September 28, 2012: Cheiron School 2012 @ SPring-8

Small-Angle X-ray Scattering Basics & Applications

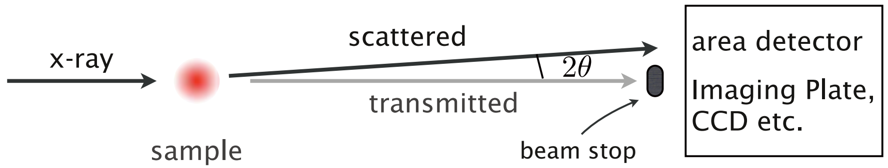
Yoshiyuki Amemiya and Yuya Shinohara

Graduate School of Frontier Sciences,

The University of Tokyo

Table of Contents

What's Small-Angle X-ray Scattering ?



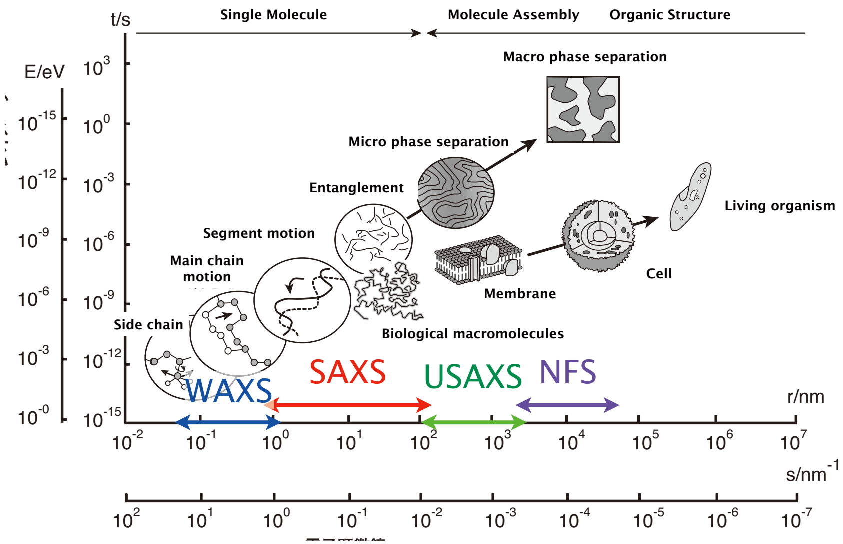
Bragg's law: $\lambda = 2d\sin\theta$

small angle → large structure (1 – 100 nm)

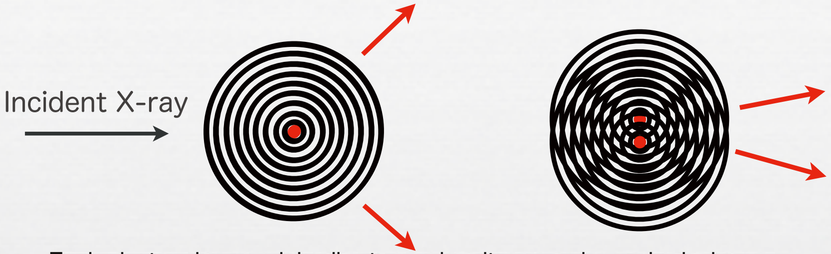
crystalline sample --> small-angle X-ray diffraction: SAXD

solution scattering / inhomogeneous structure --> SAXS

Hierarchical Structure of Soft Matter



Interference of secondary waves



Each electron in marerials vibrates and emits secondary spherical wave

<u>When there are two electrons,</u>

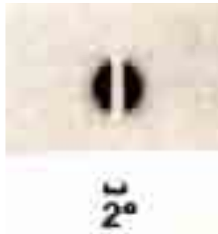
- interference between secondary waves from electrons
- when a distance between electrons is small
  --> scattering at large angle is intensified
- when a distance between electrons is large
  --> scattering at small angle is intensified --> SAXS

History of SAXS (< 1936)

Krishnamurty (1930)
Hendricks (1932)
Mark (1932)
Warren (1936)

Observation of scattering

from powders, fibers, and colloidal dispersions



carbon black

Molten silica - silica gel
(above) (below)

courtesy to Dr. I.L.Torriani

History (> 1936)

A. Guinier (1937, 1939, 1943)

Interpretation of inhomogeneities in Al alloys "G-P zones", introducing the concept of "particle scattering" and formalism necessary to solve the problem of a diluted system of particles.

O. Kratky (1938, 1942, 1962)

G. Porod (1942, 1960, 1961)

Description of dense systems of colloidal particles, micelles, and fibers.

Macromolecules in solution.

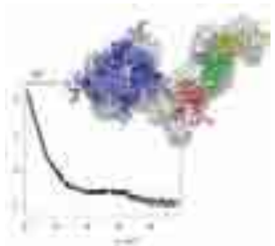
Single crystals of Al-Cu hardened alloy

Hemoglobin

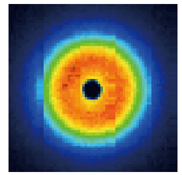
courtesy to Dr. I.L.Torriani

Application of SAXS

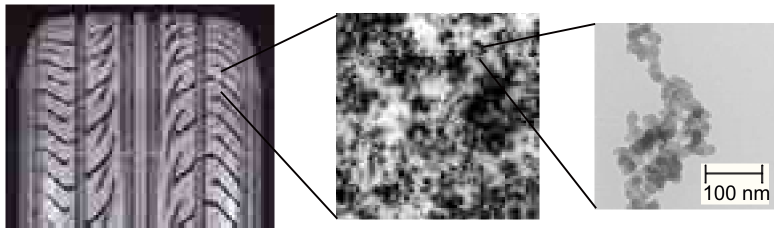
gel



Proteins in solution (Dr. Svergun, EMBL)



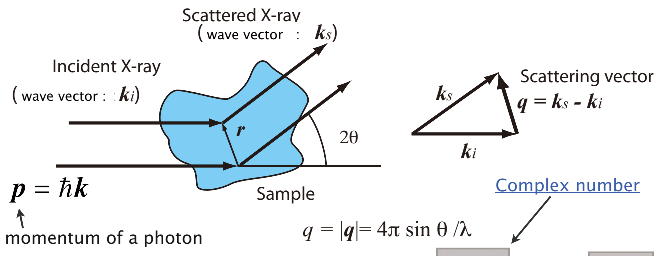
Typical SAXS image



Nanocomposite

Table of Contents

Basic of X-ray scattering



$\rho(r)$: electron density

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

Complex number

$dr = dxdydz$ around r

Amplitude of scattered X-ray $\boxed{A(q)} = \int_V \boxed{\rho(r)} \exp(-iq \cdot r)dr$

Fourier transform of electron density

Intensity of scattered X-ray : $I(q) = A(q)A^*(q) = |A(q)|^2$

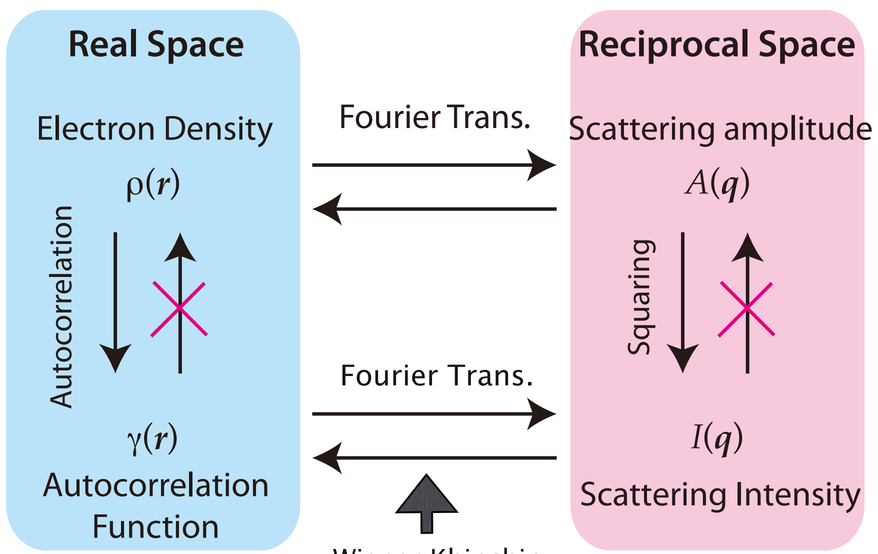
(Extensive variable)

Intensity of scattered X-ray per volume: $I(q) = \dfrac{A(q)A^*(q)}{V} = \dfrac{|A(q)|^2}{V}$

(Intensive variable)

This doesn't depend on sample volume, and is used to obtain the absolute intensity

Real space and Reciprocal Space

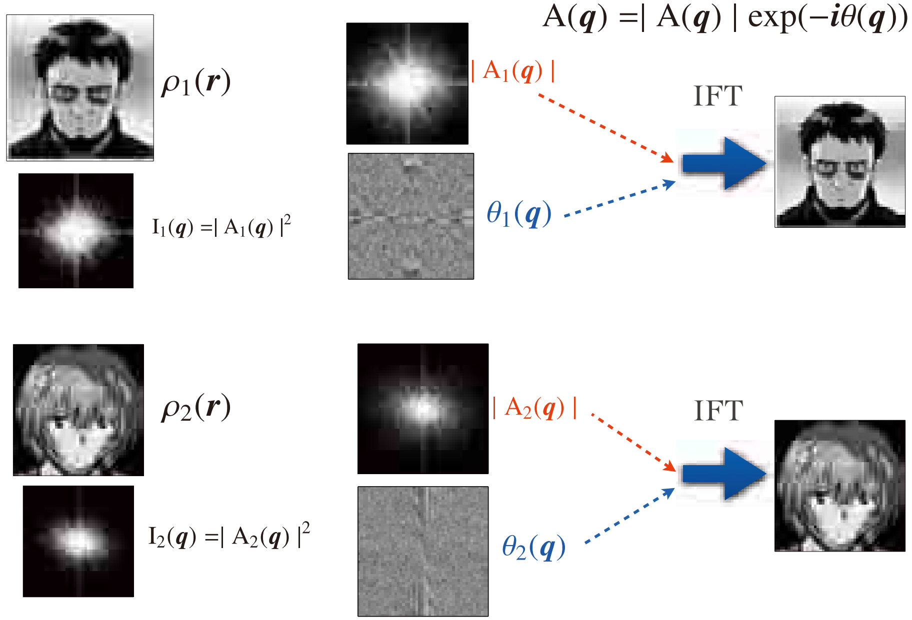


= Patterson Function

Wiener-Khinchin theorem

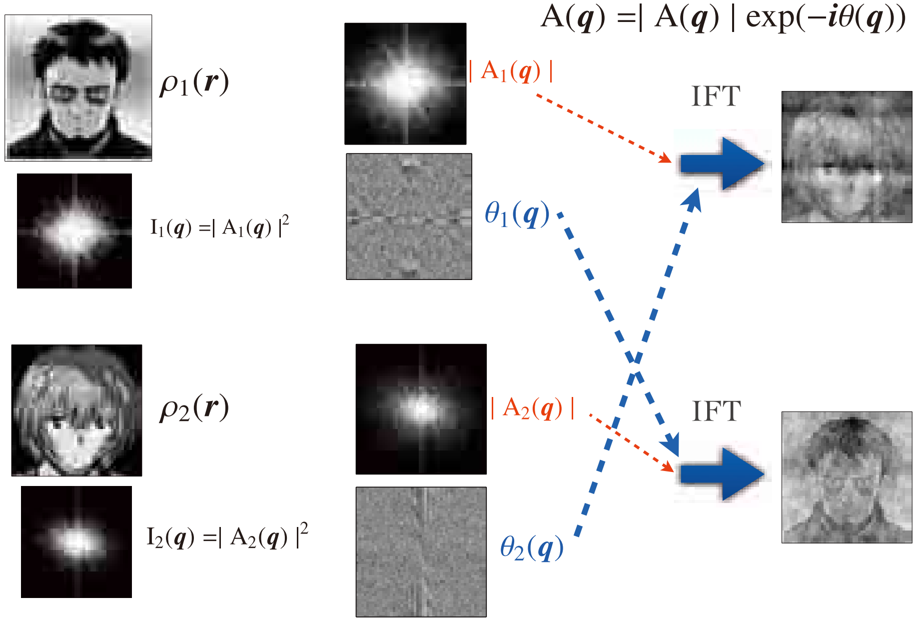
Importance of phase, $\theta(q)$ of complex amplitude

$A(q) = |A(q)| \exp(-i\theta(q))$



Importance of phase, $\theta(\boldsymbol{q})$ of complex amplitude

$$A(\boldsymbol{q}) = |A(\boldsymbol{q})| \exp(-i\theta(\boldsymbol{q}))$$



Autocorrelation Function & Scattering Intensity

Autocorrelation function of electron density

$$\gamma(\boldsymbol{r}) = \frac{1}{V}\int_V \rho(\boldsymbol{r}')\rho(\boldsymbol{r}+\boldsymbol{r}')\mathrm{d}\boldsymbol{r}' = \frac{1}{V}\underline{P(\boldsymbol{r})}$$

Patterson Function

(Debye & Bueche 1949)

asymptotic behavior of the autocorrelation function

$$\gamma(0) = \langle\rho^2\rangle \qquad \gamma(\infty) = \langle\rho\rangle^2$$

Scattering Intensity : Fourier Transform of autocorrelation function

$$\boxed{I(\boldsymbol{q})} = \int_V \boxed{\gamma(\boldsymbol{r})} \exp(-i\boldsymbol{q}\cdot\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}$$

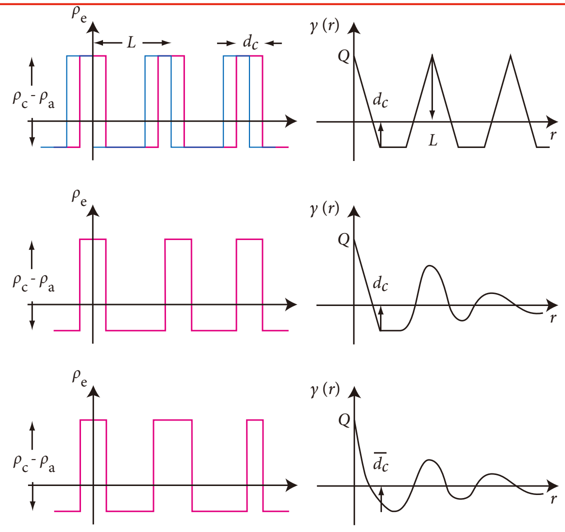
cf. Wiener-Khinchin theorem

Example of ρ(r) & γ(r) : in case of lamellar

ideal ordering

Long period changes.

Thickness of crystal changes.



real space   autocorrelation

Normalized Autocorrelation Function:

Introducing the relative electron density, $\eta(\boldsymbol{r})$, as

$$\eta(\boldsymbol{r}) = \rho(\boldsymbol{r}) - \langle\rho\rangle \longrightarrow \langle\eta^2\rangle = \langle(\rho(\boldsymbol{r}) - \langle\rho\rangle)^2\rangle = \langle\rho^2\rangle - \langle\rho\rangle^2$$

Introducing the normalized autocorrelation function, $\gamma_0(\boldsymbol{r})$, as

$$\gamma_0(\boldsymbol{r}) = \frac{1}{\langle\eta^2\rangle}\frac{1}{V}\int_V \langle\eta(\boldsymbol{r}')\eta(\boldsymbol{r}+\boldsymbol{r}')d\boldsymbol{r}'$$

then, $\gamma_0(\boldsymbol{r}) = \dfrac{\gamma(\boldsymbol{r}) - \langle\rho\rangle^2}{\langle\eta^2\rangle}$ where $\gamma_0(0) = 1 \quad \gamma_0(\infty) = 0$

then, $$\boxed{I(\boldsymbol{q}) = \underline{\langle\eta^2\rangle}\int_V \gamma_0(\boldsymbol{r})e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\mathrm{d}\boldsymbol{r} + \underline{\langle\rho\rangle^2\delta(\boldsymbol{q})}}$$

The average of the relative electron density fluctuations determines the magnitude of I(q). The normalized autocorrelation function $\gamma_0(r)$ determines the shape of I(q).

Not observable.

Invariant Q

Invariant: $Q = \int_0^\infty \mathrm{I}(\boldsymbol{q})d\boldsymbol{q} \Rightarrow \int_0^\infty \mathrm{I}(q)4\pi q^2 dq$ (when isotropic)

$= (2\pi)^3 \langle \eta^2 \rangle$ ← It doesn't depend on the structure

$$(\because) \quad Q = \int_0^\infty \mathrm{I}(\boldsymbol{q})d\boldsymbol{q} = \langle \eta^2 \rangle \int_0^\infty \int_V \gamma_0(\boldsymbol{r}) e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} d\boldsymbol{r} d\boldsymbol{q}$$

$$= \langle \eta^2 \rangle \int_V \gamma_0(\boldsymbol{r}) \int_0^\infty e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} d\boldsymbol{q} d\boldsymbol{r}$$

$$= (2\pi)^3 \langle \eta^2 \rangle \int_V \gamma_0(\boldsymbol{r}) \delta(0) d\boldsymbol{r} = (2\pi)^3 \langle \eta^2 \rangle \gamma_0(0) = (2\pi)^3 \langle \eta^2 \rangle$$

$$I(\boldsymbol{q}) = \langle \eta^2 \rangle \int_V \gamma_0(\boldsymbol{r}) e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} d\boldsymbol{r} + \underbrace{\langle \rho \rangle^2 \delta(\boldsymbol{q})}_{\text{Omitted.}}$$

Parseval's theorem

$$A(\boldsymbol{q}) \xleftrightarrow{\text{Fourier Trans.}} \eta(\boldsymbol{r})$$

$$\int |A(\boldsymbol{q})|^2 d\boldsymbol{q} = (2\pi)^3 \int |\eta(\boldsymbol{r})|^2 d\boldsymbol{r}$$

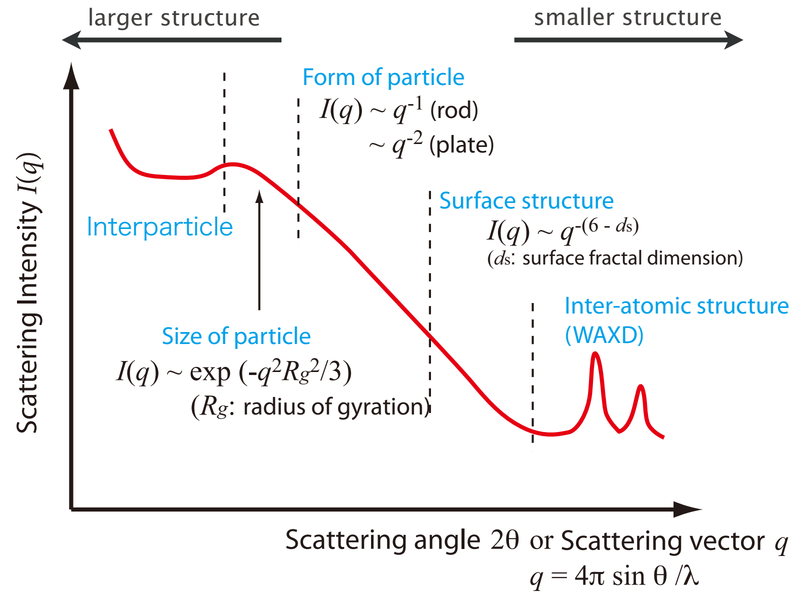
Table of Contents

Information obtained from SAXS

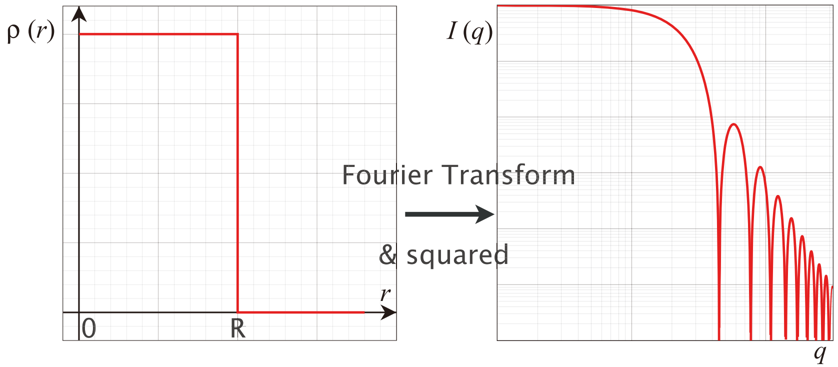
1. Size and form of particulate system
   - Colloids, Globular proteins, etc...
2. Correlation length of inhomogeneous structure
   - Polymer chain, two-phase system etc.
3. Lattice parameters of distorted crystals (para-crystal)
4. Degree of crystallinity, crystal size, crystal distortion
   - Crystalline polymer

SAXS of particulate system

Relation between SAXS pattern and Structural information



Spherical sample

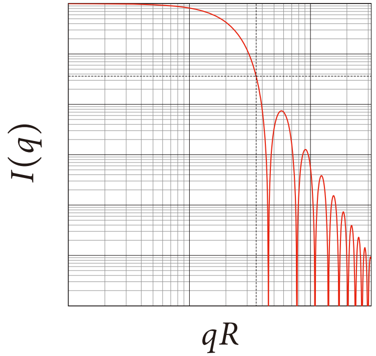


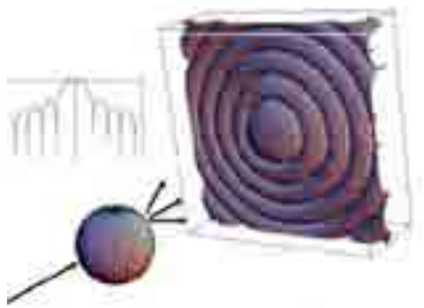
$$\rho(r) = \begin{cases} \Delta\rho & r < R \\ 0 & \text{else} \end{cases}$$

$$I(q) = \frac{(\Delta\rho)^2\, V_{\text{particle}}^{\;2}}{V}\left[3\frac{\sin qR - qR\cos qR}{(qR)^3}\right]^2$$

Homogeneous sphere

$$I(q) = \frac{(\Delta\rho)^2\, V_{\text{particle}}^{\;2}}{V}\left[3\frac{\sin qR - qR\cos qR}{(qR)^3}\right]^2$$





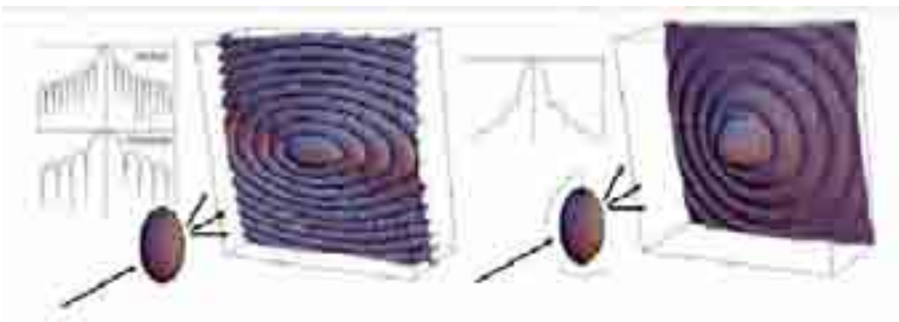
isotropic scattering

courtesy to Dr. I.L.Torriani

Homogeneous elipsiod

Fixed particle

Random orientation

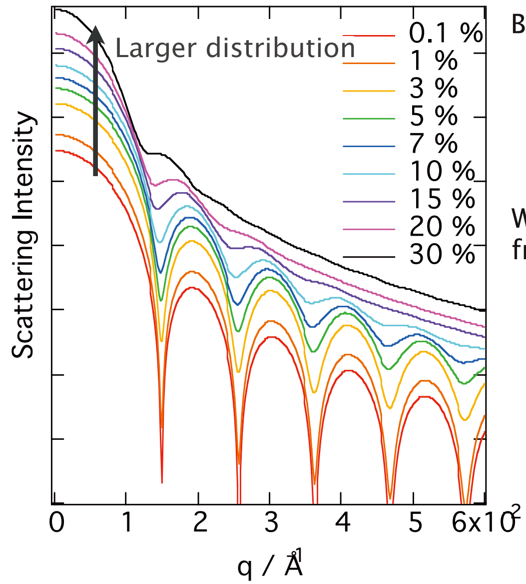


anisotropic scattering

isotropic scattering

courtesy to Dr. I.L.Torriani

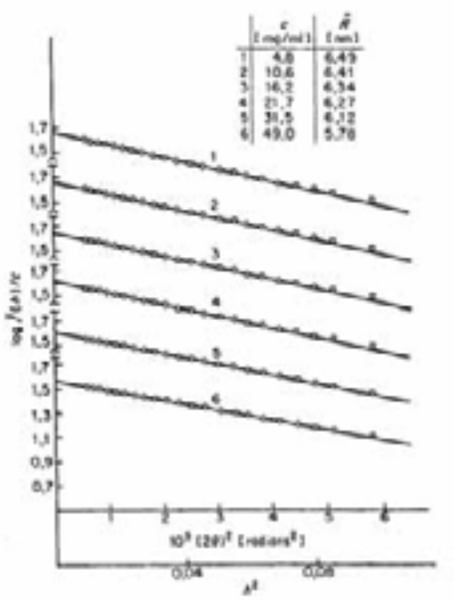
Size distribution



Based on Gaussian distribution

When the form has distribution, fringes are missed.

Radius of Gyration: R_g ($R_g^2 = \frac{\int r^2 \rho(\mathbf{r}) d\mathbf{r}}{\int \rho(\mathbf{r}) d\mathbf{r}}$) ----- Guinier Plot



$$I(q) \sim \exp\left(-\frac{q^2 R_g{}^2}{3}\right)$$

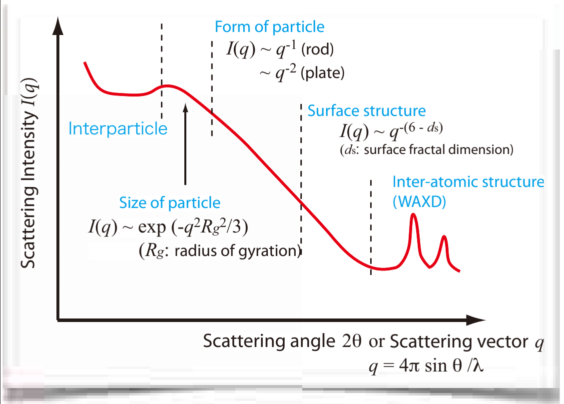
$$\downarrow$$

$$\log(I(q)) = -\frac{q^2 R_g{}^2}{3}$$

Guinier plot: log ($I(q)$) vs q^2

O. Glatter & O. Kratky ed., "Small Angle X-ray Scattering", Academic Press (1982).

Structure Factor & Form Factor



$$I(q) = \phi V_{\text{particle}} S(q) F(q)$$

Structure Factor → inter-particle structure

Form Factor → intra-particle structure

Separation of S(q) & F(q)

→ Everlasting issue

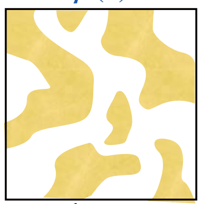
(especially, for non-crystalline sample)

Proposed remedy:

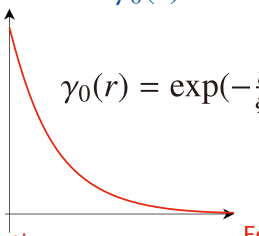
- GIFT (Generalized Inverse Fourier Trans.) by O. Glatter

Scattering from Inhomogeneous Structure

Electron Density $\rho(r)$ | Autocorrelation Function $\gamma_0(r)$ | Scattering Intensity



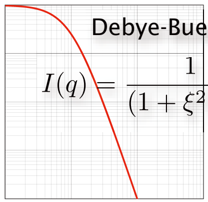
two phase system



$$\gamma_0(r) = \exp(-\tfrac{r}{\xi})$$

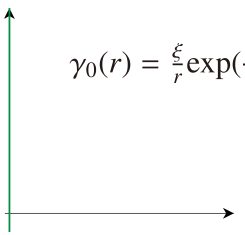
Autocorrelation →

Fourier trans. →

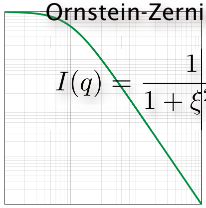


$$I(q) = \frac{1}{(1+\xi^2 q^2)^2}$$

polymer chain etc.



$$\gamma_0(r) = \tfrac{\xi}{r}\exp(-\tfrac{r}{\xi})$$



$$I(q) = \frac{1}{1+\xi^2 q^2}$$

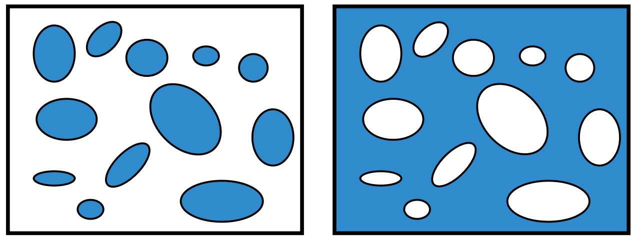
Two-phase system

Phase 1: ρ_1, volume fraction ϕ Phase 2: ρ_2 volume fraction $1 - \phi$

$$A(\mathbf{q}) = \int_{\phi V} \rho_1 e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} + \int_{(1-\phi)V} \rho_2 e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

$$= \int_{\phi V} (\rho_1 - \rho_2) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} + \rho_2 \int_V e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

$$\boxed{A(\mathbf{q}) = \int_V \Delta\rho\, e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} + \rho_2 \delta(\mathbf{q})}$$



Babinet's principle

Two complementary structures produce the same scattering.

Two-phase system -- cont.

Averaged square fluctuation of electron density

$$\langle \eta^2 \rangle = \phi(1-\phi)(\Delta\rho)^2 \qquad \text{where} \qquad \Delta\rho = \rho_1 - \rho_2$$

Φ : volume fraction

$$I(q) = 4\pi\langle \eta^2 \rangle \int_0^\infty \gamma_0(r)\frac{\sin(qr)}{qr}r^2\mathrm{d}r$$

$$I(q) = 4\pi\phi(1-\phi)(\Delta\rho)^2\int_0^\infty \gamma_0(r)\frac{\sin(qr)}{qr}r^2\mathrm{d}r$$

$$\boxed{Q = \int_0^\infty I(q)q^2\mathrm{d}q = 2\pi^2\phi(1-\phi)(\Delta\rho)^2}$$

Invariant: does not depend on the structure of the two phases but only on the volume fractions and the contrast between the two phases.

Porod's law

For a sharp interface, the scattered intensity decreases as q^{-4}.

$$I(q) \to (\Delta\rho)^2\frac{2\pi}{q^4}\underline{S}/V$$

internal surface area

Combination of Porod's law & Invariant Q

$$\pi \cdot \frac{\lim_{q\to\infty} I(q)q^4}{Q} = \boxed{\frac{S}{V}}$$

surface-volume ratio

important for the characterization of porous materials

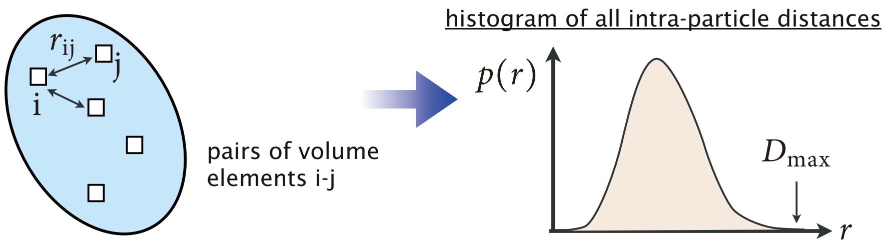
Pair Distance Distribution Function: PDDF

Scattering intensity: $I(q) = 4\pi\int_0^\infty \gamma_0(r)\frac{\sin(qr)}{qr}r^2\mathrm{d}r$
(when isotropic)

PDDF : $p(r) = r^2\gamma_0(r)$

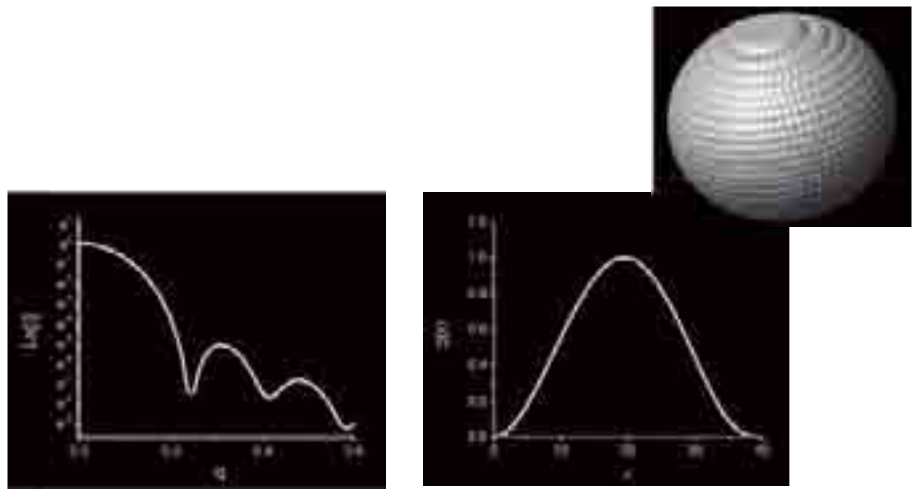
the set of distances joining the volume elements within a particle, including the case of non-uniform density distribution.

Particle's SHAPE and maximum DIMENSION.



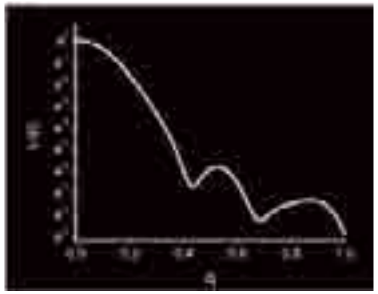
$$I(q) = 4\pi\int_0^\infty p(r)\frac{\sin(qr)}{qr}\mathrm{d}r$$

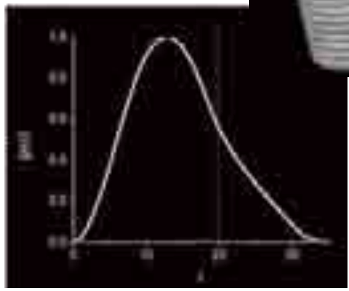
I(q) & P(r) of Spherical particle



courtesy to Dr. I.L.Torriani

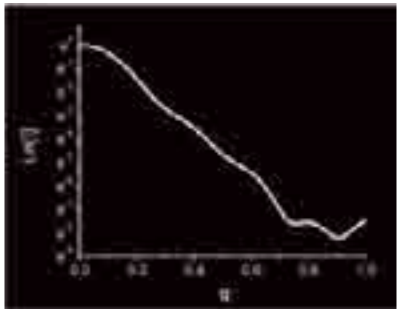
I(q) & P(r) of Cylindrical particle

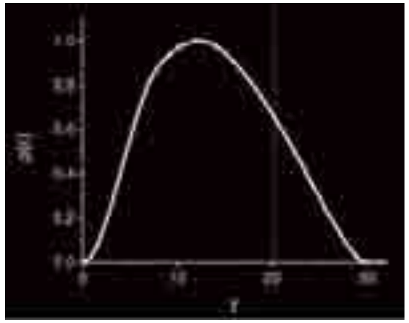




courtesy to Dr. I.L.Torriani

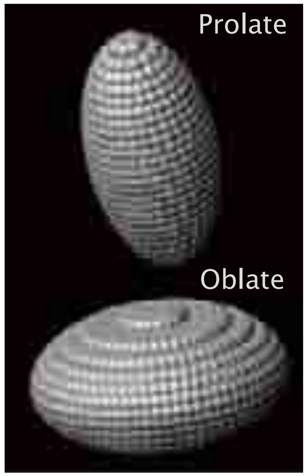
I(q) & P(r) of Flat particle

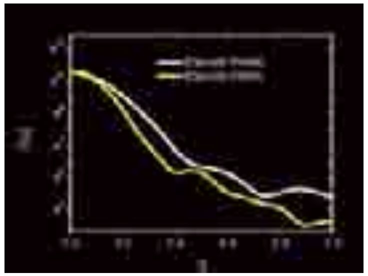


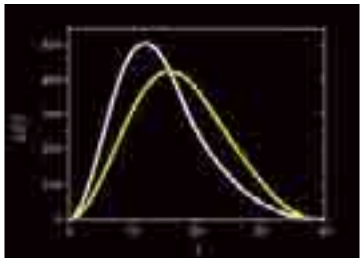


courtesy to Dr. I.L.Torriani

I(q) & P(r) of Ellipsoids

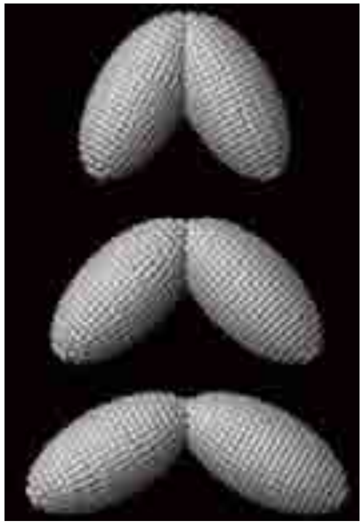


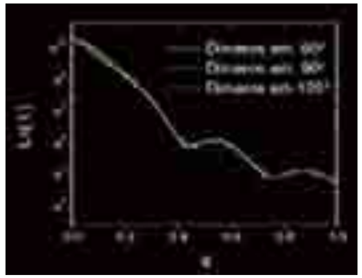


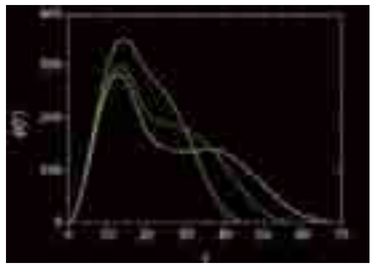


courtesy to Dr. I.L.Torriani

I(q) & P(r) of Two ellipsoid = dimer

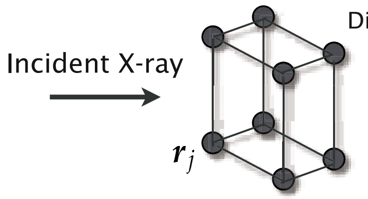






courtesy to Dr. I.L.Torriani

Diffraction from Periodic Structure



Diffraction from Unit cell (Crystalline structure factor)

$$F(\boldsymbol{q}) = \sum_j f(\boldsymbol{q}) \exp(-i\boldsymbol{q}\cdot\boldsymbol{r}_j)$$

$f(\boldsymbol{q})$: Atomic Form Factor

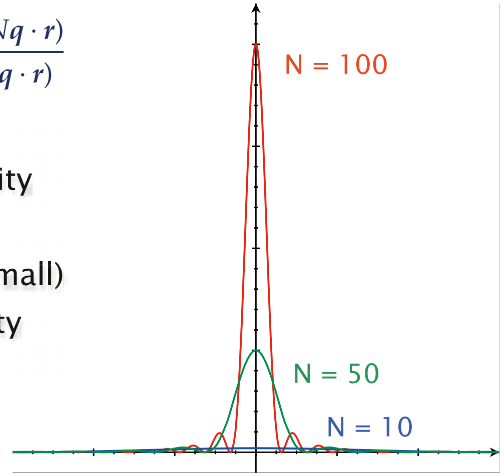
Diffraction Intensity: $I(\boldsymbol{q}) \sim \underline{G(\boldsymbol{q})}^2 \; F(\boldsymbol{q})^2$

Laue function: $|G(\boldsymbol{q})|^2 = \dfrac{\sin^2(\pi N \boldsymbol{q}\cdot\boldsymbol{r})}{\sin^2(\pi \boldsymbol{q}\cdot\boldsymbol{r})}$

- Maximum ~ N^2
- FWHM ~ 2π/N
  - FWHM --> Size of crystal

Laue Function

Laue function: $|G(\boldsymbol{q})|^2 = \dfrac{\sin^2(\pi N \boldsymbol{q}\cdot\boldsymbol{r})}{\sin^2(\pi \boldsymbol{q}\cdot\boldsymbol{r})}$

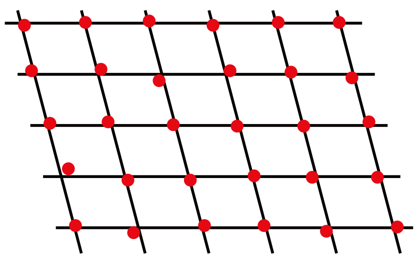


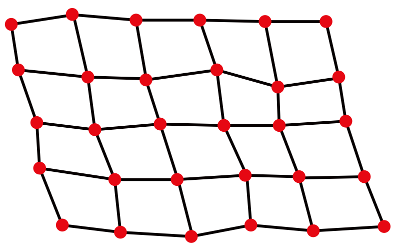
- Large crystal
  - High diffraction intensity
  - Narrow FWHM
- Soft matter (crystal size: small)
  - Low diffraction intensity
  - Wide FWHM

  → low S/N

Crystal size --> Intensity & FWHM of diffraction

Imperfection of crystal (2D)





Imperfection of 1st kind

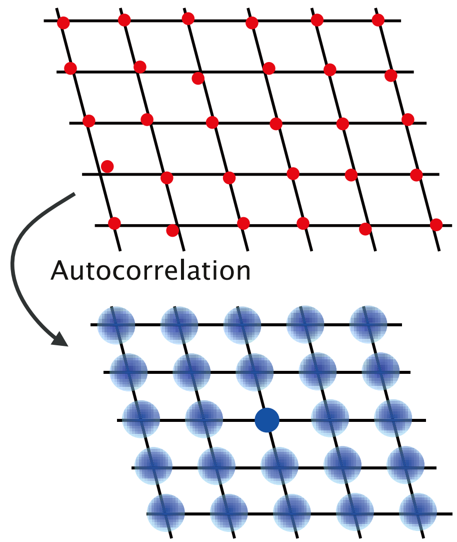
Thermal fluctuation etc.

Imperfection of 2nd kind

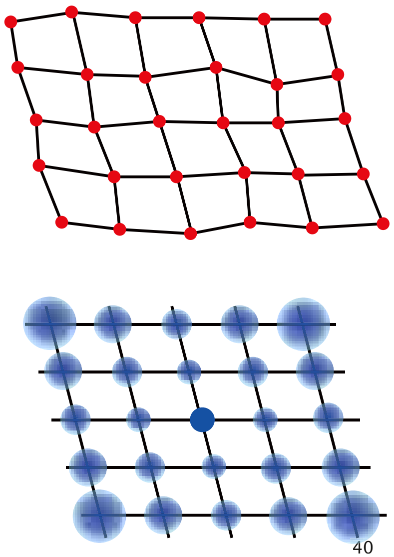
in the case of soft matter

Imperfection of crystal

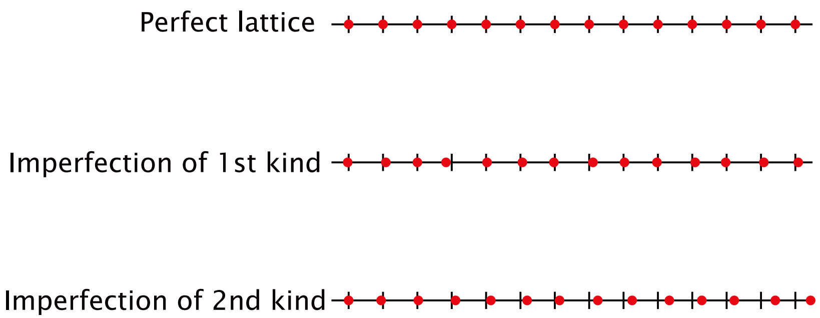
Imperfection of 1st kind



Imperfection of 2nd kind

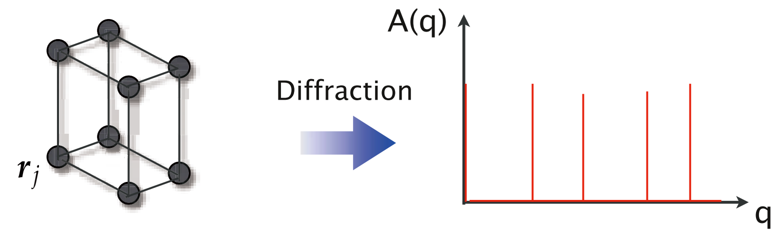


Imperfection of lattice (1D)



- Effect of imperfections on diffraction ?

Diffraction from lattice-structure



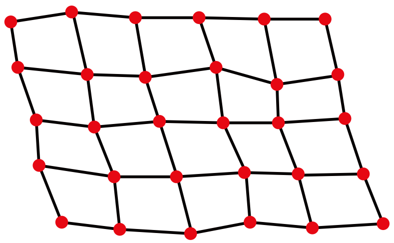
$$\rho(\boldsymbol{r}) = \rho_u(\boldsymbol{r}) * \underline{z(\boldsymbol{r})} \qquad A(\boldsymbol{q}) = F(\boldsymbol{q}) \cdot \underline{Z(\boldsymbol{q})}$$

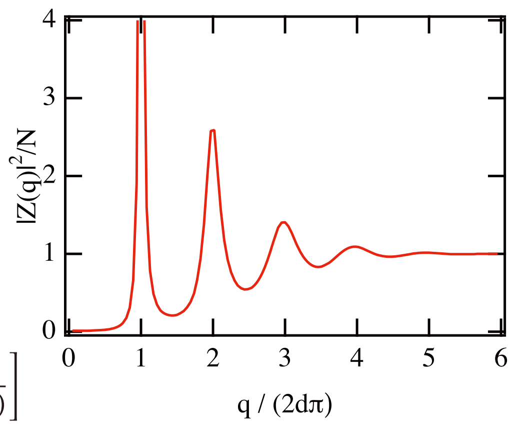
convolution

Form of lattice

z(**r**) with imperfection ---> calculate Z(**q**)

Imperfection of 2nd kind





Paracrystal theory

$$|Z(q)|^2 = N\left[1 + \frac{P(q)}{1 - P(q)} + \frac{P^*(q)}{1 - P^*(q)}\right]$$

Decrease of diffraction intensity and
Increase of FWHM

R. Hosemann, S. N. Bagchi, Direct Analysis of Diffraction by Matter, North-Holland, Amsterdam (1962).

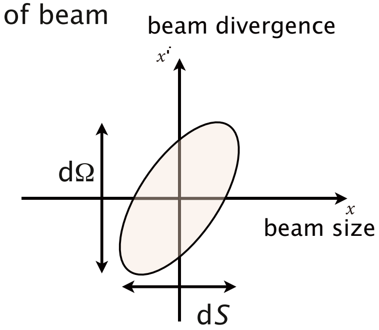
Table of Contents

X-ray Source for SAXS

Emittance -- Product of size and divergence of beam

$$\text{Brilliance} = \frac{d^4 N}{dt \cdot d\Omega \cdot dS \cdot d\lambda/\lambda}$$

[photons/(s·mrad^2·mm^2·0.1% rel.bandwidth)]

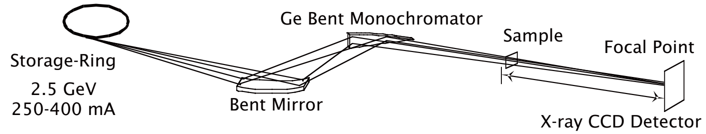


SAXS needs to use a low divergence and small beam

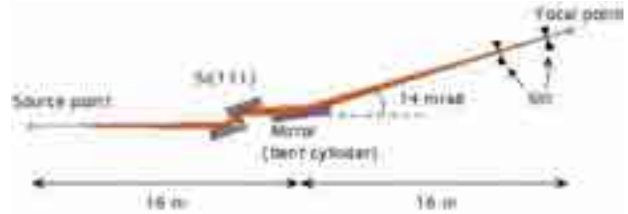
⟶ High brilliance beam is required !

X-ray Optics for SAXS

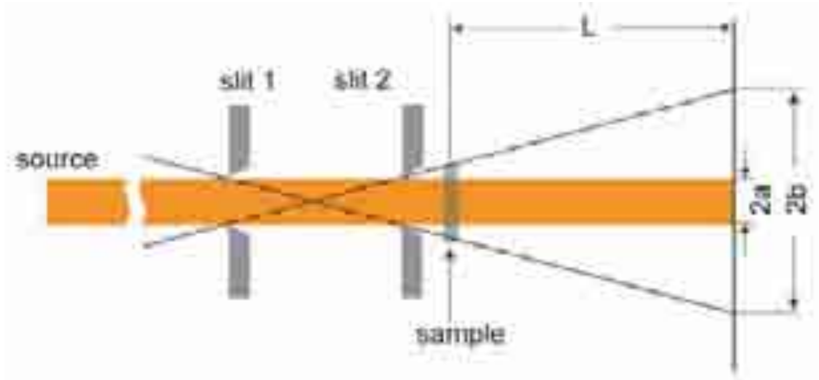
PF BL-15A



PF BL-10C



Slits for SAXS



Detectors for SAXS

	Good Point	Drawback
PSPC	• time-resolved • photon-counting • low noise	• counting-rate limitation
Imaging Plate	• wide dynamic range • large active area	• slow read-out
CCD with Image Intensifier	• time-resolved • high sensitivity	• image distortion • low dynamic range
Fiber-tapered CCD	• fast read-out • automated measurement	• not good for time-resolved

X-ray CCD detector with Image Intensifier

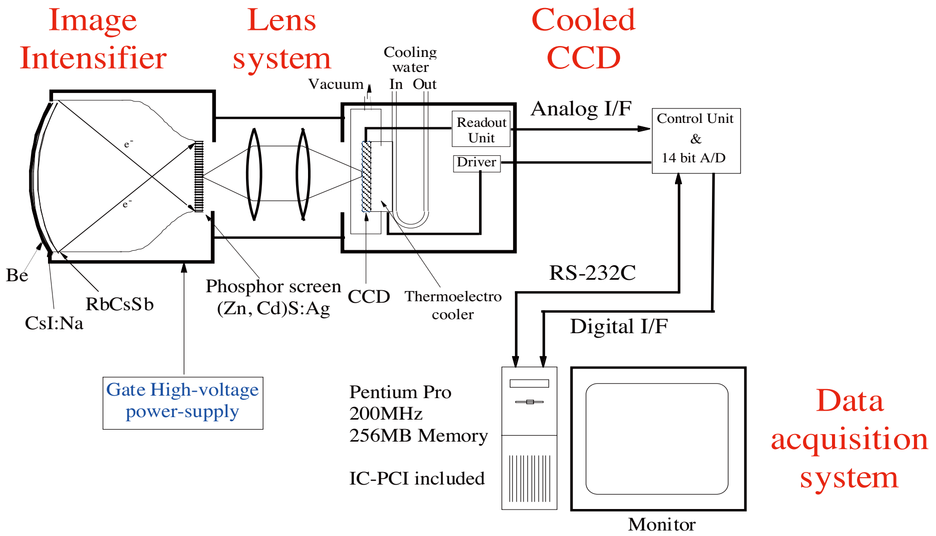


Table of Contents

Advanced SAXS

Microbeam X-ray
- Inhomogeneity of nano-structure
- local time evolution of structure

Time-resolved
- time evolution of structure

GI-SAXS
- surface, interface, thin films

SAXS

XPCS
- structural fluctuation
- dynamics

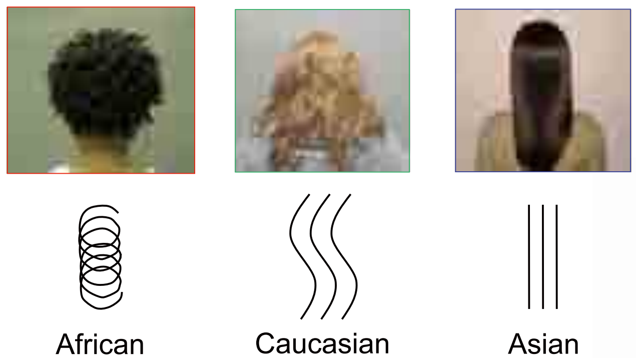
Combined measurement with DSC, viscoelasticity

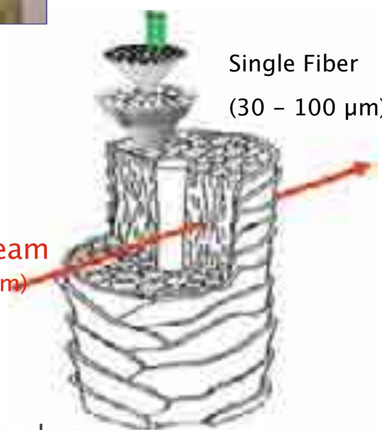
wide-q (USAXS-SAXS-WAXS)
- hierarchical structure

2D measurement
- anisotropic structure

Application of paracrystal theory

Collab. with Kao ltd.





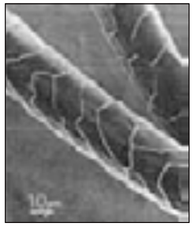
X-ray Microbeam
(5 μm x 5 μm)

Relationship between macroscopic form and nano structure?

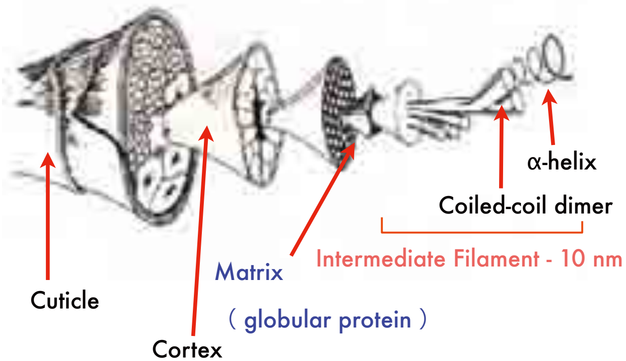
Local observation with an X-ray microbeam

Internal structure of wool

SEM 像



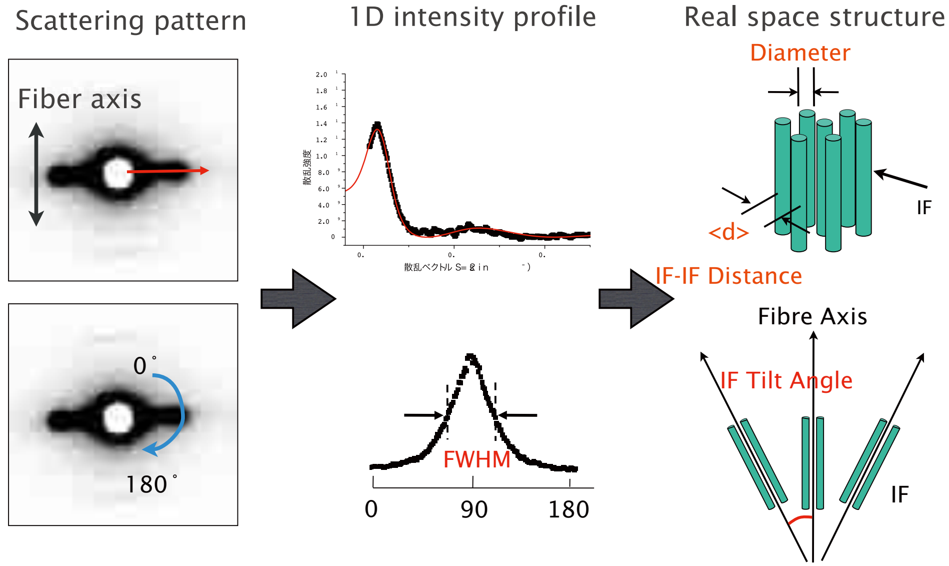
H. Ito et al., Textile Res. J. **54**, 397–402 (1986).



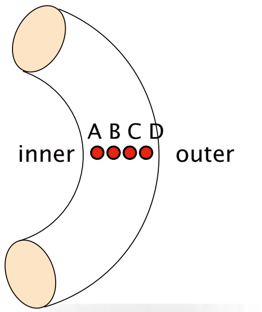
R. D. B. Fraser et al., Proc. Int. Wool Text. Res. Conf., Tokyo, II, **37**, (1985) partially changed.

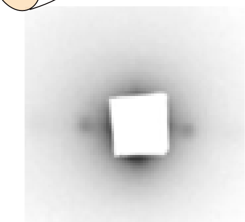
Relationship between IF distribution and hair curlness?

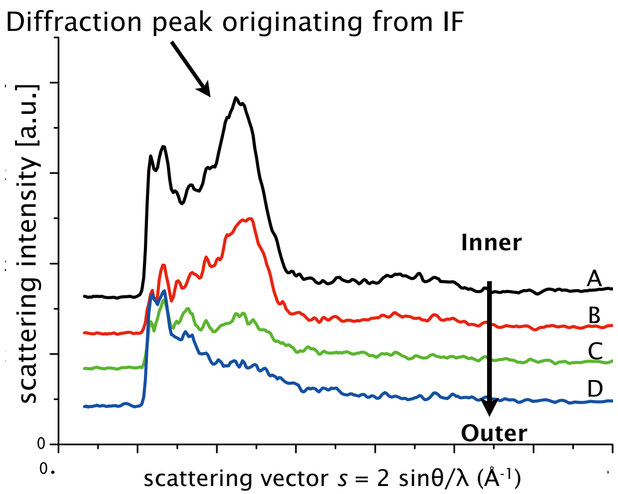
Structure of Intermediate Filament



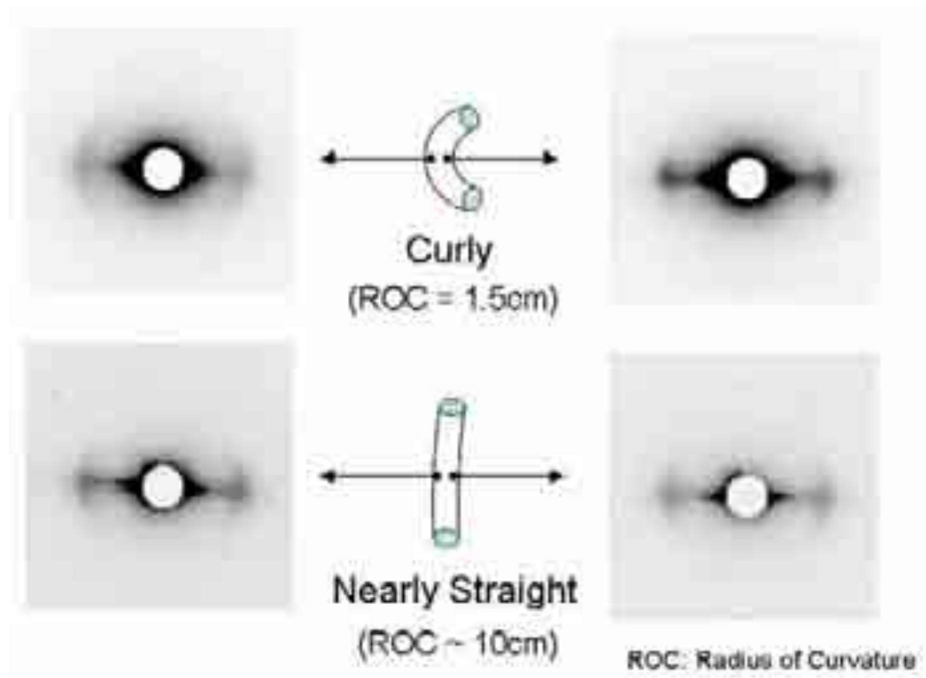
Diffraction intensity profiles



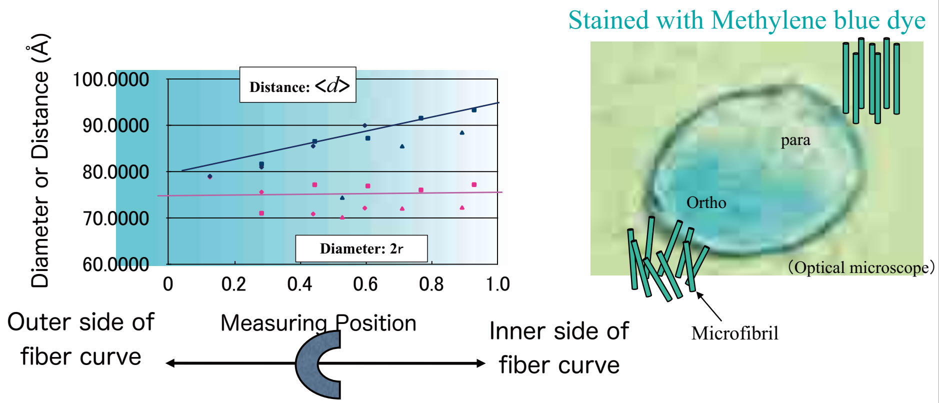




Difference in diffraction intensity
--> Structural difference in cortex.

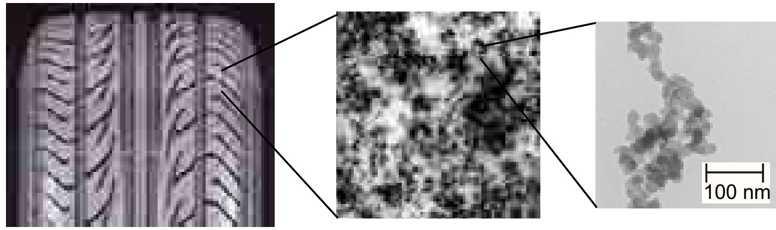


Distribution of Intermediate Filament (IF)



- Diameter of Intermediate filament (IF) is almost constant
- Distance between IFs increases from outer to inner sides.

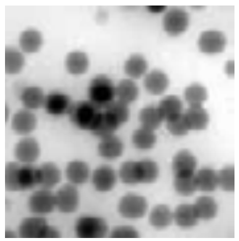
USAXS for nano-composite in rubber



Nanocomposite

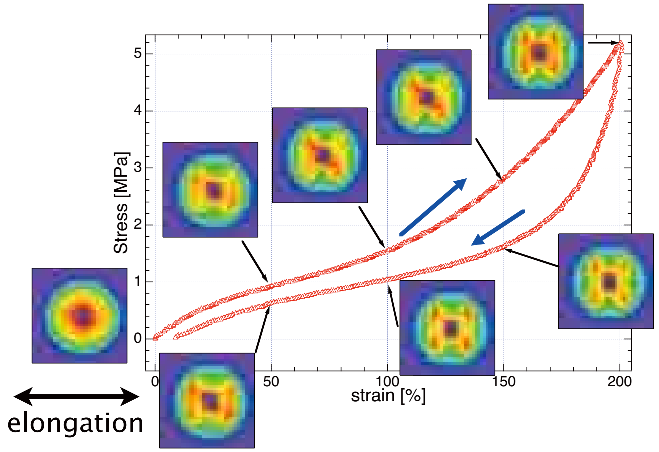
USAXS using medium-length beamline

USAXS patterns from elongated rubber



TEM image

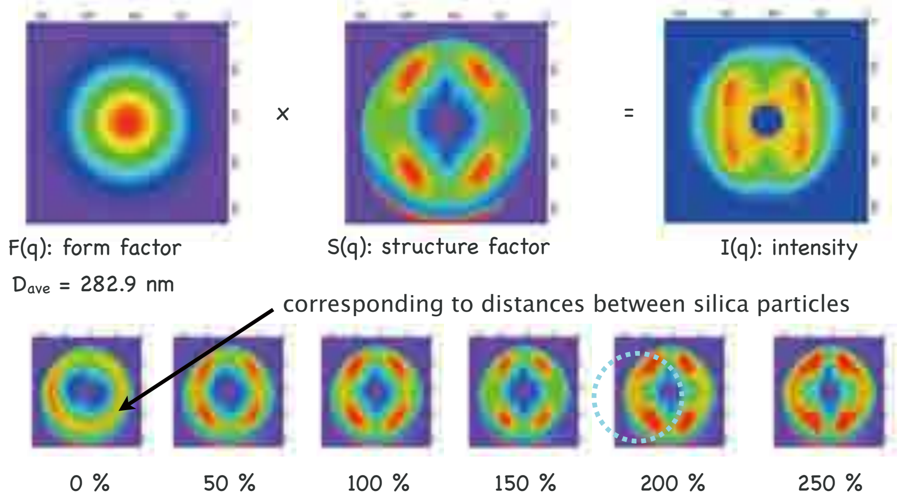
Rubber filled with spherical silica



Scattering pattern also shows hysteresis.

Y. Shinohara et al., J. Appl. Cryst., **40**, s397 (2007).

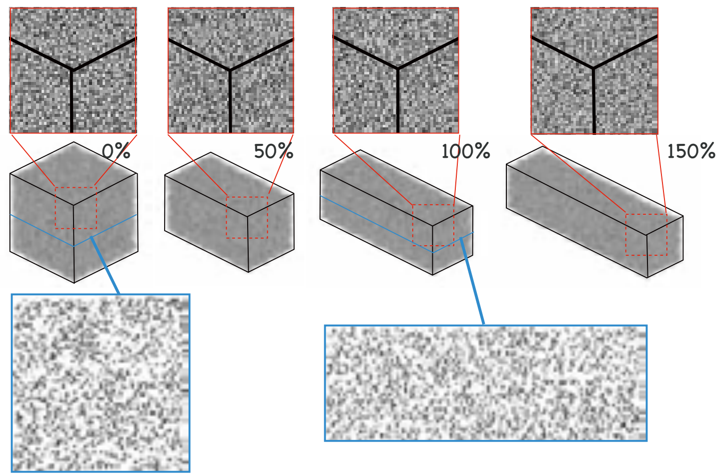
Separation of Structure factor S(q)



Y. Shinohara et al., J. Appl. Cryst., **40**, s397 (2007).

Analysis by RMC (Reverse Monte Carlo)

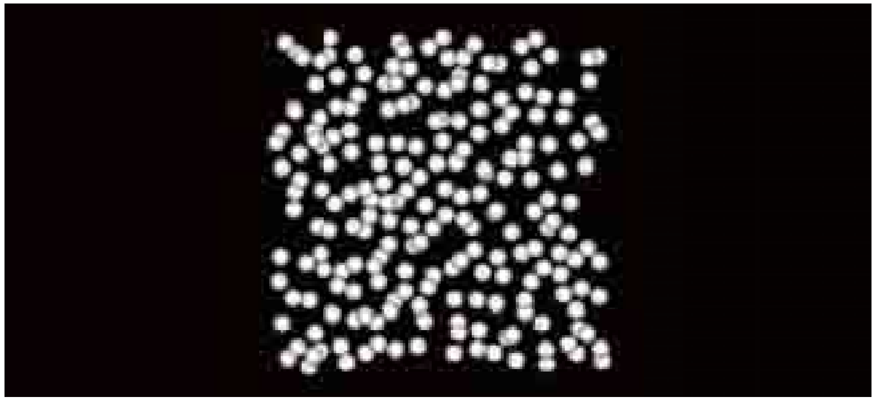
Sample : monodispersive silica spheres in rubber



Courtesy to Dr.Hagita & Prof. Arai

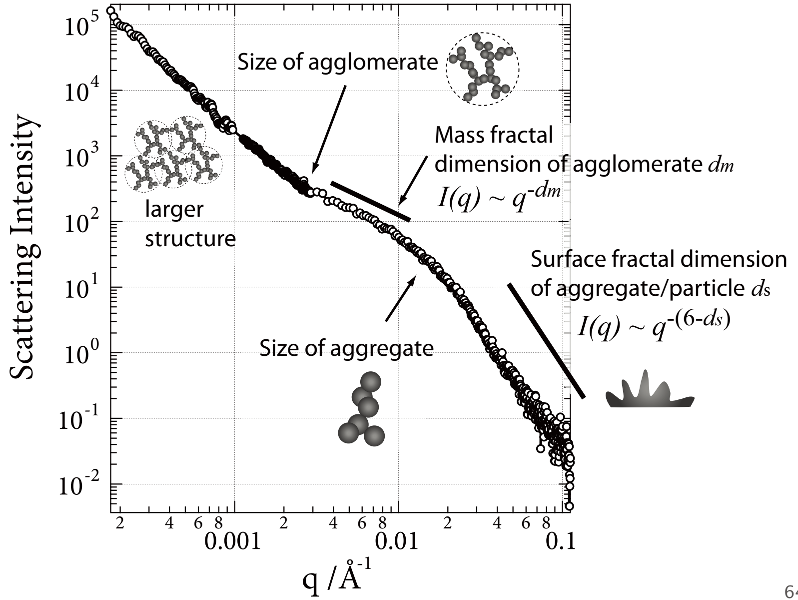
Visualization of structure change of fillers during elongation of rubber by using SAXS and RMC

0→150% : elongation process



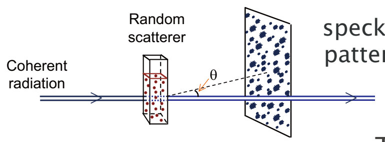
non-uniformity increases along the elongation direction.

Structural information from USAXS



X-ray Photon Correlation Spectroscopy: XPCS

- Measurement of fluctuation of X-ray scattering intensity
  --> Structural fluctuation in sample

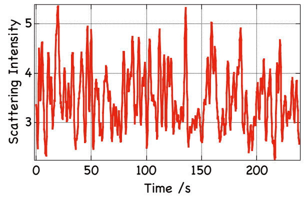


speckle pattern

$$g^{(2)}(q,\tau) = \frac{\langle I(q,0)I^{*}(q,\tau)\rangle}{\langle I(q)\rangle^{2}}$$

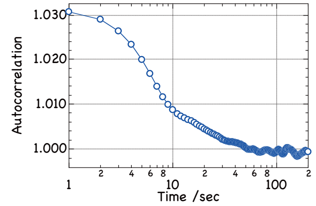
Time-resolved SAXS with coherent X-ray

Fluctuation of intensity

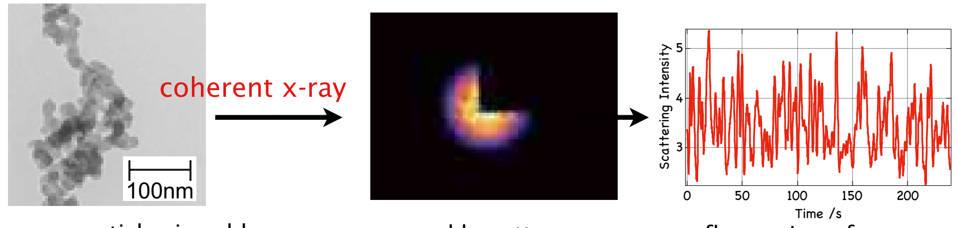


Autocorrelation

relaxation time in system



Dynamics of nanoparticles observed with XPCS



nano-particles in rubber

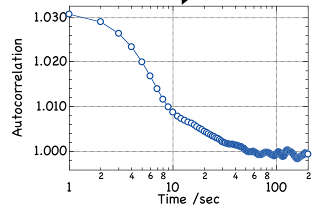
speckle pattern

fluctuation of scattering intensity

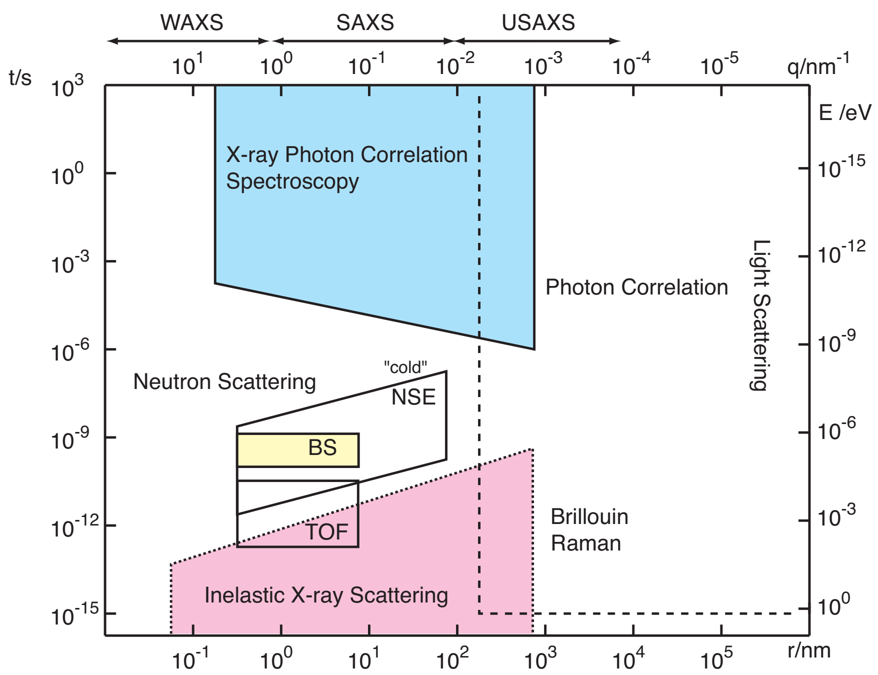
<u>Dependence of dynamics on...</u>

- Volume fraction of nano-particles
- Vulcanization (cross-linking)
- Type of nano-particles
- Temperature

etc.



Dynamics of Filler in Rubber



Bibliography

- A. Guinier and A. Fournet (1955) “Small angle scattering of X-rays” Wiley & Sons, New York. out-of-print
- O. Glatter and O. Kratky ed. (1982) “Small Angle X-ray Scattering” Academic Press, London. out-of-print
- L. A. Feigin and D. A. Svergun (1987) “Structure Analysis by Small Angle X-ray and Neutron Scattering” Plenum Press.
- P. Lindner and Th. Zemb ed. (2002) “Neutron, X-ray and Light Scattering: Soft Condensed Matter”, Elsevier.
- Proceedings of SAS meeting (2003 & 2006). Published in J. Appl. Cryst.
- R-J. Roe (2000) “Methods of X-ray and Neutron Scattering in Polymer Science”, Oxford University Press.