Small-Angle X-Ray Scattering for nanostructures, with a focus on bio-related soft matter

http://web11.nsrrc.org.tw/endstation/saxs/

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National Synchrotron Radiation Research Center

"Just as eating against one's will is injurious to health
so studying without a liking, for it spoils the memory, and it retains nothing it takes in."

- Leonardo Da Vinci

Structure & Technology

對結構理解與控制的尺度精度

- 公分 → 厘米 → 微米 → 次微米 → 奈米

VS.

當代的文明特徵

- 石器 → 鐵器 → 橡膠 → 矽晶片 → 奈米科技（分子科技）

Desire to understand and control structures

Interactions of Probing Particles with Materials for structural understanding

- **Hierachical structure of matter**

Molecule@atom@nucleus@quark

- **Interactions types**

(1) Strong interaction – nucleus distribution

(2) Weak interaction – quark distribution

(3) Electromagnetic interaction

Charge distribution

(4) Gravity – mass distribution

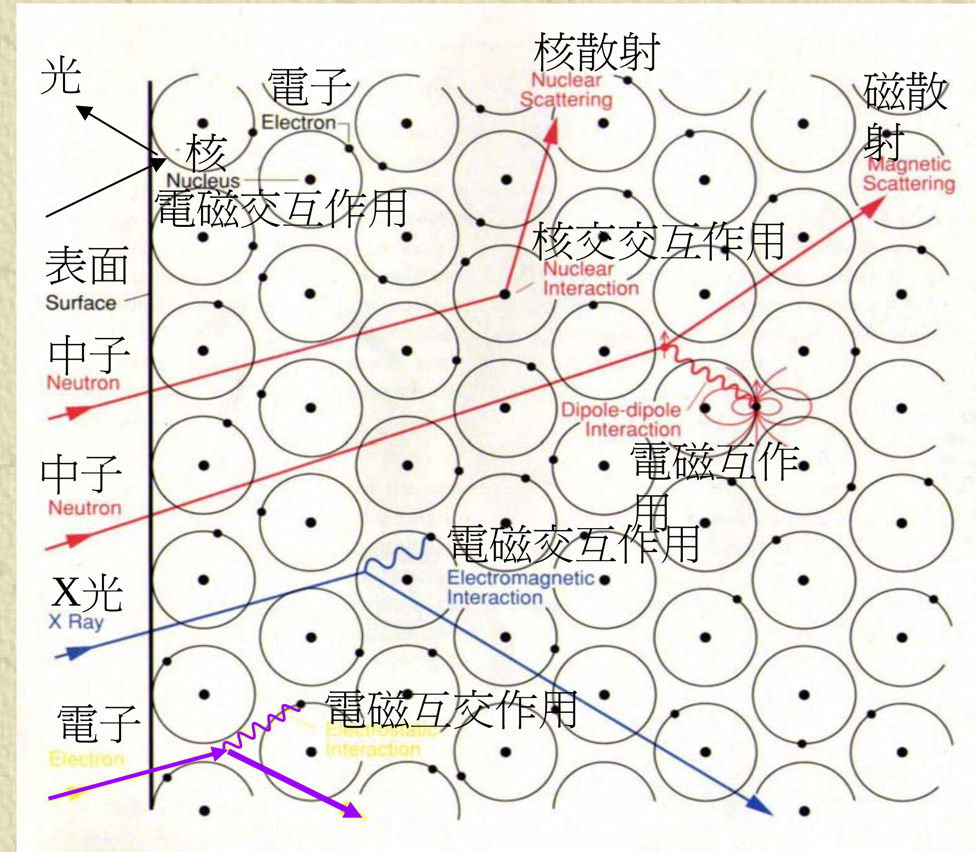
- **Sensitivity of Probes**

(1) Characteristic length of the probe

(2) Penetration depth (Absorption)

Buried structures (photons, electrons, X-rays)

Scattering Tools for structural study



Structure VS Probe Methodology

- **Probing methodology - depending on the probe size and penetration power**

(1) Imaging

TEM, SEM, confocal microscopy, XEM

field-Ion microscopy

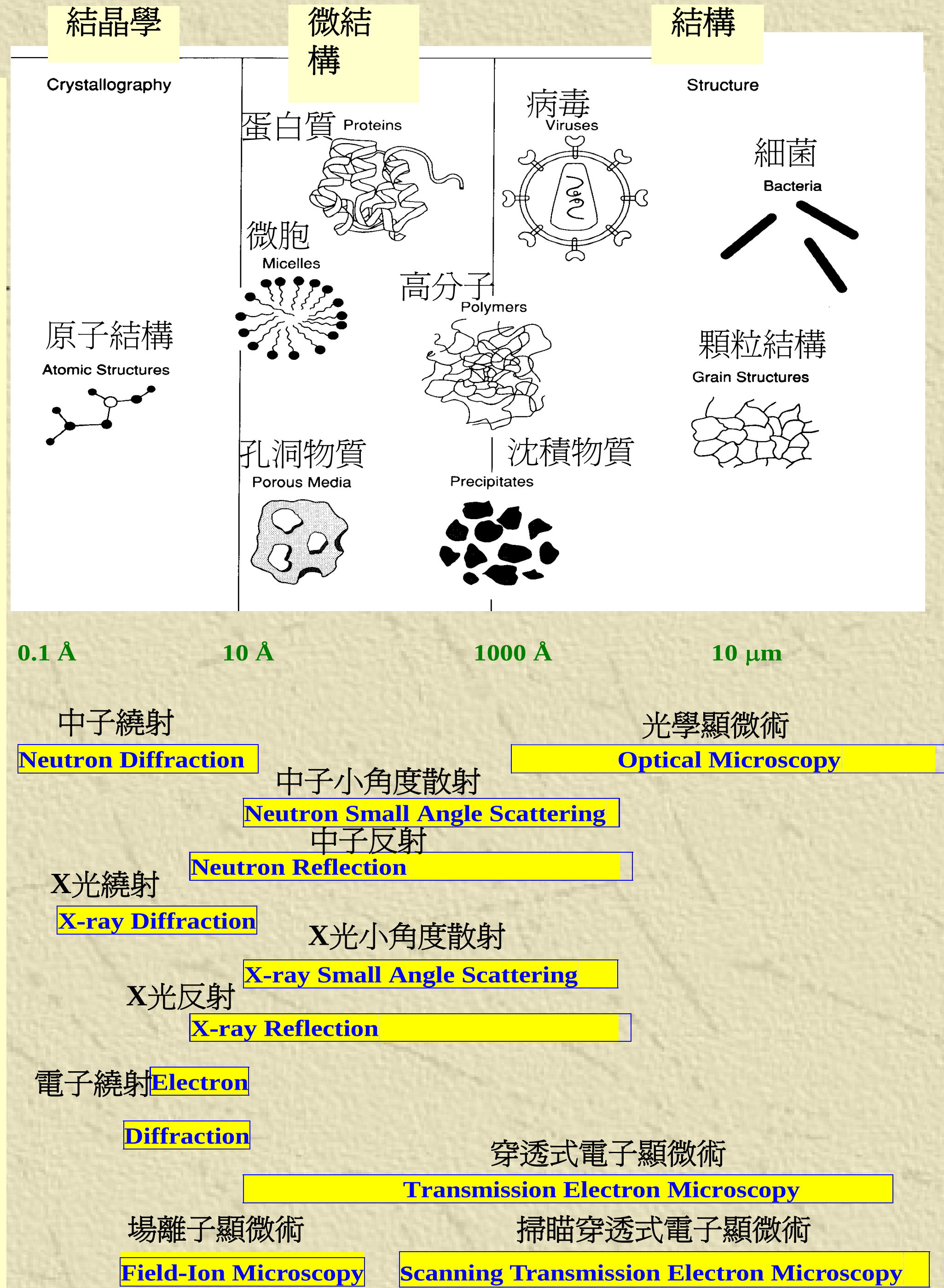
(2) Scattering

Diffraction for crystal structure (atomic resolution crystallography, powder diffraction)

Reflection for depth density profile, surface & interface structure of lipid membranes or monolayers

Small-angle scattering, coherent scattering for non-crystalline structures like proteins in solutions

Inelastic scattering for structural dynamics, phonons in a liquid crystalline phase of Na-DNA



Introduction of small-angle X-ray scattering (SAXS)

Basics of X-ray & Neutron scattering, based on the wave properties of the radiation quanta

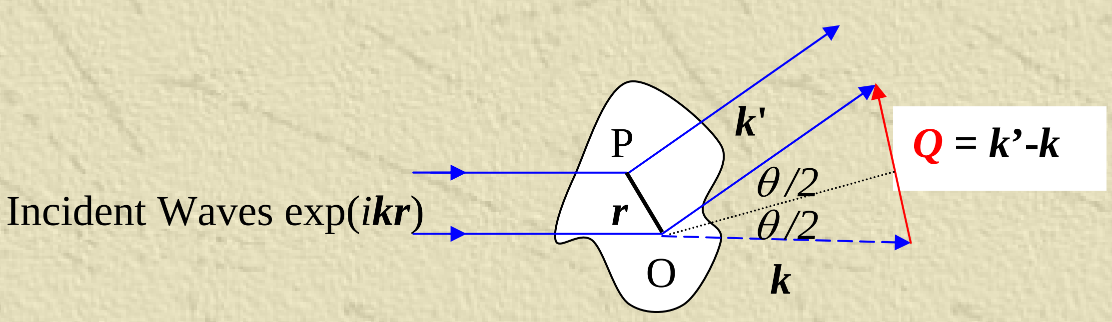


Illustration of Neutron/X-ray Scattering by a single particle

- $\boldsymbol{Q} \bullet \boldsymbol{r} \Rightarrow$ Phase difference between the scattered beams
- $Q = 4\pi \sin(\theta/2)/\lambda \Rightarrow$ Momentum transfer of neutrons/X-rays
- $\theta \Rightarrow$ scattering angle

“Q- (or angle-) dependent” Scattering Differential Cross Section, for the scattering distribution I(Q) = I_o (dσ(Q)/dΩ)

⇒

$$\frac{d\sigma(Q)}{d\Omega} = \left\langle \left| \int e^{ik\cdot r} V(r) e^{-ik'\cdot r} d^3 r \right|^2 \right\rangle = \left\langle \left| \int e^{iQ\cdot r} V(r) d^3 r \right|^2 \right\rangle$$

Scattering Potential (or density distribution of scatterer $V(r) = \sum_j b_j \delta(r - r_j)$

describes the interactions between the probe and the scatterer

***b_j* : Interaction strength or scattering amplitude (length) of the scatter (electrons for X-ray, nucleus for neutrons)**

Q-dependent Scattering intensity

I(Q) = $$\frac{d\sigma(Q)}{d\Omega} = \left\langle \left| \int e^{ik\cdot r} V(r) e^{-ik'\cdot r} d^3r \right|^2 \right\rangle = \left\langle \left| \int e^{iQ\cdot r} V(r) d^3r \right|^2 \right\rangle$$

(1) When I(Q) is modulated by periodic phase difference

- **Bragg scattering from periodic structures ⇒** $Q \bullet (r_i - r_j) = 2n\pi$

Arrange the object to be in an ordered structure
for observation - crystallization

$$\textbf{I(Q)} = \frac{d\sigma(Q)}{d\Omega} = \left\langle \left| \int e^{ik\cdot r} V(r) e^{-ik'\cdot r} d^3 r \right|^2 \right\rangle = \left\langle \left| \int e^{iQ\cdot r} V(r) d^3 r \right|^2 \right\rangle$$

(2) When there is no periodic structure :

I(Q) is modulated by the density distribution function only at a small Q region (small scattering angle region) with slow phase variation $\mathbf{Q \bullet (r_i - r_j) << 1}$

$$I(Q) = \frac{d\sigma}{d\Omega} = \left\langle \sum_i \sum_j b_i b_j e^{i\mathbf{Q}\bullet(\mathbf{r}_i - \mathbf{r}_j)} \right\rangle = \left| \int \rho(\mathbf{r}) e^{-i\mathbf{Q}\bullet\mathbf{r}} d^3 r \right|^2$$

Summation of each individual atoms b_i is replaced by an integration of an approximated density distribution function ρ(r)

Small angle X-ray scattering for soft materials lack of long-range ordering but rich in nanostructures

$$\mathbf{I(Q)} = \left| \int \rho(\mathbf{r}) e^{-i\mathbf{Q}\bullet\mathbf{r}} d^3 r \right|^2$$

SAXS or SANS in search of nanostructure described by a mean electron or nucleus density function $\rho(\mathbf{r})$

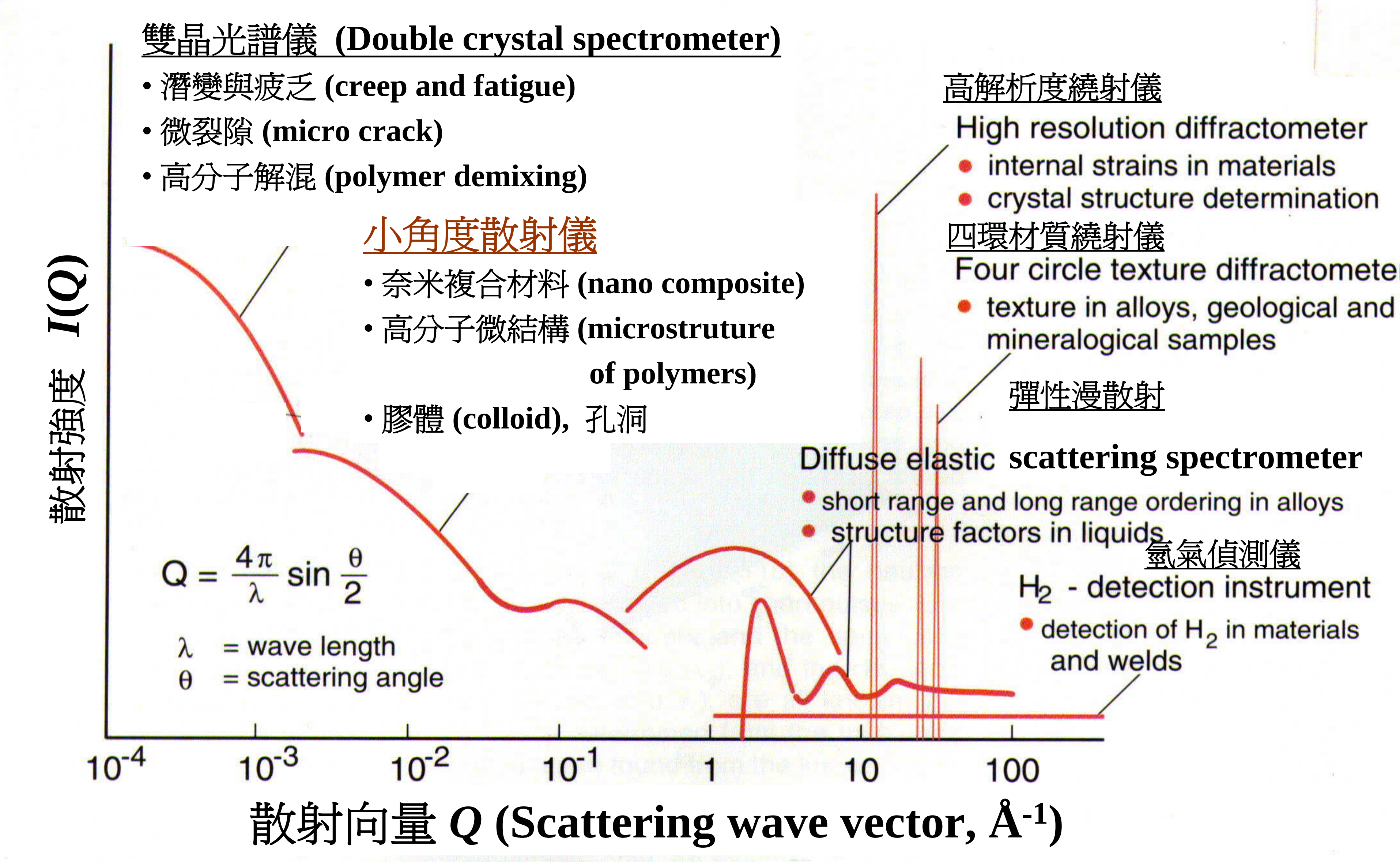
Practical steps:

(1) Measure the scattering distribution in Q-space, $I(Q)$.

(2) From ***I*(*Q*)**, deduce **$\rho(\mathbf{r})$ by model simulation**

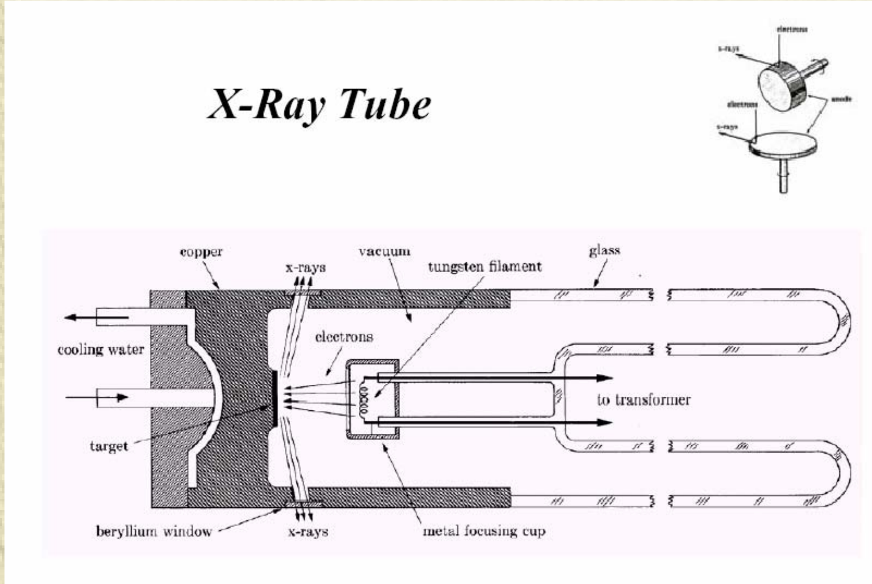
(Inverse Fourier transformation for ρ(r) is hindered by the lack of phase information)

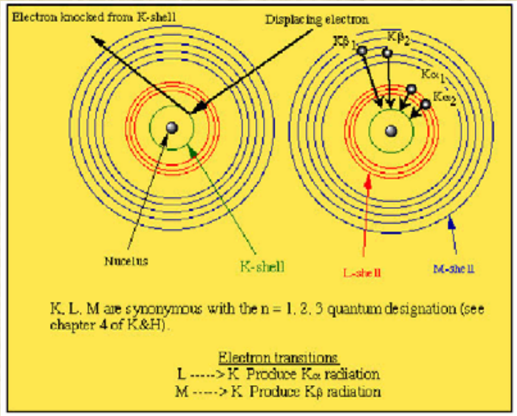
Correlation between the instruments (Q-range covered) and the characteristic length-scale *D* probed : *Q* ~ 1/*L*

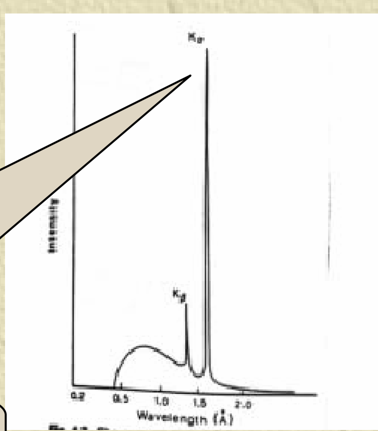


Introduction of X-ray source for scattering

Traditional X-ray Source



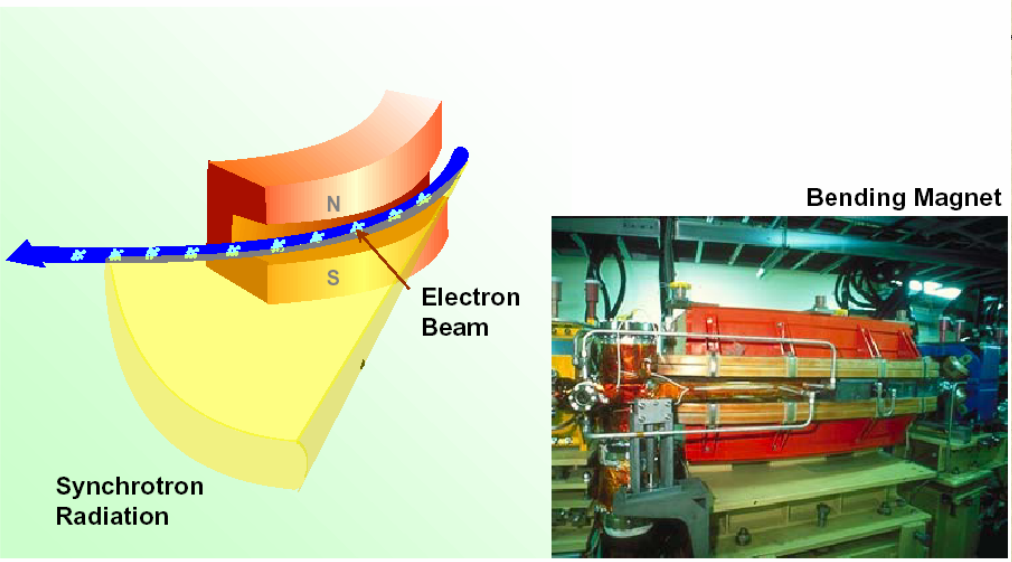


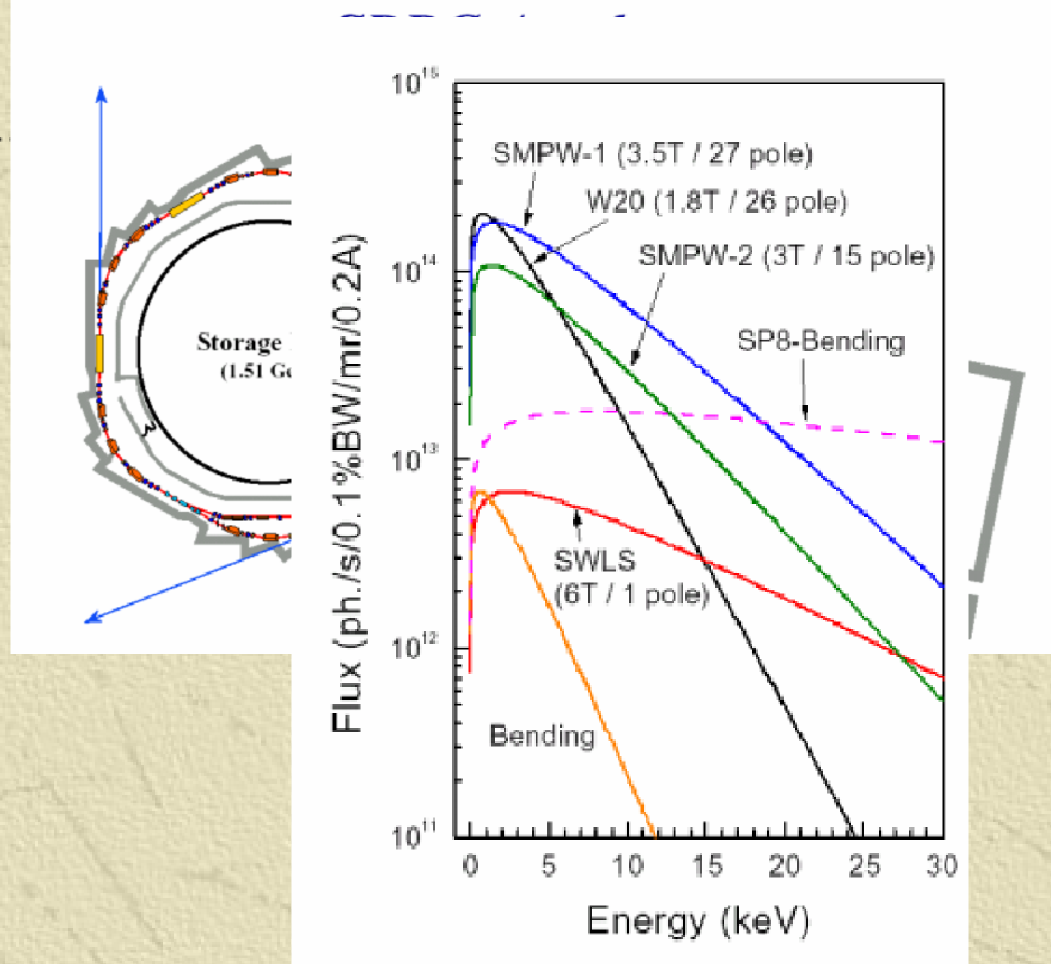


- Single characteristic wavelength
- Flux~ 10^6 photons/s

Synchrotron Radiation X-ray Source

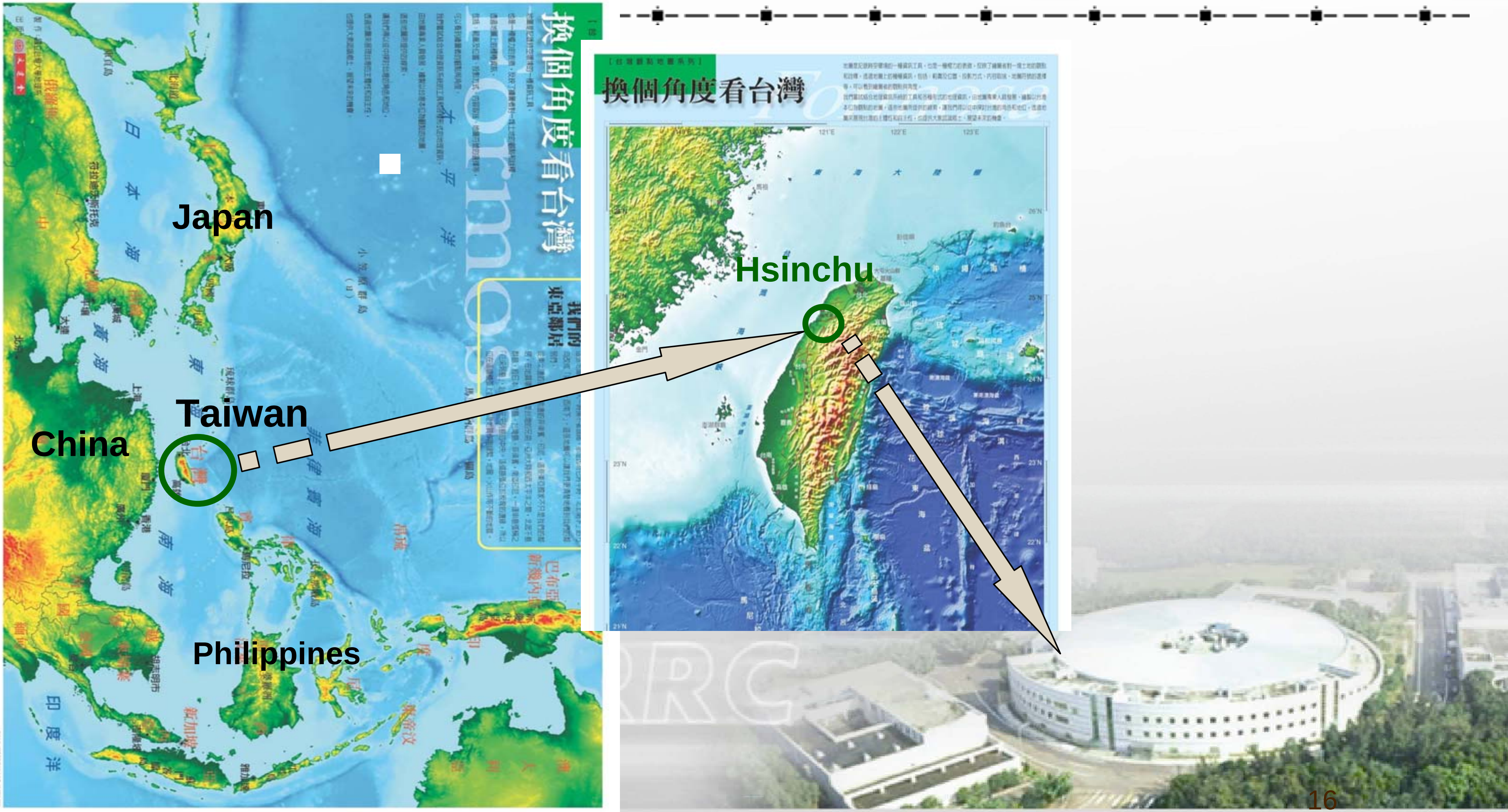
Principle of Synchrotron Radiation Emission





Advantage of using Synchrotron Radiation X-ray

- High Flux 3×10^{11} photon/s (time-resolved measurement)
- Tunable wavelength (anomalous scattering for multiphase structure)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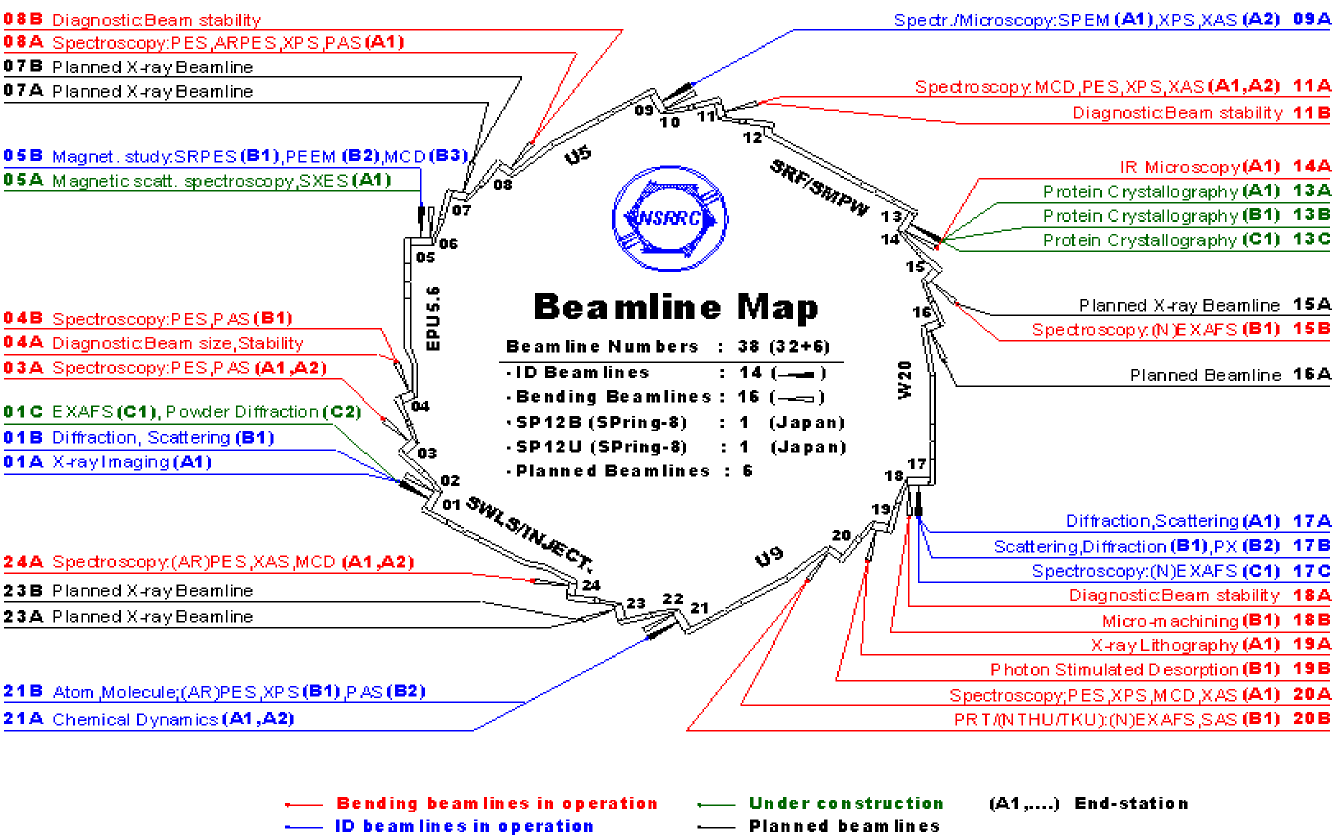

- ➲1.5 GeV Storage Ring
- ➲ 120 m circumference
- ➲ Total 32 beamlines
- ➲ 6 insertion devices

➲ **11 X-ray beamlines : - --**

- Power X-ray diffraction,
- EXAFS,
- General X-ray scattering,
- X-ray microscopy,
- Soft-X-ray scattering

➲ 3 InAcroma Superconducting Wiggler to be installed for X-ray applications

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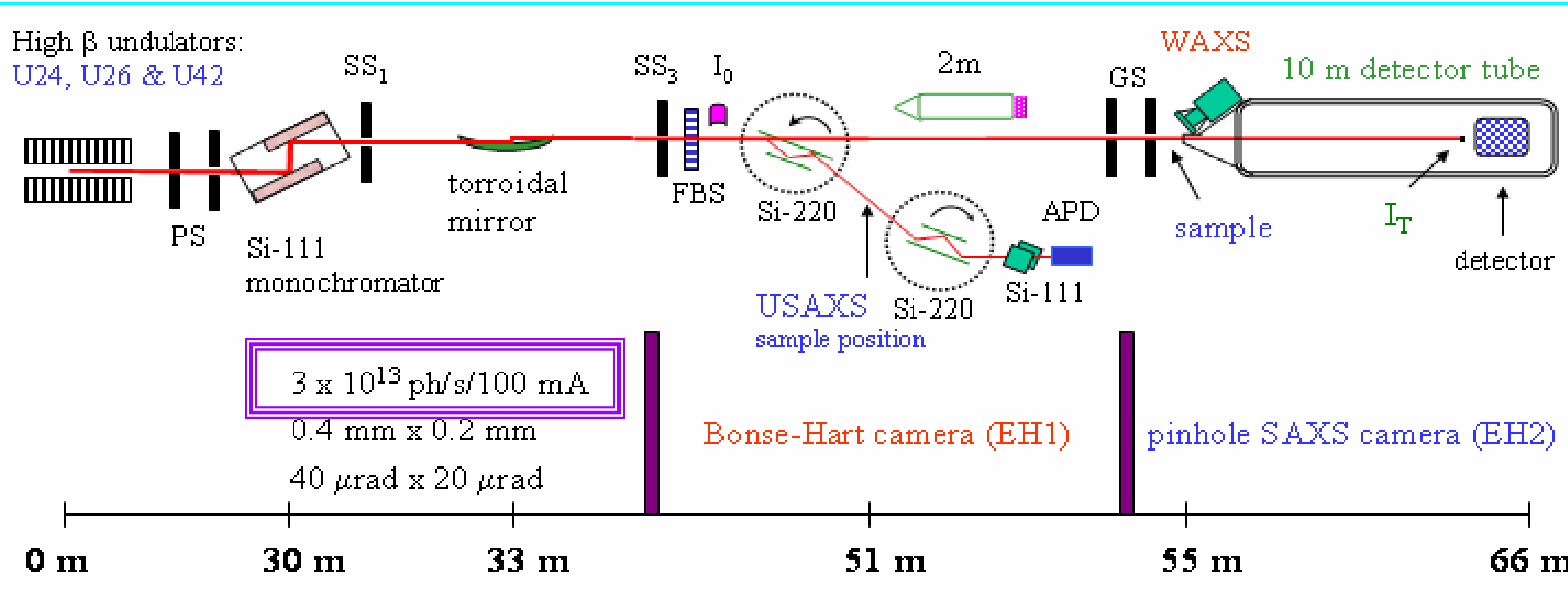
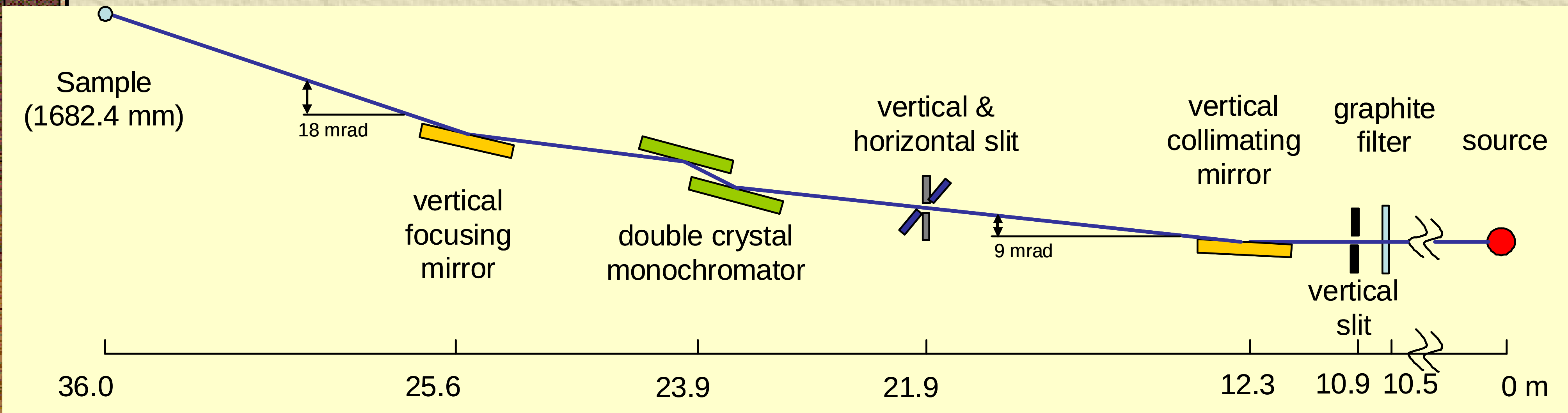
SAXS-based instrumentation

ESRF ID2 SAXS/WAXS beamline scheme



ESRF ID2 SAXS/WAXS beamline

Small- & wide-angle X-ray Scattering (SWAXS) end-station at BL17B3, NSRRC



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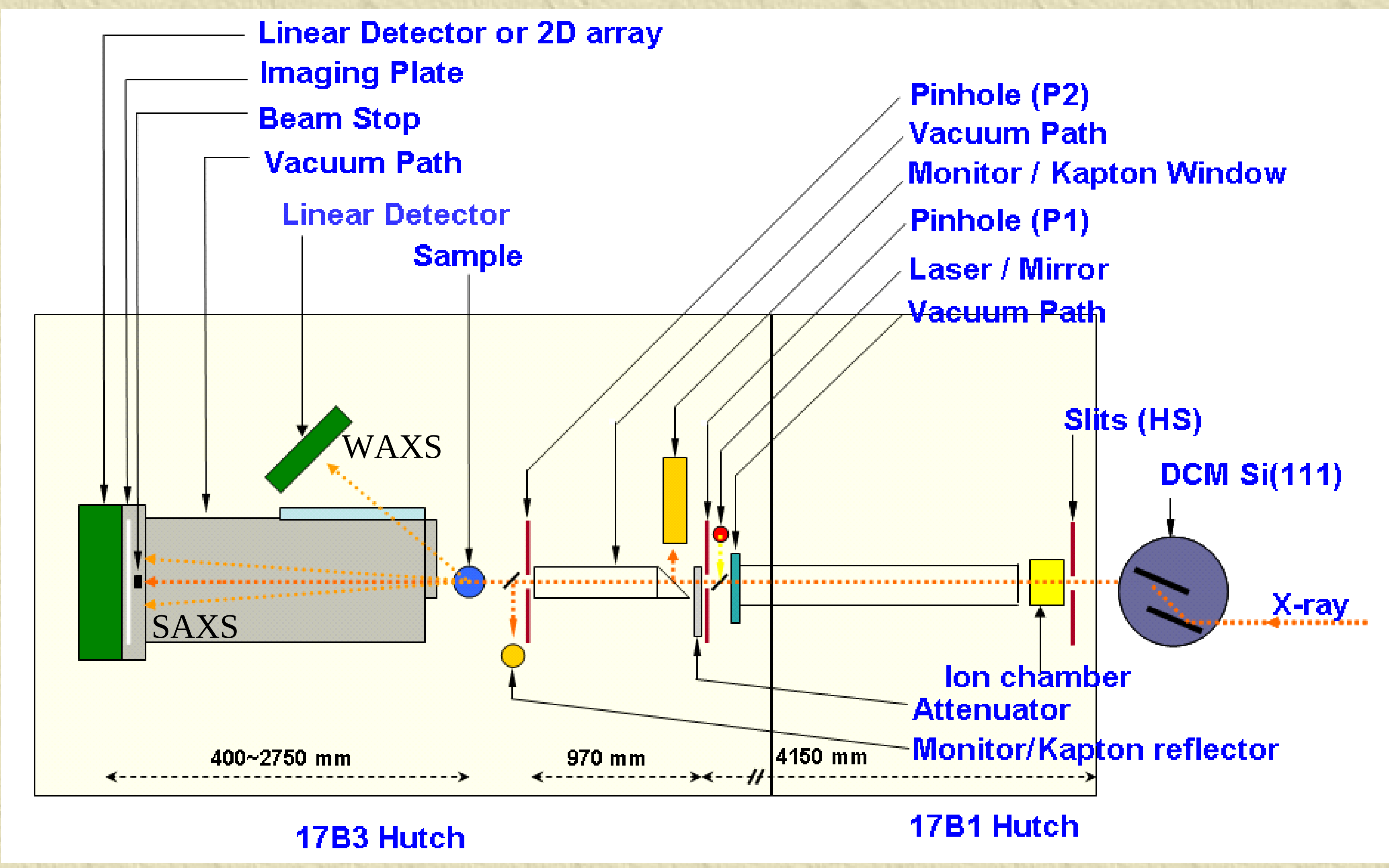
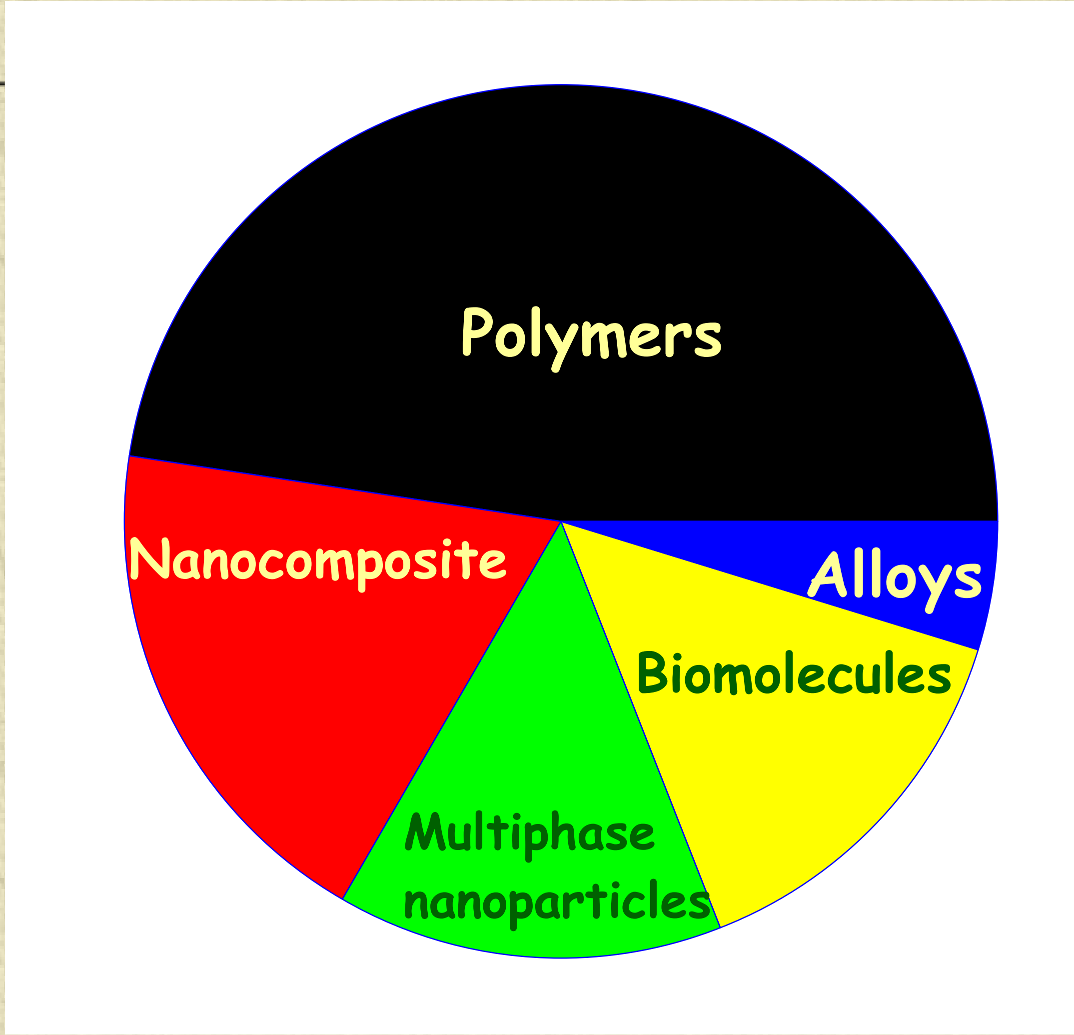
- Tunable wavelength (anomalous scattering for mulphase structure)

Schematic view of the SWAXS setup at BL17B3, NSRRC



Small Angle X-ray Scattering at BL17B3 End Station

SAXS Activities at NSRRC



Practical Consideration for Doing SAXS

- What Q-range is interested?

⇨Smaller Q for larger dimension ; $Q \sim 1/L$

Rules of thumb –

1. Lamellar spacing of L, $Q_{Bragg} = 2\pi/L$
   For $L = 10$ nm, $Q_{min} = 0.628$ nm^{-1} for the first peak.

2. For general aggregate or particle size estimation
   Guinier approximation for radius of gyration
   $I(Q) = I(0) \exp(-R_g^2 Q^2)$
   $(Q R_g < 1)$

For particles (aggregates) of size $R_g = 5$nm
The target SAXS Q-range should include in Q-range smaller than 0.2 nm^{-1}

• SAXS Intensity Considerations

$$I(Q) \propto (\Delta\rho)^2 = (\rho-\rho_{matrix})^2$$

$\Delta\rho$ **: contrast, (product of charge density difference and scattering length *b*)**

- **For water, scattering length per unit volume or scattering length density** ρ

Molecule number density ↓ ; *b* ↓ ; ↑ No. e^- /molecules

$$\rho = \frac{1.0[g/cm3]}{18[g/mole]} \times 6.02\times10^{23}[mol./mole] \times (10e^- \times 2.82\ fm)$$

$$= 9.43\times10^{-6}\ \text{Å}^{-2}$$

- For organic or bio molecules of density close to unity, $\rho \approx \rho_{water}$

⇨Contrast is low

- For polymers of CH_2 chain mainly, $\rho \approx \rho_{water}$

Scattering intensity increase when the density changes due to partial crystallization or density fluctuation

Sample geometry considerations

- The optimum sample thickness

$$I(Q) = tT\Phi\ (d\Sigma/d\Omega)_Q A(\Delta\Omega)e_{det}$$

t: sample thickness, T: sample transmission

$dI(Q)/dt = 0 \Rightarrow T=\exp(-\sigma t)=e^{-1}$, or $\sigma t = 1$

σ: linear absorption coefficient

At photon energy 8 keV,

$\sigma_{water} = 9.81\ cm^{-1}$, $t_{opt.} = 1$ mm

$\sigma_{toluene} = 3.9\ cm^{-1}$, $t_{opt.} = 2.6$mm

$\sigma_{DMF} = 6.2\ cm^{-1}$, $t_{opt.} = 1.6$ mm

$\sigma_{polyethylene} = 3.4\ cm^{-1}$, $t_{opt.} = 2.9$ mm

- **Watch for heady atoms, for instances Cl, embedded in samples They attenuate X-ray significantly.**

- **Sample lateral size can be few mm by few mm, to cover the whole incident beam size, typically 0.5 mm by 0.5 mm**

Colloidal solution containing monodisperse particles

$I(Q) = n_p P(Q) S(Q)$

$n_p = N/Vs$: Number density of particles

$P(Q)$: $\int_V \rho(r) d^3 r$, Particle form factor (intra-particle interference)

$S(Q)$: Structure factor (interference between scattering particles)

$$S(Q) = \frac{1}{N} \left\langle \sum_i^N \sum_j^N e^{i\mathbf{Q}\cdot(\mathbf{R}_i - \mathbf{R}_j)} \right\rangle$$

$$= 1 + n_p \int_0^\infty 4\pi r^2 (g(r) - 1)(\sin(Qr)/Qr) dr$$

$g(r) = (1/\langle\rho(\mathbf{r})\rangle^2)\int\rho(\mathbf{r}')\rho(\mathbf{r}'-\mathbf{r})d^3r \Rightarrow$ pair correlation function

$[s(0)]^{-1} = (1/k_bT)(\partial\Pi/\partial n_p) = 1 + 2 B_2 n_p$; (related to compressibility)

$B_2 \Rightarrow$ the second Virial coefficient

形狀因子(form factor) *P*(*Q*)

- 球體 (sphere)

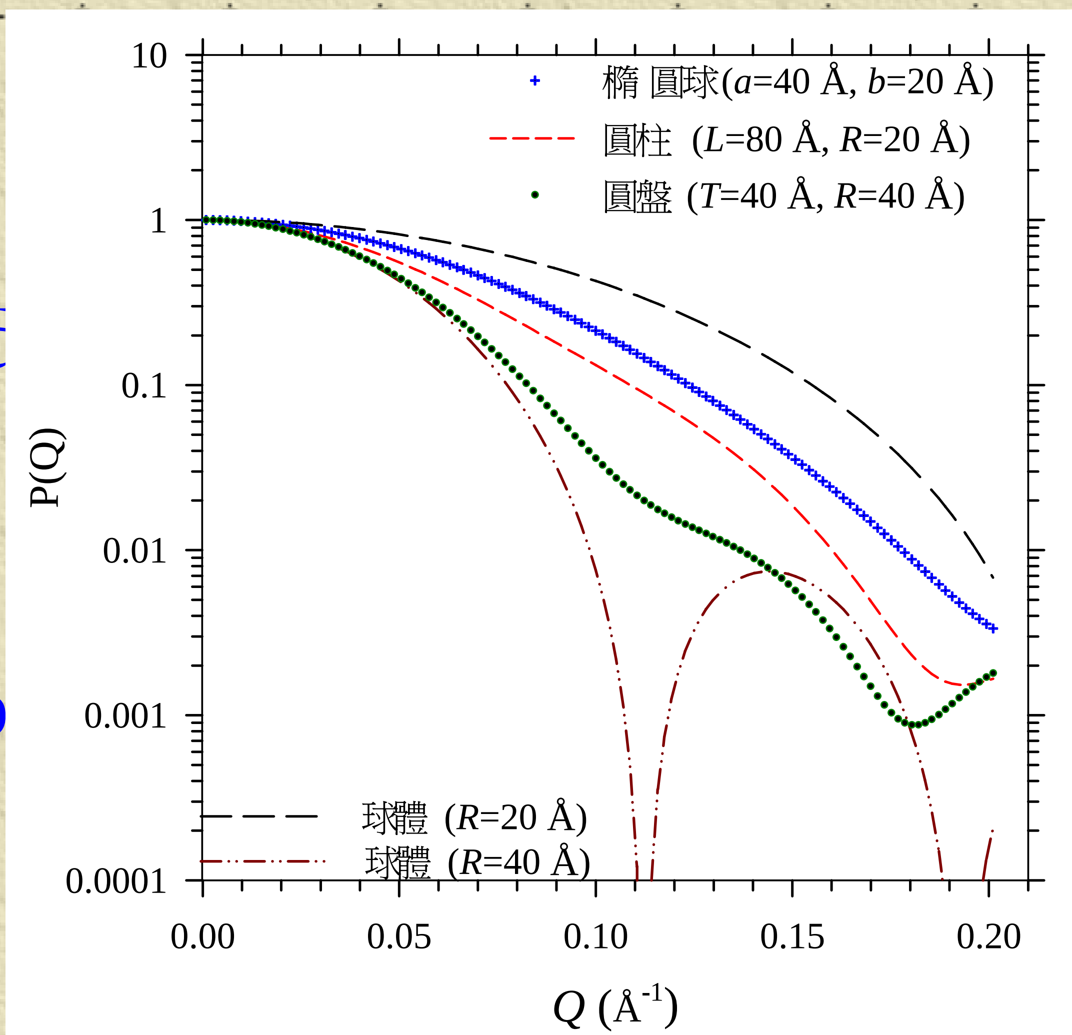
$$\tilde{P}(Q) = \left(3 j_1(QR)/QR\right)^2$$

- 橢圓球體 (ellipsoid

$$\tilde{P}(Q) = \int_0^1 \left| \frac{3 j_1(v)}{v} \right|^2 d\mu$$

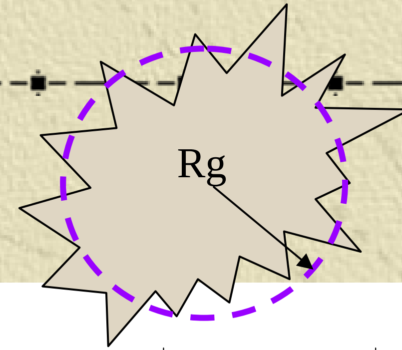
- 圓柱體, 或圓盤 (ro

$$\tilde{P}(Q) = \int_0^1 \left| \frac{2 J_1(v)}{v} \frac{\sin(w)}{w} \right|^2 d\mu$$



Guinier approximation for size information

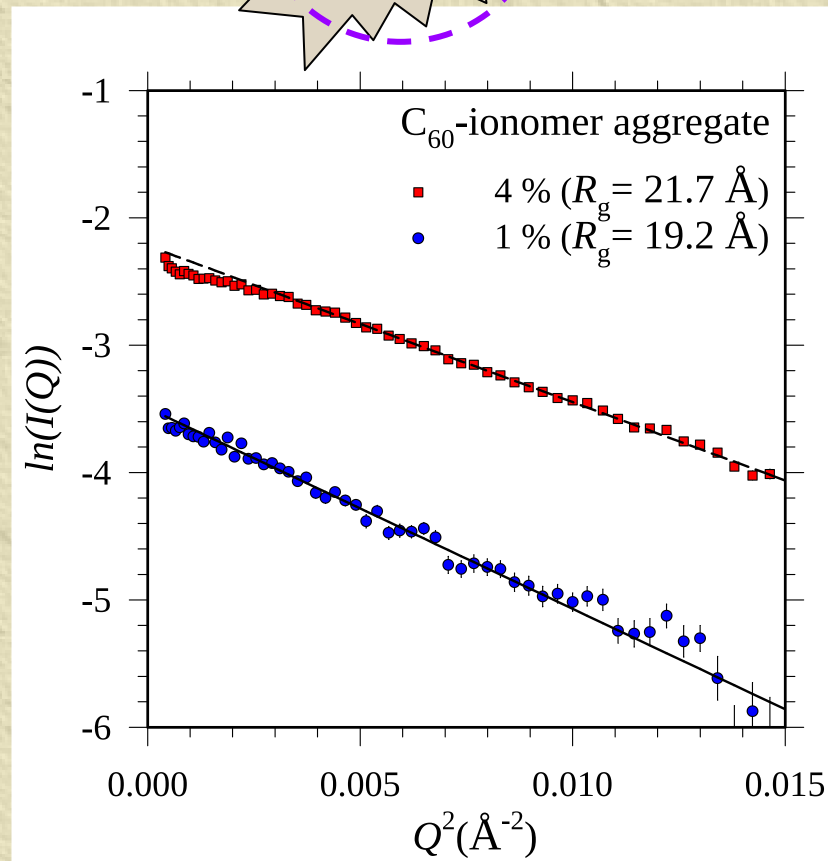
- Particles of irregular shapes



$$I(Q) \approx I_o \exp(-Q^2 R_g^2 / 3)$$

$$\mathrm{Ln}(Q) = -(1/3)R_g^{\,2}Q^2$$

(Guinier Approximation)



For spheres of uniform density ρ

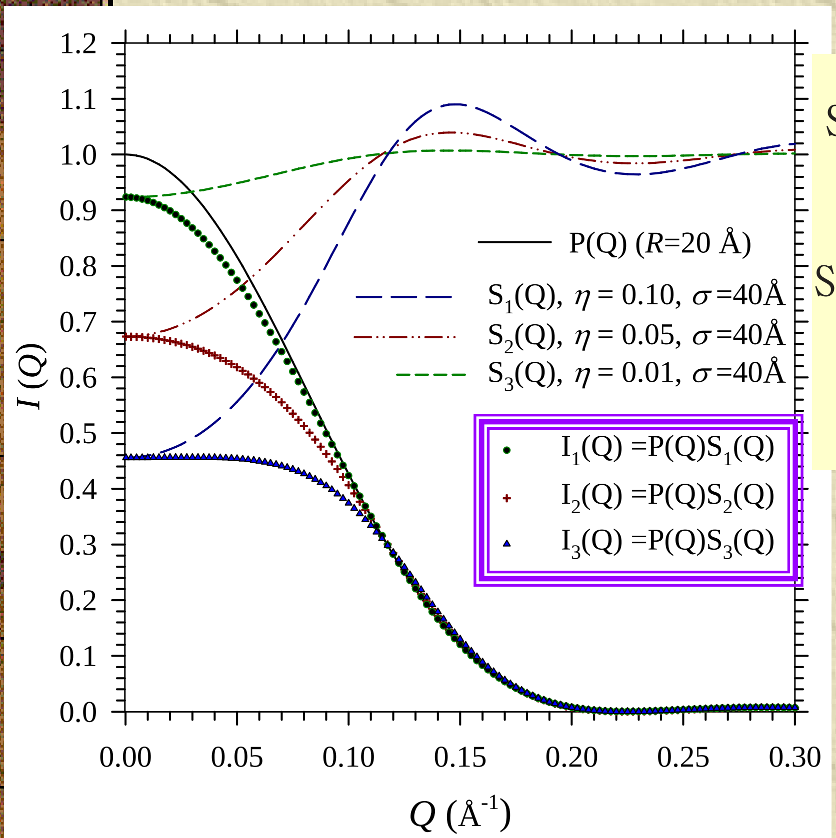
$$R_g^2 = 4\pi\rho \int_0^R \left(r^2\right) r^2 dr = (3/5)R^2$$

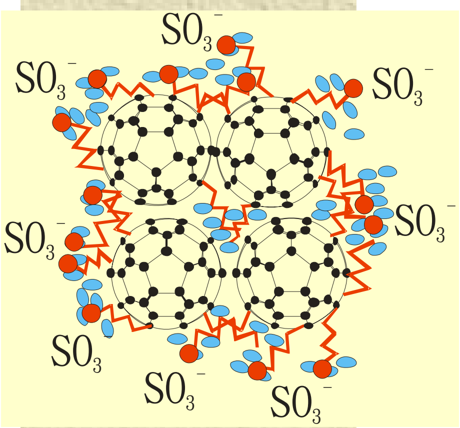
$C_{60}[(CH_2)_4SO_3Na]_6$之碳六十-離聚物小角度X光散射

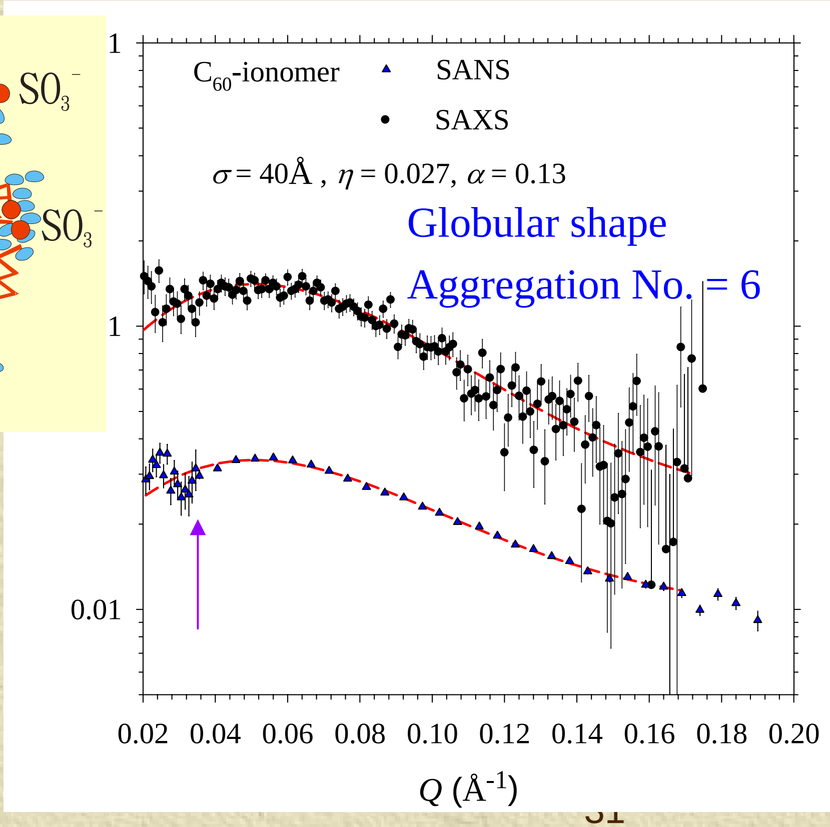
$I(Q) = P(Q)\boldsymbol{S(Q)}$

- 硬球(Hard Sphere)結構因子
- (硬球+電荷作用力)結構因子

帶電碳六十-離聚物(C60-ionomer)的聚集在水溶液的X光小角度散射(SAXS)與中子小角度散射(SANS)數據。圖中，σ，η分別是聚集體的等效硬球直徑，體積分率。圖中虛曲線爲對*SANS和*SAXS實驗數據所作的同步擬合，以找出最恰當的碳六十-離聚物的解離率，α。







親水性碳六十衍生分子$C_{60}(OH)_{18}$在水溶液的碎形聚集

- **Pair correlation funciton**

$$\bar{g}^{N^*}(r) \propto r^{D-d} \exp(-r/\xi)$$

- **S(Q) for fractal structure**

$$S(Q) \sim \frac{1}{Q^D} \frac{D\Gamma(D-1)}{\left(1+(Q\xi)^{-2}\right)^{(D-1)/2}} \sin[(D-1)\tan^{-1}(Q\xi)]$$

P(Q) ~ 1 ⇨ I(Q) =P(Q)S(Q)~S(Q)

C (wt %)	I(0) (cm^{-1})	R_g (Å)	R_g^* (Å)	ξ (Å)	N	N'
0.625	0.21	22.4 ± 3.0	28.3	13.4	48	40
1.25	0.39	25.6	31.7	15.0	55	54
2.5	1.04	26.9	37.2	17.6	74	80
4.0	3.21	34.3	44.2	20.9	113	125
*10.0	5.18	–	37.4	17.7	–	–