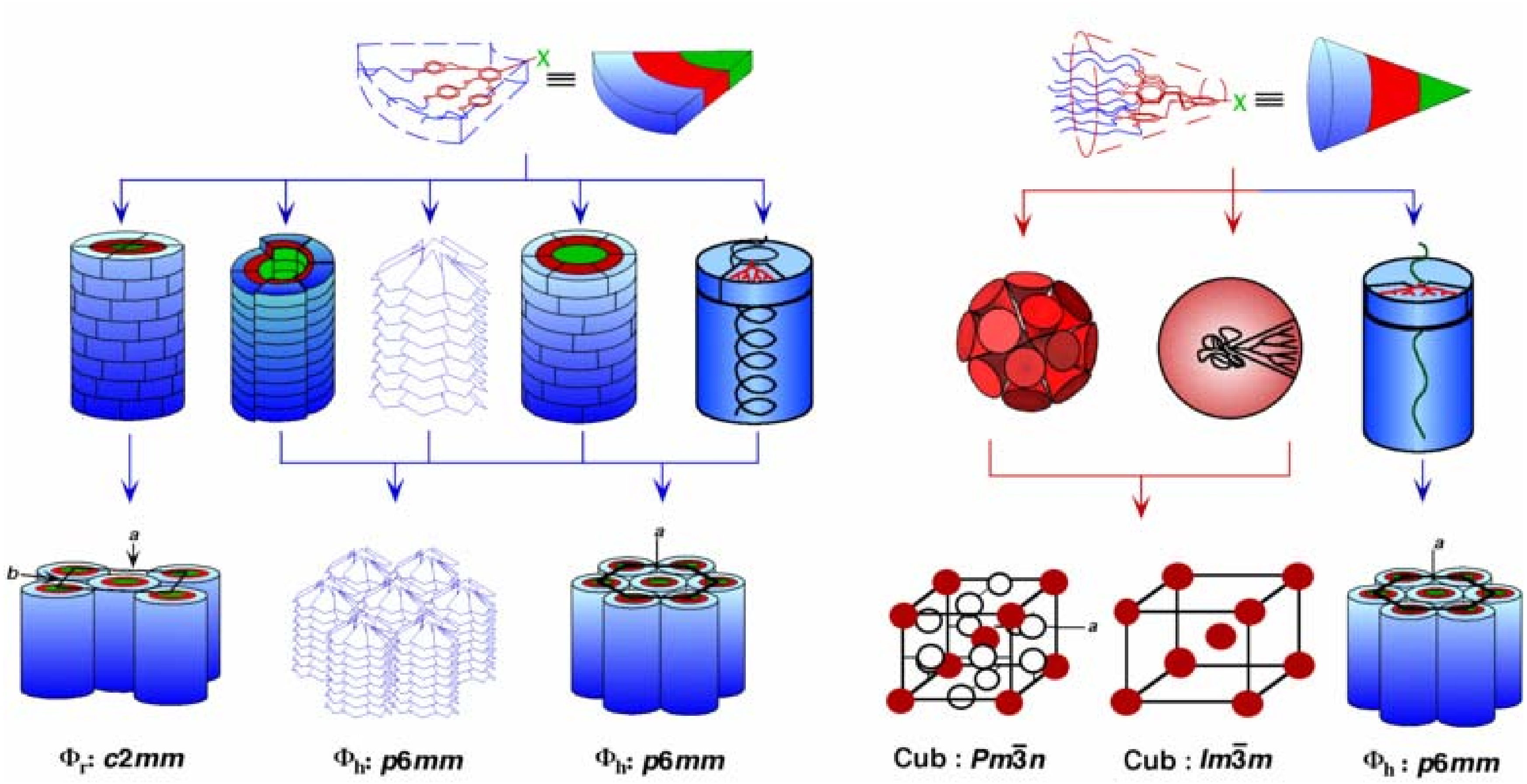


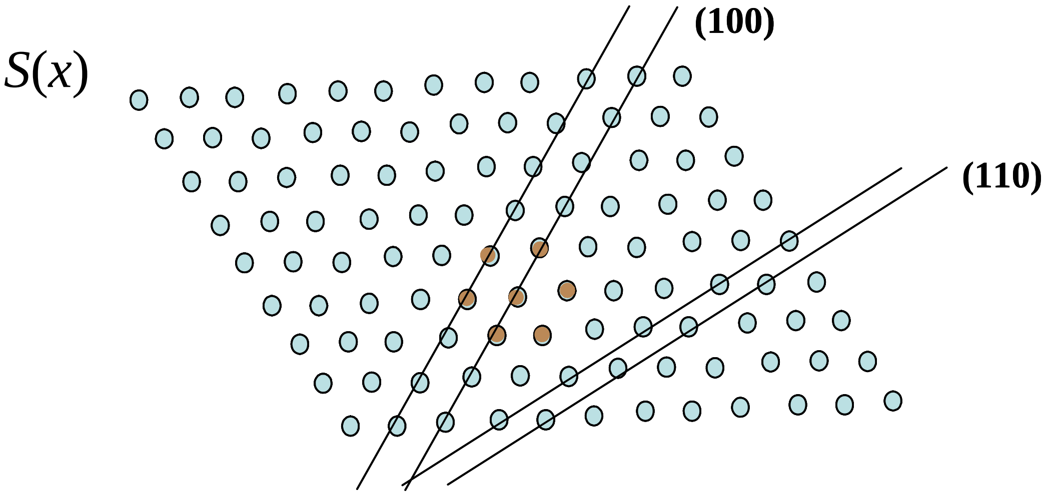


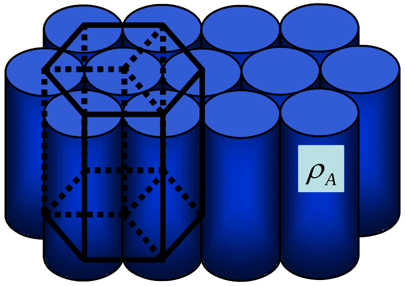


H.H. Song et al., *Macromolecules*, 36, 9873 (2003)

Nanostructures



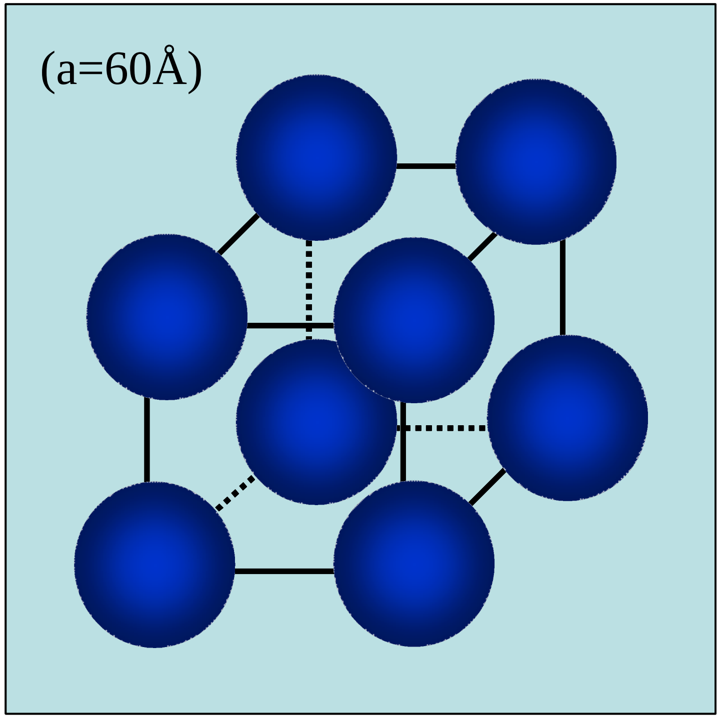

$S(x)$
(100)
(110)


ρ_A

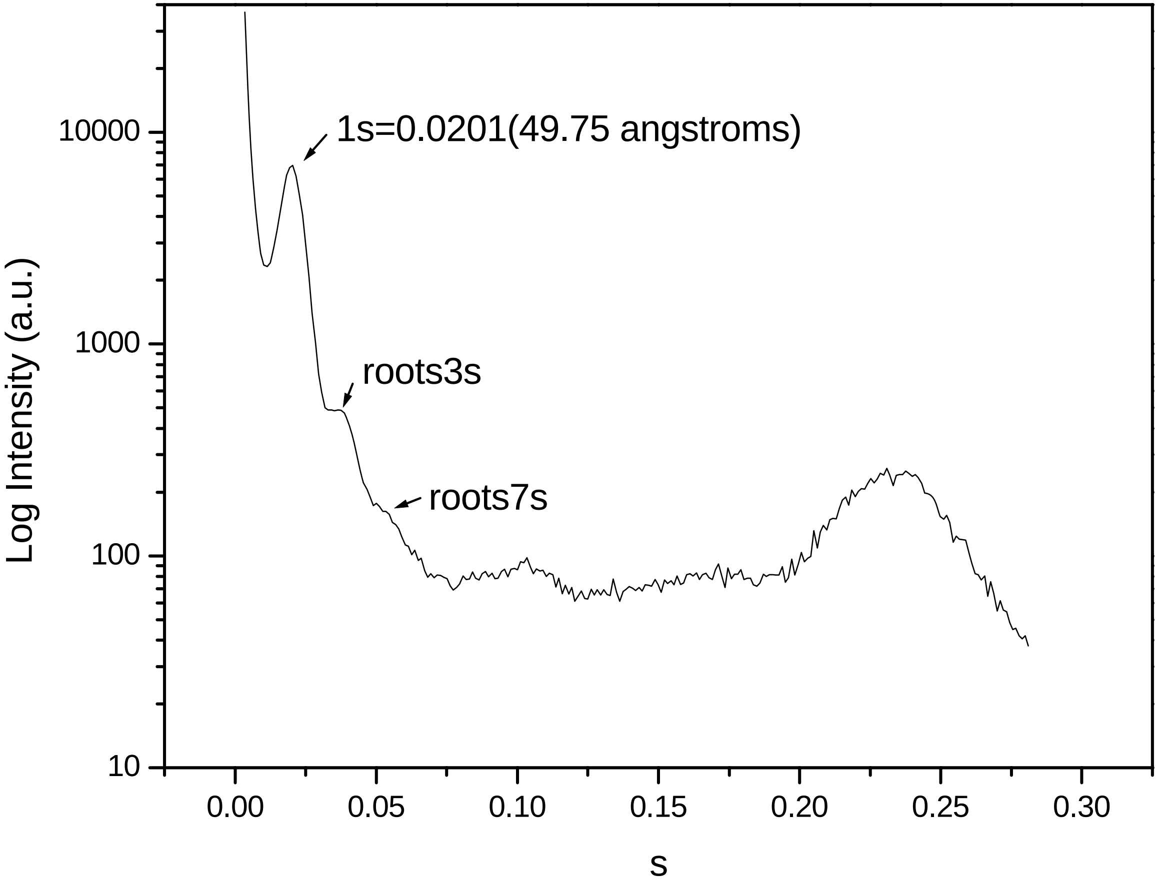
Sphere cubic packing

h	k	l	s^2	s	order	d
1	0	0	2.78E-04	0.016667	1	60.00
1	1	0	5.56E-04	0.02357	√2	42.43
1	1	1	8.33E-04	0.028868	√3	34.64
2	0	0	0.00111	0.033333	√4	30.00
2	1	0	0.00139	0.037268	√5	26.83
2	1	1	0.00167	0.040825	√6	24.49
2	2	0	0.00222	0.04714	√8	21.21
2	2	1	0.0025	0.05	√9	20.00
2	2	2	0.00333	0.057735	√12	17.32
3	0	0	0.0025	0.05	√9	20.00
3	1	0	0.00278	0.052705	√10	18.97
3	1	1	0.00306	0.055277	√11	18.09
3	2	0	0.00361	0.060093	√13	16.64
3	2	1	0.00389	0.062361	√14	16.04

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$



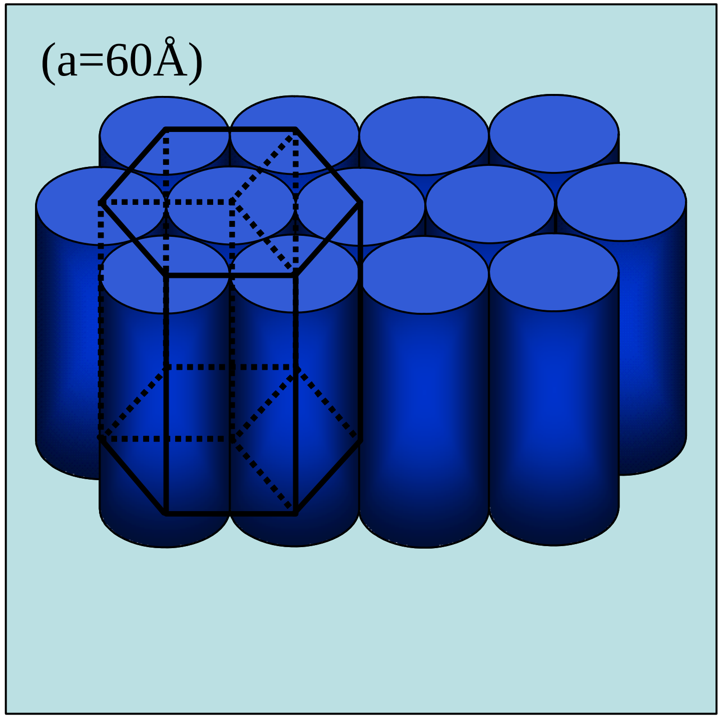
Hexagonal cylinder



Columnar hexagonal packing

h	k	l	s^2	s	order	d
1	0	0	0.00037	0.019245	1	51.96
1	1	0	0.001111	0.033333	√3	30.00
2	0	0	0.001481	0.03849	√4	25.98
2	1	0	0.002593	0.050918	√7	19.64
2	2	0	0.004444	0.066667	√12	15.00
3	0	0	0.003333	0.057735	√9	17.32
3	1	0	0.004815	0.069389	√13	14.41
3	2	0	0.007037	0.083887	√19	11.92
3	3	0	0.01	0.1	√27	10.00
4	0	0	0.005926	0.07698	√16	12.99
4	1	0	0.007778	0.088192	√21	11.34
4	2	0	0.01037	0.101835	√28	9.82
4	3	0	0.013704	0.117063	√37	8.54
4	4	0	0.017778	0.133333	√48	7.50

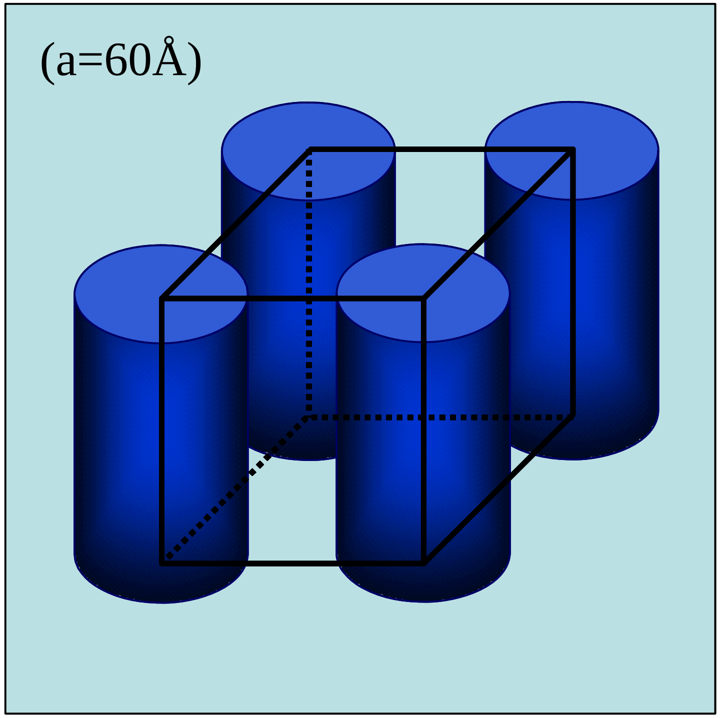
$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$



Columnar quadratic packing

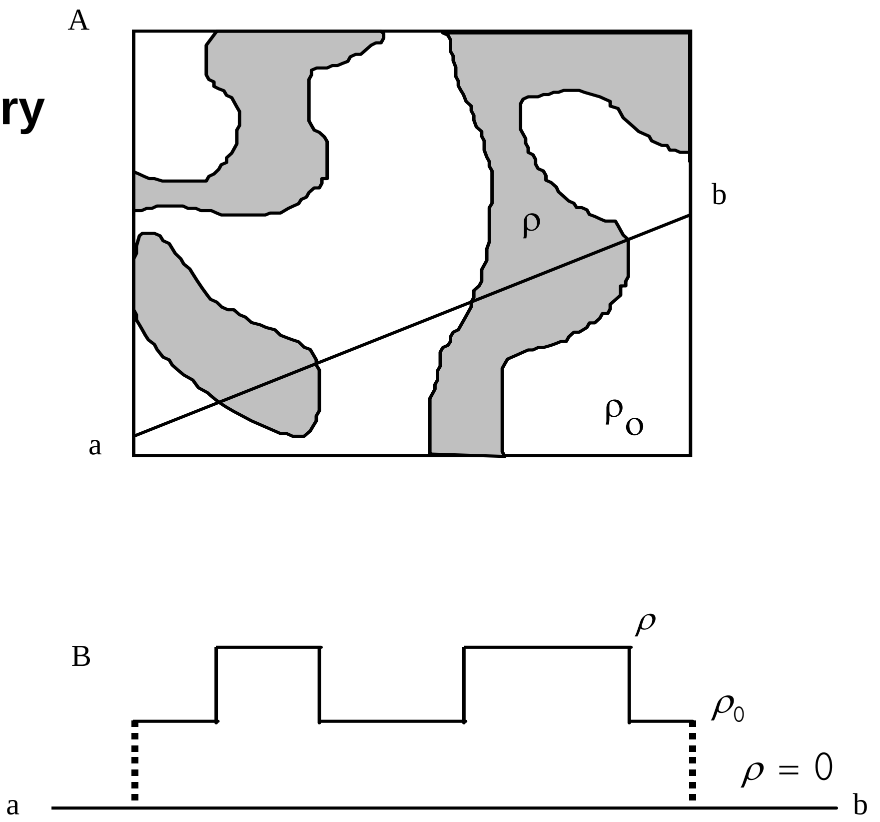
h	k	l	s^2	s	order	d
1	0	0	0.000278	0.016667	1	60.00
1	1	0	0.000556	0.02357	√2	42.43
2	0	0	0.001111	0.033333	√4	30.00
2	1	0	0.001389	0.037268	√5	26.83
2	2	0	0.002222	0.04714	√8	21.21
3	0	0	0.0025	0.05	√9	20.00
3	1	0	0.002778	0.052705	√10	18.97
3	2	0	0.003611	0.060093	√13	16.64
3	3	0	0.005	0.070711	√18	14.14
4	0	0	0.004444	0.066667	√16	15.00
4	1	0	0.004722	0.068718	√17	14.55
4	2	0	0.005556	0.074536	√20	13.42
4	3	0	0.006944	0.083333	√25	12.00
4	4	0	0.008889	0.094281	√32	10.61

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$


(a=60Å)

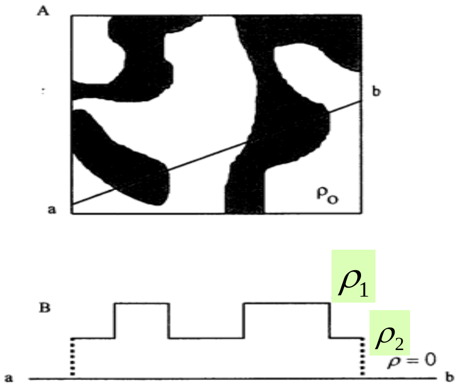
Two Phase System

Sharp boundary



Model of two phase system (A) and electron density distribution follow up line a-b (B).

Condensed Multi-phase



ρ_1, ρ_2 : *densities of particle and matrix*

ϕ_1, ϕ_2 : *volume fractions* $\quad \rho_0 = \rho_1\phi_1 + \rho_2\phi_2$ *average density*

$$\eta(r) = \rho(r) - \rho_o$$

$$\langle \eta^2 \rangle = \Delta\rho^2 \phi_1\phi_2 \qquad \Delta\rho = \rho_1 - \rho_2$$

$$I_{obs}(\mathbf{s}) = \langle \eta^2 \rangle V \Im\{\gamma(\mathbf{r})\} = \Delta\rho^2 \phi_2\phi_1 V \cdot \Im\{\gamma(\mathbf{r})\}$$

$$I_{obs}(\mathbf{s}) = 2\pi(\Delta\rho)^2 \phi_1\phi_2 V \cdot \Im\{\gamma(\mathbf{r})\}$$

Invariant

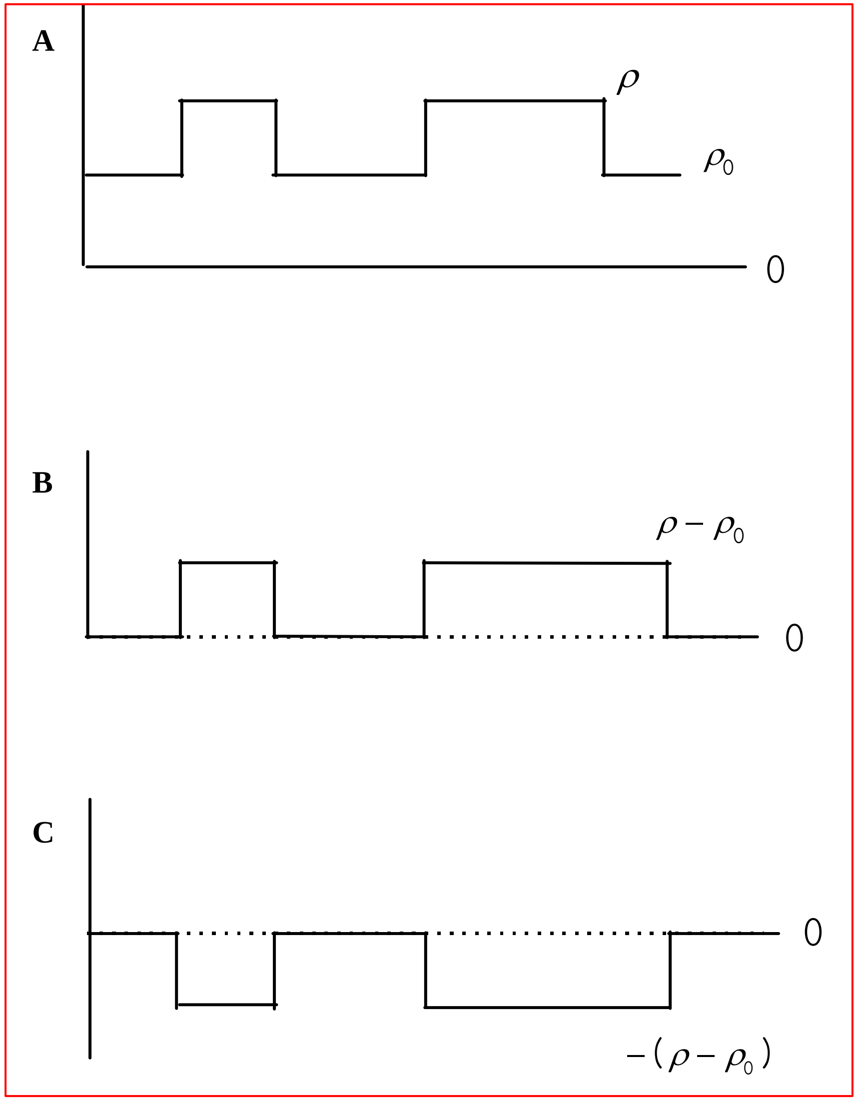
$$\int I_{obs}(\mathbf{s}) ds = \int I_{obs}(\mathbf{s}) e^{i2\pi(\mathbf{s}\cdot\mathbf{r})} ds \quad (\mathbf{r} = 0)$$

$$(\Delta\rho)^2 \phi_1\phi_2 V \gamma(\mathbf{r}),\ \mathbf{r} = 0$$

Surface Area

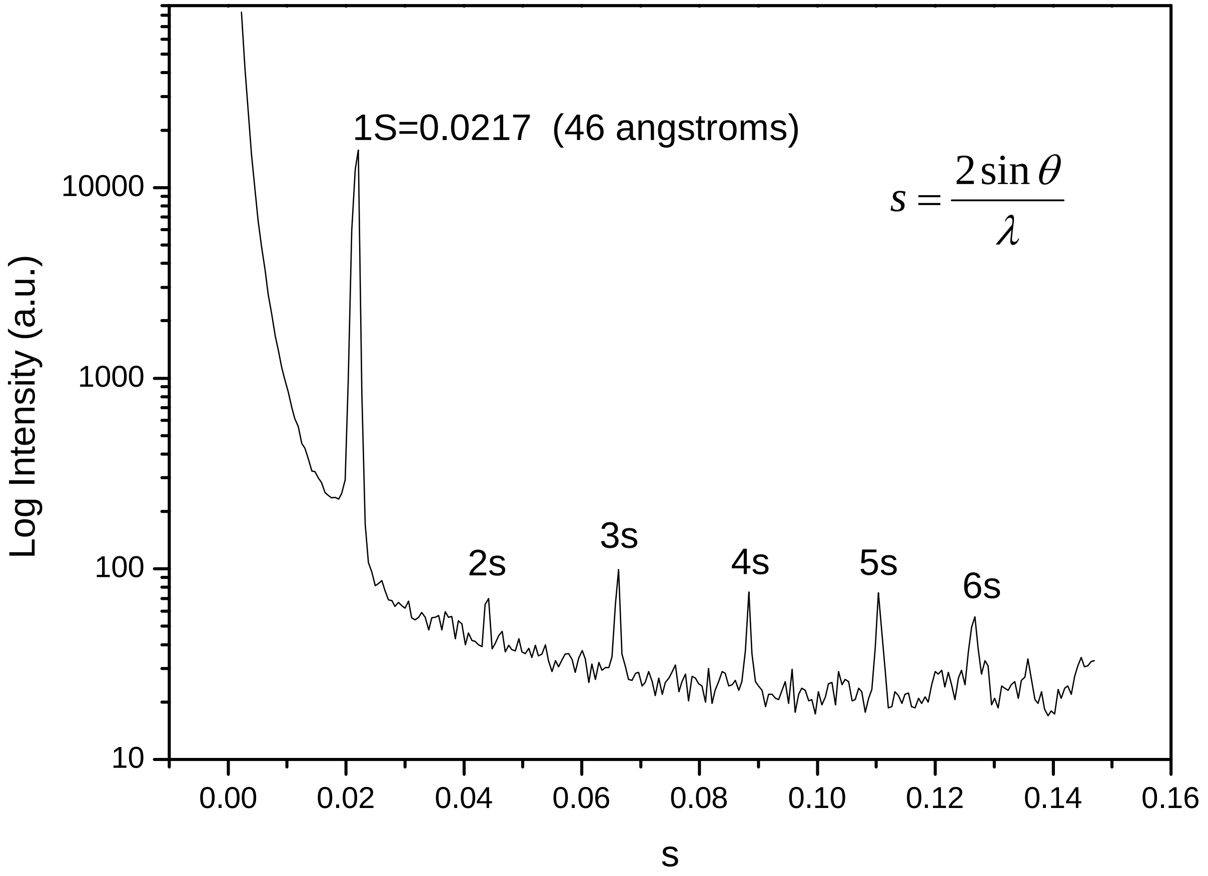
$$\gamma'(0) = -\frac{1}{4\phi_1\phi_2}\frac{A}{V}$$

Babinet’s Reciprocity Principle



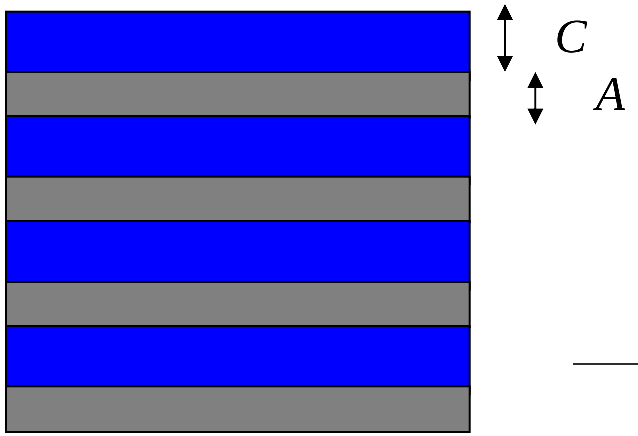
All produces identical I_{obs}

Lamella

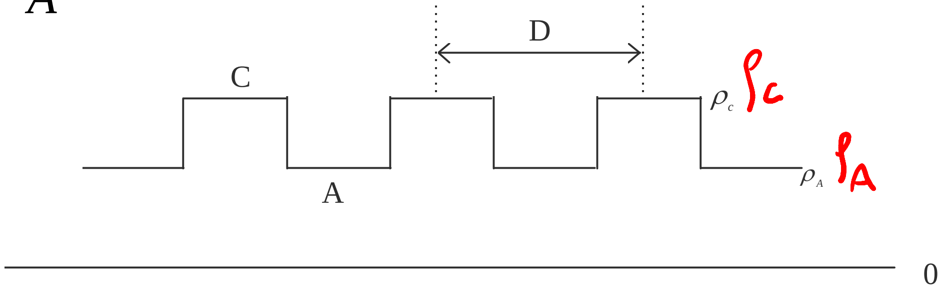


1S=0.0217 (46 angstroms)
$s = \frac{2\sin\theta}{\lambda}$
2s
3s
4s
5s
6s
Log Intensity (a.u.)
10
100
1000
10000
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
s

Polymer Crystals (Lamellae)

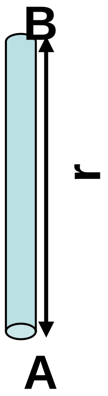


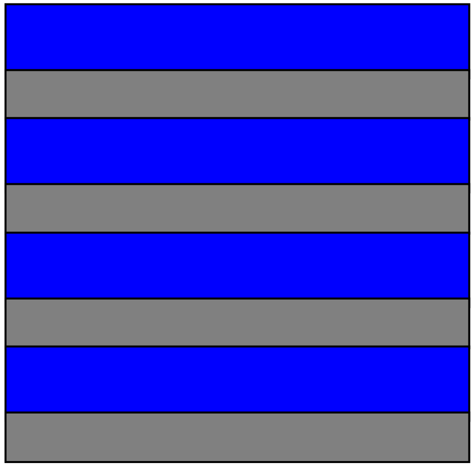
$D = C + A$



$$I_{1obs}(s) = 4\pi s^2 I_{obs}(s)$$

Correlation Function

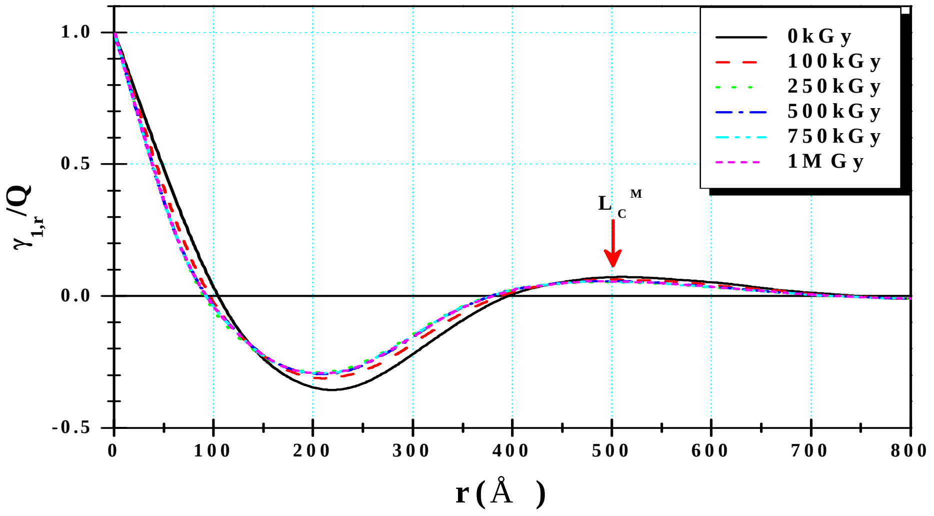




$$\eta_A,\ \eta_B\ \left(\eta = \rho - \langle \rho \rangle\right)$$

$$\gamma_1(r) = \frac{\int \eta(r+u)\eta(u)du}{\langle \eta^2 \rangle} = \frac{\langle \eta_A \eta_B \rangle}{\langle \eta^2 \rangle}$$

$$\gamma_1(r) = \frac{\int I_1(s)\cos 2\pi rs\,ds}{\int I_1(s)ds}$$



Porod Law (for high scattering angle, Porod region)

For spherical particle

$$I_{obs}(s) = \frac{\rho - \rho_0}{8\pi^3}\left[\frac{4\pi R^2}{s^4} + \frac{1}{\pi s^6} + \frac{4R}{s^5}\sin 4\pi Rs + \left(\frac{4\pi a^2}{s^4} - \frac{1}{\pi s^6}\right)\cos 4\pi Rs\right]$$

when s is large

$$I_{obs}(s) = \frac{\rho - \rho_0}{8\pi^3}\frac{A}{s^4}$$

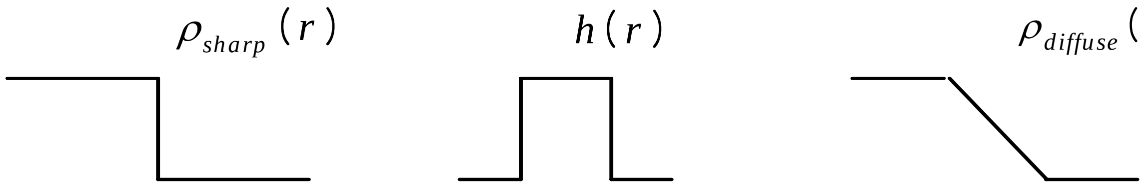
A is surface area of the particle

Satisfies regardless of particle shape, size and concentration

Surface area A can be obtained from the plot of $s^4 I_{obs}(s)$ vs. s

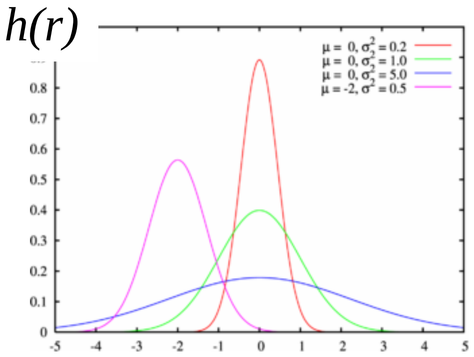
This is also used for intensity fit at high angles

Interface Thickness



$$\rho_{diffuse}(r) = \rho_{sharp}(r) * h(r)$$

$$h(r) = \frac{1}{\left(\sqrt{2\pi}\sigma\right)^3} exp(-\frac{r^2}{2\sigma^2})$$



$$I_{diffuse}(\mathbf{s}) = I_{sharp}(\mathbf{s}) \left|\Im\{h(\mathbf{r})\}\right|^2$$

Here, $\left|\Im\{h(\mathrm{r})\}\right|^2 = e^{-4\pi^2\sigma^2 s^2}$

$$I_{diffuse}(s) = I_{sharp}(s) e^{-4\pi^2\sigma^2 s^2} \sim I_{sharp}(s)(1-4\pi^2\sigma^2 s^2)$$

$$I_{diffuse}(s) \sim \frac{1}{8\pi}(\Delta\rho)^2 \frac{A}{s^4}(1-4\sigma^2\pi^2 s^2)$$

Porod region

POSTECH
Polymer Synthesis and Physics Laboratory

Guinier Approximation

$$I_{obs}(s) = N\langle \eta^2 \rangle V^2 e^{-\frac{4}{3}\pi^2 R_g{}^2 s^2}$$

$$lnI_{obs}(s) = lnNV^2\langle \eta^2 \rangle - \frac{4}{3}\pi^2 R_g{}^2 s^2$$

R_g : radius of gyration

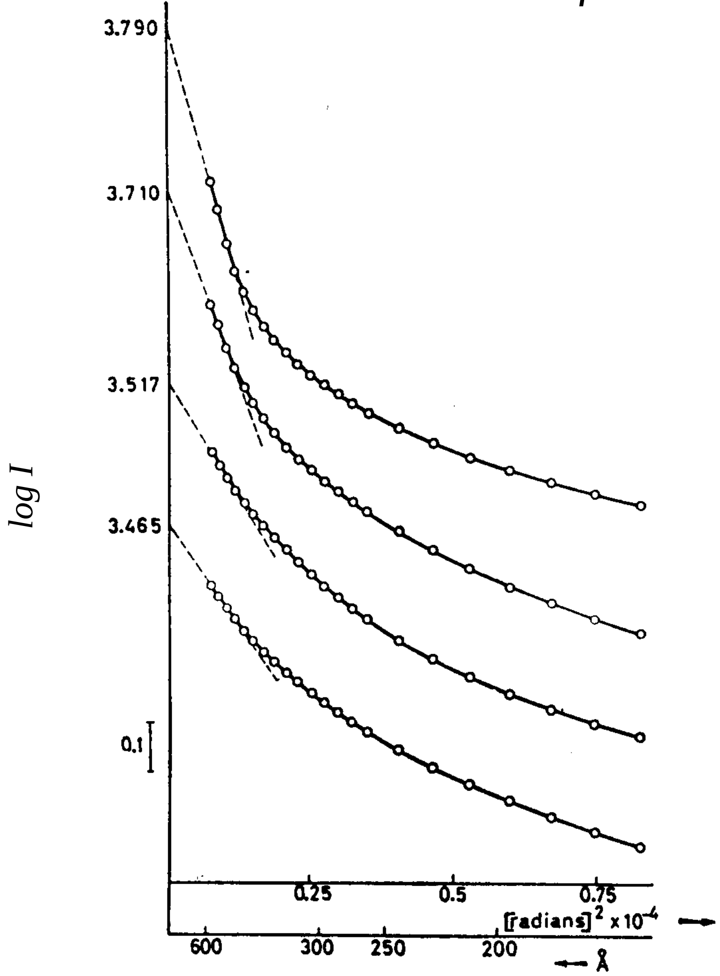
V : scattering volume

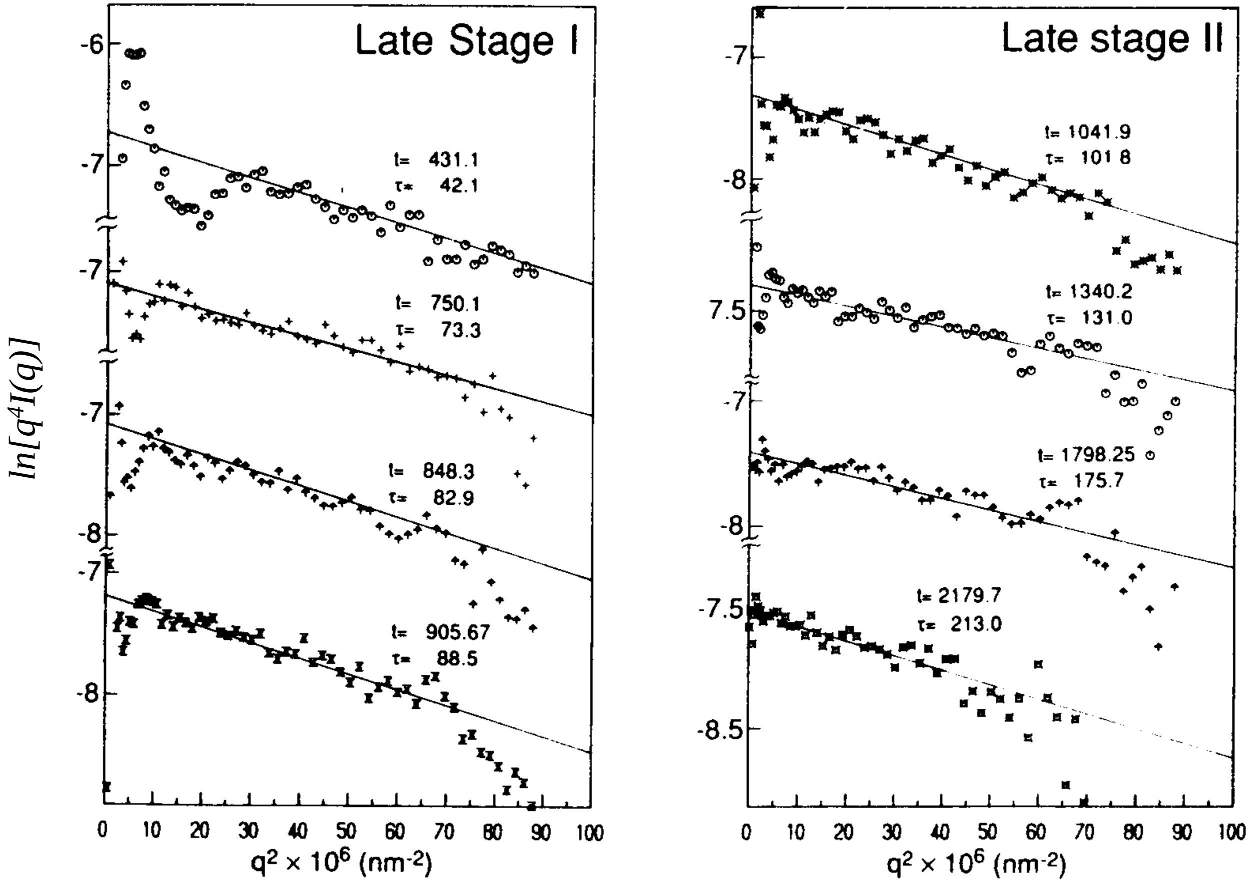
R_g from the slope

$$I(0) = NV^2\langle \eta \rangle^2$$

Applicable only at very small angles
Must be sufficiently dilute

Guinier plot of cellulose nitrate in acetone solution of 0.5 %.




Late Stage I
t= 431.1
τ= 42.1
t= 750.1
τ= 73.3
t= 848.3
τ= 82.9
t= 905.67
τ= 88.5
-6
-7
-7
-7
-8
-7
-8
ln[q^4I(q)]
0 10 20 30 40 50 60 70 80 90 100
q² × 10⁶ (nm⁻²)
Late stage II
t= 1041.9
τ= 101.8
t= 1340.2
τ= 131.0
t= 1798.25
τ= 175.7
t= 2179.7
τ= 213.0
-7
-8
7.5
-7
-8
-7.5
-8.5
0 10 20 30 40 50 60 70 80 90 100
q² × 10⁶ (nm⁻²)

(*a*)

(*b*)

Density Fluctuation

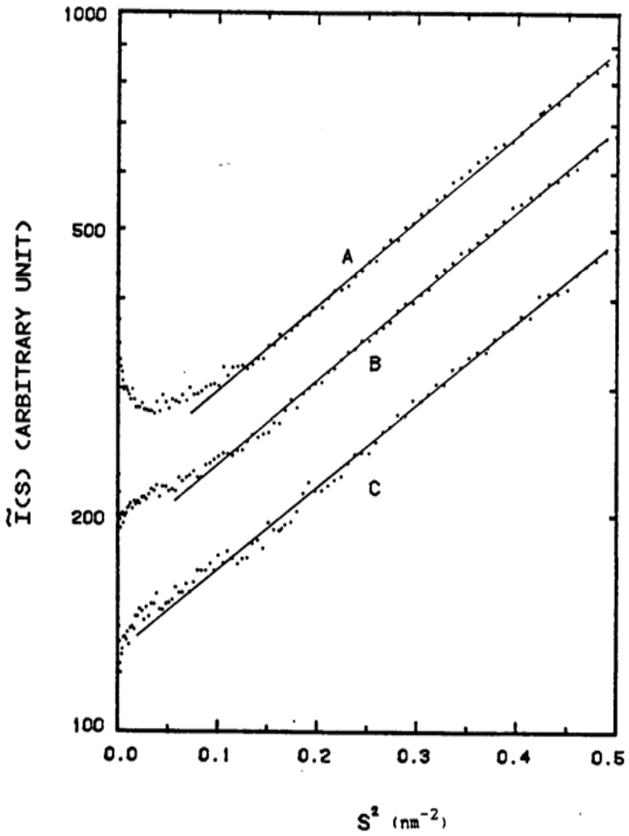
$$Fl(V) = \frac{\left\langle (N - <N>)^2 \right\rangle}{<N>}$$

$$Fl(V) = \int_{Vr} \frac{1}{\rho_0} I(s) \frac{1}{V} (\Sigma^2(s))ds$$

Ruland (1975)

$$Fl(\infty) = \frac{1}{\rho_0} I(0)$$

$$Fl(\infty) = \rho \kappa T \beta_T$$



Correlation and Interface Distribution Functions Analysis on Lamellar Structure

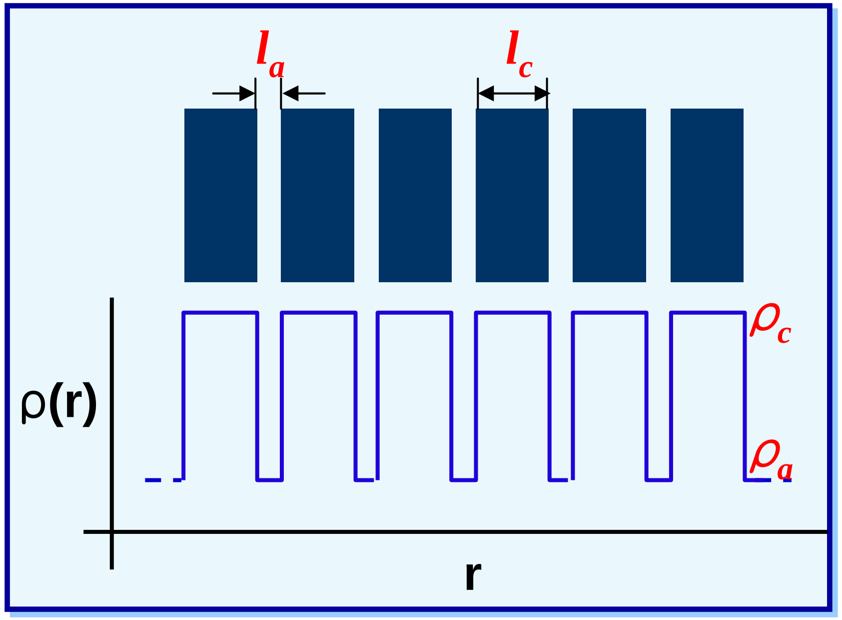
Examples of various arbitrary models

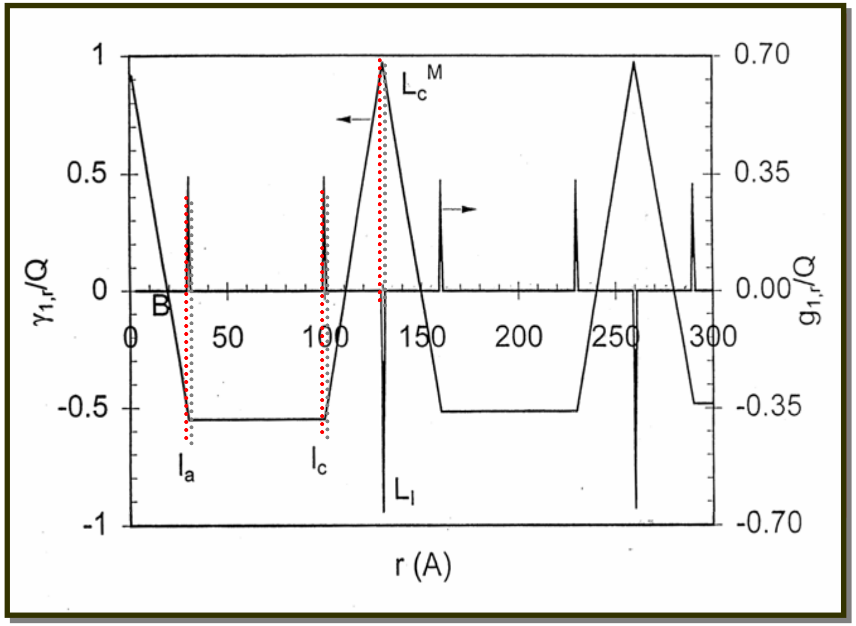
$$Z''(r) = \frac{2}{r_e^2(2\pi)^2}\int_0^\infty \left[\lim_{q\to\infty} q^4 I(q) - q^4 I(q)\right]\cos qr\,dq$$

Ideal Two Phase Model

$$I_{ideal} = \Im\left(\rho_{ideal} * \rho_{ideal}\right)$$

l_c=100Å, l_a=30Å, finite no. of lamellae in the stack is 20

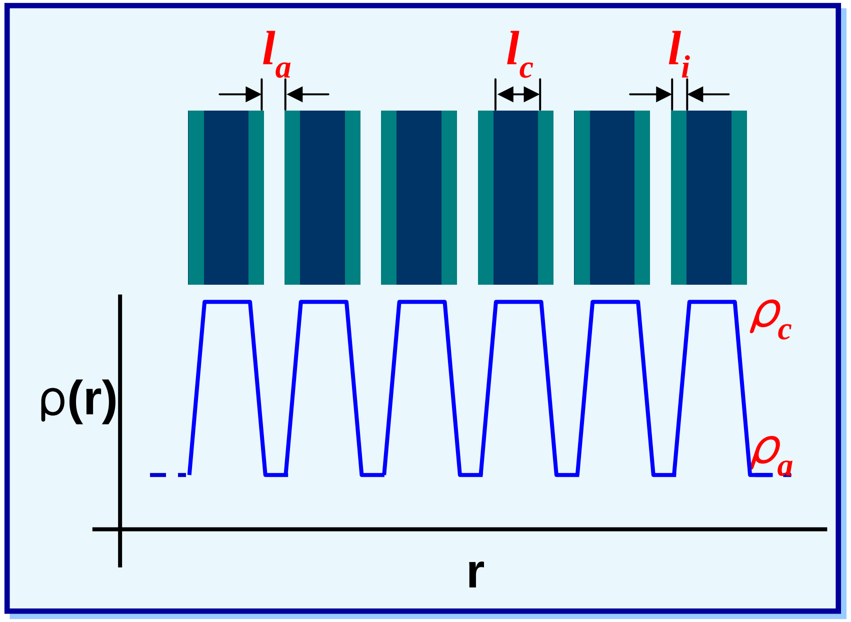


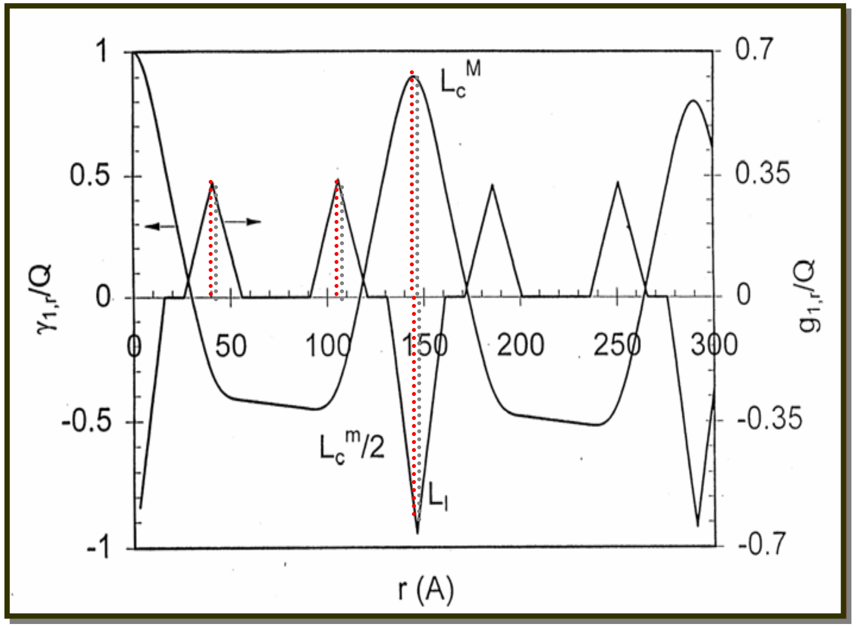


Model With Interface (I)

The ideal two phase model with a finite crystal amorphous transition zone

l_c=100Å, l_a=30Å, l_i=12Å

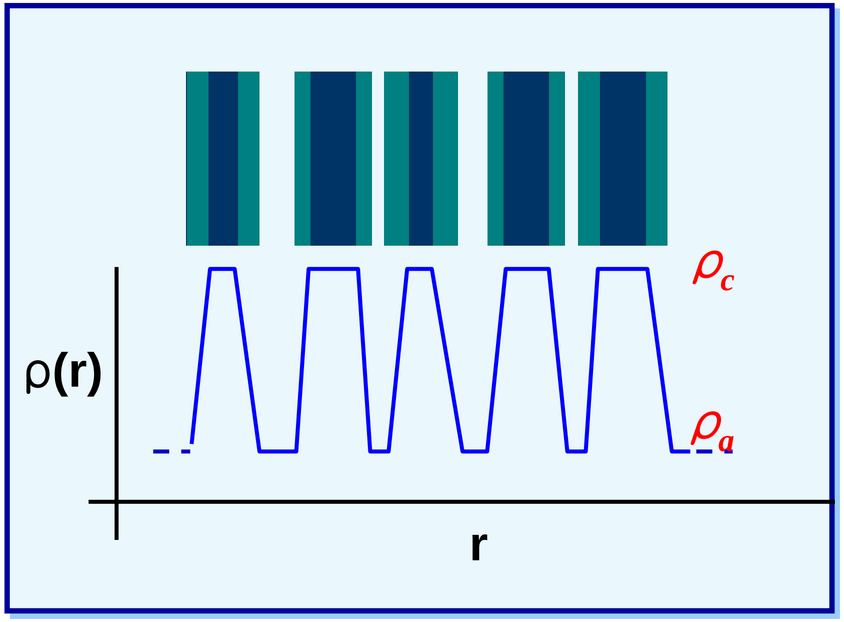


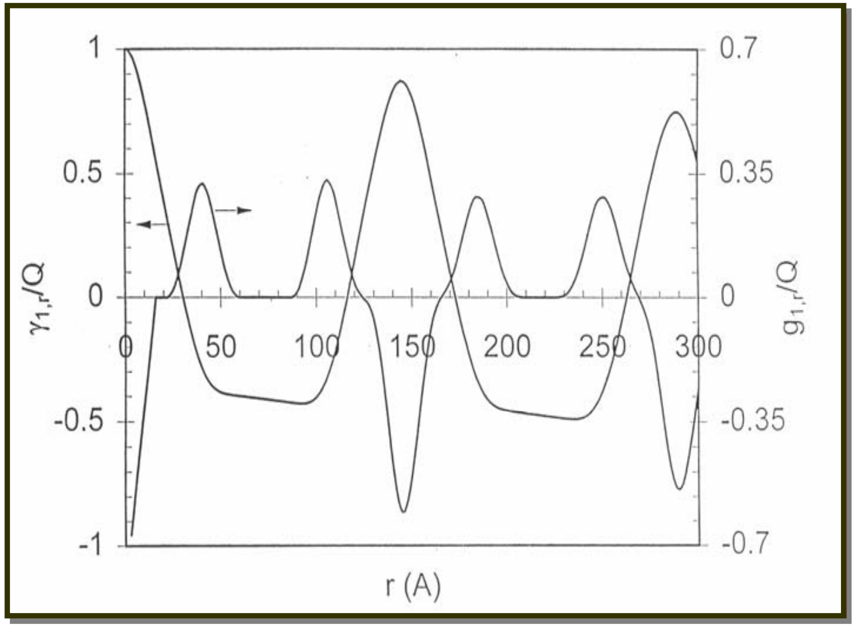


Model With Interface (II)

Distribution of lamellar and amorphous layer sizes

l_c=90Å, w_c=10Å, l_a=25Å, w_a=10Å, l_i=15Å, w_i=1Å





$$L_{model} = L_c^M \geq L_c^m \quad for\, w_2 \leq w_1$$

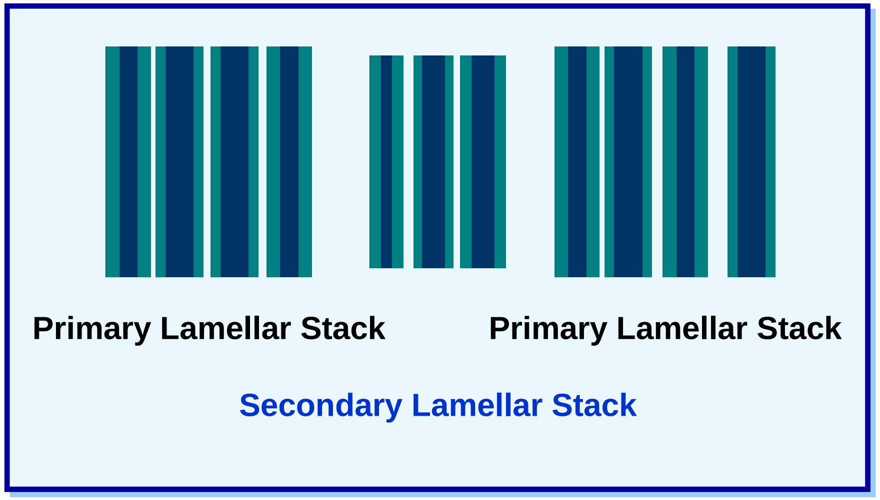
$$L_{model} = L_c^M \leq L_c^m \quad for\, w_2 \geq w_1$$

2 ; thicker phase
w; width of the thickness distribution
L_{model}; average long spacing in the model

Dual Lamellar Stack Model

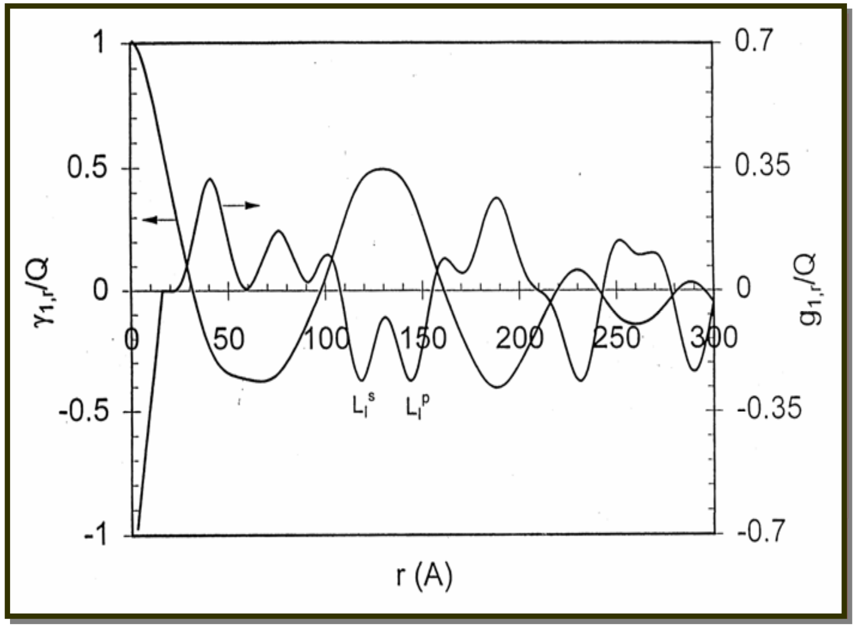
Stack 1 $l_c=90$Å, $w_c=10$Å, $l_a=25$Å, $w_a=10$Å, $l_i=15$Å, $w_i=1$Å

Stack 2 $l_c=60$Å, $w_c=10$Å, $l_a=25$Å, $w_a=10$Å, $l_i=15$Å, $w_i=1$Å



Primary Lamellar Stack **Primary Lamellar Stack**

Secondary Lamellar Stack



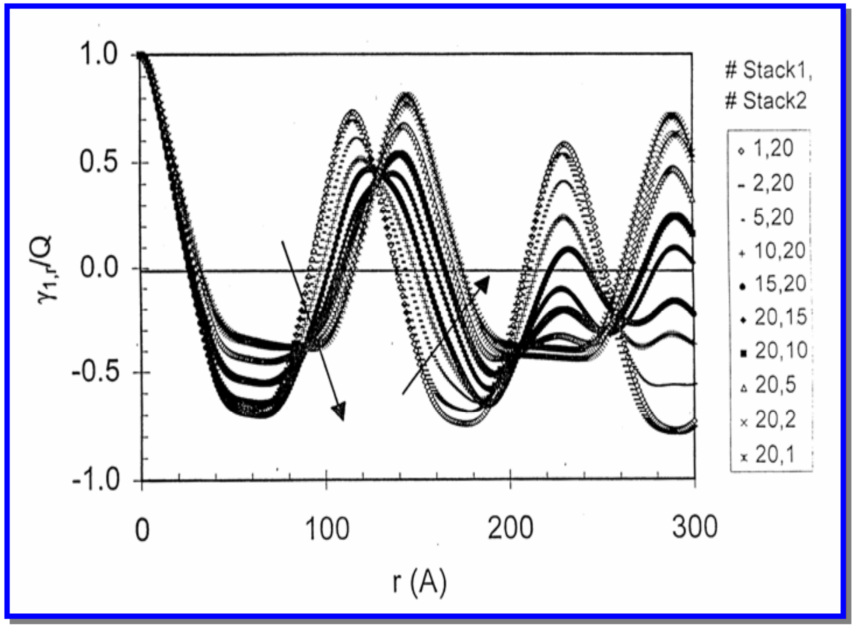
$$L_c^M \geq L_I\,, \quad L_c^m \geq L_I$$

$$L_c^M \geq L_c^m \geq L_I \quad \text{for } w_2 \leq w_1$$

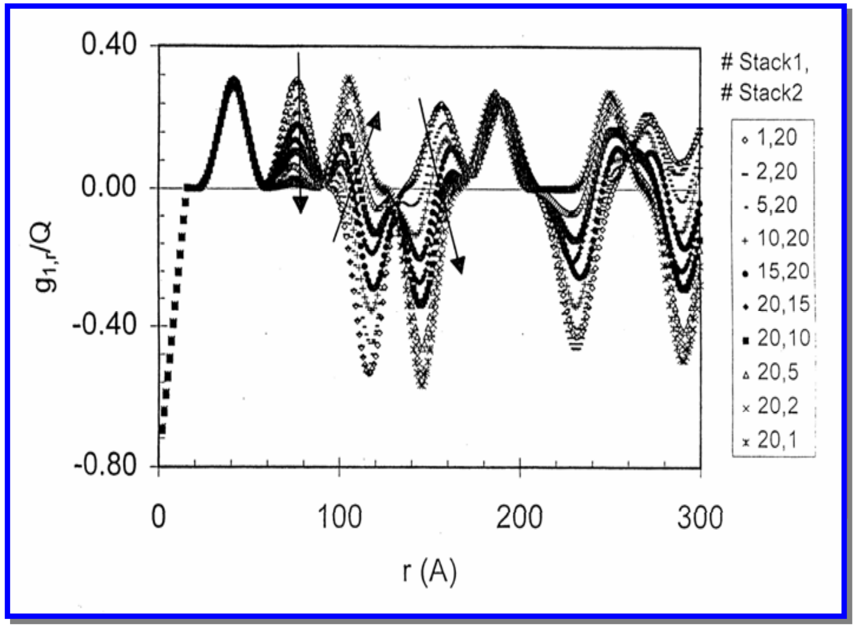
$$L_c^m \geq L_c^M \geq L_I \quad \text{for } w_2 \geq w_1$$

Examples

Correlation function

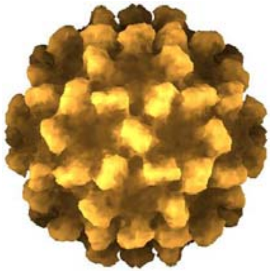


Interface distribution function



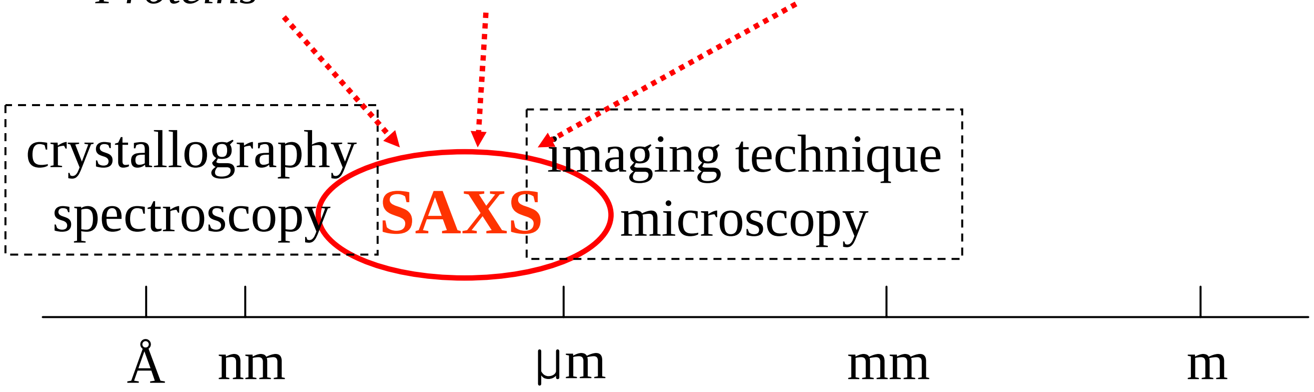
Biological Systems

Proteins



Viruses

Subcellular structures



crystallography
spectroscopy

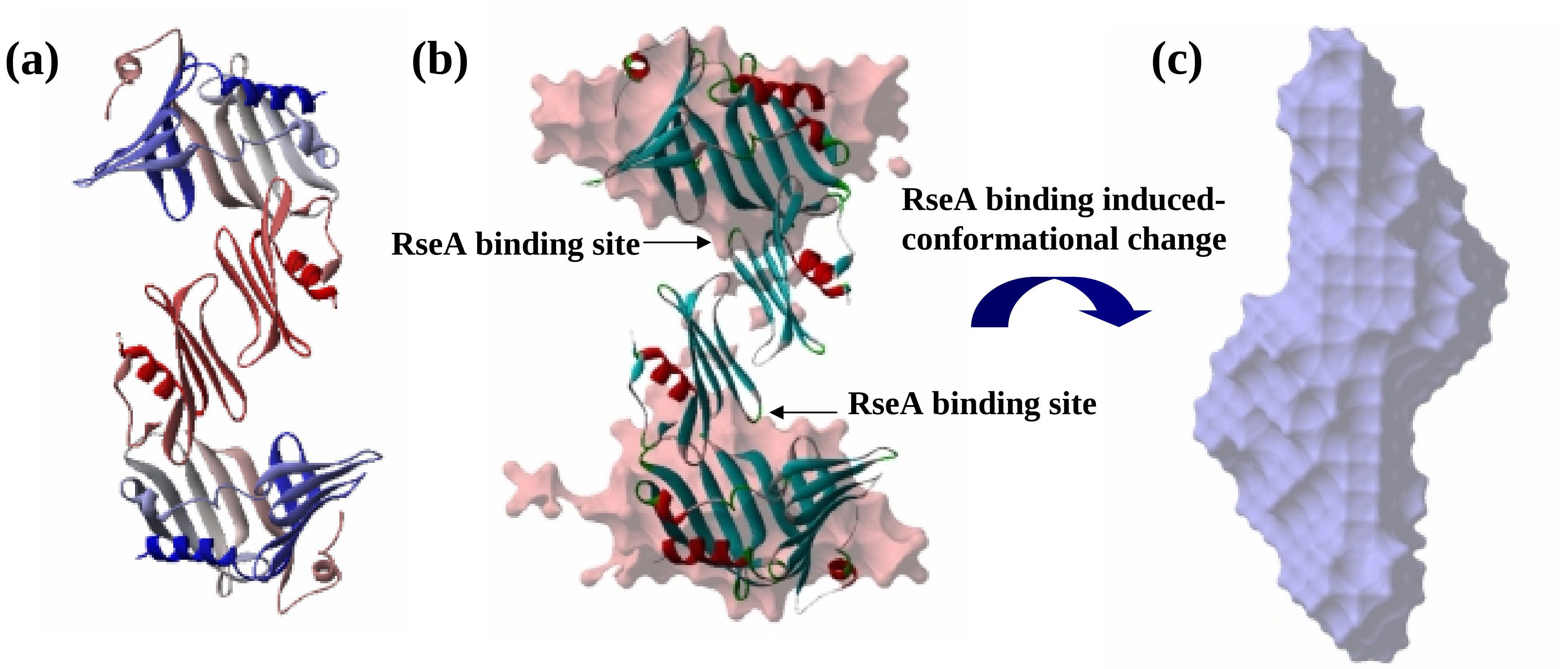
SAXS

imaging technique
microscopy

Å nm µm mm m

Characteristic length

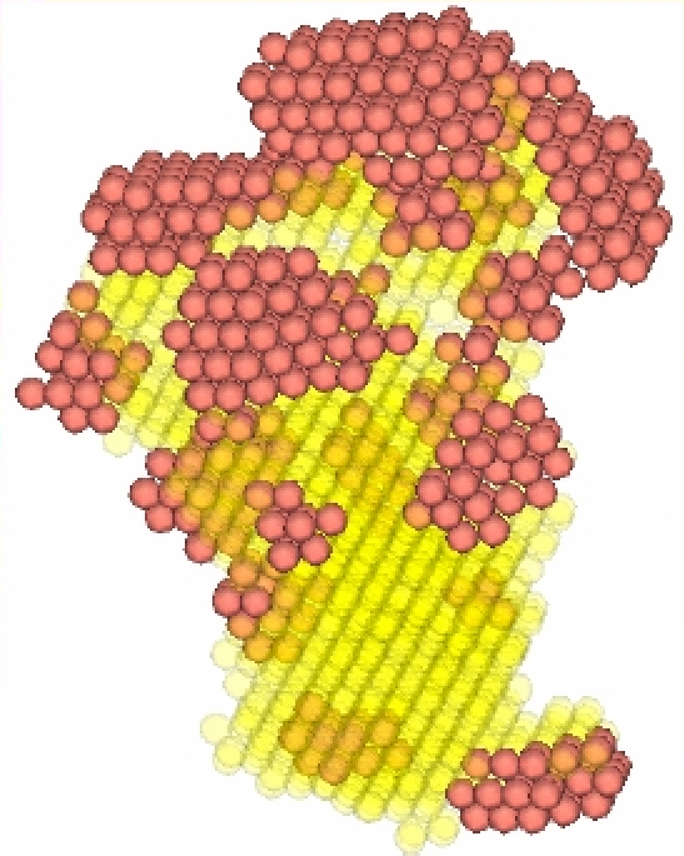
Solution SAXS *versus* Single Crystallography



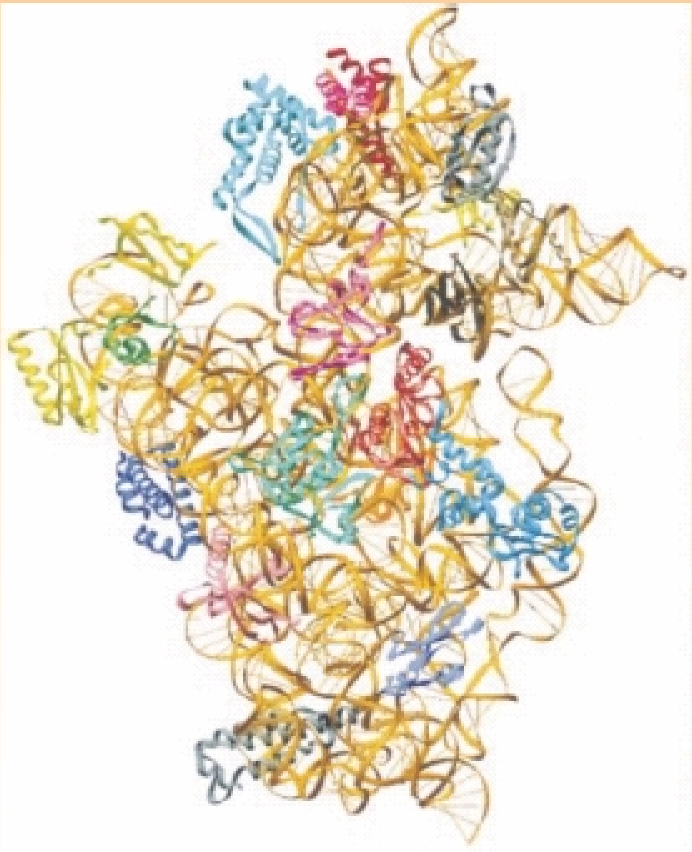
(a) Crystal structure of *Escherichia coli* RseB at a resolution of 0.24 nm

The solution models of RseB (b) and RseA$_{121–216}$/RseB complex (c) restored from the SAXS data at a resolution of 1.25 nm. The ribbon diagram of the RseB is overlapped onto the solution model of RseB for the comparison of overall shape and dimension.

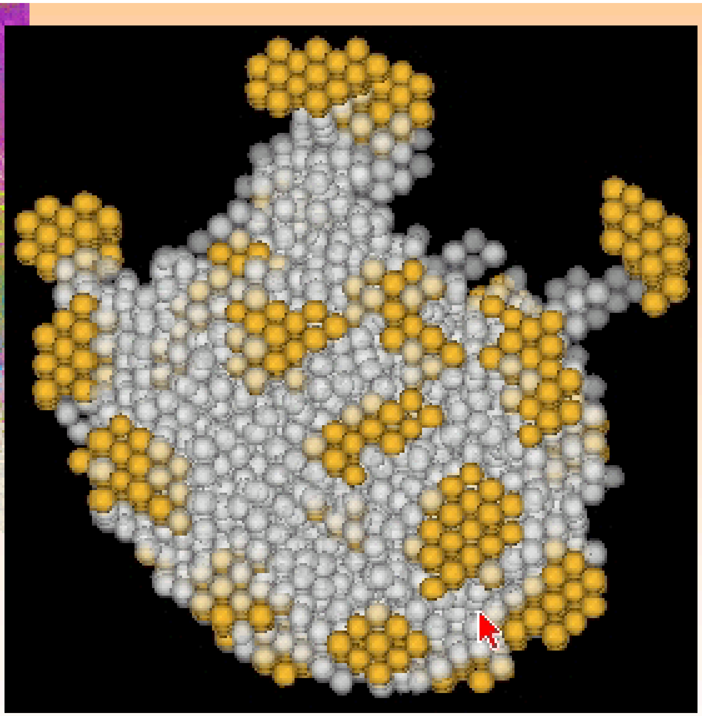
D.Y. Kim, K.S. Jin, E. Kwon, M. Ree, K. K. Kim, *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 8779-8784.



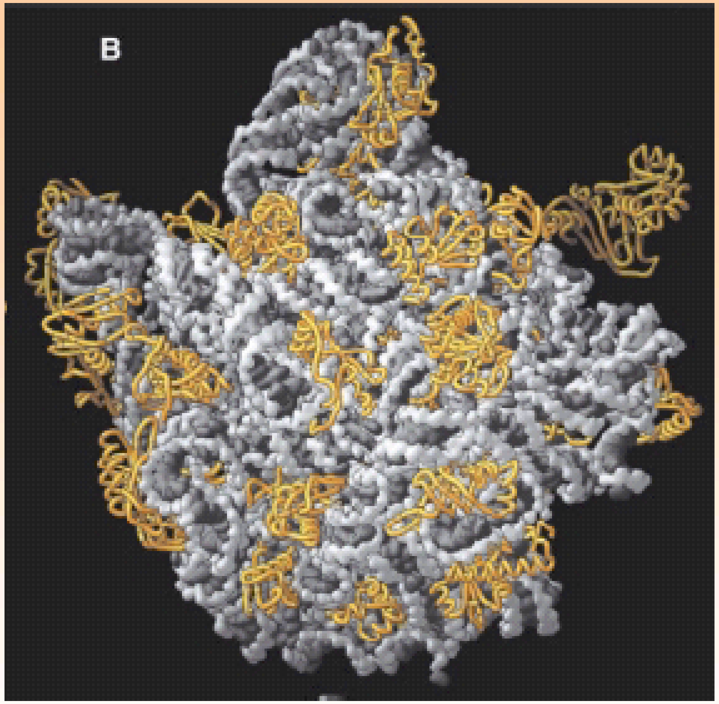
3 nm resolution model of the 30S subuinit in the 70S ribosome *E.coli* (Svergun & Nierhaus, May 2000)



0.33 nm resolution model of the 30S subunit *Th. Thermophilus* (Yonath group, September 2000)



3 nm resolution neutron scattering model of the 50S subunit in the 70S ribosome *E.coli* (Svergun & Nierhaus, May 2000)

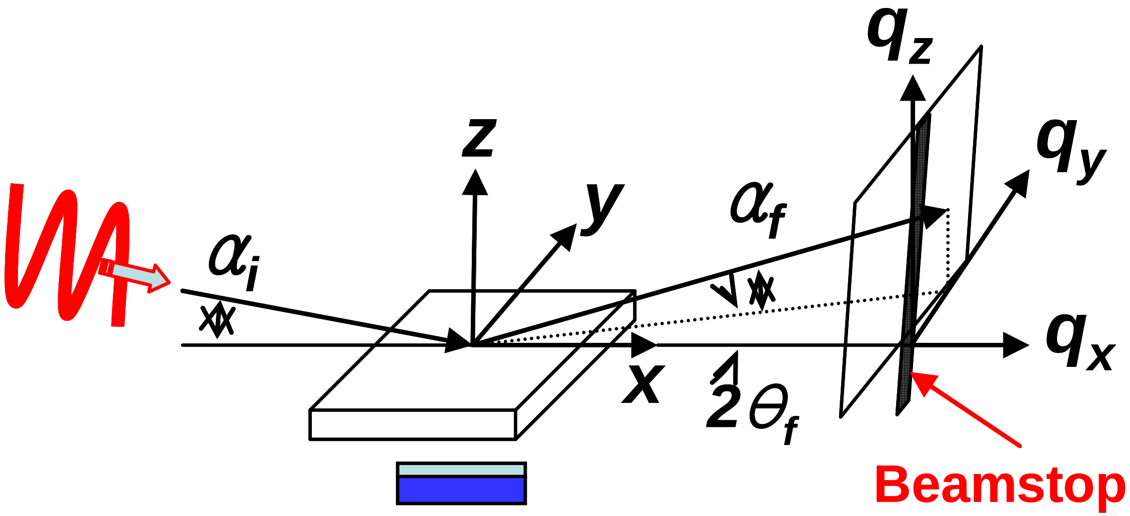


0.24 nm resolution crystallographic model of the 50S subunit *H.marismortui* (Steitz group, August 2000)

Outline

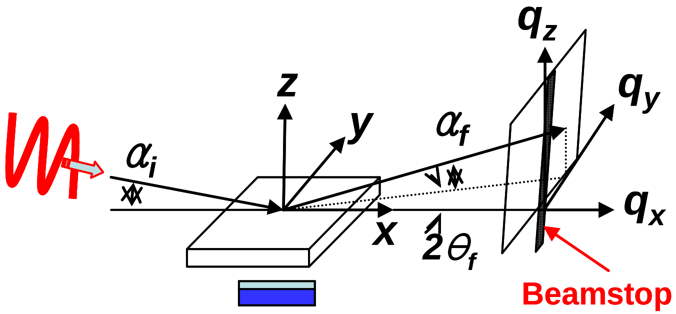
1. Introduction – POSTECH & Pohang Light Source
2. Optics, Beamlines and Equipments of SAXS
3. Data Collection and Samples
4. Fundamentals of SAXS
5. Fundamentals of Conventional, Transmission SAXS (TSAXS)
    (1) Single Molecule (or Particle)
    (2) Multiple Molecules (or Particles) and Their Assemblies
6. **Fundamentals of Grazing Incidence SAXS (GISAXS)**
    (1) Static GISAXS
    (2) In-Situ GISAXS
1. Conclusions – I, II
2. References
3. Introduction – M. Ree's Group at Postech
4. Acknowledgments

Grazing Incidence
Small Angle X-ray Scattering
(GISAXS)

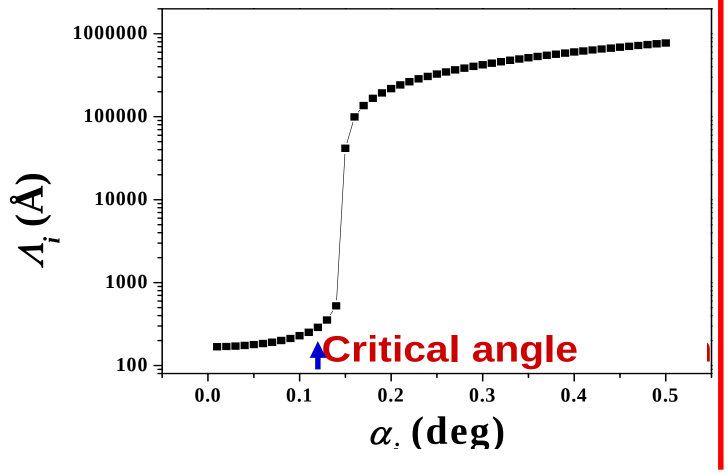


Grazing Incidence X-ray Scattering (GIXS)

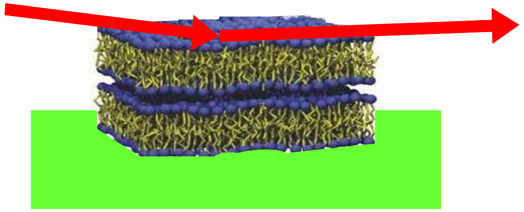
GIXS



Penetration depth profile

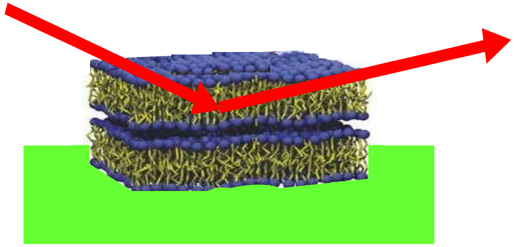


$\alpha_i \leq \alpha_c$



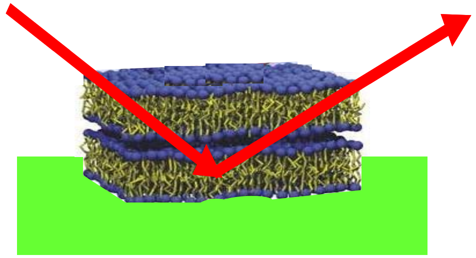
Surface structure >> Internal structure

$\alpha_i \geq \alpha_c$



Surface structure + Internal structure

$\alpha_i > \alpha_c$



Surface structure << Internal structure

- Surface
- Interfaces
- Sub-layers
- Electron density
- etc.

PENETRATION DEPTH

$$\zeta = \frac{\lambda}{\sqrt{2}\pi} \times \frac{1}{\sqrt{\sqrt{\left(\alpha_i^2 - \alpha_c^2\right)^2 + 4\beta^2} - (\alpha_i^2 - \alpha_c^2)}}$$

α_i : **incidence angle**

α_c : **critical angle of the sample**

$$\delta = \frac{\alpha_c{}^2}{2}, \delta = \frac{1}{2\pi}\gamma_e \lambda^2 \rho_e$$

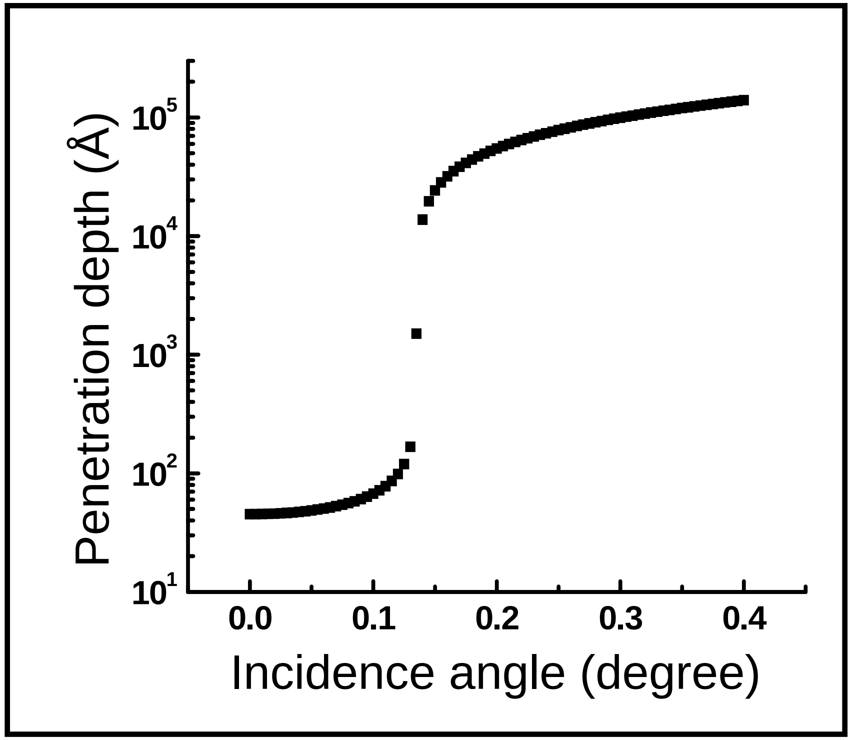
$$\beta = \frac{\lambda\mu}{4\pi} = \frac{\lambda}{4\pi} \times \overline{\rho} \sum_j \left(\frac{\mu}{\overline{\rho}}\right)_j \omega_j$$

μ: **linear absorption coefficient**

$\overline{\rho}$: **mass density of the sample**

ω: **weight fraction**

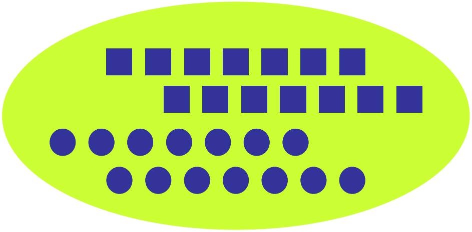
γ_e: **classical radius of electron**



M. Tolan, *X-ray Scattering from Soft-Matter Thin films.* (1999) Springer, NY.

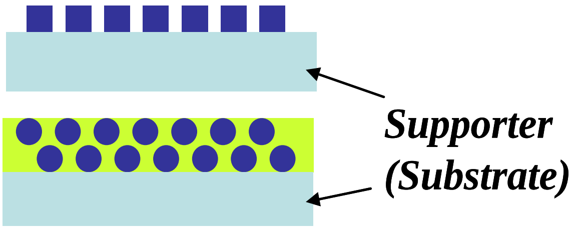
Challenges in Characterization of Nano-Products

Nanostructures



Materials
Fabrications
Characterizations

Nanostructures



Bulk Specimens

Nanotechnology
Era (21st Century)

Nanoscale Specimens

small mass, volume ⇨ weak signal

Analytical Techniques

Transmission:
WAXD, SAXS, WAND, SANS
SALS
Reflection: WAXD, SAXS
Reflectivity

TEM, SEM
AFM

Spectroscopies
etc.

Analytical Techniques

One of Major Issues:
How to characterize?

Scatterings ? → **GIXS**
GINS

Reflectivity → **X-ray**
Neutron

Microscopies ?

Spectroscopies ?
etc.

Concerns and Complexity in GIXS

and

GIXS Theory Development

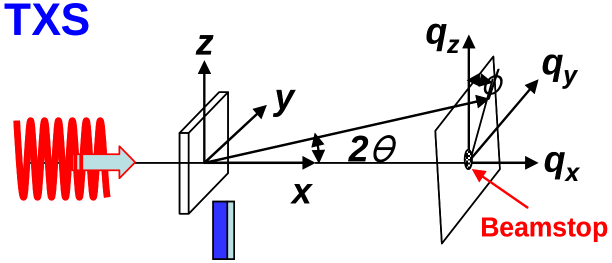
for

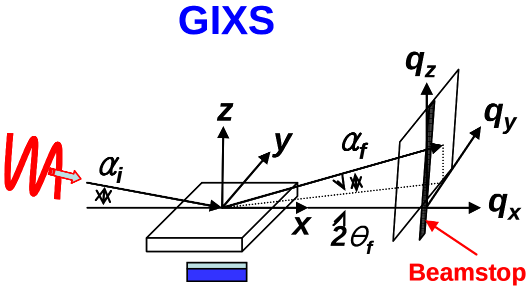
characterizing

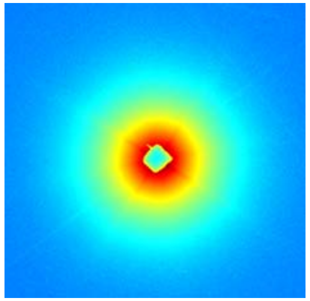
Nanostructures in nanoscale specimens

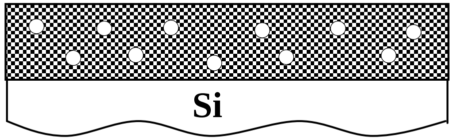
supported with substrates

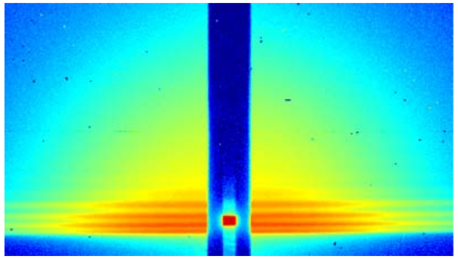
TSAXS vs GISAXS for Characterizing Nanotructure on Substrate





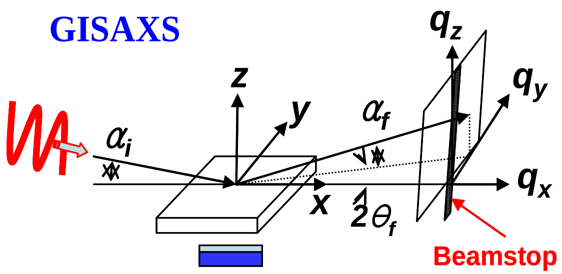






Merit	- Easy measurement - Easy analysis	- Strong intensity - Easy preparation of samples - More informations
Concerns	- Any possible scattering from substrate - Transparency of substrate to X-ray beam - High energy and high flux X-ray beam	- Scattering from surface structure - Scattering from internal structure * Scattering from reflected beam * Scattering from transmitted beam - Refraction effect involved • Need a special setup • Need new scattering theory

GIXS Analysis of Nanotructure in supported with Substrate



Concerns

- Scattering from internal structure
  - Scattering from reflected beam
  - Scattering from transmitted beam
- Refraction effect involved

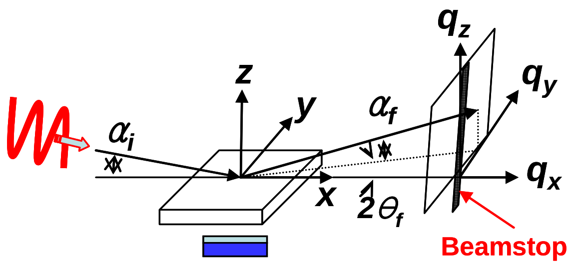
Ree, et al.,
***Macomolecules* (2005) 39, 3395; (2005) 39, 4311.**
***Nature Materials* (2005) 4, 147.**
***Adv. Mater.* (2005) 17, 696.**
Other Groups
etc.

- Scattering from surface structure

Sinha, et al., *Phys. Rev. B.* (1988) 38, 2297.
Rauscher, et al., *Phys. Rev. B* (1995) *52*, 16855.
etc.

Nanostructure on Substrate

GIXS



Concerns

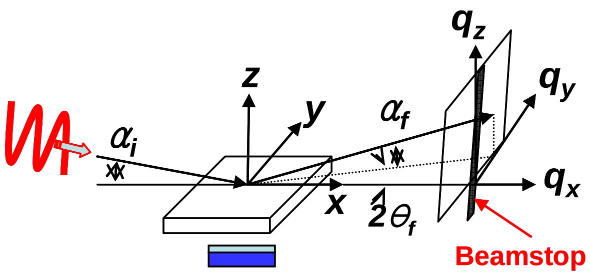
- Scattering from surface roughness : **diffuse scattering**

*** usually very weak,**
but depending on the degree of roughness or surface structure.

(This is not discussed in this presentation.
Further information available: Sinha, et al., *Phys. Rev. B.* (1988) 38, 2297, etc.)

Nanostructure on Substrate

GIXS



Concerns

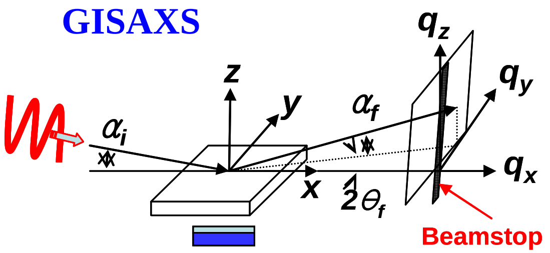
- Scattering from surface roughness : **diffuse scattering**

  *** usually very weak,**

  but depending on the degree of roughness or surface structure.

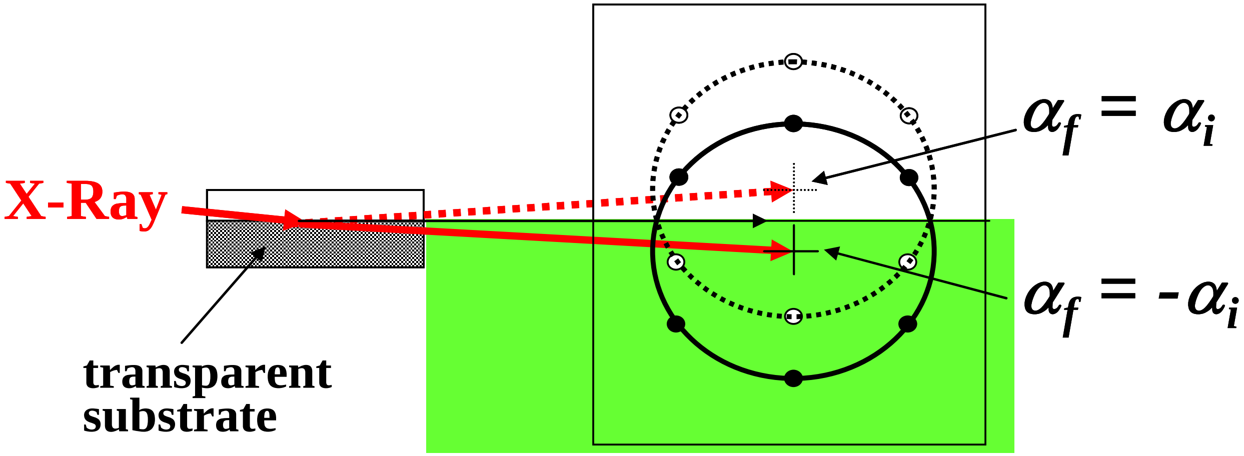
(This is not discussed in this presentation.
Further information available: Sinha, et al., *Phys. Rev. B.* (1988) 38, 2297, etc.)

Nanostructure on Substrate



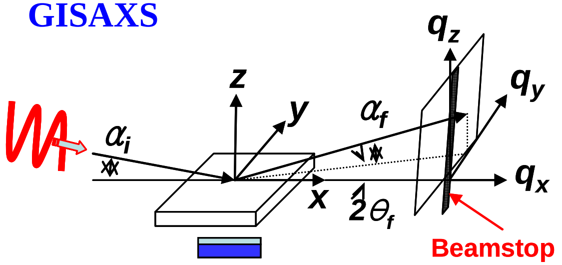
Concerns

- Scattering from internal structure
  - * Scattering from reflected beam
  - * Scattering from transmitted beam



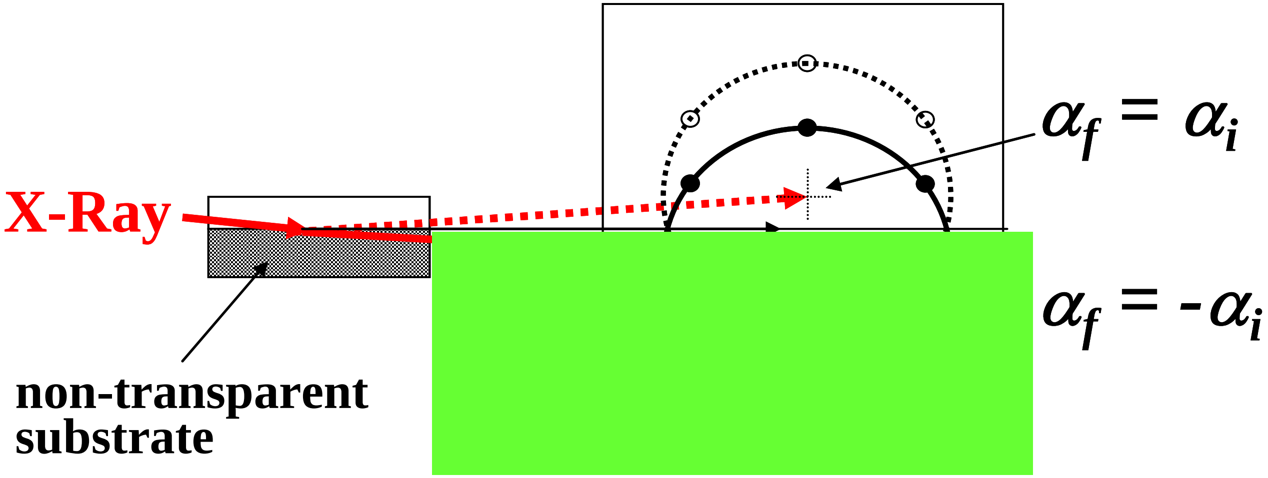
Nanostructure on Substrate

GISAXS



Concerns

- Scattering from internal structure
  - * Scattering from reflected beam
  - * Scattering from transmitted beam



$\alpha_f = \alpha_i$

X-Ray

$\alpha_f = -\alpha_i$

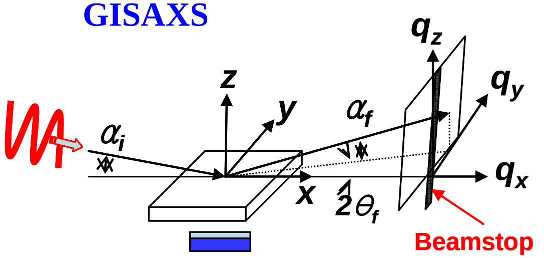
non-transparent
substrate

Nanostructure on Substrate

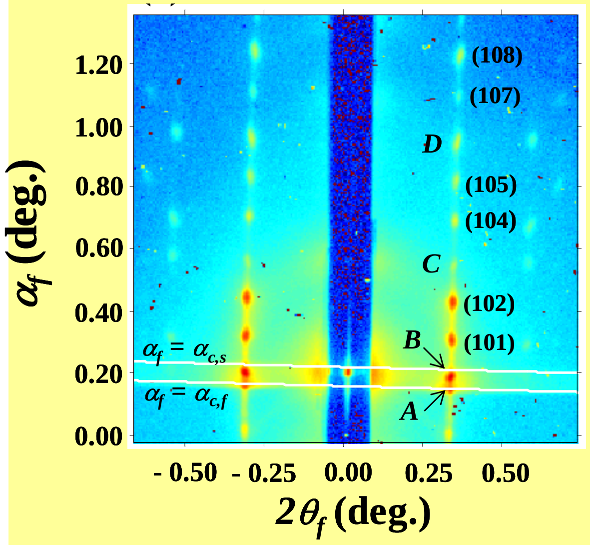
Concerns

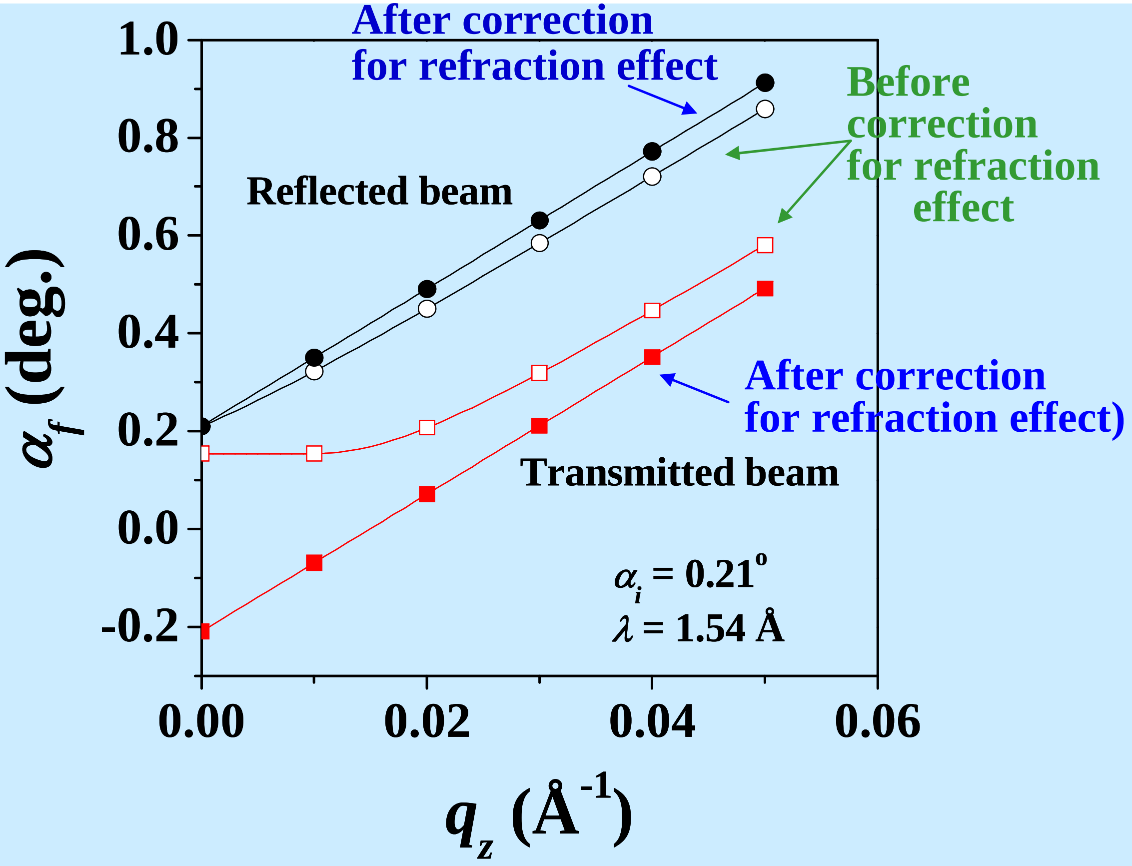
- Scattering from internal structure
  - * Scattering from reflected beam
  - * Scattering from transmitted beam
  - * Refraction effect

GISAXS



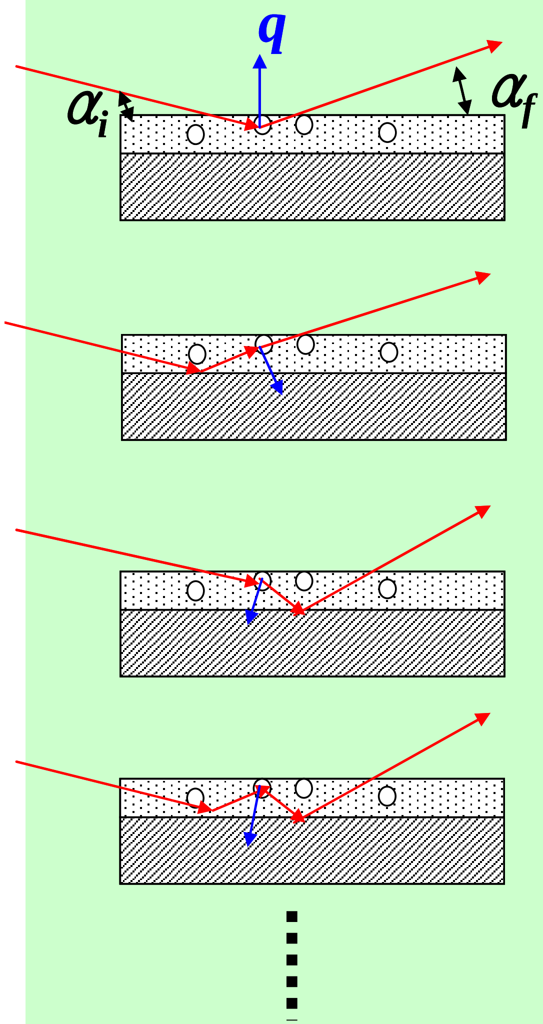
PS-*b*-PI(37/63) film
(HPL; ρ_e = 360 nm^{-3})

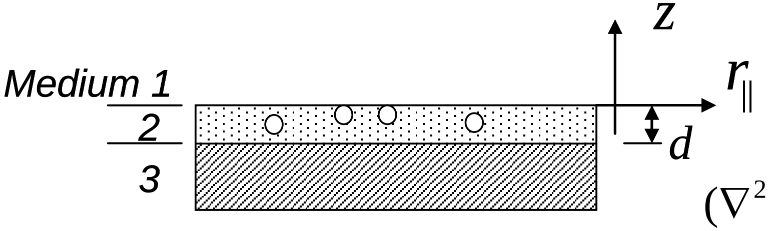




GIXS Intensity : DWBA

Scattering process





$(V = V_1 + V_2)$

$$(\nabla^2 + k_0^2 - V_1)\Psi = 0$$

$$\Psi_{sc}(\mathbf{r}) = -\frac{ik_0 r}{4\pi r}\int d^3 r' \Psi^1(\mathbf{r}', -\mathbf{k_f}) V_2(\mathbf{r}') \Psi^1(\mathbf{r}', \mathbf{k_i})$$

(DWBA)

$$I_{GIXS}(\alpha_f, 2\theta_f) = \frac{1}{16\pi^2} \cdot \frac{1 - e^{-2\,\mathrm{Im}(q_z)\cdot \mathbf{d}}}{2\,\mathrm{Im}(q_z)} \cdot \left| \begin{matrix} T_i T_f F(q_{\|}, \mathrm{Re}(q_{1,z})) + \\ T_i R_f F(q_{\|}, \mathrm{Re}(q_{2,z})) + \\ T_f R_i F(q_{\|}, \mathrm{Re}(q_{3,z})) + \\ R_i R_f F(q_{\|}, \mathrm{Re}(q_{4,z})) \end{matrix} \right|^2$$

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot I_{independent}$$

$$= \frac{1}{16\pi^2} \cdot \frac{1 - e^{-2\,\mathrm{Im}(q_z)\cdot \mathrm{d}}}{2\,\mathrm{Im}(q_z)} \cdot \left[\begin{matrix} |T_i T_f|^2 I_1(q_{\|}, \mathrm{Re}(q_{1,z})) + \\ |T_i R_f|^2 I_1(q_{\|}, \mathrm{Re}(q_{2,z})) + \\ |T_f R_i|^2 I_1(q_{\|}, \mathrm{Re}(q_{3,z})) + \\ |R_i R_f|^2 I_1(q_{\|}, \mathrm{Re}(q_{4,z})) \end{matrix} \right]$$

$$q_{\square} = \sqrt{q_x^2 + q_y^2}$$

$$q_{1,z} = k_{z,f} - k_{z,i}$$

$$q_{2,z} = -k_{z,f} - k_{z,i}$$

$$q_{3,z} = k_{z,f} + k_{z,i}$$

$$q_{4,z} = -k_{z,f} + k_{z,i}$$

$$\mathrm{k}_{z,i} = \mathrm{k}_o\sqrt{n^2 - \cos^2\alpha_i}$$

$$\mathrm{k}_{z,f} = \mathrm{k}_o\sqrt{n^2 - \cos^2\alpha_f}$$

$$k_o = 2\pi/\lambda$$

R_i , T_i : incoming wave
R_f , T_f: outgoing wave
F : amplitude of scattering
from the internal structure
$I_1 = FF^*$; intensity

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2}\cdot\frac{1-e^{-2\,\mathrm{Im}(q_z)\cdot\mathbf{d}}}{2\,\mathrm{Im}(q_z)}\cdot\begin{bmatrix} |T_iT_f|^2\, I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ |T_iR_f|^2\, I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ |T_fR_i|^2\, I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ |R_iR_f|^2\, I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{bmatrix}$$

I_1, scattered intensity from scatters in nanoscales

(1) Spherical structures:

$$I_1 = c\int_0^\infty n(r)\upsilon^2(r)\,|F(qr)|^2\, S(qr)\,dr$$

$$n(r) = \frac{1}{\sqrt{2\pi}\,r_o\sigma e^{\sigma^2/2}}\, e^{\frac{-\ln(r/r_o)^2}{2\sigma^2}}$$

(2) Random two-phase structures:

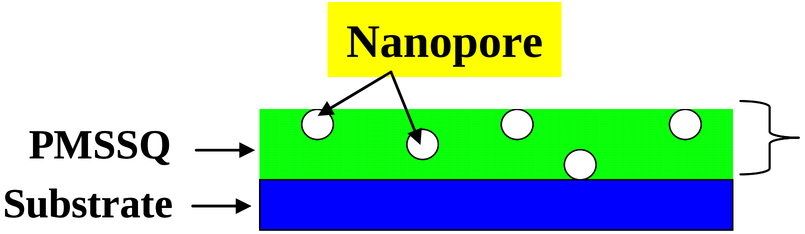
$$I_1 = \frac{8\pi\phi(1-\phi)(\rho_{e(film\ medium)} - \rho_{e(scatter)})^2\,\xi^3}{(1+q^2\xi^2)^2}$$

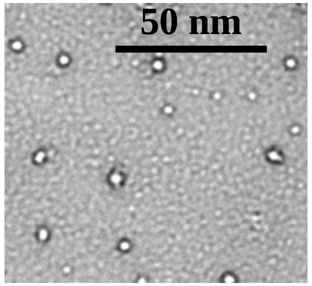
(3) Structures in Crystal lattices:

$$I_1(\mathbf{q}) = S(\mathbf{q})\cdot P(\mathbf{q})$$

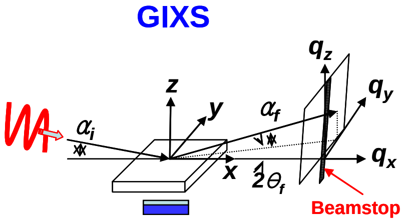
Ree, et al.,
***Macomolecules* (2005) 38, 3395**
***Macromolecules* (2005) 38, 4311.**
***Nature Materials* (2005) 4, 147**
***Adv. Mater.* (2005) 17, 696**

2D GIXS Pattern measured for a nanopous dielectric thin film

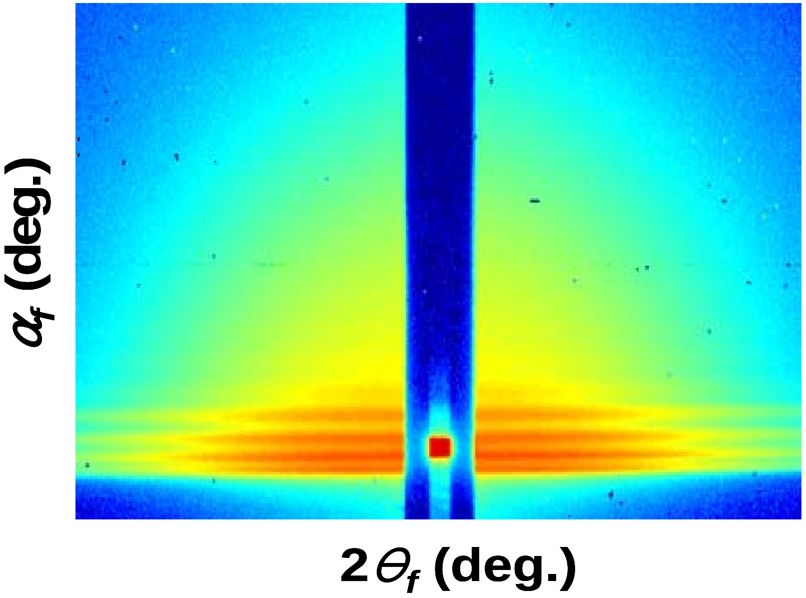




TEM

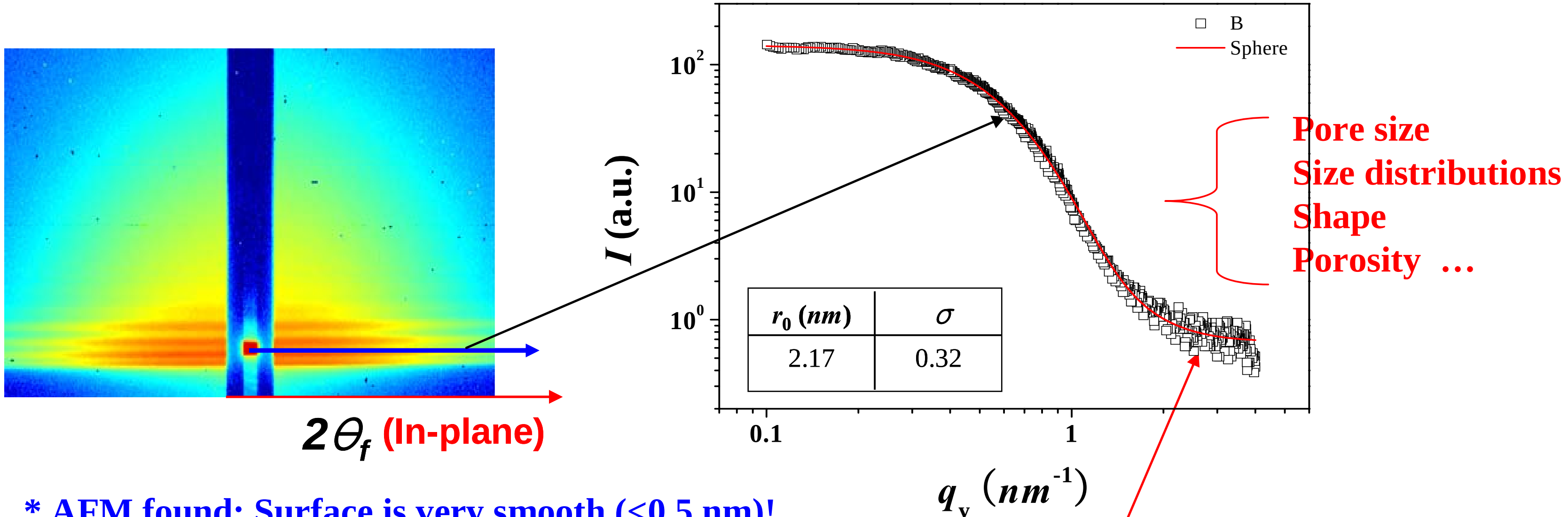


* AFM found: Surface is very smooth (<0.5 nm)!
* Nanospcimen thickness: ca. 100 nm.



2D GIXS Pattern
(experimental data)

(1) Data Analysis with GIXS of Spherical Structures (Pores)



r_0 (nm)	σ
2.17	0.32

Pore size
Size distributions
Shape
Porosity …

*** AFM found: Surface is very smooth (<0.5 nm)!**

*** Nanospcimen thickness: ca. 100 nm.**

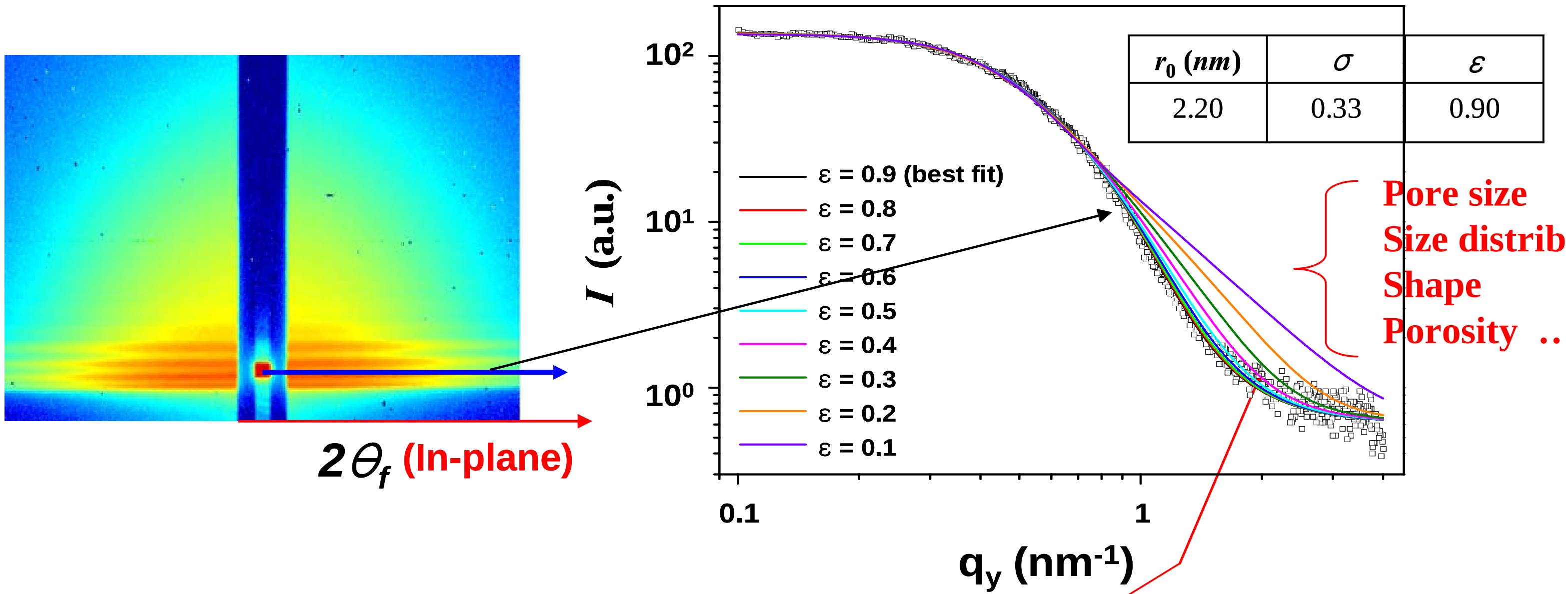
$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot \frac{1-e^{-2\,\mathrm{Im}(q_z)\cdot d}}{2\,\mathrm{Im}(q_z)} \cdot \begin{bmatrix} \left|T_i T_f\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ \left|T_i R_f\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ \left|T_f R_i\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ \left|R_i R_f\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{bmatrix}$$

$$I_1 = \int n(r) \left(\frac{4\pi r^3}{3}\right)^2 \left(\frac{\sin(qr) - qr\cos(qr)}{(qr)^3}\right)^2 S(qr)\,dr$$

$$n(r) = \frac{1}{\sqrt{2\pi\, r_0 \sigma e^{0.5\sigma^2}}}\, e^{\frac{-\ln(r/r_0)^2}{2\sigma^2}}$$

Sphere Form Factor: $F_{sphere}(q,r) = \frac{3[\sin(qr) - qR\cos(qr)]}{(qr)^3}$

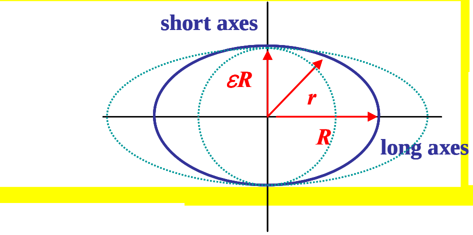
(2) Data Analysis with GIXS of Ellipsoidal Structures (Pores)



r_0 (nm)	σ	ε
2.20	0.33	0.90

Pore size
Size distributions
Shape
Porosity …

$$I_{GIXS}(\alpha_f,2\theta_f)\cong\frac{1}{16\pi^2}\cdot\frac{1-e^{-2\,\mathrm{Im}(q_z)\cdot d}}{2\,\mathrm{Im}(q_z)}\cdot\left[\begin{array}{l}\left|T_iT_f\right|^2 I_1(q_\parallel,\mathrm{Re}(q_{1,z}))+\\ \left|T_iR_f\right|^2 I_1(q_\parallel,\mathrm{Re}(q_{2,z}))+\\ \left|T_fR_i\right|^2 I_1(q_\parallel,\mathrm{Re}(q_{3,z}))+\\ \left|R_iR_f\right|^2 I_1(q_\parallel,\mathrm{Re}(q_{4,z}))\end{array}\right]$$



$$I_1\quad)=\int n(r)\left(\frac{4\pi r^3}{3}\right)^2 F^2_{elliposid}\,S(qr)\,dr$$

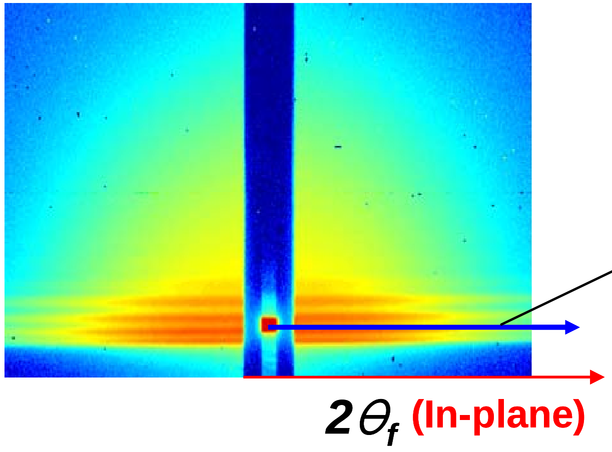
$$n(r)=\frac{1}{\sqrt{2\pi r_0\sigma e^{0.5\sigma^2}}}e^{\frac{-\ln(r/r_0)^2}{2\sigma^2}}$$

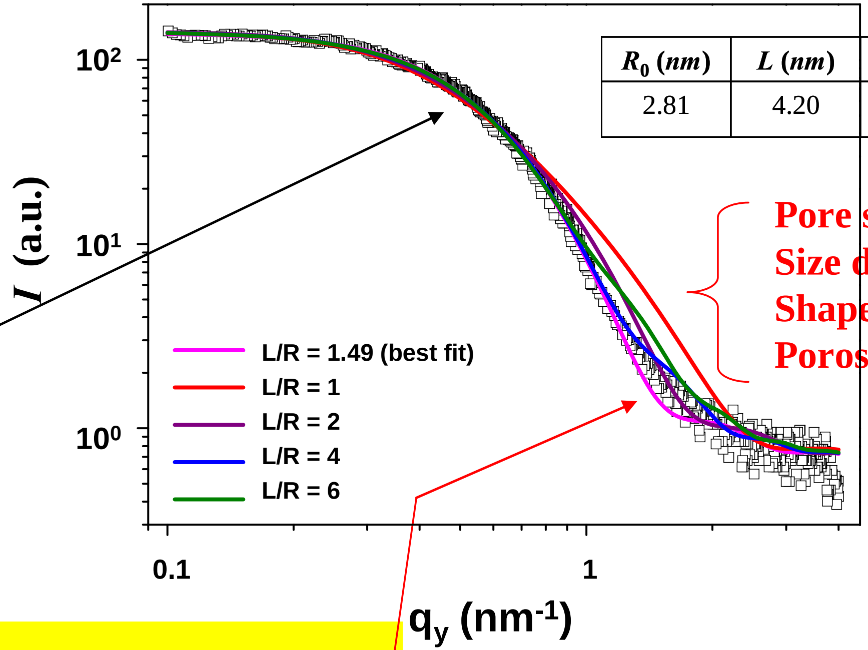
$$F_{ellipsoid}(q,R,\varepsilon)=\int_0^{\pi/2}F^2_{sphere}\left[q,r(R,\varepsilon,\alpha)\right]\sin\alpha\,d\alpha$$

$$r(R,\varepsilon,\alpha)=R\sqrt{\sin\alpha^2+\varepsilon^2\cos\alpha^2}$$

(ε : aspect ratio)

(3) Data Analysis with GIXS of Cylindrical Structures (Pores)





R_0 (nm)	L (nm)	σ
2.81	4.20	0.33

Pore size
Size distributions
Shape
Porosity …

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot \frac{1-e^{-2\,\mathrm{Im}(q_z)\cdot d}}{2\,\mathrm{Im}(q_z)} \cdot \left[\begin{array}{l} |T_i T_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ |T_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ |T_f R_i|^2 I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ |R_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{array} \right]$$

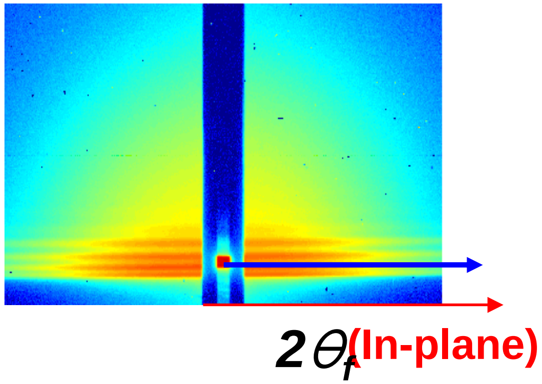
$$I_1 = \int n(R,L) V^2 F_{cylinder}^2 S(qr) dr$$

$n(R,L)$: lognormal function

$$F_{cylinder}(q,R,L) = \int_0^{\pi/2} \left[\frac{2B_1(qR\sin\alpha)}{qR\sin\alpha} \frac{\sin(qL\cos\alpha)/2}{qL\cos\alpha/2} \right]^2 \sin\alpha\, d\alpha$$

R : radius, L : length

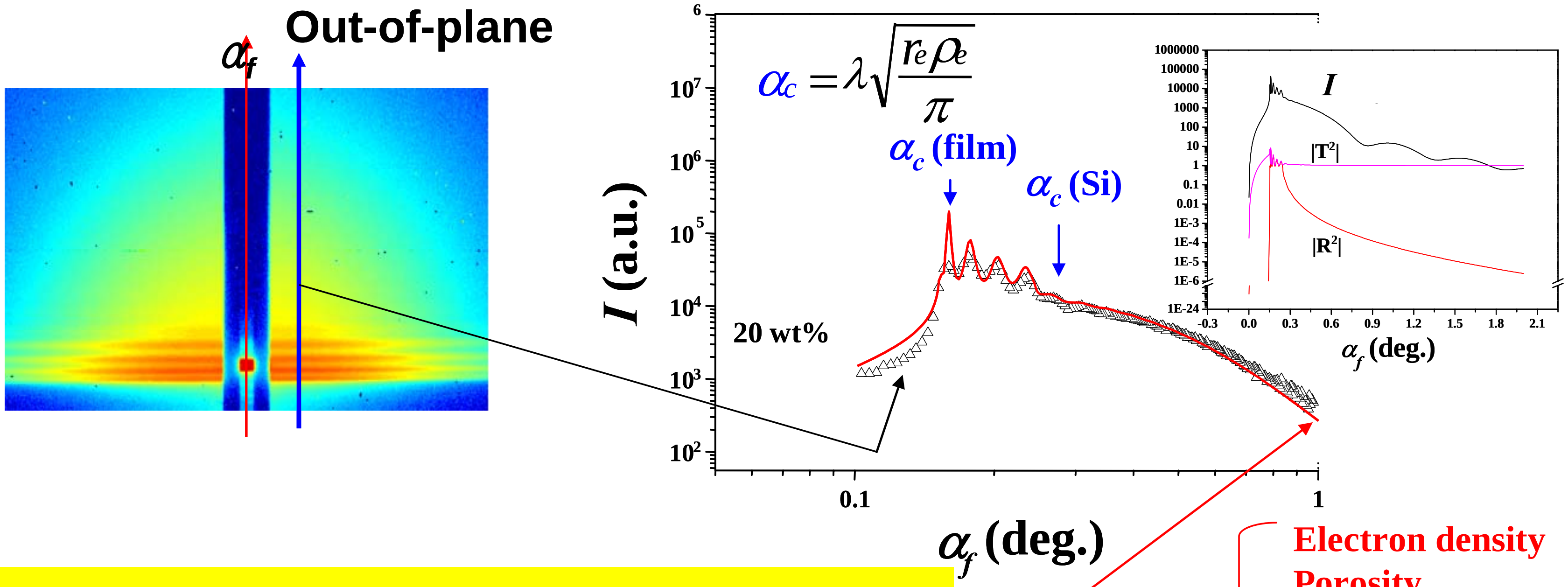
B_1 : first order Bessel function)



This Series of GIXS Analyses gives Conclusions:

- Nanopore shape: “Sphere (hard sphere)”
- Packing order: “None”
  (randomly dispersed in the film plane)

(4) Structural Information in the Out-of-Plane

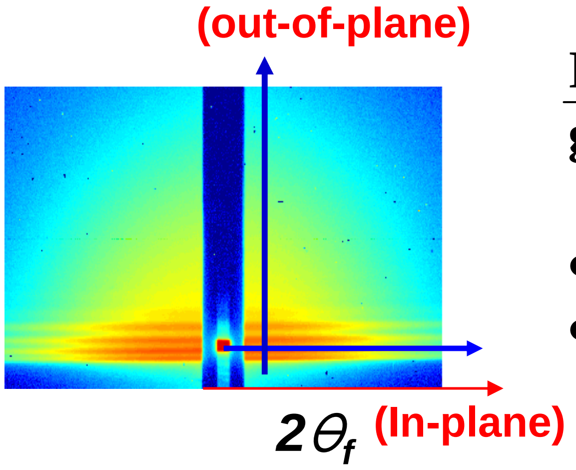


Electron density
Porosity
Thickness
Orientation

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2}\cdot\frac{1-e^{-2\mathrm{Im}(q_z)\cdot d}}{2\mathrm{Im}(q_z)}\cdot\begin{bmatrix} \left|T_iT_f\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ \left|T_iR_f\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ \left|T_fR_i\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ \left|R_iR_f\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{bmatrix}$$

$$I_1 = \int n(r)\left(\frac{4\pi r^3}{3}\right)^2\left(\frac{\sin(qr) - qr\cos(qr)}{(qr)^3}\right)^2 S(qr)\,dr$$

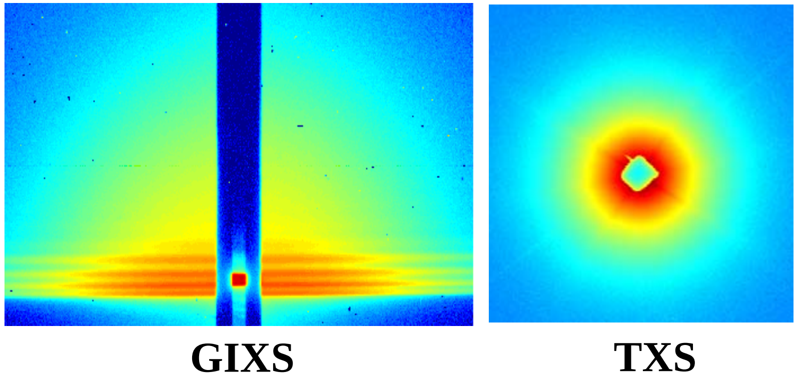
$$n(r) = \frac{1}{\sqrt{2\pi r_0\sigma e^{0.5\sigma^2}}}\, e^{\frac{-\ln(r/r_0)^2}{2\sigma^2}}$$



In- and Out-of-Plane GIXS Profiles Analysis gives Conclusions:

- **Nanopore shape: “Sphere (hard sphere)”**
- **Packing order: “None”**
  (randomly dispersed within the thin film)

*** Further, We have verified these GIXS Analysis Results by the TXS Measurement and Data Analysis!**



M. Ree et al., *Macromolecules* 39, 8991 (2005)

Comparison of GIXS and TXS Analysis

Pore structures and properties of nanoporous PMSSQ films imprinted with PCL4 porogen

Porogen loading (wt%)	Cure temp. (°C)	$\overline{R_g}$ [a] (nm)		ρ_e [b] (nm^{-3})	P [c] (%)	n [d]	k [e]
		GIXS	TXS				
0	400	-	-	399	-	1.3960	2.70
PCL4							
10	400	5.3(0.01)	4.4 (0.06)	373	6.5	1.3587	2.44
20	400	10.0(0.02)	11.3 (0.10)	338	15.3	1.3207	2.16
30	400	>40 [g]	>40 [g]	302	24.3	1.2795	1.85
30	200	-	>40 [g]	398	-	-	-

[a] Average radius of gyration estimated from the radius r and number distribution of pores obtained by the analysis of SAXS profile.

[b] Electron density determined from the out-of-plane GISAXS profile.

[c] Porosity estimated from the electron density of the film.

[d] Refractive index measured at 633 nm using spectroscopic ellipsometry.

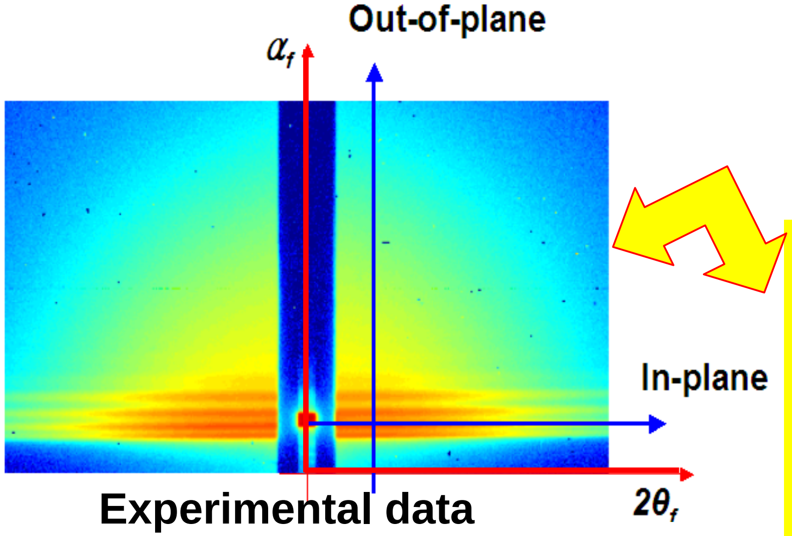
[e] Dielectric constant measured at 1 MHz using an impedance analyzer.

[f] Standard deviation in the determined $\overline{R_g}$ value.

[g] Not detected due to the out of the detection limit (ca. 40 nm).

M. Ree et al., *Macromolecules* 39, 8991 (2005)

(5) 2D GIXS Simulation

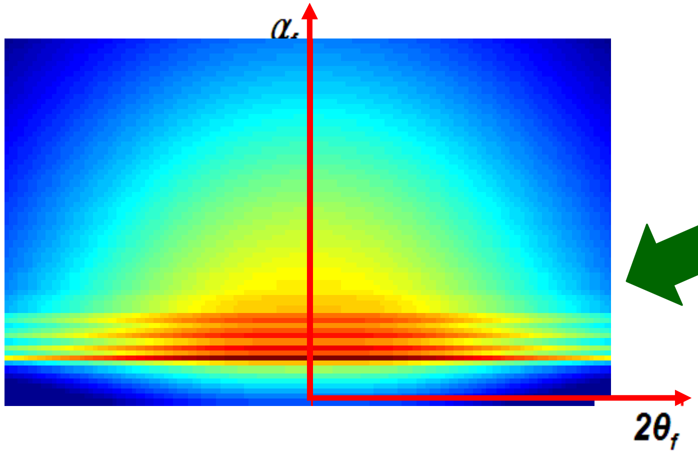


Experimental data

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot \frac{1 - e^{-2\,\mathrm{Im}(q_z)\cdot d}}{2\,\mathrm{Im}(q_z)} \cdot \begin{bmatrix} \left|T_i T_f\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ \left|T_i R_f\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ \left|T_f R_i\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ \left|R_i R_f\right|^2 I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{bmatrix}$$

$$\boldsymbol{I_1} = \int n(r) \left(\frac{4\pi r^3}{3}\right)^2 \left(\frac{\sin(qr) - qr\cos(qr)}{(qr)^3}\right)^2 S(qr)\,dr$$

$$n(r) = \frac{1}{\sqrt{2\pi r_0 \sigma e^{0.5\sigma^2}}}\, e^{\frac{-\ln(r/r_0)^2}{2\sigma^2}}$$



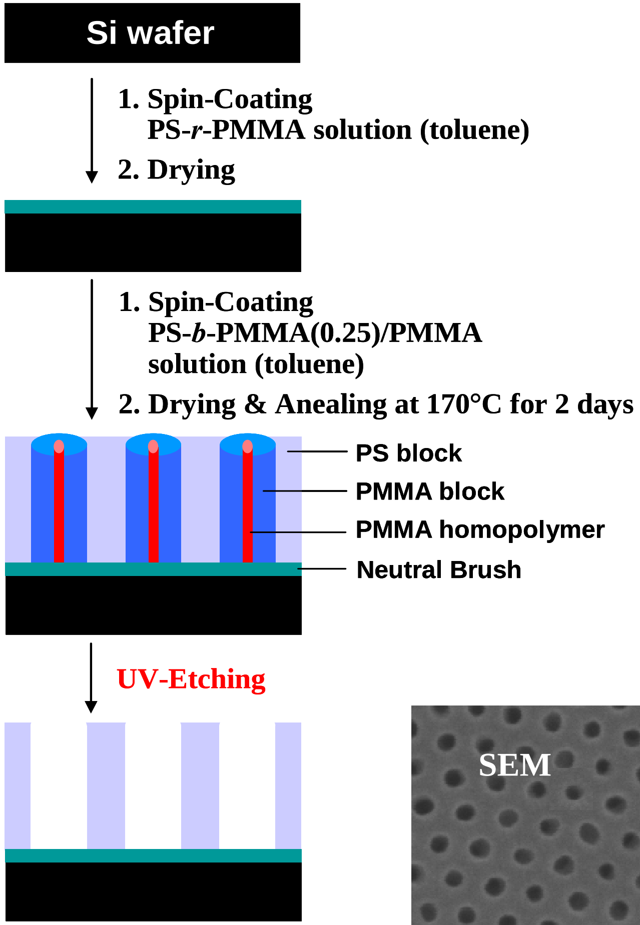
Simulated GIXS pattern

Ree et al.,
***Nature Materials* (2005) 4, 147**
***Adv. Mater.* (2005) 17, 696**
Patents filed

Surface Structures of a Nano-Template on Substrate

PS-b-PMMA Film (25-90 nm thick)

***Co-worked with Prof. Jin Kon Kim (Postech)**

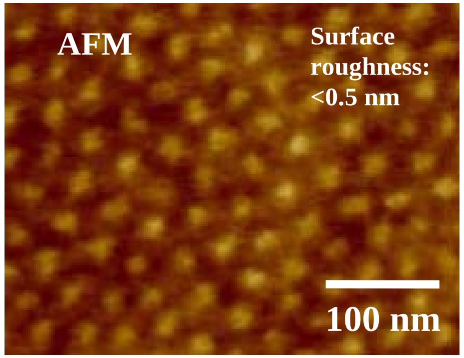


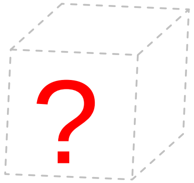
Si wafer

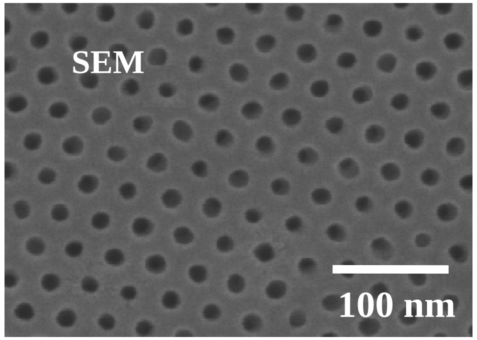
1. Spin-Coating
   PS-*r*-PMMA solution (toluene)
2. Drying

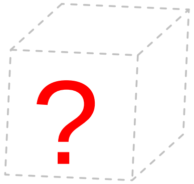
1. Spin-Coating
   PS-*b*-PMMA(0.25)/PMMA solution (toluene)
2. Drying & Anealing at 170°C for 2 days

UV-Etching









(1) $R_{cylinder}$ & Distribution ?

(2) $L_{cylinder}$ & Distribution ?

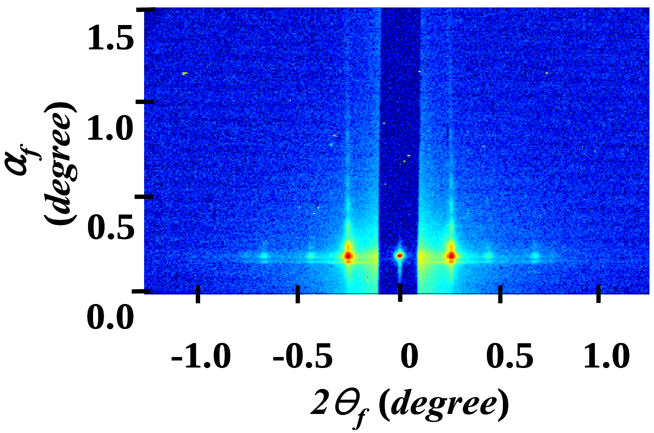
(3) Cylindrical Pore Depth & Its Quality ?

Ree et al.,
J. Appl. Cryst. 40, 305 (2007)

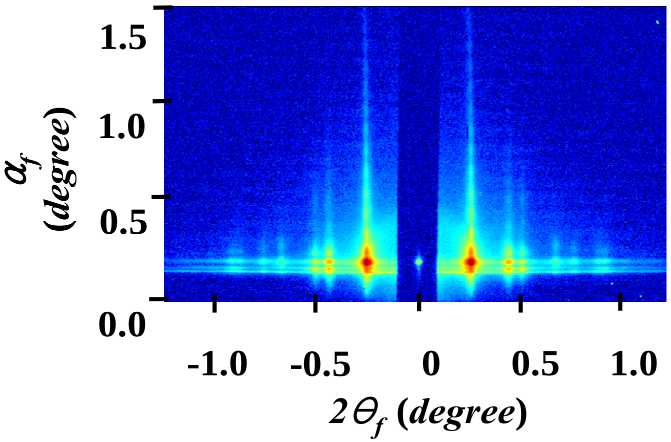
GIXS

Measured

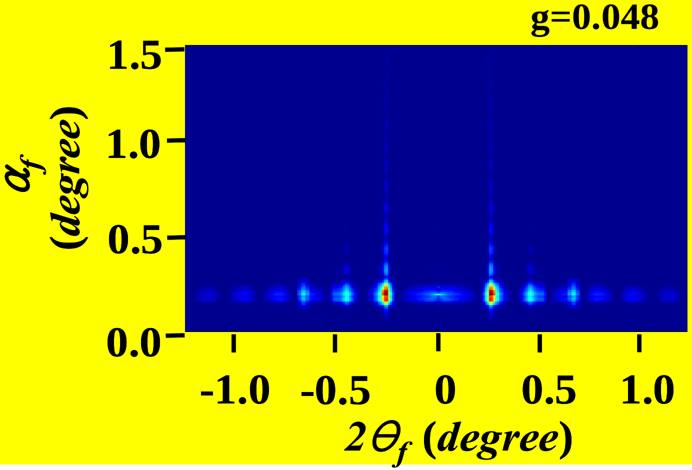
Before UV-Etching

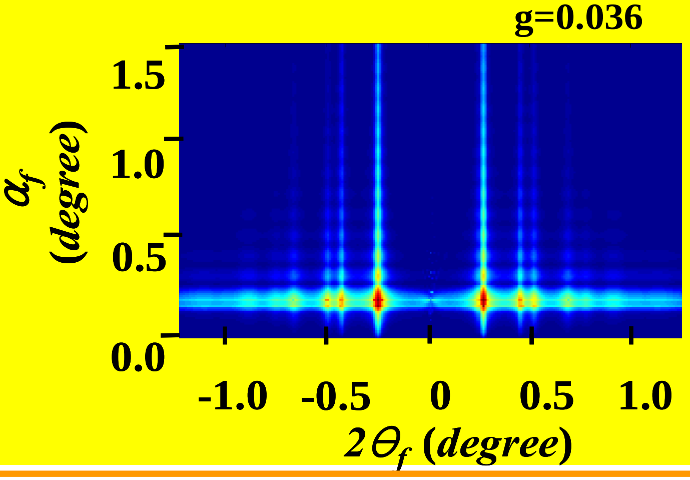


After UV-Etching



Calculated





Parameters in calculating 2D GIXS pattern:

$\alpha_i = 0.20°$
L = 78.8 nm
R = 11.8 nm
σ_r = 2.95 nm
D_{sp} = 34.0 nm
ρ_e(film)=348 nm^{-3}

Parameters in calculating 2D GIXS pattern:

$\alpha_i = 0.20°$
L = 86.1 nm
R = 11.7 nm
σ_r = 2.90 nm
D_{sp} = 34.0 nm
ρ_e(film)=261nm^{-3}

Internal Structure of a Nano-Template on Si Substrate

PS-b-PMMA Film (25-90 nm thick)

$$I_{GIXS}(\alpha_f,2\theta_f)\cong\frac{1}{16\pi^2}\cdot\frac{1-e^{-2\mathrm{Im}(q_z)\cdot d}}{2\mathrm{Im}(q_z)}\cdot\begin{bmatrix}\left|T_iT_f\right|^2 I_1(q_{\|},\mathrm{Re}(q_{1,z}))+\\ \left|T_iR_f\right|^2 I_1(q_{\|},\mathrm{Re}(q_{2,z}))+\\ \left|T_fR_i\right|^2 I_1(q_{\|},\mathrm{Re}(q_{3,z}))+\\ \left|R_iR_f\right|^2 I_1(q_{\|},\mathrm{Re}(q_{4,z}))\end{bmatrix}$$

$$I_1(q)=\left|F(q)\right|^2 Z(q)$$

$$F(q,R,L)=2\pi R^2L\frac{J_1(qR)}{qR}\sin(qL/2)\exp(-iqL/2)$$

$$G(R)=\frac{1}{\sqrt{2\pi}\sigma_R}\exp\left[-\frac{(R-\bar{R})^2}{2\sigma_R^2}\right]$$

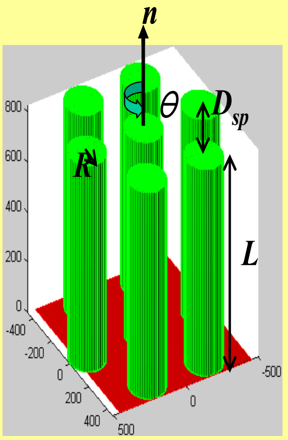
$$Z(q)=\prod_{k=1}^{d}Z_k(q)$$

$$Z(q)=\mathrm{Re}\left\{\frac{1+F_k(q)}{1-F_k(q)}\right\}=\frac{1-\left|F_k\right|^2}{1-2\left|F_k\right|\cos(a_k\cdot q)+\left|F_k\right|^2}$$

$$F_k(q)=\left|F_k(q)\right|\exp(-iqa_k)$$

$$\left|F_k(q)\right|=\prod_{j=1}^{2}\exp\left[-\frac{1}{2}g^2(qa_j)^2\right]$$

$$g^2=\Delta^2a_j/a_j^2$$



R_{cylinder}**=11.5 nm**
L **= 25 – 100 nm**

g: paracrystal distortion factor

Structural and property characteristics of thin films of the PS-*b*-PMMA/PMMA mixtures before and after UV-etching

Sample	t^a (nm)	Structural parameters					Properties		
		L^b (nm)	$\overline{R}^c$ (nm)	$\sigma_R{}^d$ (nm)	$d_{sp}{}^e$ (nm)	g^f	$\alpha_c{}^g$ (deg.)	$\rho_e{}^h$ (nm^{-3})	$P_e{}^i$ (%)
Before etching									
Film-1	**28.5**	**28.5**	**11.0**	**3.01**	**34.0**	**0.053**	**0.156**	**348**	**–**
Film-2	**78.8**	**78.8**	**11.4**	**3.00**	**34.0**	**0.048**	**0.156**	**348**	**–**
After UV-etching									
Film-3	**25.0**	**25.0**	**11.8**	**2.95**	**34.0**	**0.040**	**0.136**	**265**	**25.3**
Film-4	**86.1**	**86.1**	**11.7**	**2.90**	**34.0**	**0.036**	**0.135**	**261**	**26.6**

[a] Film thickness.

[b] Length of the cylindrical pores.

[c] Pore radius determined from the peak maximum of the radius *r* and the number distribution of pores.

[d] Standard deviation of the pore radius.

[e] Center-to-center distance of the cylindrical pores (*d*-spacing of the hexagon).

[f] Paracrystal distortion factor

[g] Critical angle of the film determined from the out-of-plane GIXS profile.

[h] Electron density determined from the critical angle of the film.

[i] Porosity estimated from the electron density of the film with respect to the electron density of PS.

Self-Assembled PS-b-PMMA Diblock Copolymer on Substrate

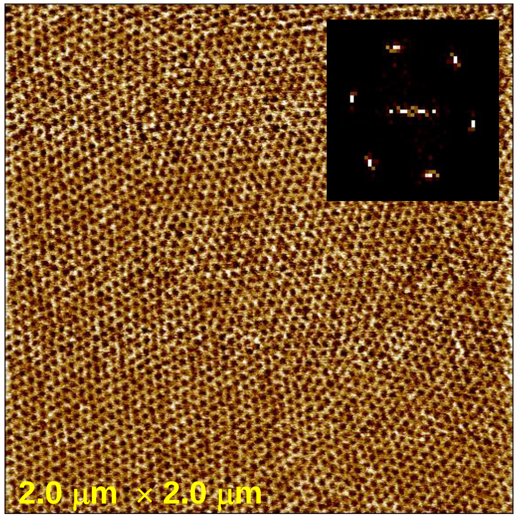
PS-b-PMMA Film (200 nm thick)

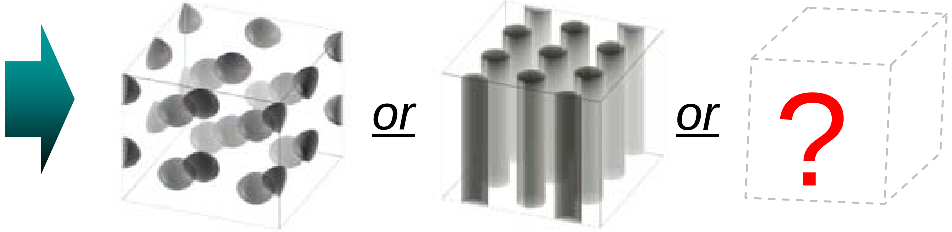
rms roughness: 0.1-0.3 nm

***Macromolecules*, 38, 10532 (2005)**

Fractionated (FM)
(wt_{PMMA} = 0.345)

AFM





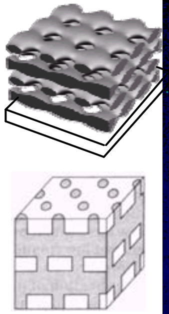
***Co-worked with**
Prof. Taihyun Chang
(Postech)

PS-b-PMMA Film (200 nm thick)

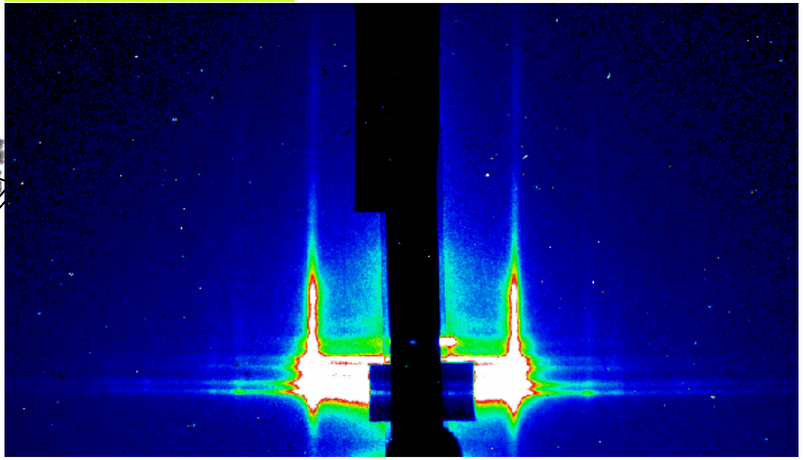
Ree et al.,
***Macromolecules*, 38, 4311 (2005)**
***Macromolecules*, 38, 10532 (2005)**
***Macromolecules*, 39, 684 (2006)**
***Macromolecules*, 40 (2007), ASAP**
***J. Appl. Crystal.* (submitted)**

Fractionated (FM)
(wt_{PMMA} = 0.345)

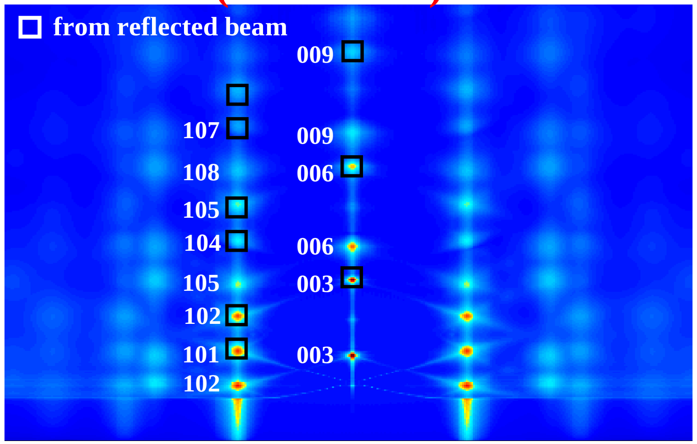
HPL



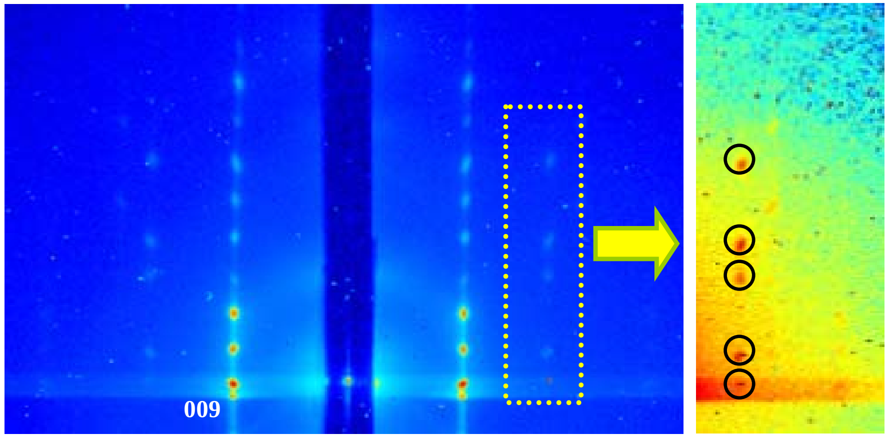
$\alpha_c \le \alpha_i \le \alpha_s$



(Calculated)



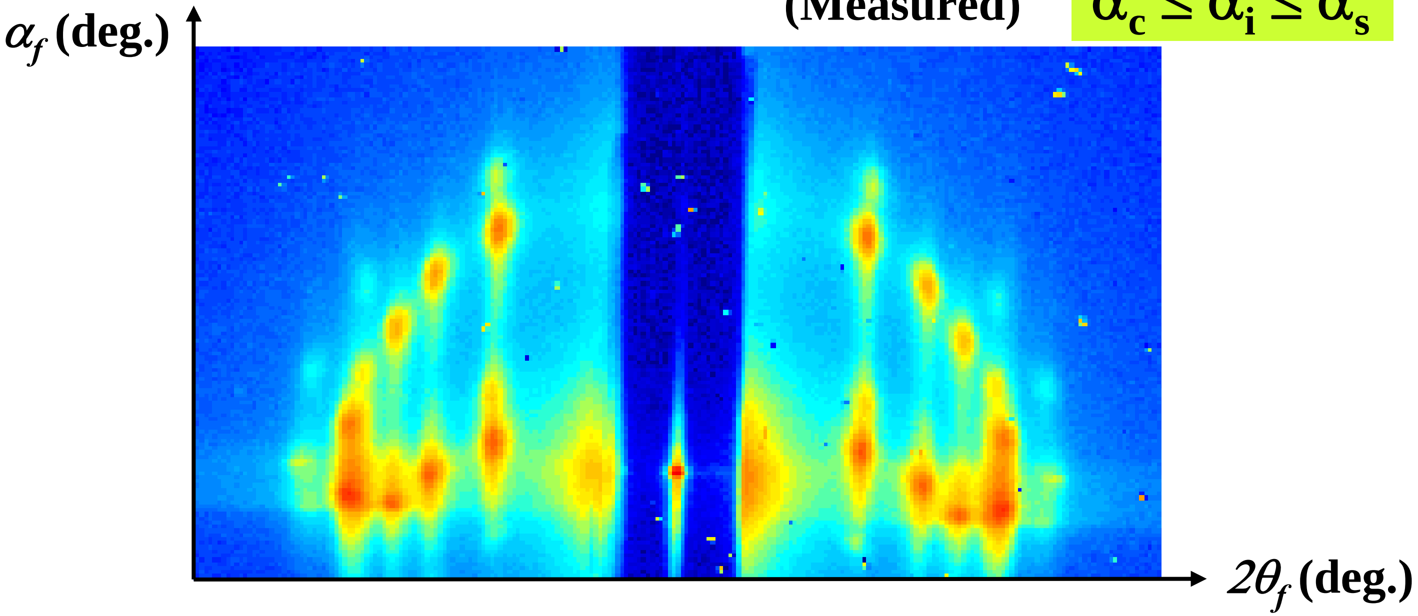
(Measured)

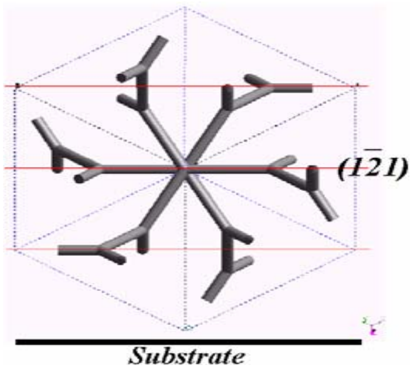


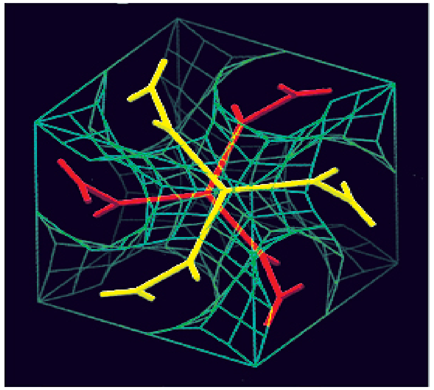
Self-Assembled PS-b-PI Diblock Copolymer on Substrate

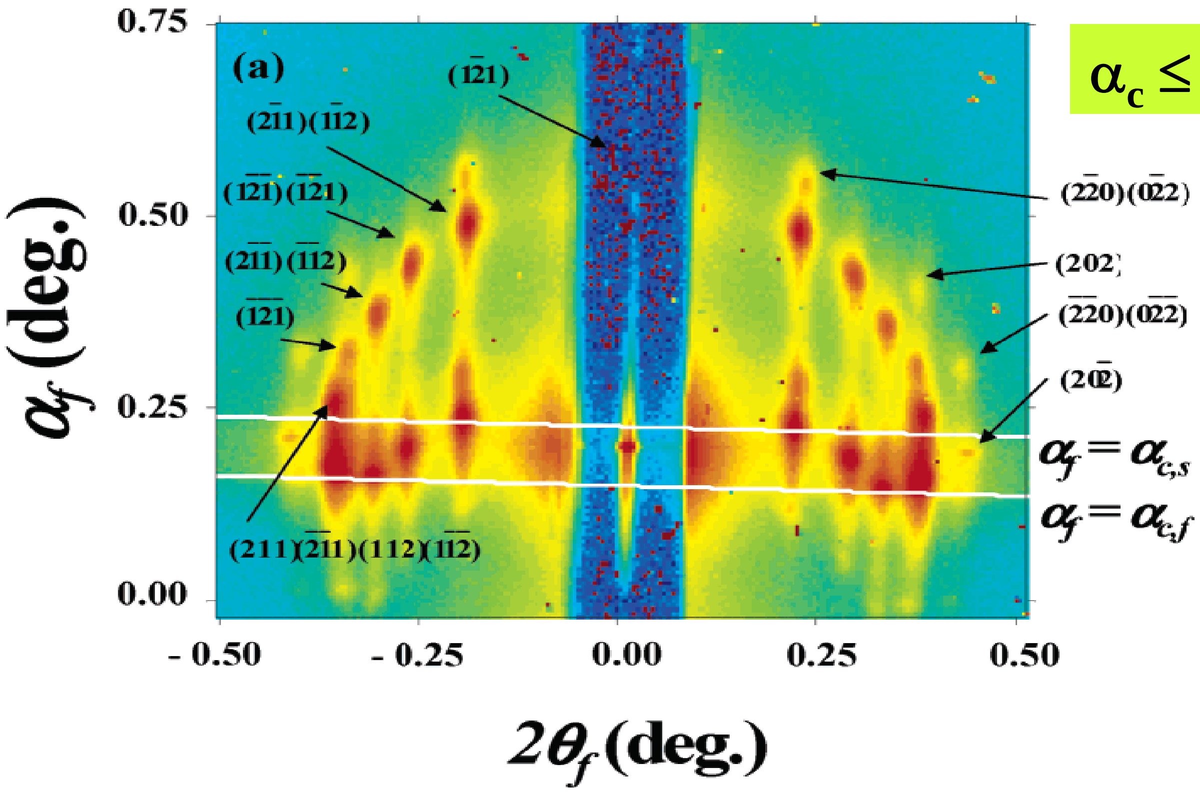
PS-*b*-PI (wt_{PI}=0.634) film (1254 nm thick) rms roughness: 0.1-0.3 nm

(Measured) $\alpha_c \leq \alpha_i \leq \alpha_s$

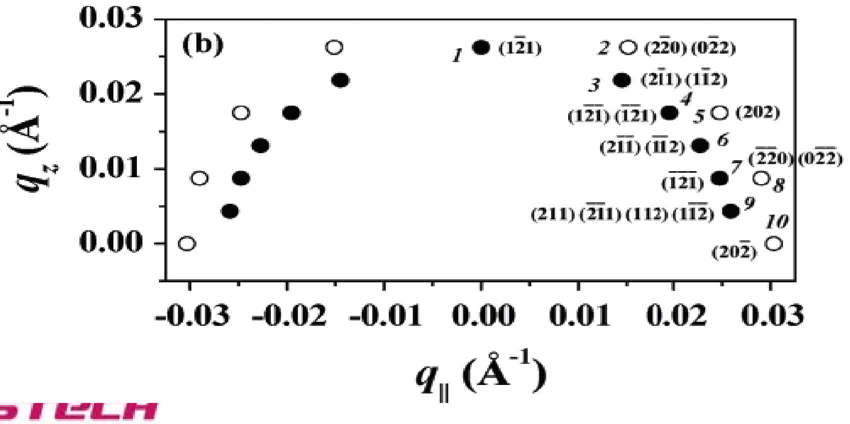


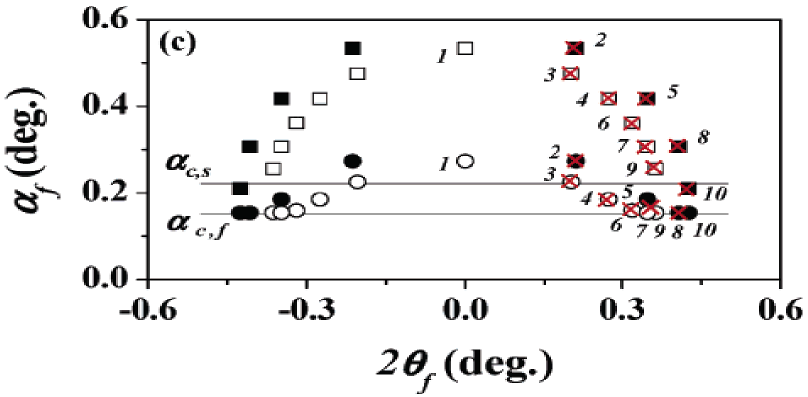




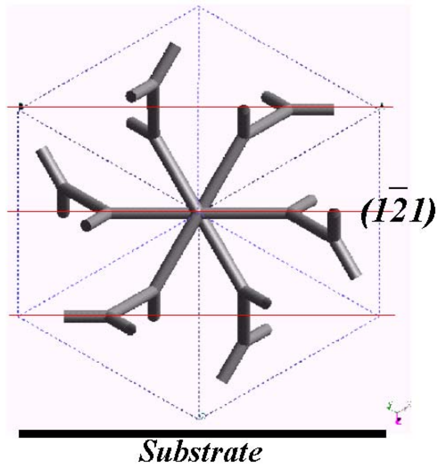


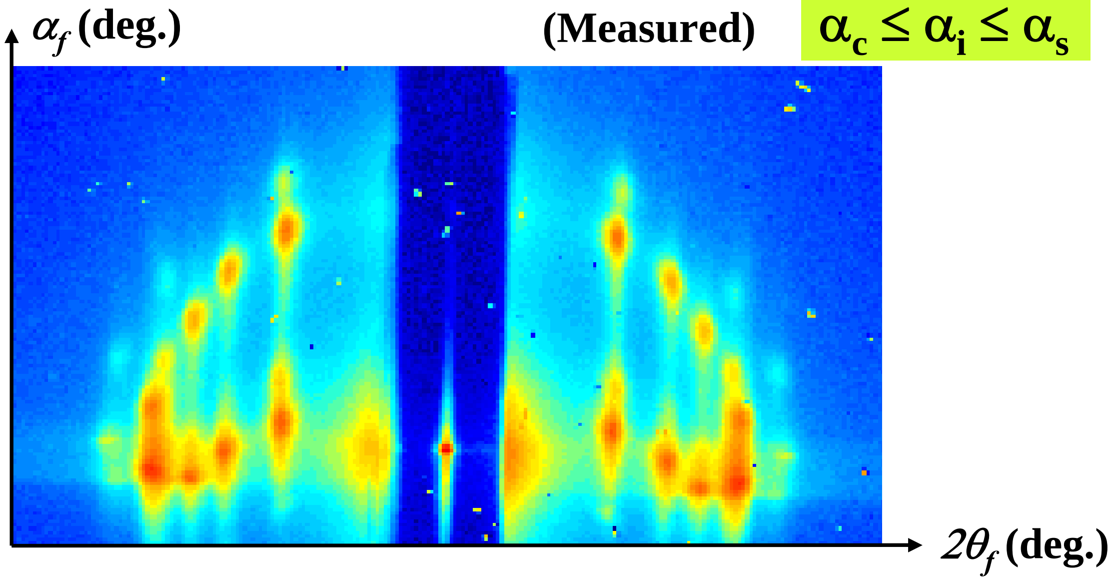
$\alpha_c \leq \alpha_i \leq \alpha_s$

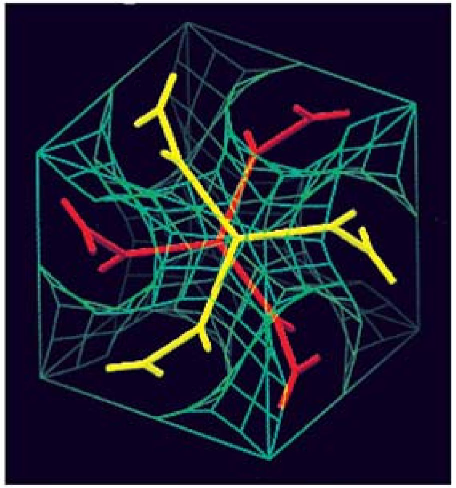


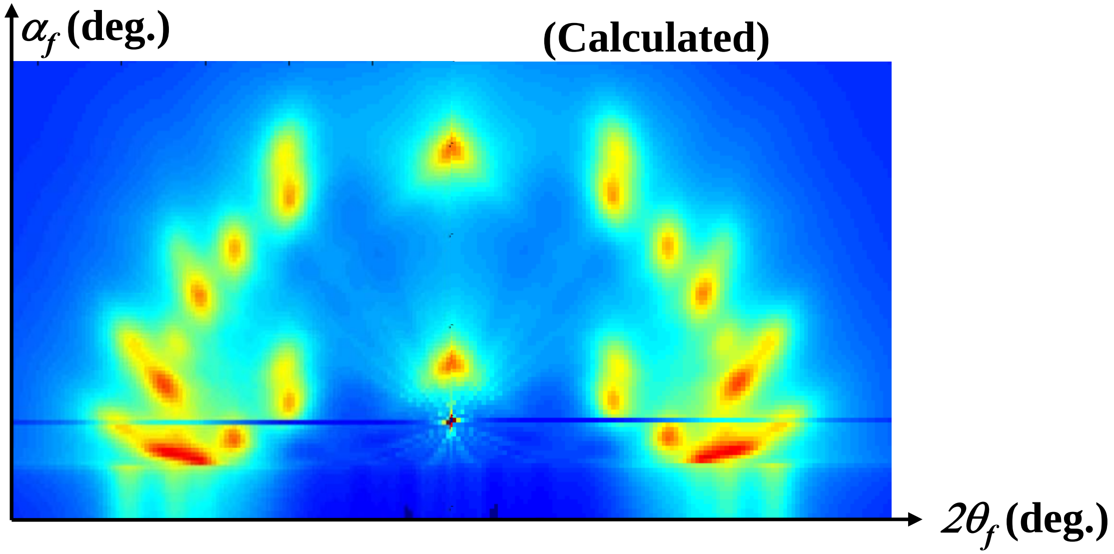


$\alpha_c \le \alpha_i \le \alpha_s$





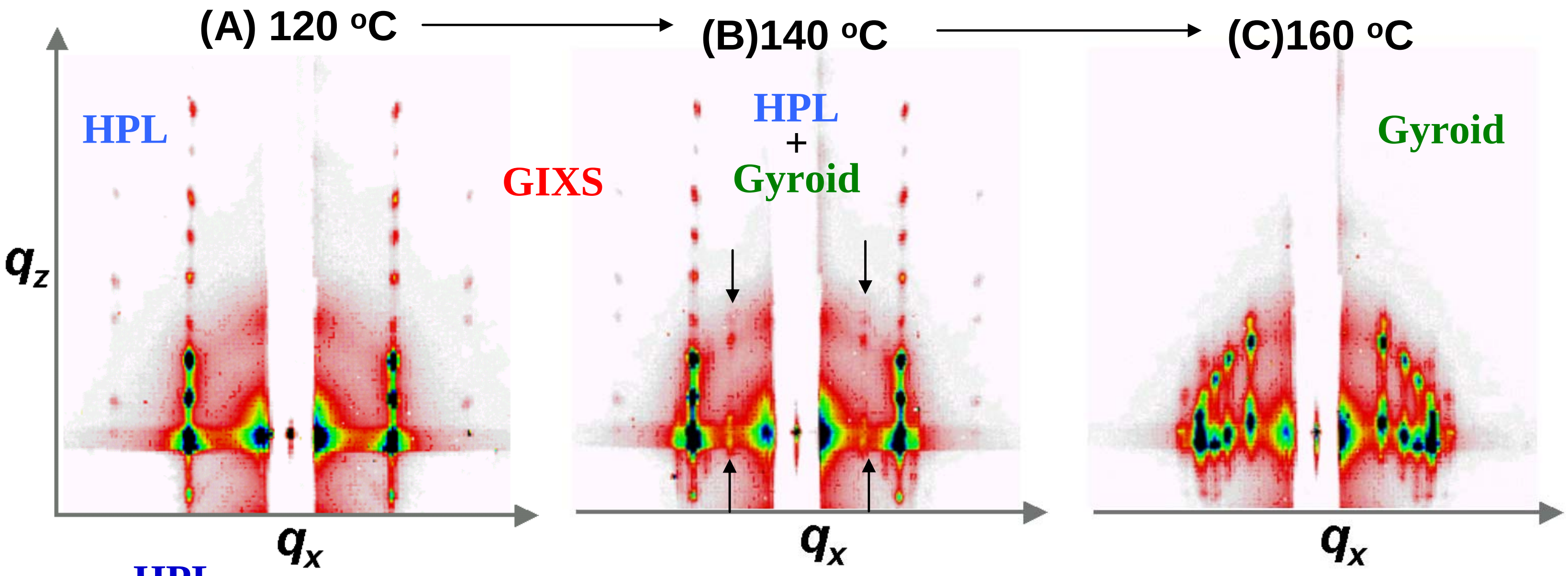




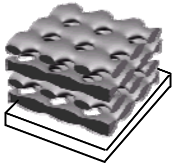
Ree et al.**,**
Macromolecules**, 38, 4311 (2005);** ***Macromolecules*****, 38, 10532 (2005)**
Macromolecules**, 40 (2007), ASAP;** ***J. Appl. Crystal.*** **(in press)**

Phase Transition of HPL phase to Gyroid

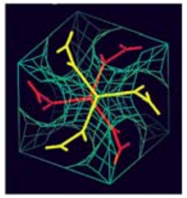
PS-*b*-PI (wt$_{PI}$=0.634) film (1254 nm thick) **rms roughness: 0.1-0.3 nm**



HPL



$\alpha_c \leq \alpha_i \leq \alpha_s$



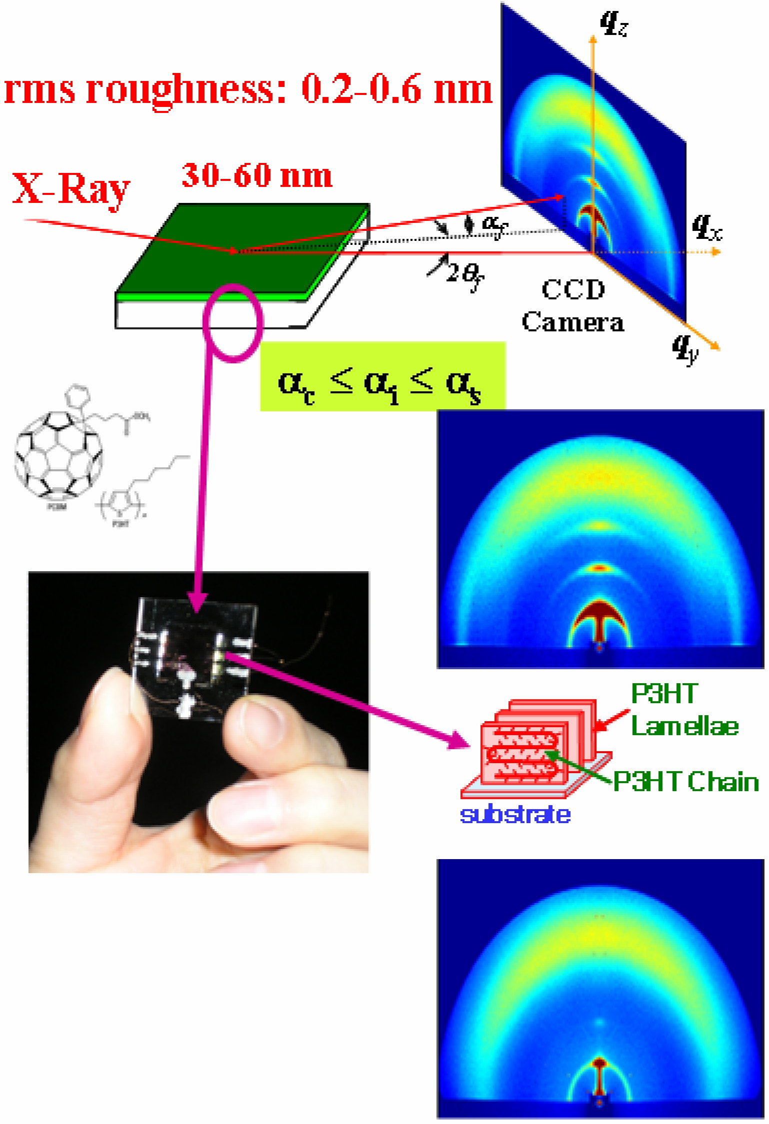
Gyroid

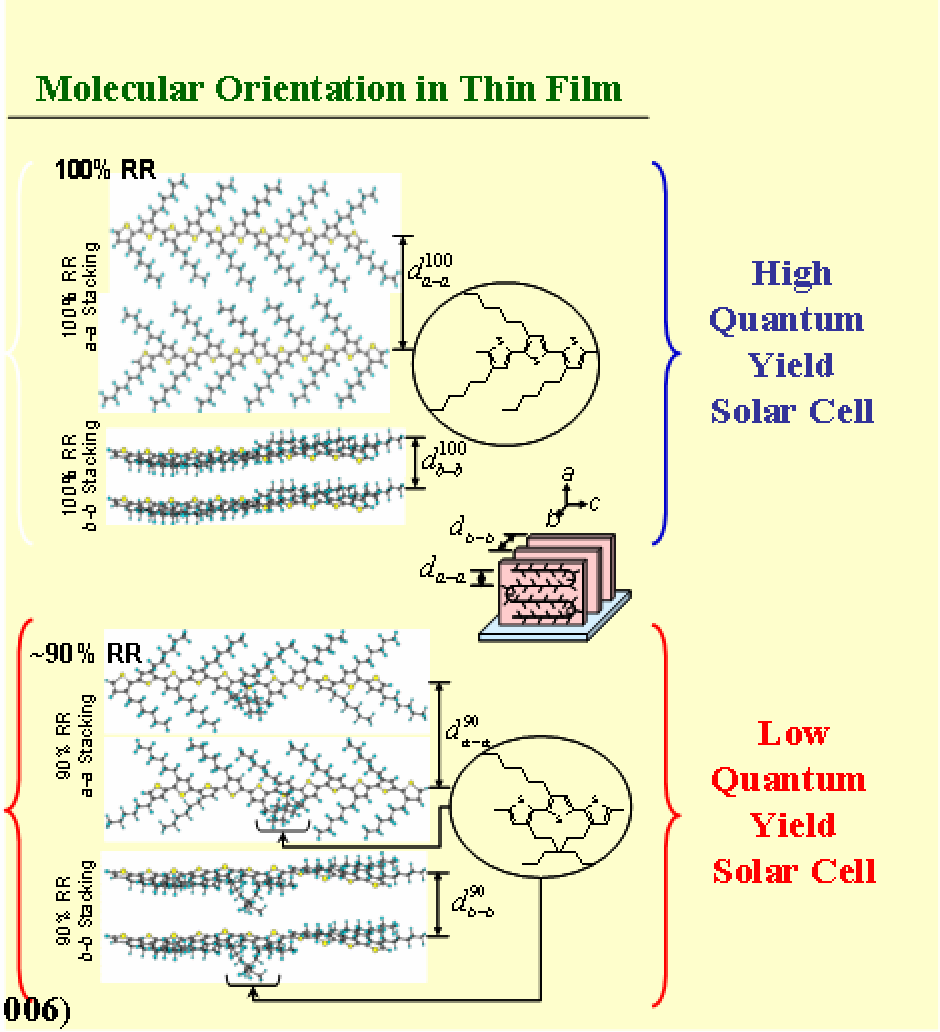
- **Gyroid-structured microdomains perfectly oriented along the {121} plane parallel to the in-plane of a film.**

Ree, Chang, et al.,
***Macromolecules*, 38, 10532 (2005)**
***Macromolecules*, 40 (2007), ASAP**

***Co-worked with**
Prof. Taihyun Chang
(Postech)

Solar Cell : Nanofilms of Poly(3-hexylthiophene)(P3HT)/Fullerene




Molecular Orientation in Thin Film

High Quantum Yield Solar Cell

Low Quantum Yield Solar Cell

Kim, Ha, Ree et al., *Nature Materials* , 5, 197 (2006)

Outline

1. Introduction – POSTECH & Pohang Light Source
2. Optics, Beamlines and Equipments of SAXS
3. Data Collection and Samples
4. Fundamentals of SAXS
5. Fundamentals of Conventional, Transmission SAXS (TSAXS)
    (1) Single Molecule (or Particle)
    (2) Multiple Molecules (or Particles) and Their Assemblies
6. **Fundamentals of Grazing Incidence SAXS (GISAXS)**
    (1) Static GISAXS
    (2) In-Situ GISAXS
1. Conclusions – I, II
2. References
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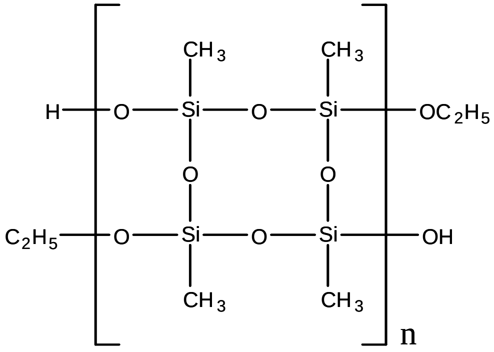
4. Acknowledgments

In-Situ GIXS Measurements

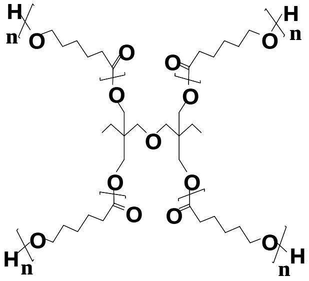
In-situ GIXS - Nanopous dielectric thin films: Low-k nanofilms



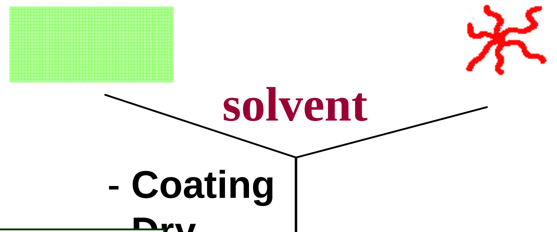
PMSSQ Precursor
10,000 $\overline{\mathrm{M}}$w

Matrix

Porogen

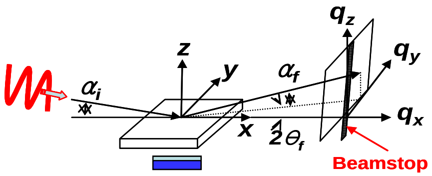


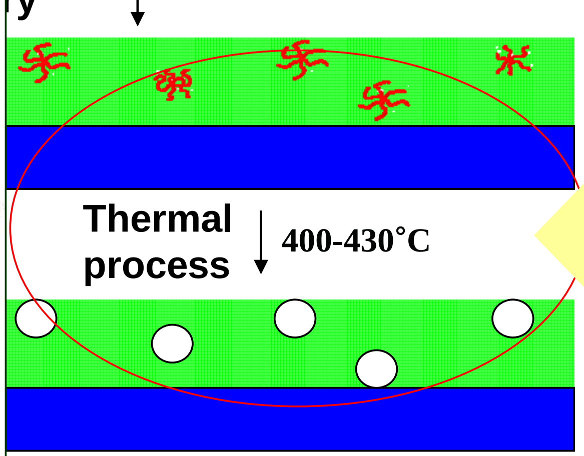
PCL4 Porogen



- Coating
Dry

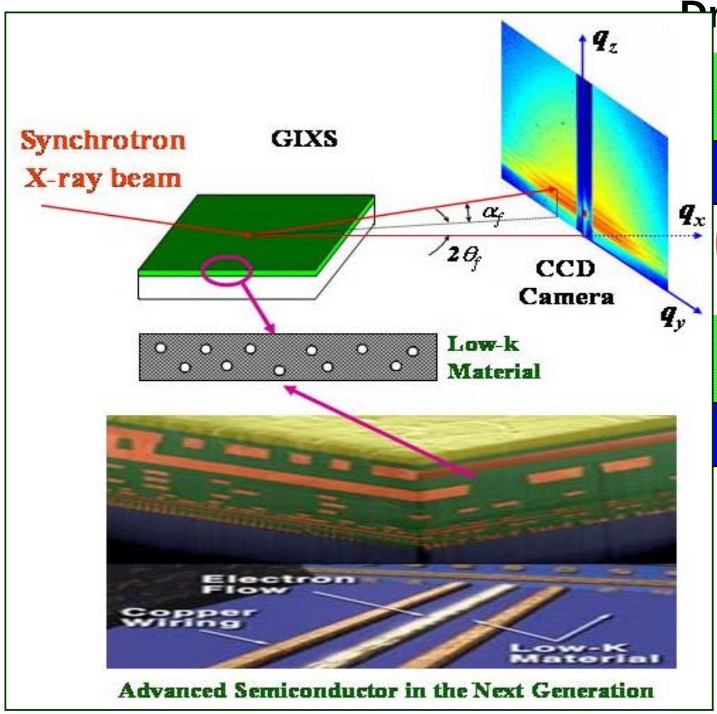
GIXS



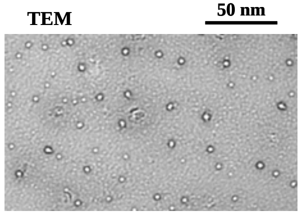


Thermal process ↓ 400-430°C

in-situ GIXS Measurements conducted



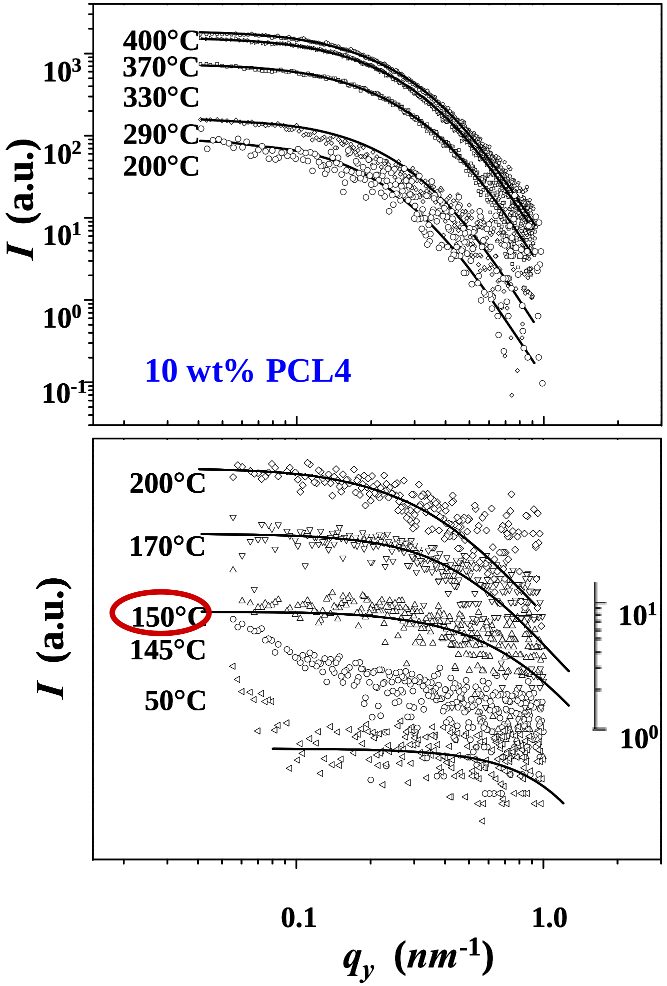
Advanced Semiconductor in the Next Generation

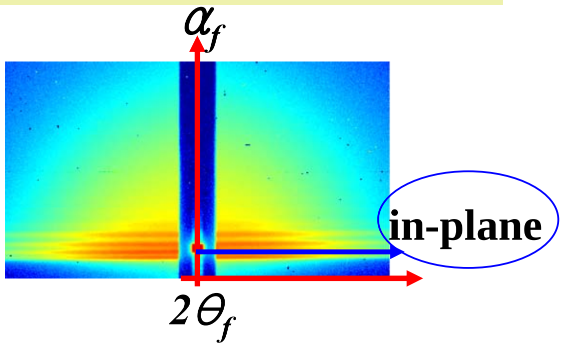


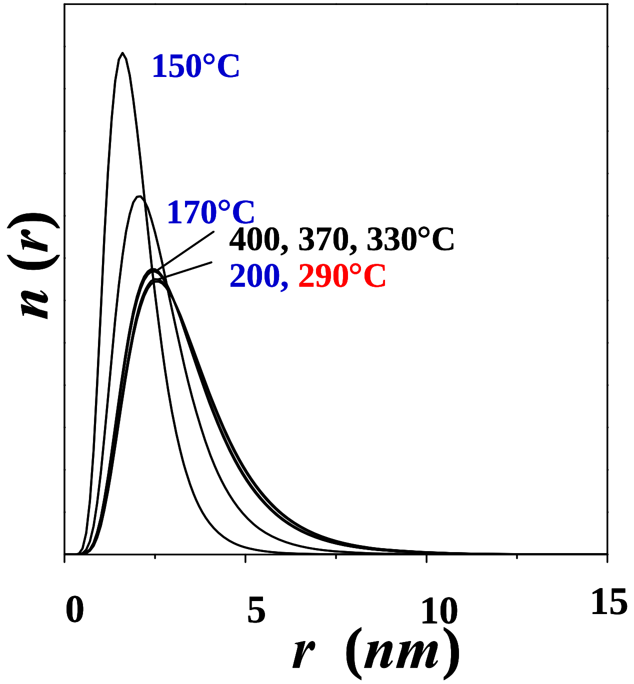
Ree et al.,
J. Phys. Chem. B, 110, 15887 (2006)
J. Mater. Chem. 16, 685 (2006)
Nanotechnology 17, 3490 (2006)
Macromolecules 38, 8991 (2005)
Macromolecules 38, 3395 (2005)

In-situ GIXS Measurements: PCL4/PMSSQ film

PCL4/PMSSQ precursor Thin Film (25°C) $\xrightarrow[\text{vacuum}]{\text{2°C/min}}$ (400°C) **PCL4/PMSSQ Thin Film** $\xrightarrow[\text{vacuum}]{\text{2°C/min}}$ (25°C)

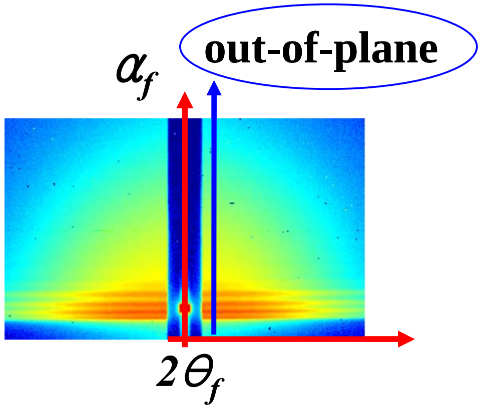


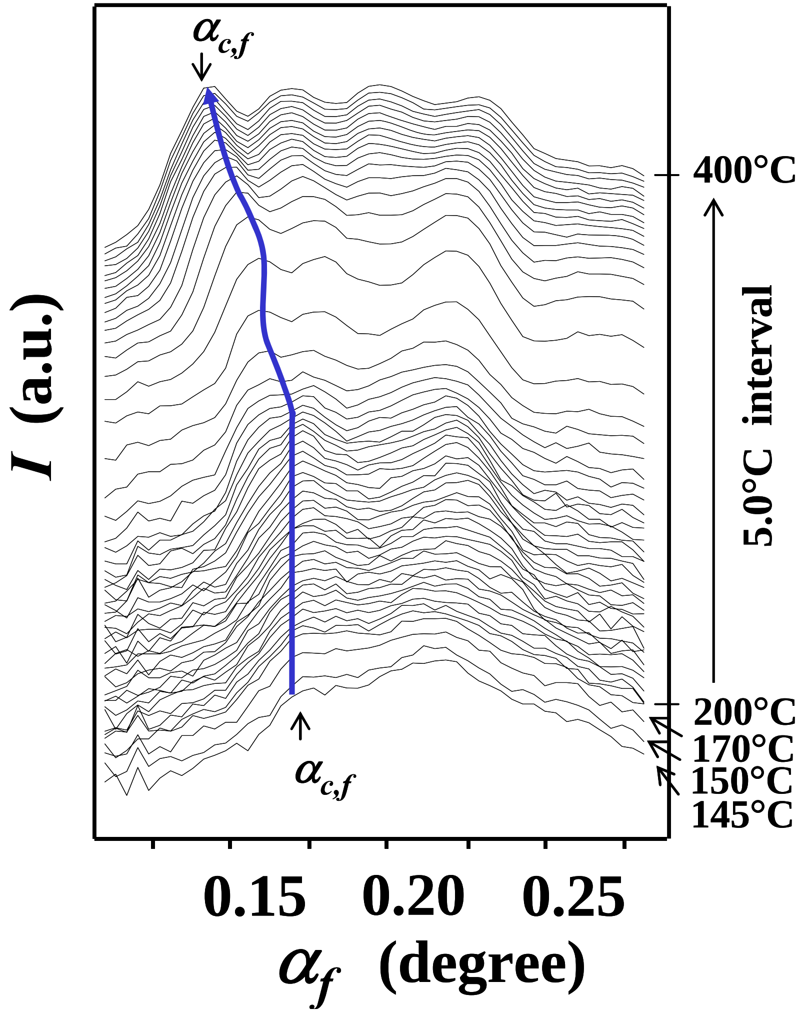




In-situ GIXS Measurements: PCL4/PMSSQ film

PCL4/PMSSQ precursor Thin Film (25°C) $\xrightarrow[\text{vacuum}]{\text{2°C/min}}$ (400°C) **PCL4/PMSSQ Thin Film** $\xrightarrow[\text{vacuum}]{\text{2°C/min}}$ (25°C)





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    (2) In-Situ GISAXS

1. **Conclusions – I, II**
2. **References – TSAXS, GISAXS**
3. **Introduction – M. Ree's Group at Postech**
4. **Acknowledgments**

Conclusions – TSAXS

- **SAXS Optics and Sample Stage Related Equipments Reviewed.**
- **Theoretical Fundamentals of TSAXS Reviewed.**
- **TSAXS is Very Powerful to Analyze Single Particles (Molecules) and Their Assemblies in Solutions and Solids.**
- **TSAXS is Very Powerful to Analyze Proteins and Other Biomacrmolecules in Nature.**
- **TSAXS is Very Powerful to Characterize Structural Changes in Time-Resolved Mode.**
- **GIXS is the Nondestructive analysis technique.**

Conclusions – GISAXS

- **GISAXS Optics, Theory and Data Analysis Methods Reviewed.**

- **GISAXS is Very Powerful to Analyze Structures in Nanoscaled Samples and Products.**

- **GISAXS is Very Powerful to Characterize Structural Changes in Time-Resolved Mode.**

- **GISAXS is the Nondestructive analysis technique.**

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M. Ree's Group at Postech

1. Research Fields

<Polymer Physics>

- Polymer chain conformation
- Structures and morphology
- Nanostructuring
- Electric, dielectric, optical, thermal, mechanical properties
- Sensor properties
- Surface, interfaces

<Polymer Synthesis>

- Functional polymers
- Structural polymers
- Polypeptides, DNA, RNA

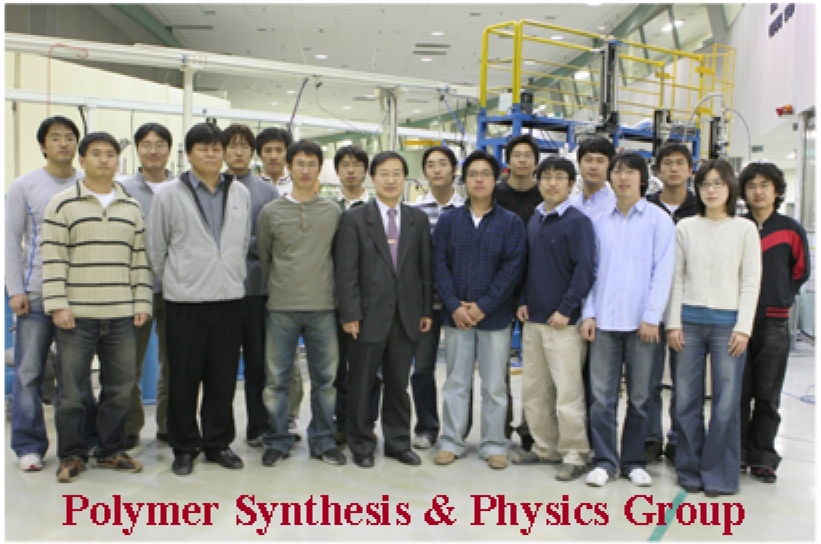
◆ Polymers for Microelectronics,
Displays, &
Sensors

◆ Polymers for Implants &
Biological Systems

◆ Proteins & Polynucleic acids (DNA, RNA)

2. Group Members (25)

2 Postdoctoral Fellows
14 Ph.D. candidates
5 Undergraduates
2 Technicians
2 Secretary
3 Scientists (Ph.D., PLS: Coworkers)



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Thank you very much for your attention !!!