Small-Angle X-ray Scattering

Basics & Applications

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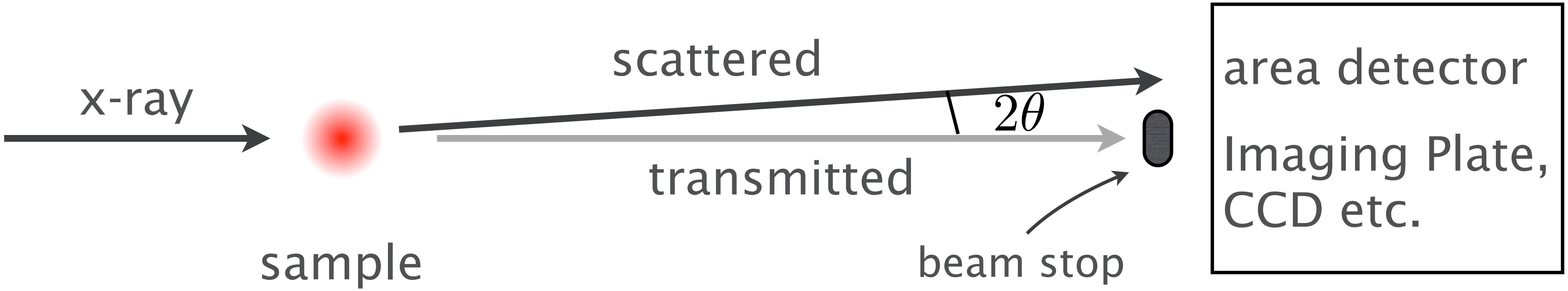
Overview

- Introduction
  - What's SAXS ?
  - History
  - Application field of SAXS
- Theory
  - Structural Information obtained by SAXS
- Experimental Methods
  - Optics
  - Detectors
- Advanced SAXS
  - Microbeam, GI-SAXS, USAXS, XPCS etc...

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

History of SAXS (< 1936)

Krishnamurty (1930)

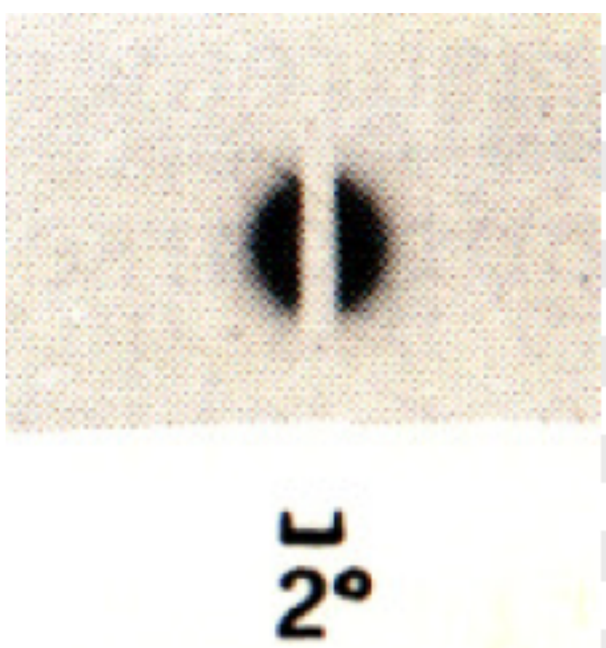
Hendricks (1932)

Mark (1932)

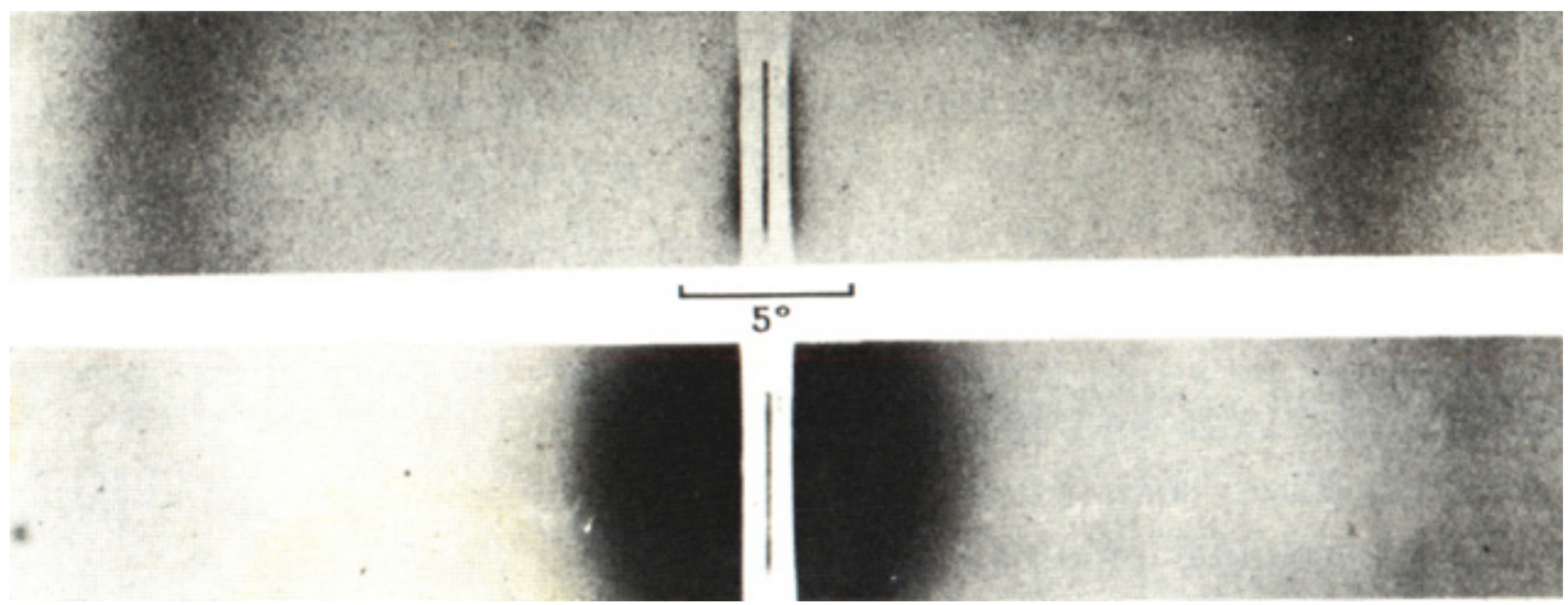
Warren (1936)

Observation of scattering

from powders, fibers, and colloidal dispersions



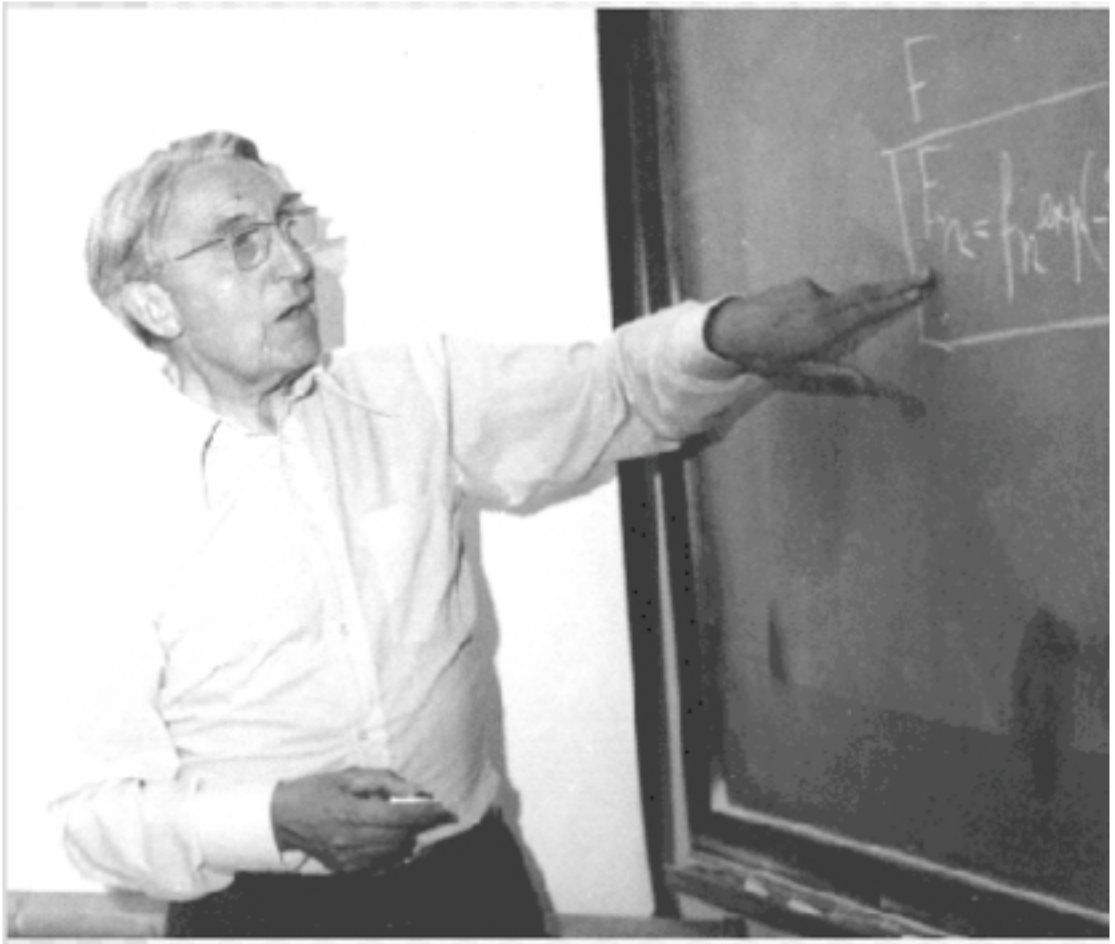
carbon black



Molten silica - silica gel

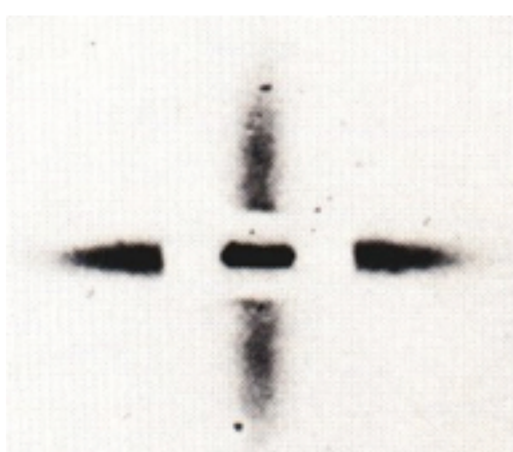
courtesy to Dr. I.L.Torriani

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.



Single crystals of Al-Cu hardened alloy

O. Kratky (1938, 1942, 1962)

G. Porod (1942, 1960, 1961)

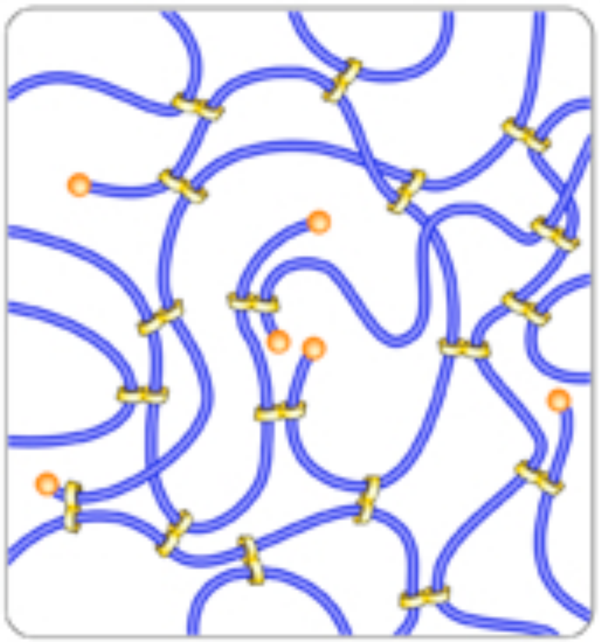
Description of dense systems of colloidal particles, micelles, and fibers.

Macromolecules in solution.

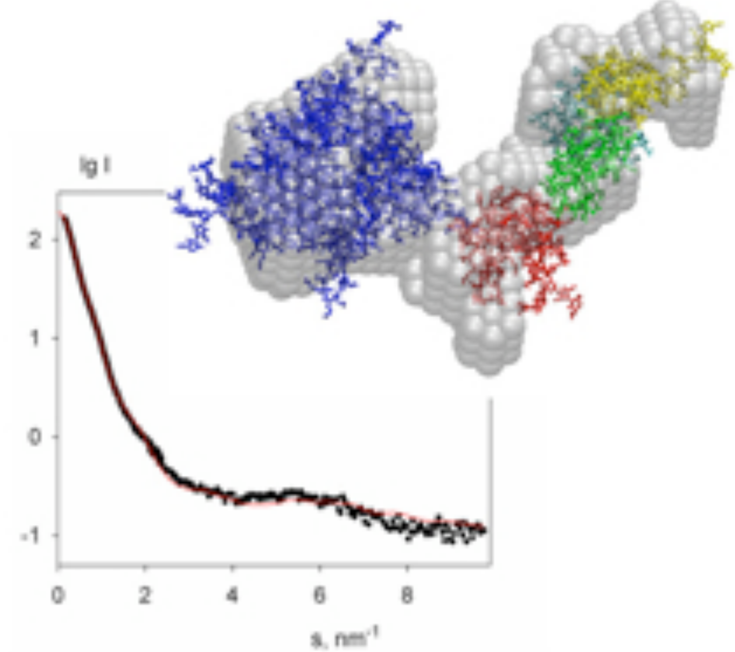
Hemoglobin

courtesy to Dr. I.L.Torriani

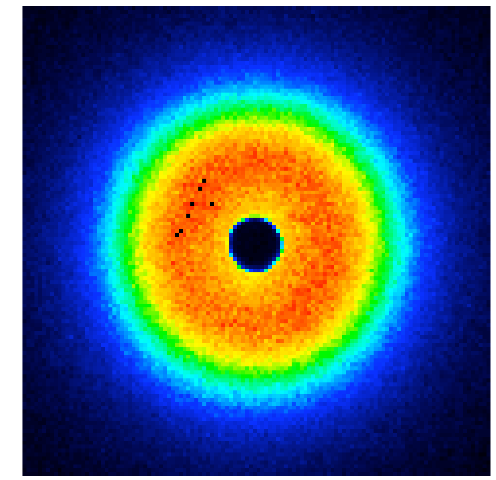
Application of SAXS



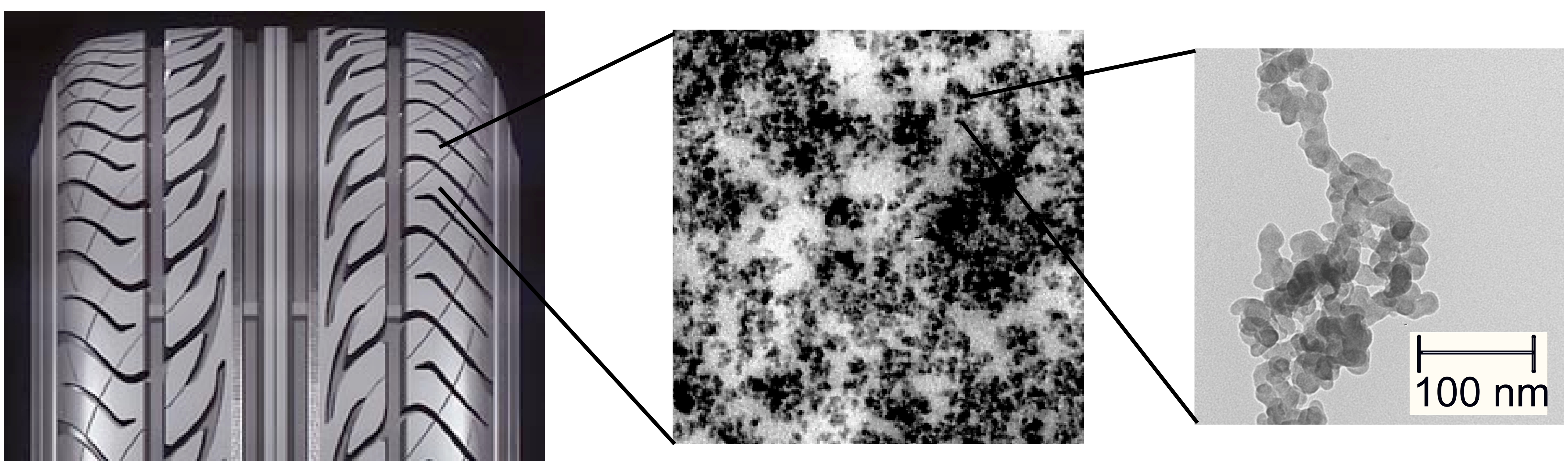
gel



Proteins in solution (Dr. Svergun, EMBL)



Typical SAXS image

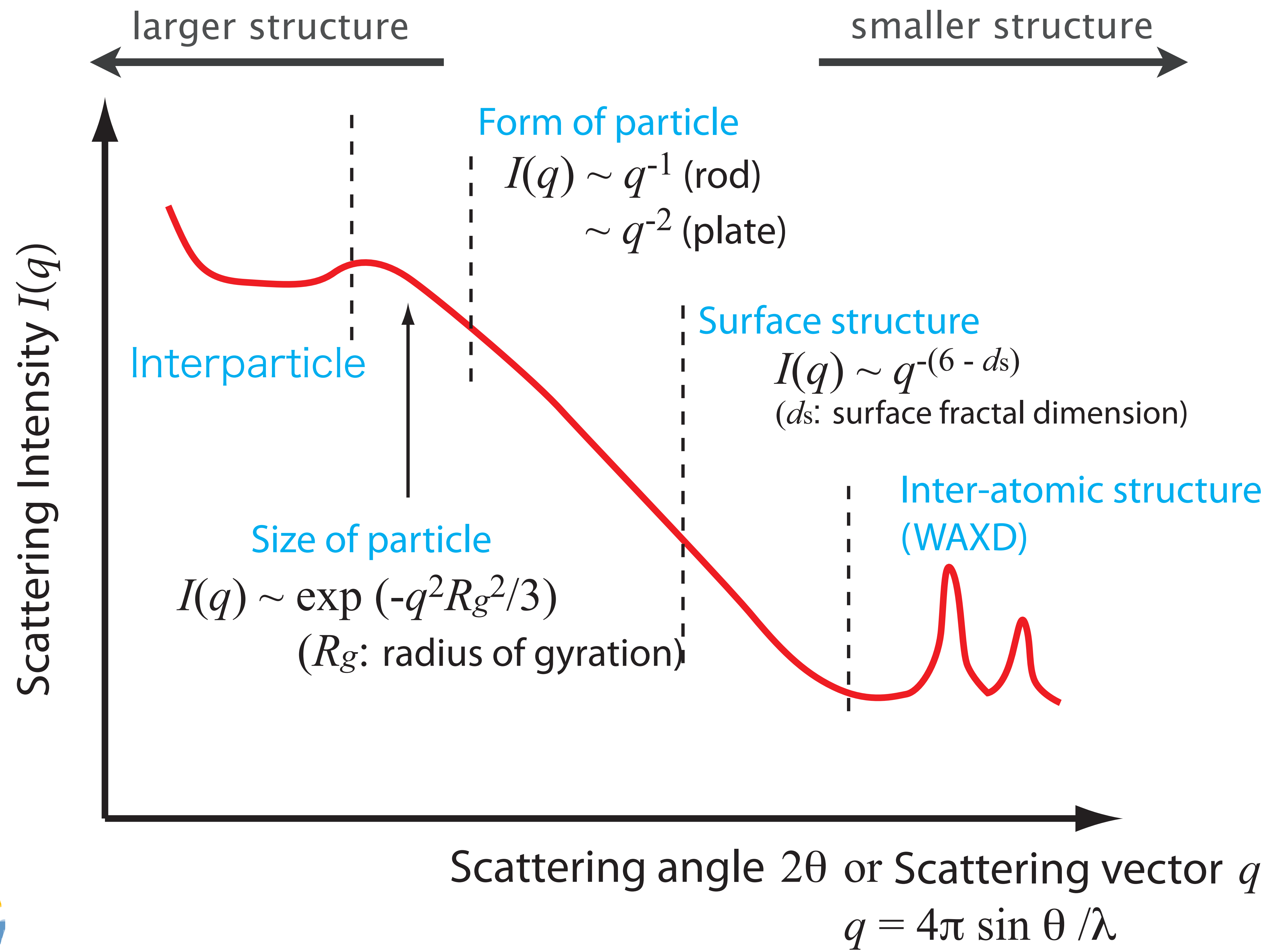


Nanocomposite

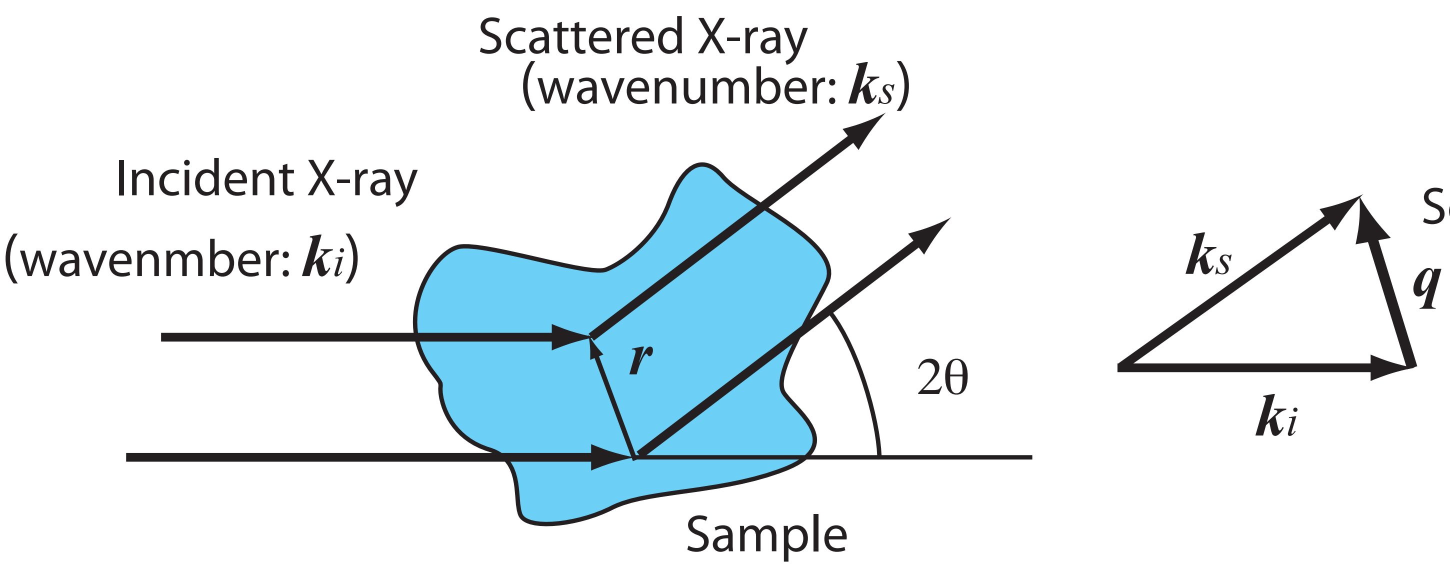
Application of SAXS

- Size and form of particulate system
  - Colloids, Globular proteins, etc...
- Inhomogeneous structure
  - Polymer chain, two-phase system etc.
- Distorted crystalline structure
  - Crystal of soft matter

SAXS of particulate system



Basic of X-ray scattering



$\rho(\boldsymbol{r})$: electron density

$q = |\boldsymbol{q}| = 4\pi \sin\theta / \lambda$

Amplitude of scattered X-ray $$A(\boldsymbol{q}) = \int_V \rho(\boldsymbol{r}) \exp(-\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{r}) \mathrm{d}\boldsymbol{r}$$

Fourier transform of electron density

Scattering intensity per unit volume: $$I(\boldsymbol{q}) = \frac{A(\boldsymbol{q}) A^*(\boldsymbol{q})}{V}$$

Correlation Function & Scattering Intensity

Correlation function of electron density per unit volume

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

Patterson Function

(Debye & Bueche 1949)

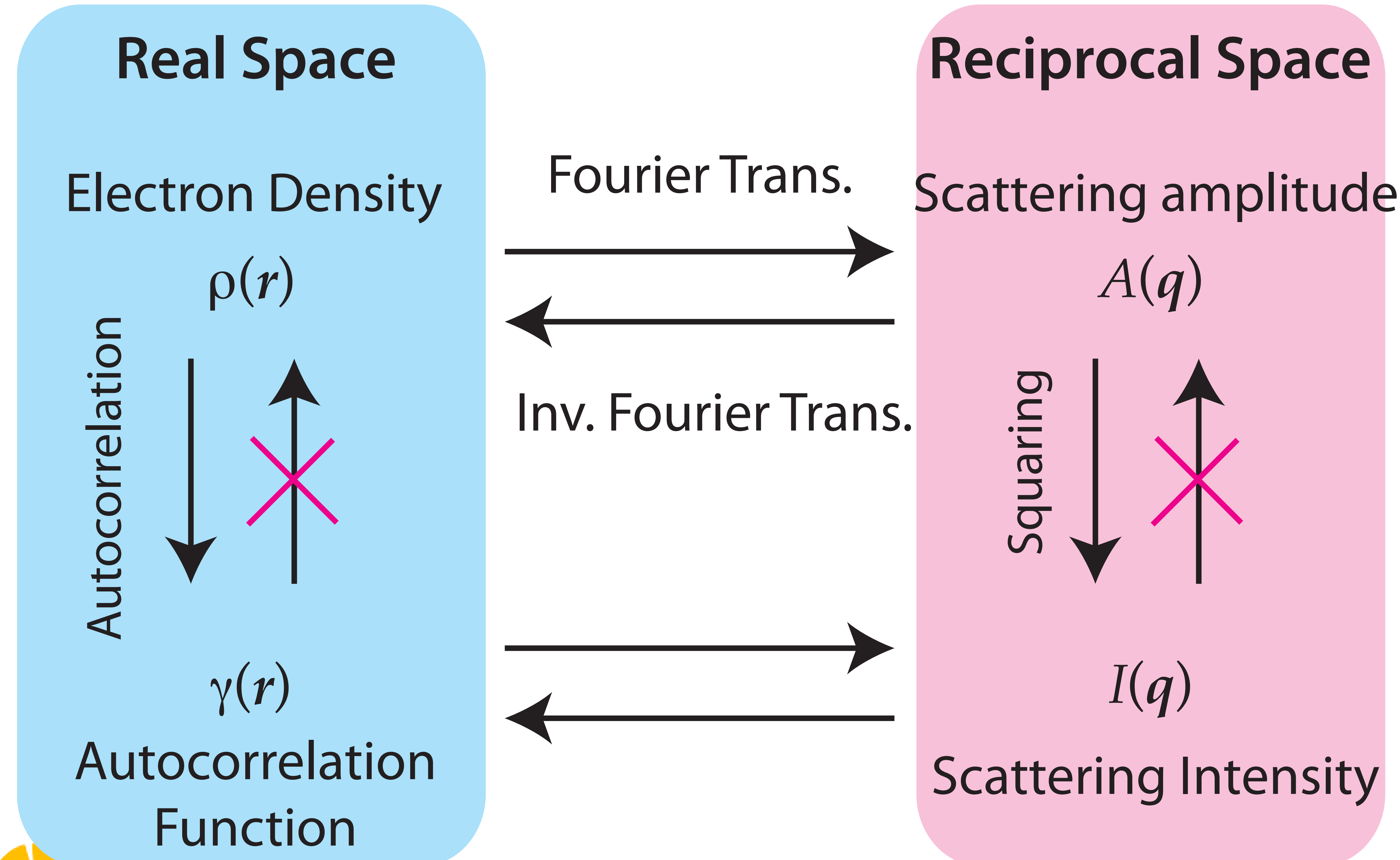
asymptotic behavior of the correlation function

$$\gamma(\boldsymbol{r}=0) = \langle \rho^2 \rangle \qquad \gamma(\boldsymbol{r}\to\infty) \to \langle \rho \rangle^2$$

Scattering Intensity : Fourier Transform of correlation function

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

Real space and Reciprocal Space

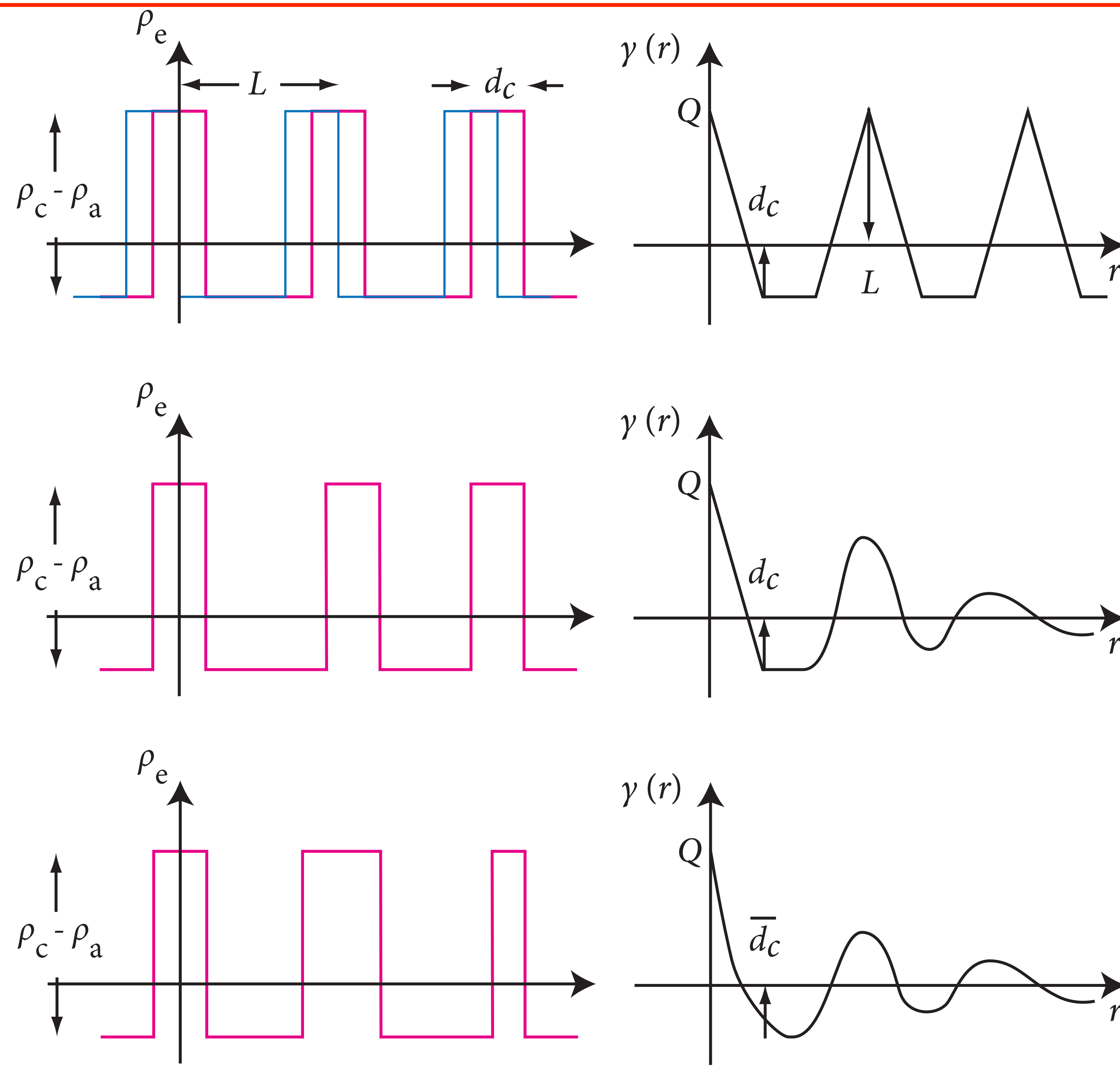


Diffraction from Lamellar Structure

ideal ordering

Long period changes.

Thickness of crystal changes.



real space

autocorrelation

Normalized Correlation Function

Local electron density fluctuations: $\eta(\boldsymbol{r}) = \rho(\boldsymbol{r}) - \langle\rho\rangle$

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

average density fluctuaitons

Normalized Correlation Function

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

substitution

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

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

Only the average density fluctuations contribute to the signal.

Not observable.

Invariant Q

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

Parseval's equality

Omitted.

$$\int I(\boldsymbol{q}) d\boldsymbol{q} = (2\pi)^3 \langle \eta^2 \rangle$$

$$4\pi \int I(q) q^2 dq$$

Parseval's equality

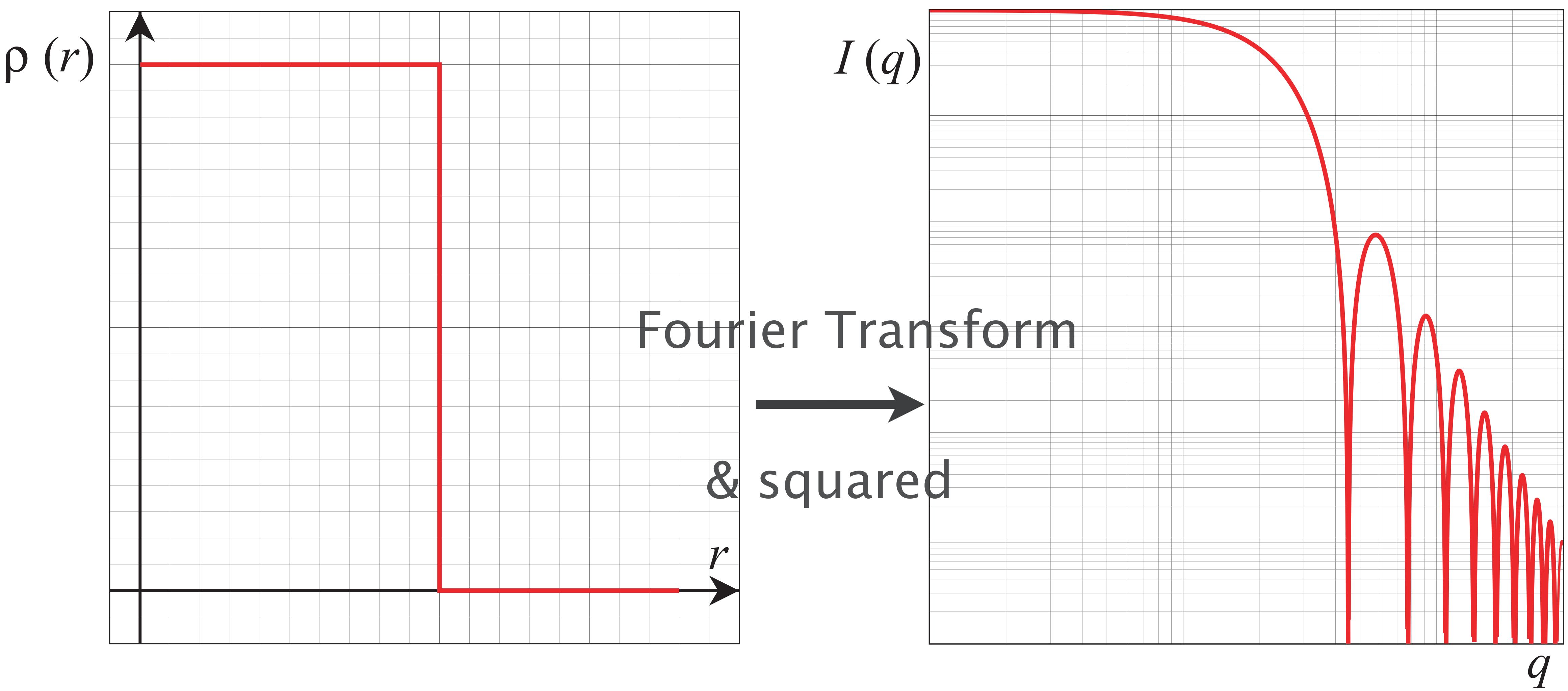
Fourier Trans.

$$A(\boldsymbol{q}) \longleftrightarrow \eta(\boldsymbol{r})$$

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

Invariant: $Q = \int_0^\infty I(q) q^2 dq = 2\pi^2 \langle \eta^2 \rangle$

Spherical sample

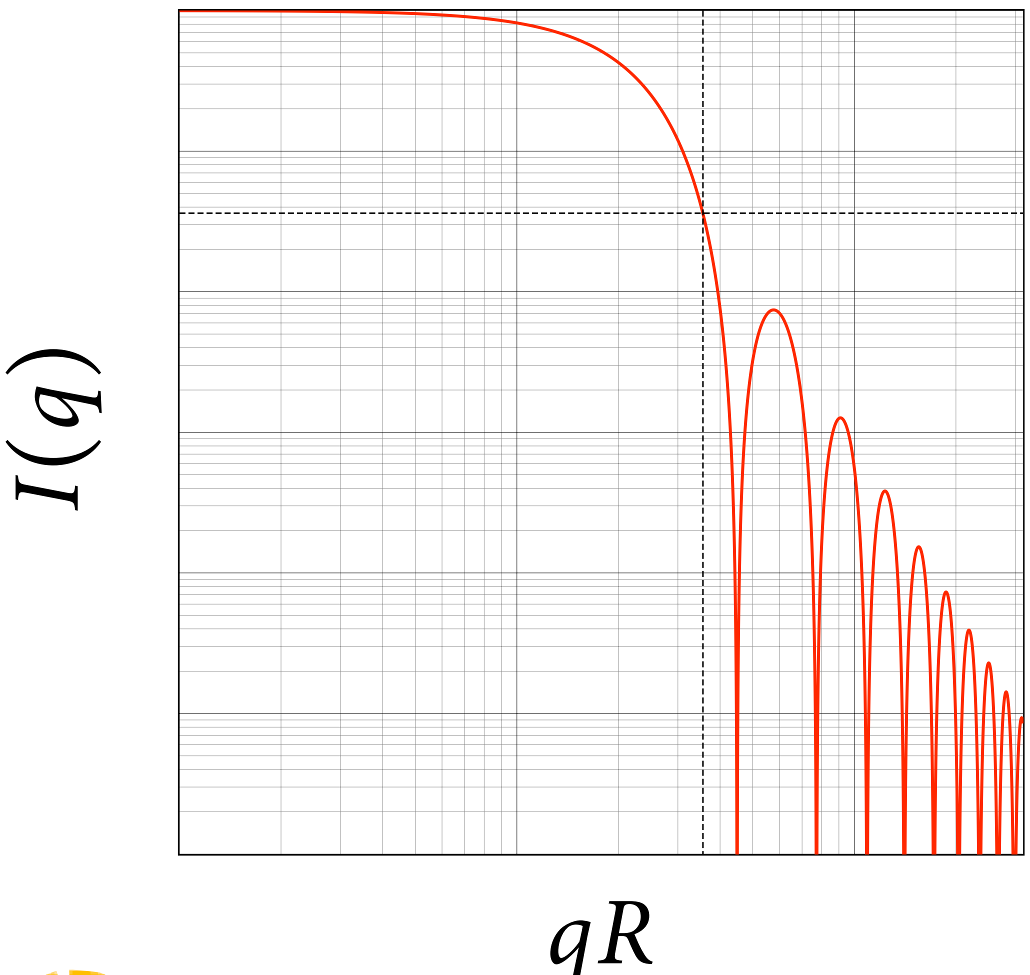


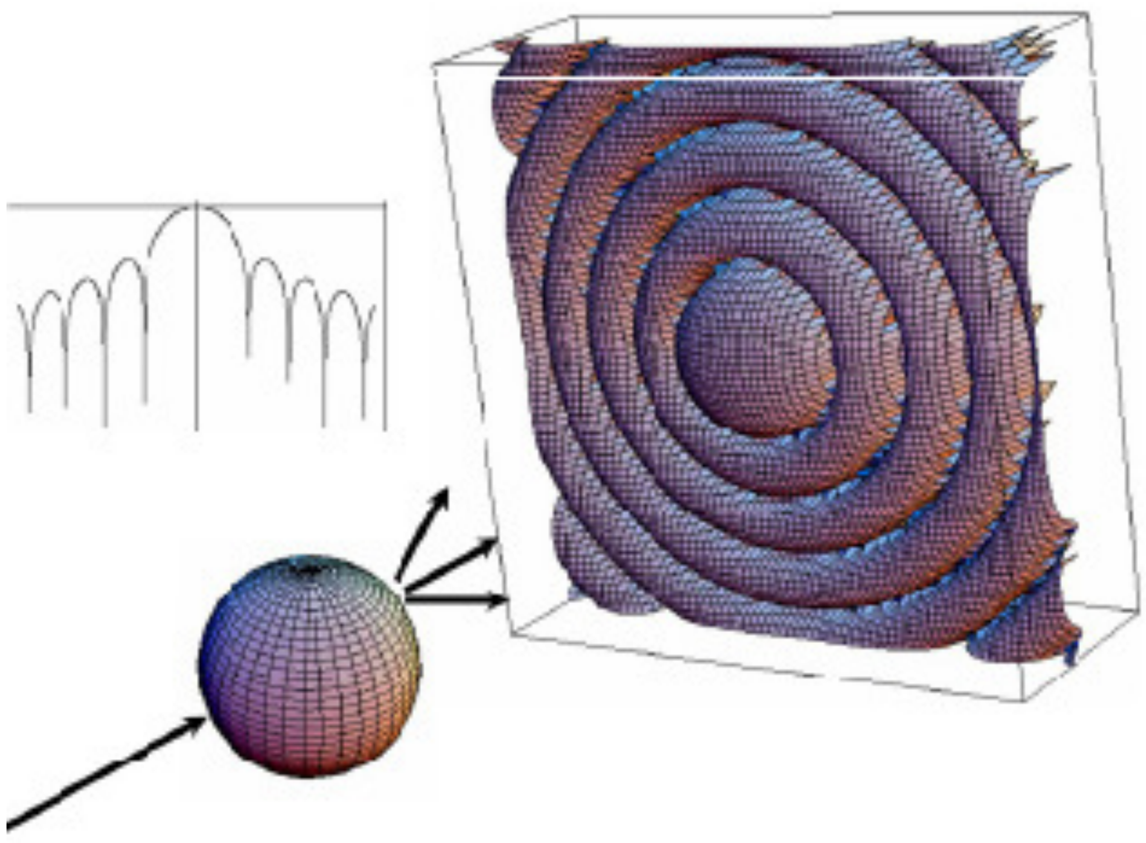
$$\rho(r) = \begin{cases} \Delta\rho & r < R \\ 0 & \text{else} \end{cases}$$

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

Homogeneous sphere

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





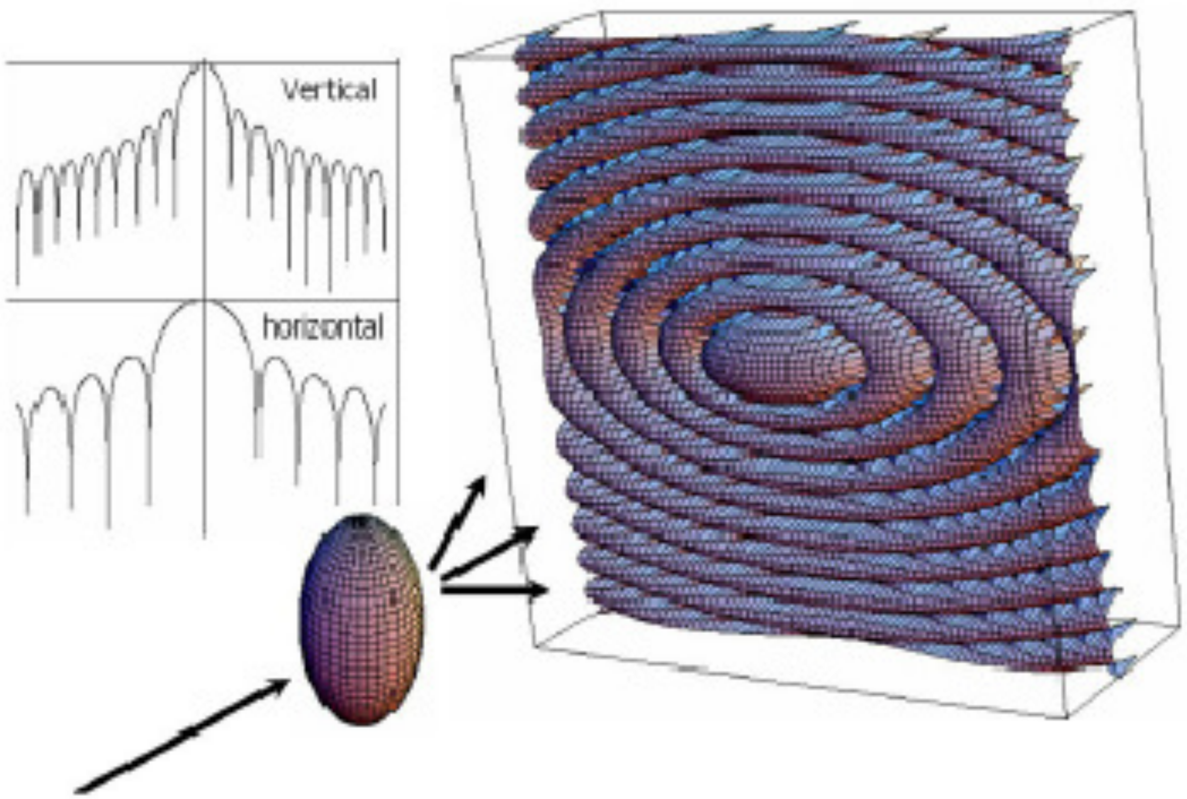
isotropic scattering

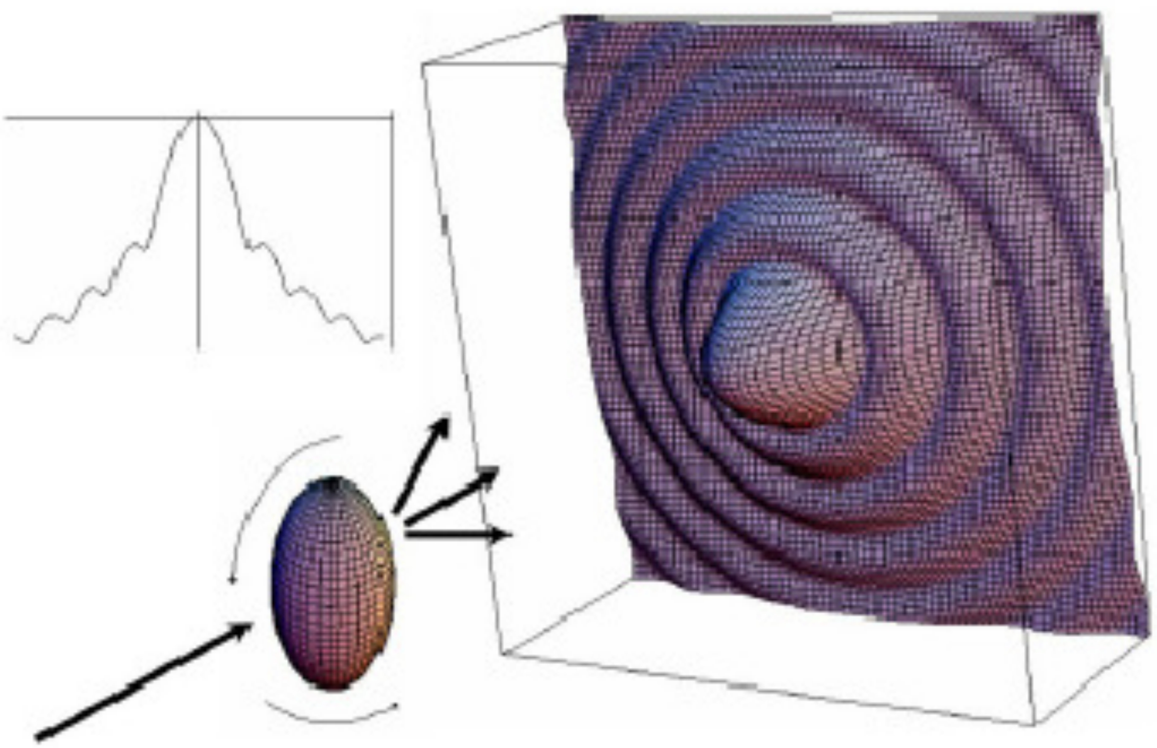
courtesy to Dr. I.L.Torriani

Homogeneous elipsiod

Fixed particle

Random orientation



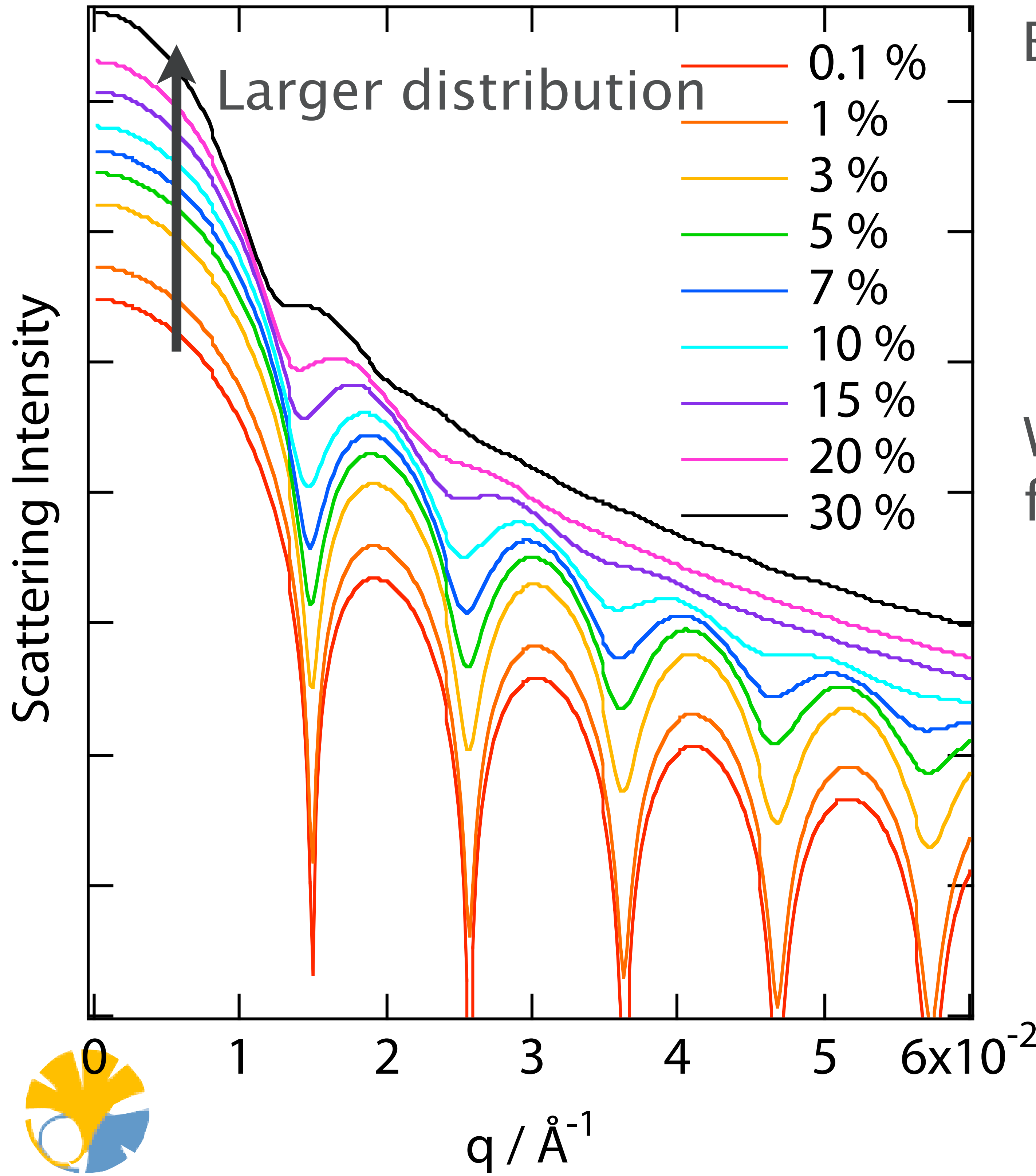


anisotropic scattering

isotropic scattering

courtesy to Dr. I.L.Torriani

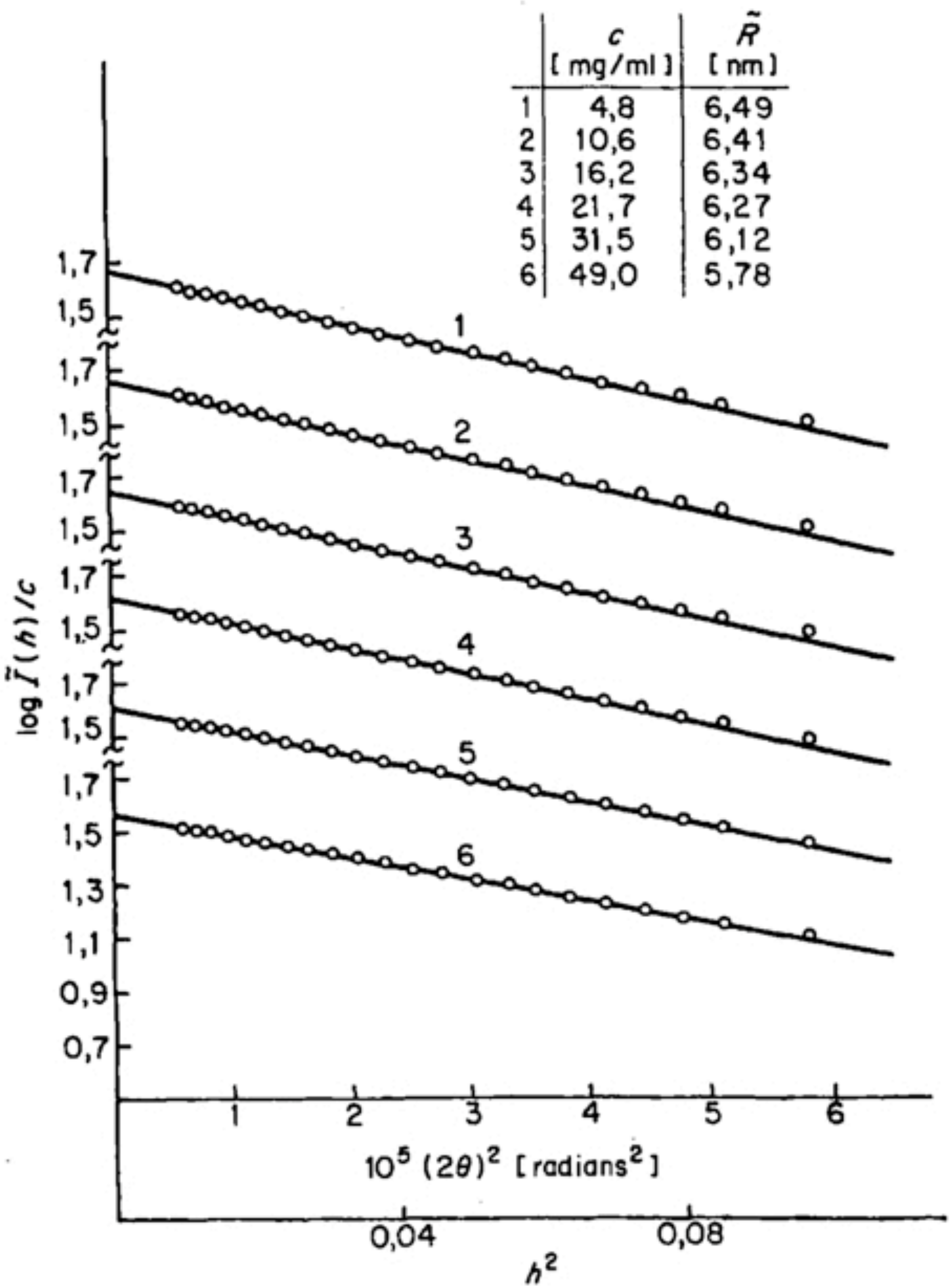
Size distribution



Based on Gaussian distribution

When the form has distribution, fringes are missed.

Radius of Gyration -- Guinier Plot



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

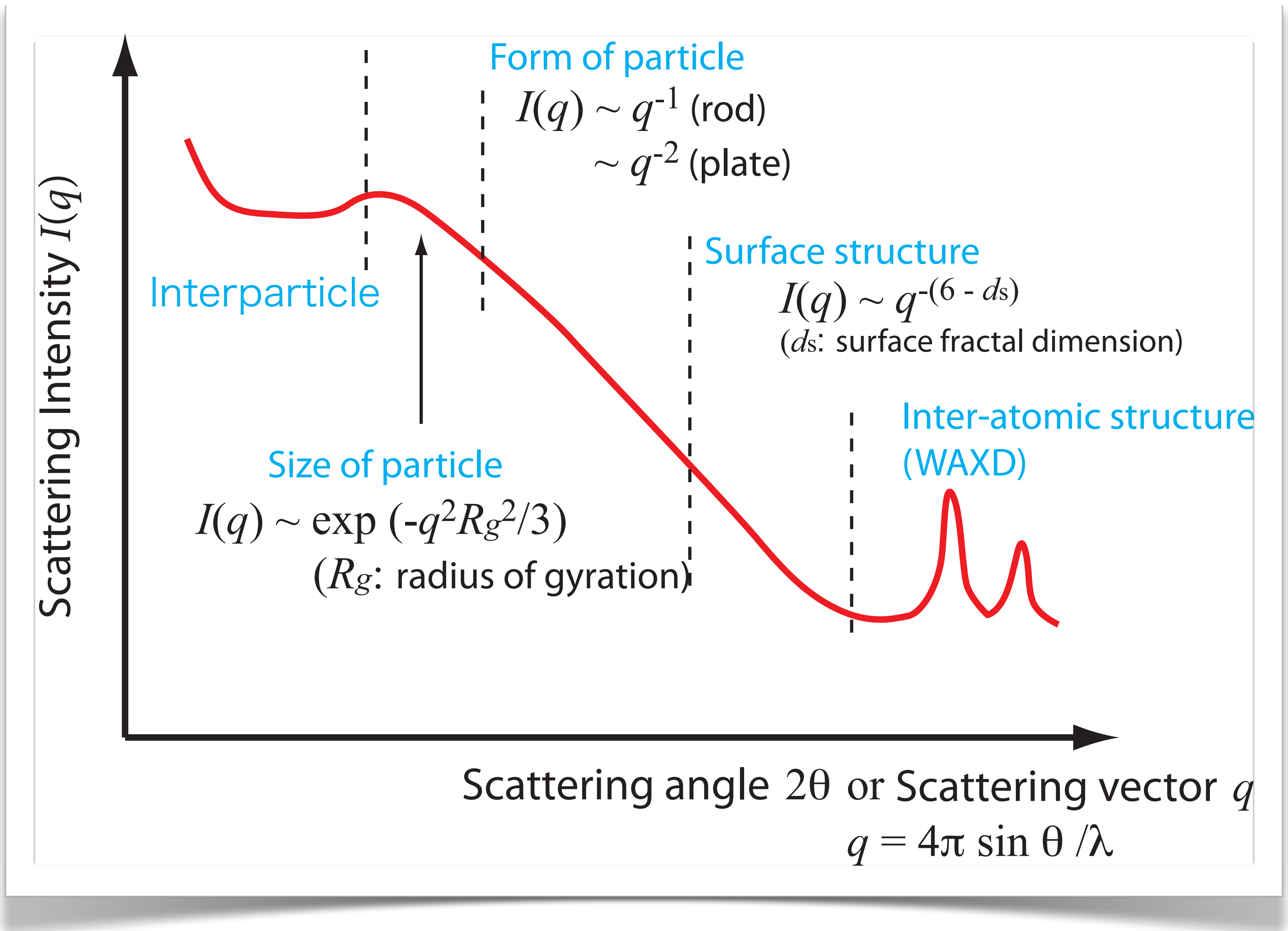
↓

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

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)

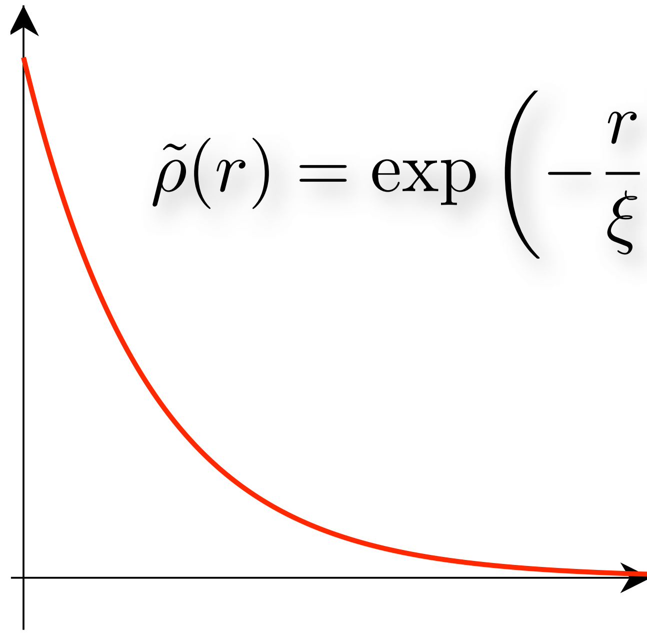
Proposed remedy:

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

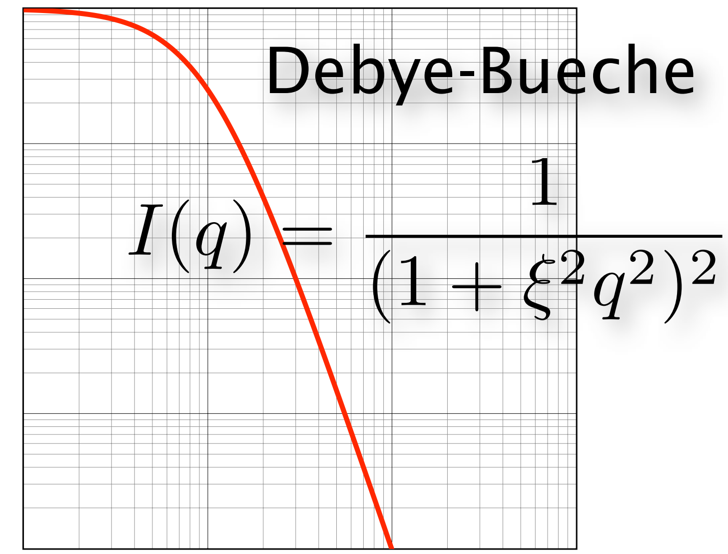
Scattering from Inhomogeneous Structure

Electron Density | **Autocorrelation Function** | **Scattering Intensity**

two phase system



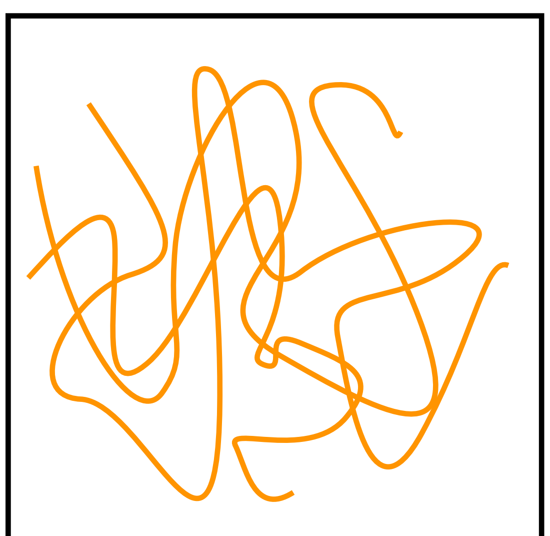
$$\tilde{\rho}(r) = \exp\left(-\frac{r}{\xi}\right)$$



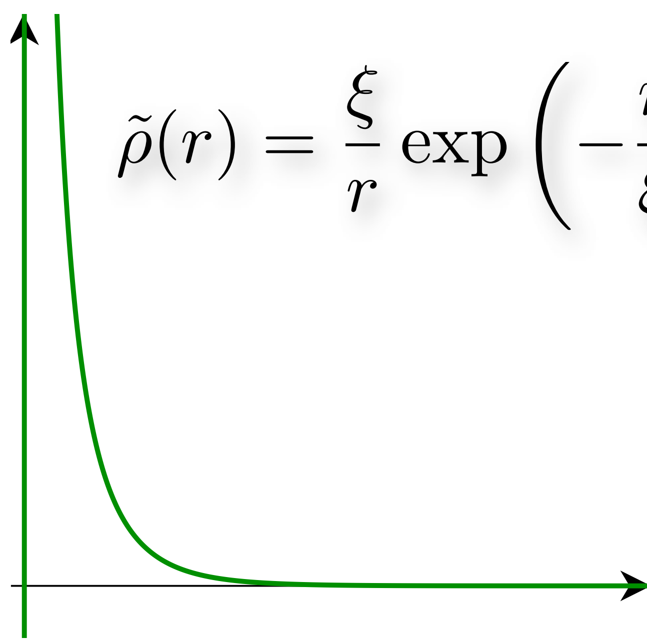
$$I(q) = \frac{1}{(1+\xi^2 q^2)^2}$$

Autocorrelation →

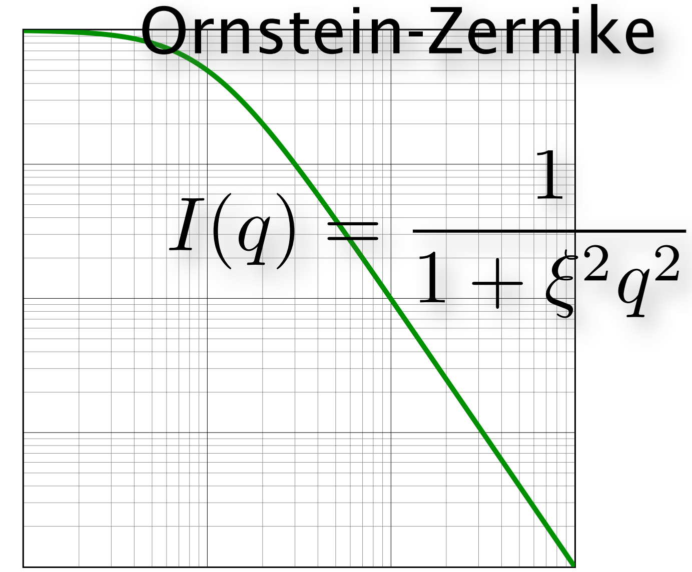
Fourier trans. →



polymer chain etc.



$$\tilde{\rho}(r) = \frac{\xi}{r}\exp\left(-\frac{r}{\xi}\right)$$



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

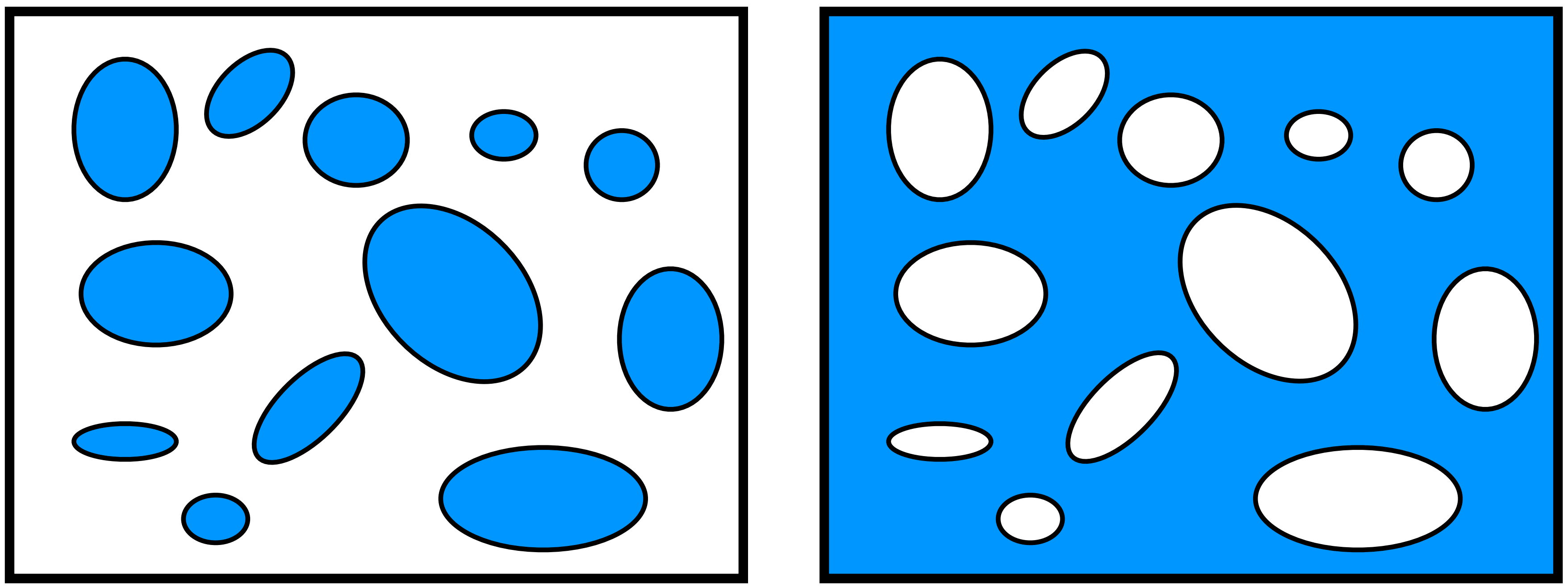
Two-phase system

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

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

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

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



Babinet's principle

Two complementary structures produce the same scattering.

Two-phase system -- cont.

Averaged square fluctuation of electron density

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

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

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

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

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}.

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

internal surface area

Combination of Porod's law & Invariant

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

surface-volume ratio

important for the characterization of porous materials

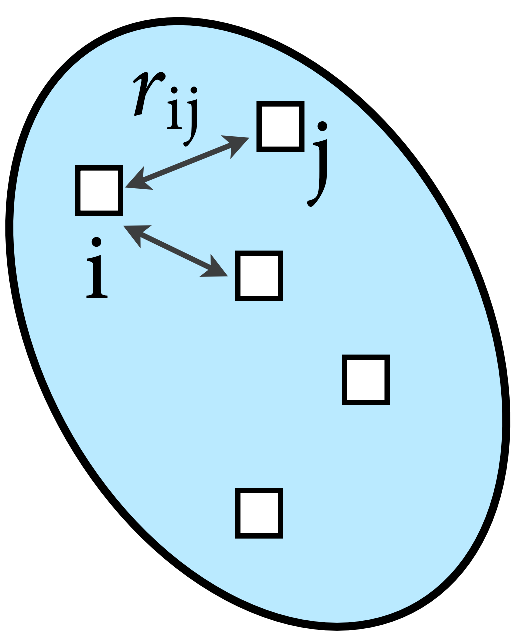
Intensity for random particle system

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

Pair distance distribution function :PDDF $\quad p(r) = r^2 \gamma_0(r)$

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.

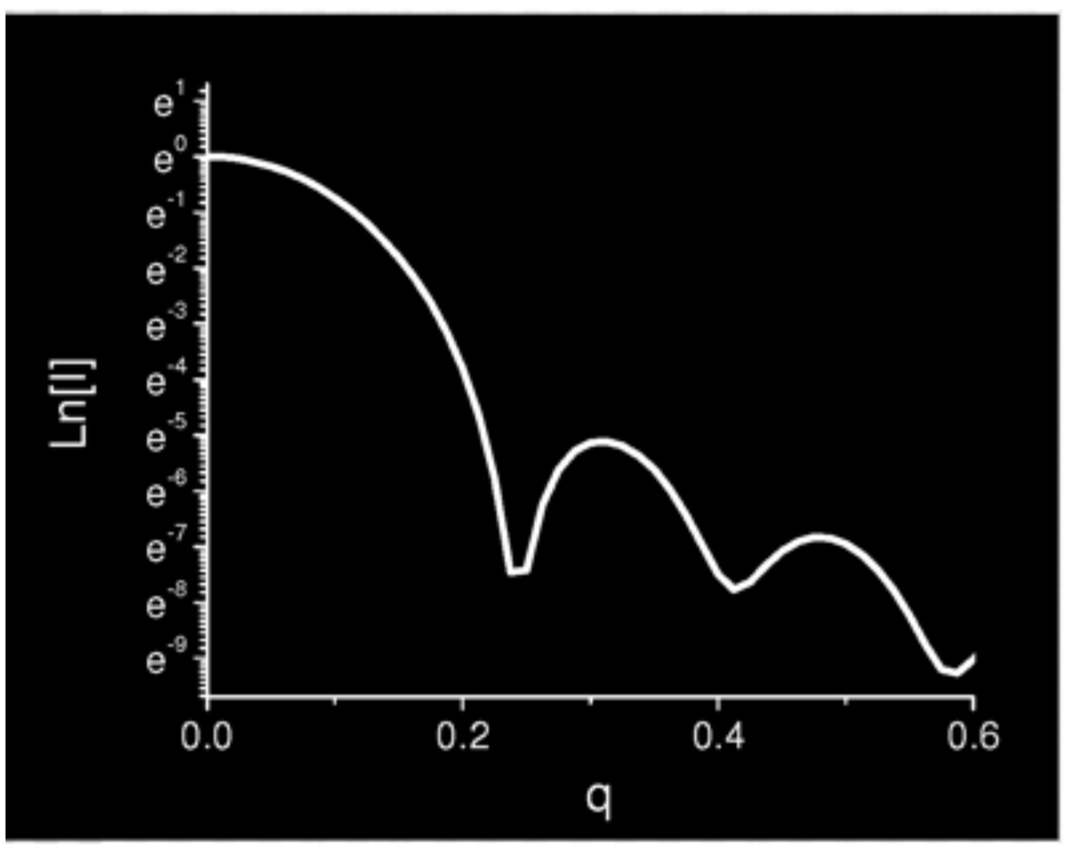


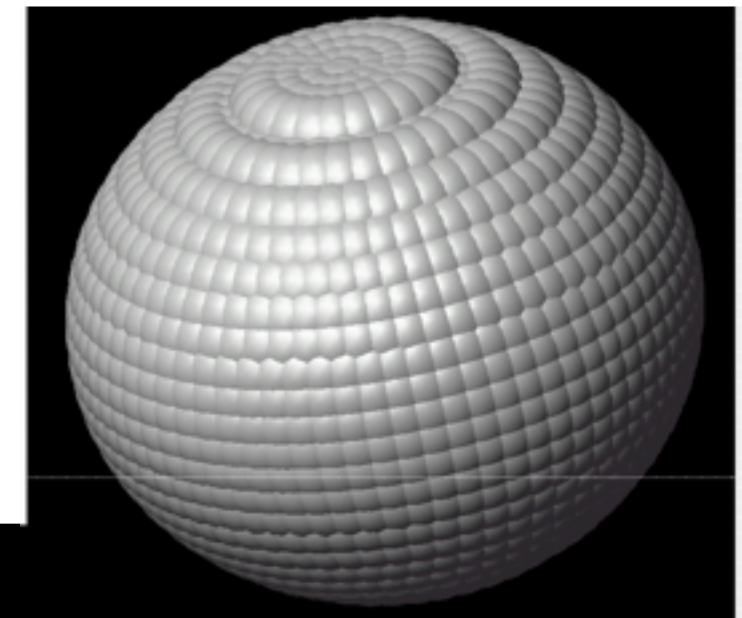
pairs of volume elements i-j

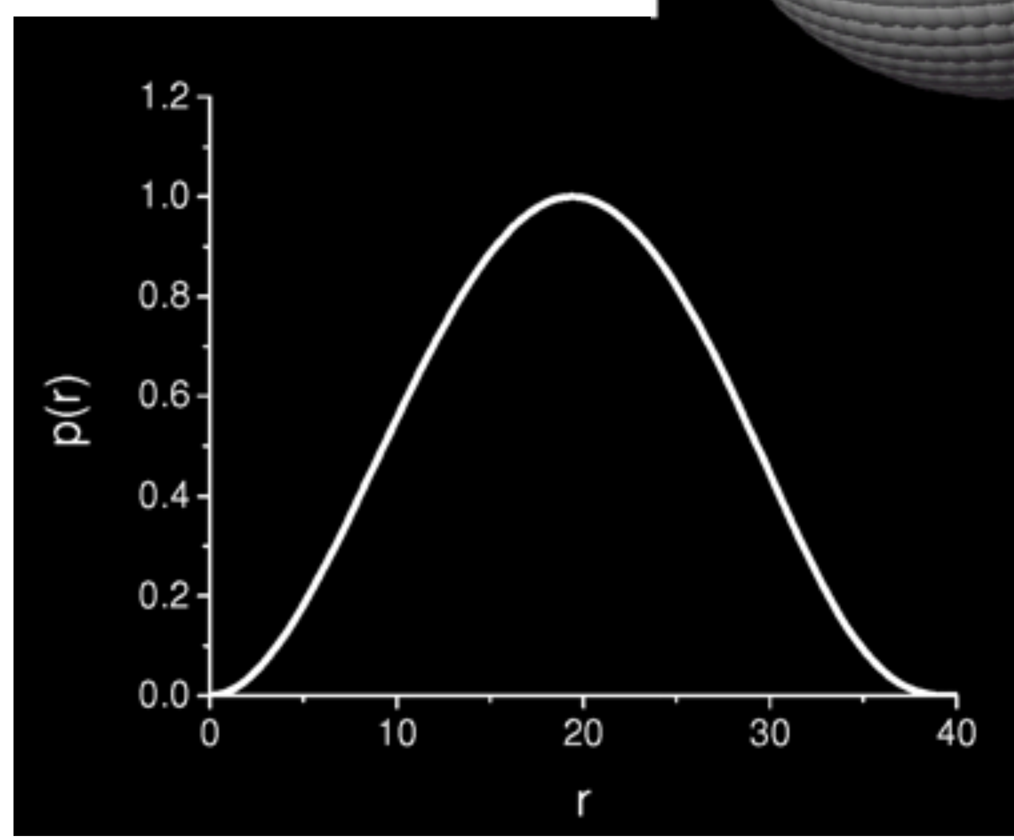
histogram o all intra-particle distances

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

Spherical particle

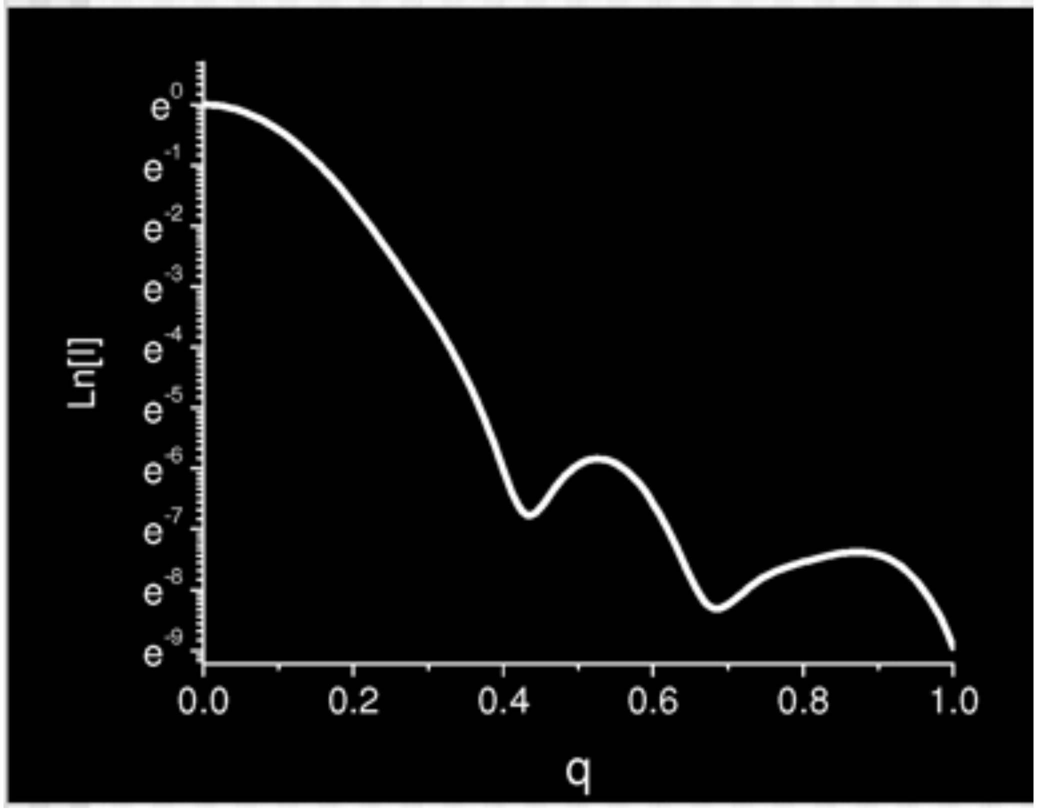


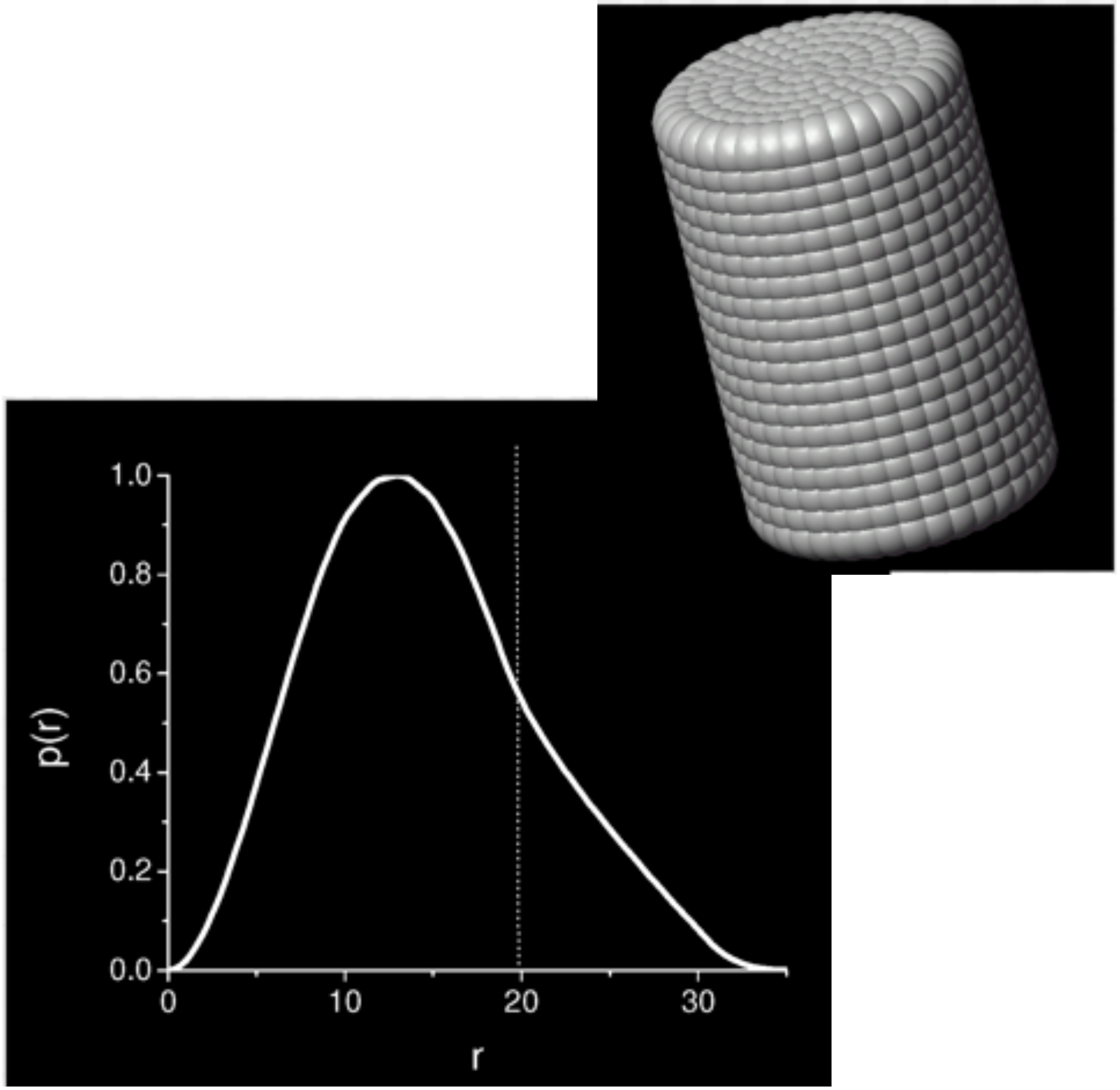




courtesy to Dr. I.L.Torriani

Cylindrical particle





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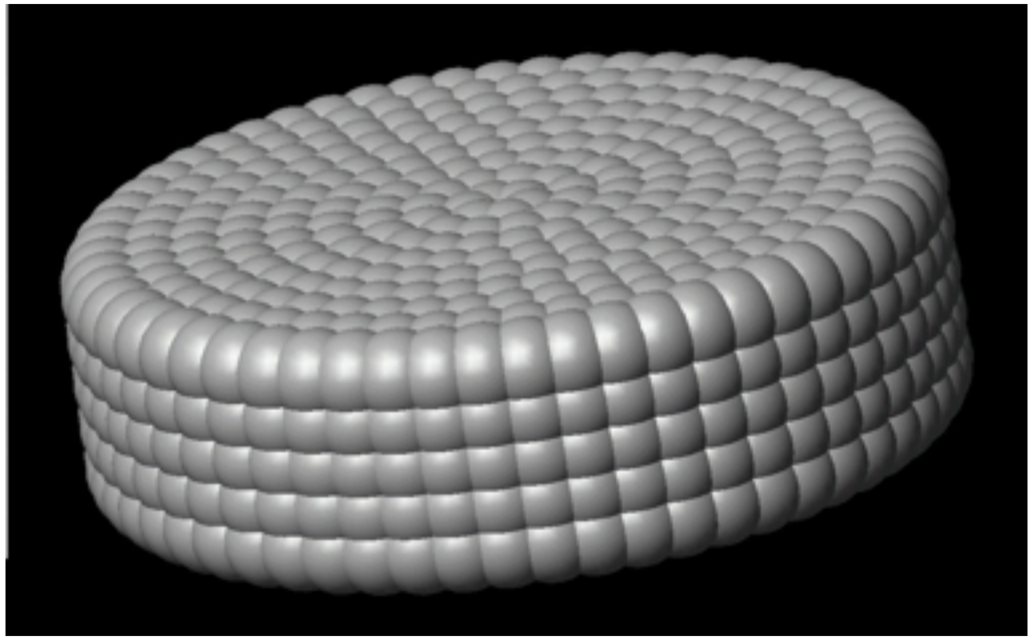
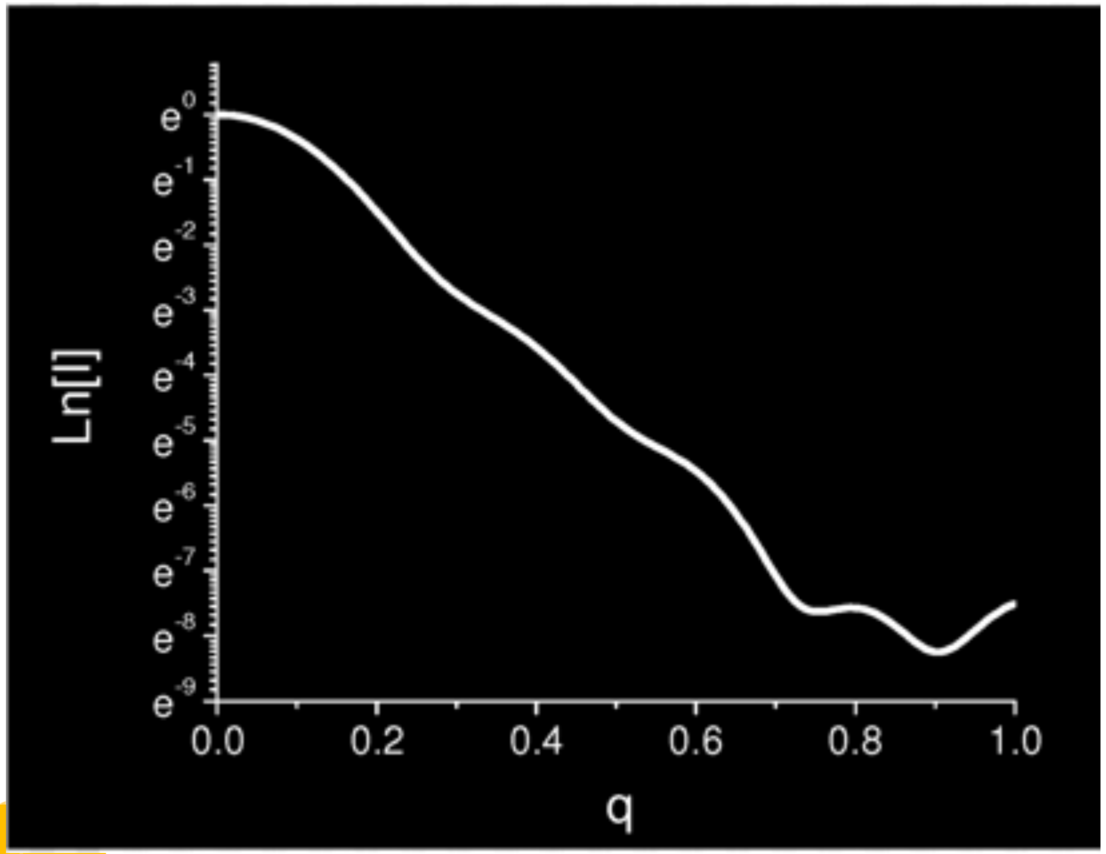
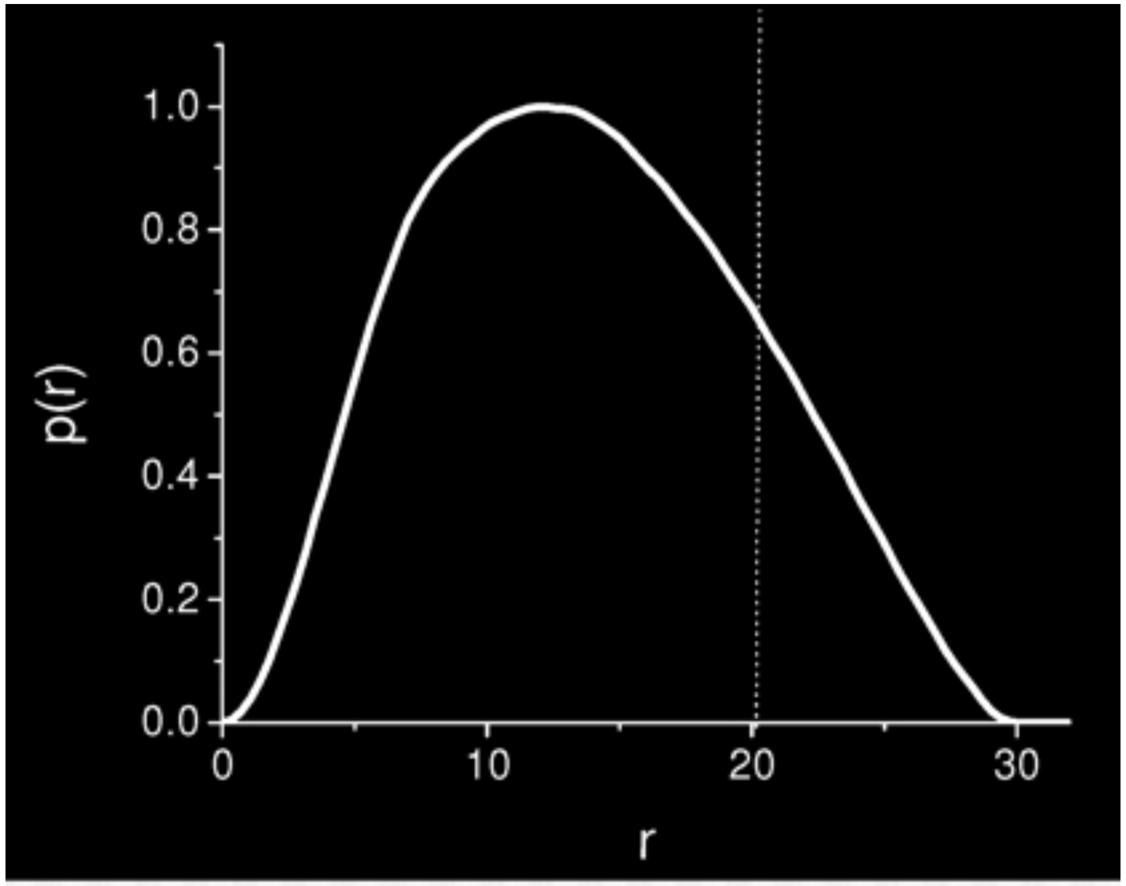
Flat particle







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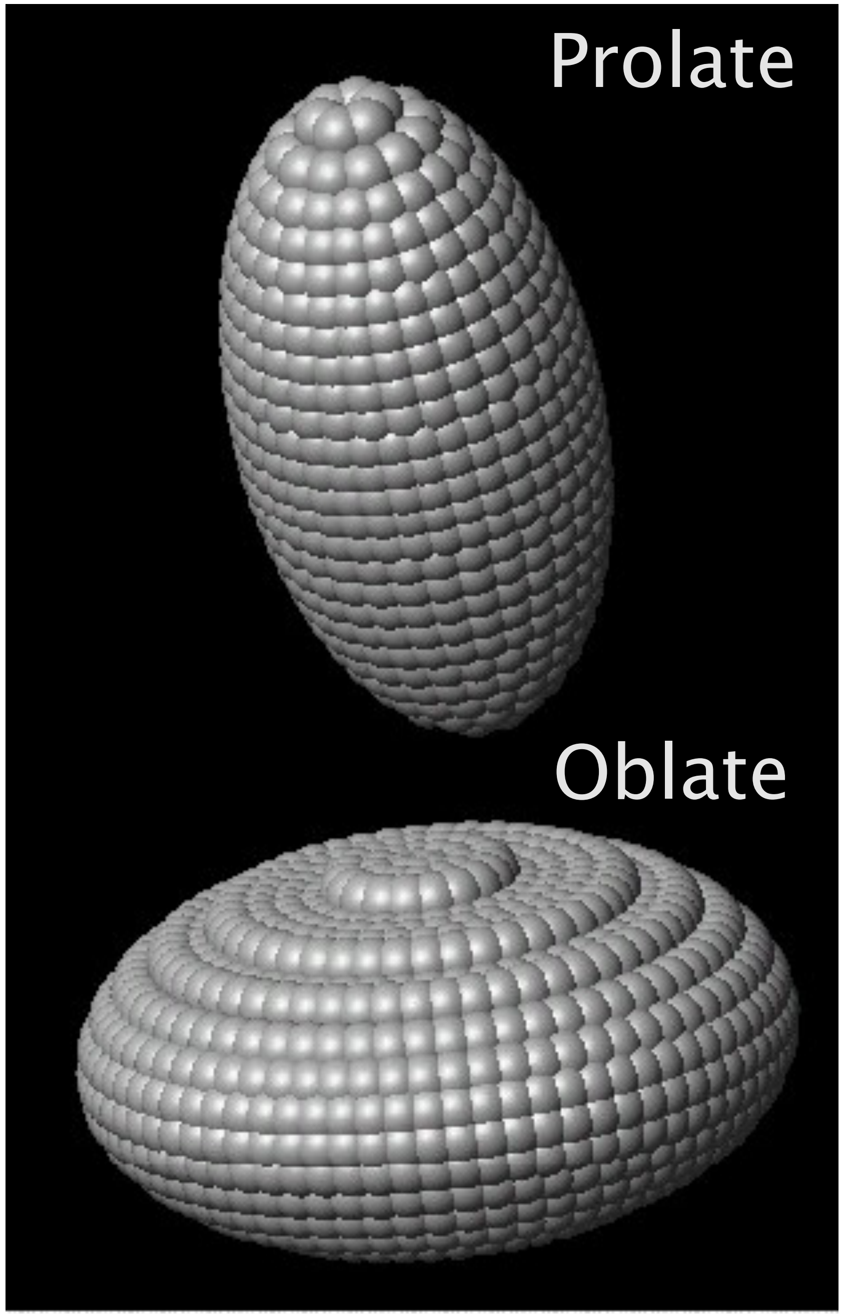
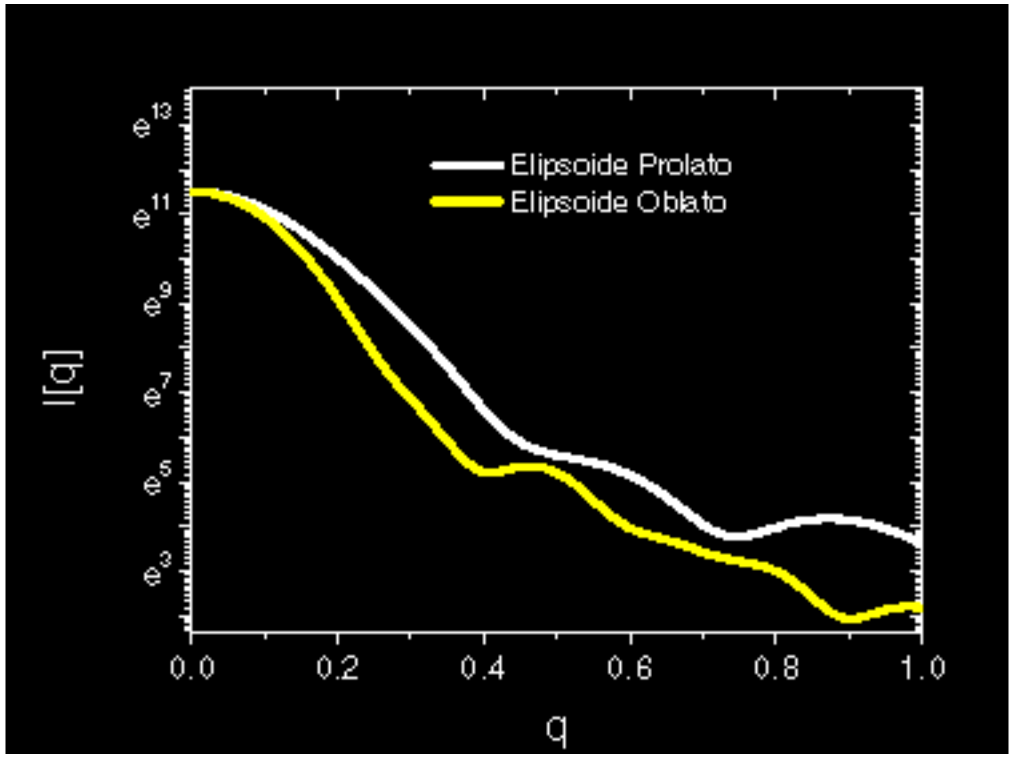
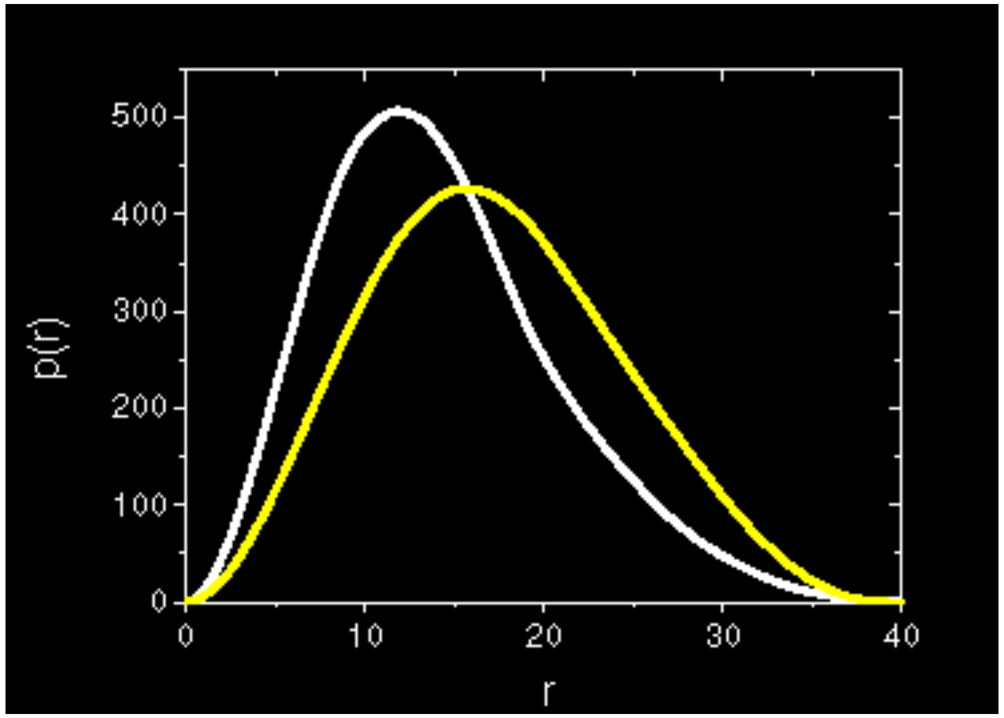
Ellipsoids







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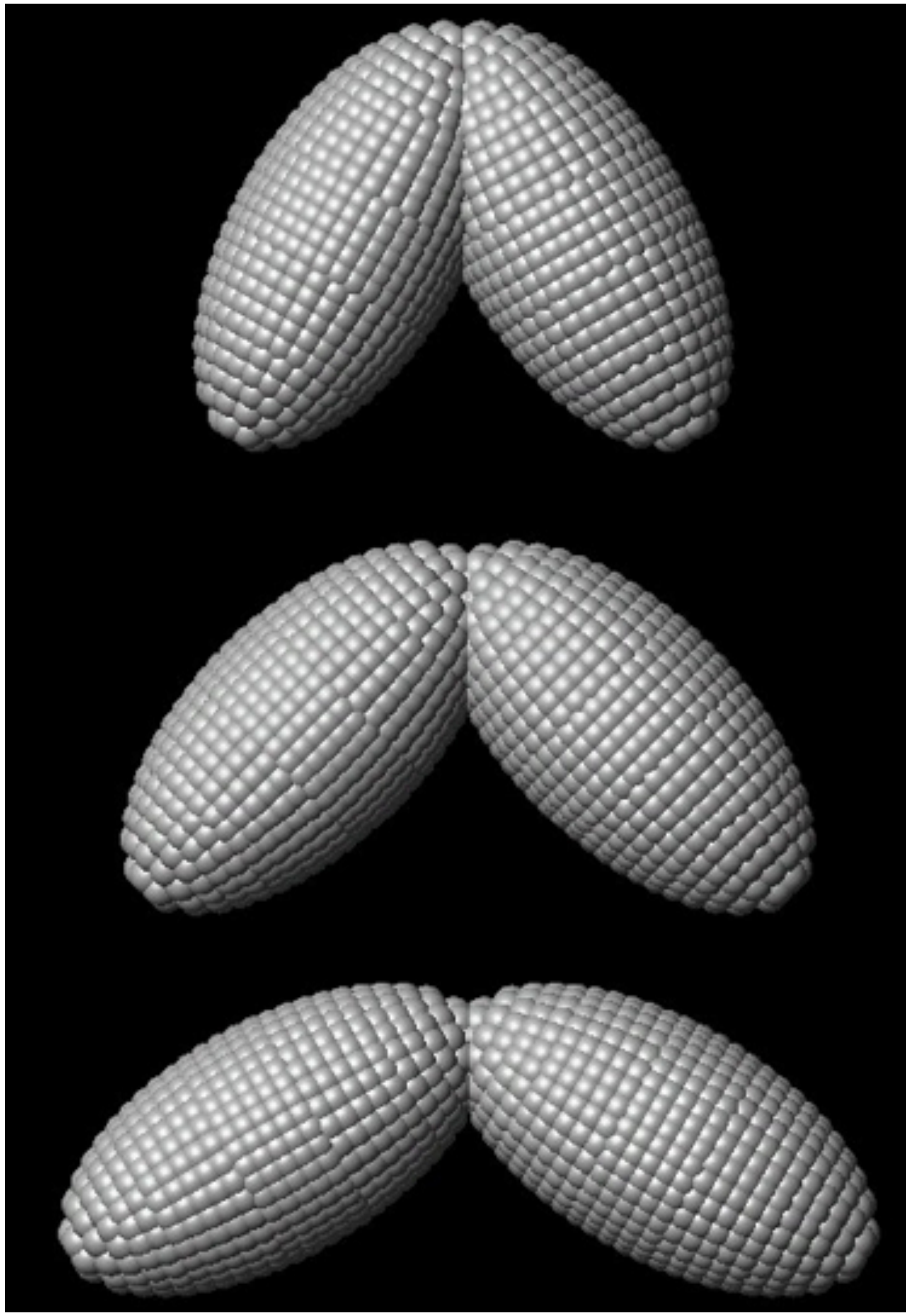
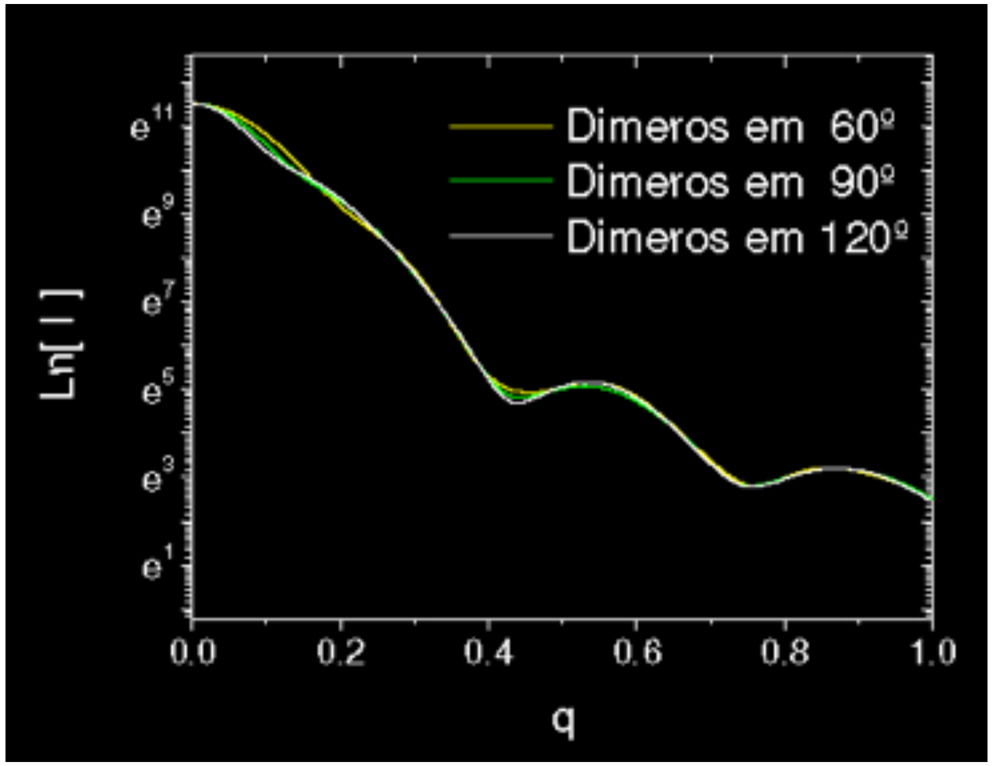
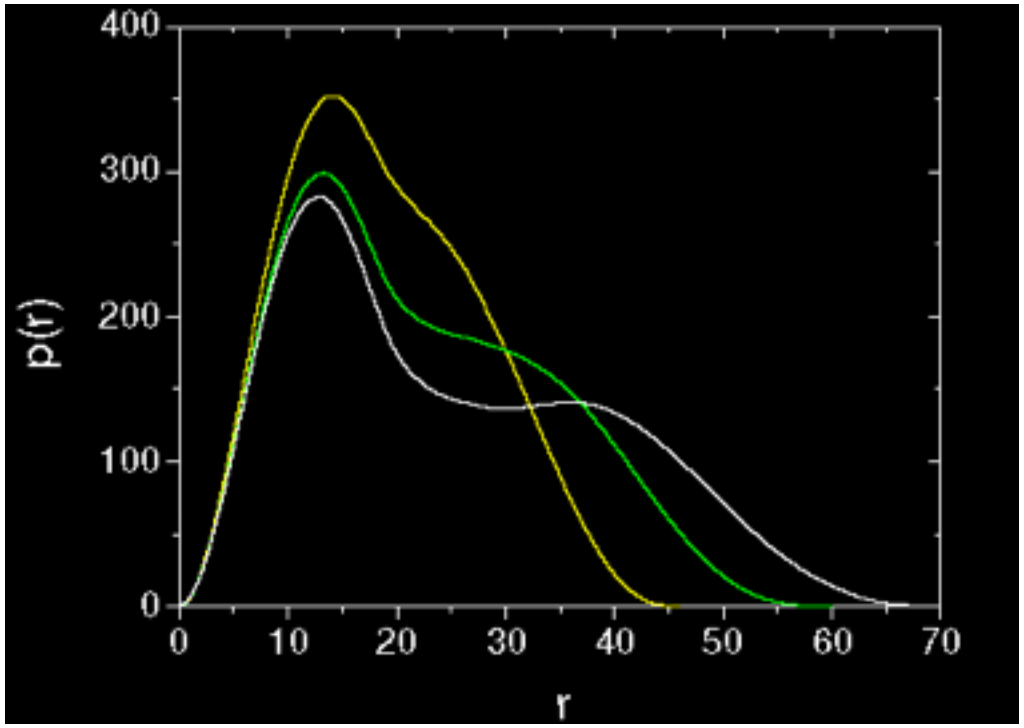
Two ellipsoid = dimer







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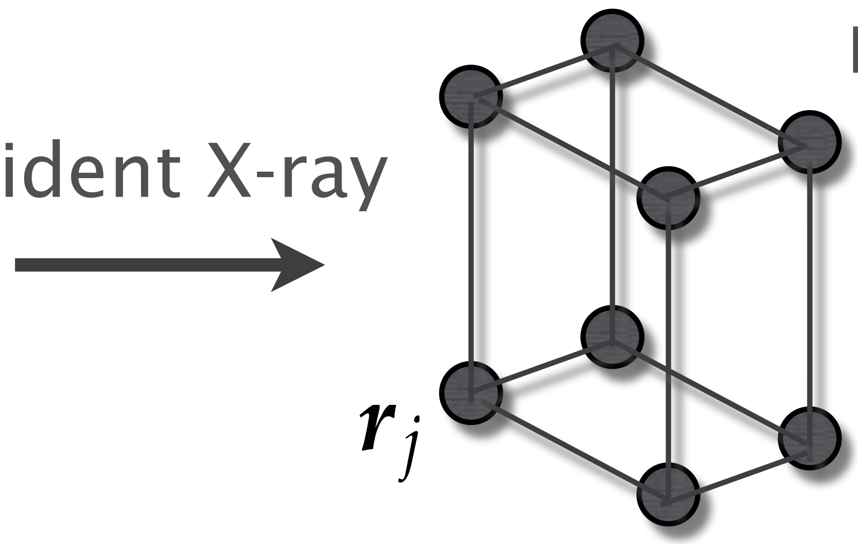
Diffraction from Periodic Structure

Incident X-ray



Diffraction from Unit cell (Crystalline structure factor)

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

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

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

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

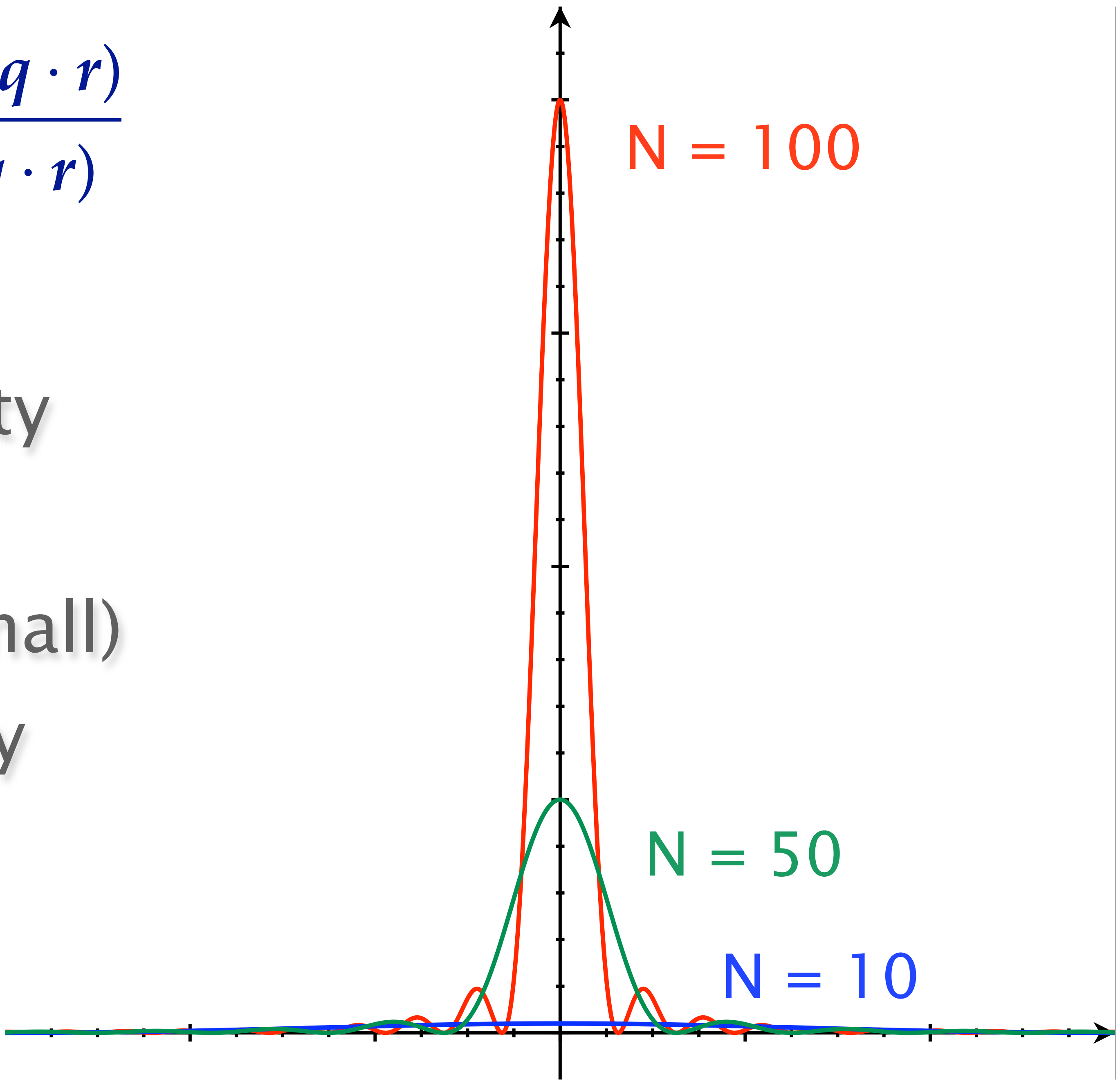
- Maximum ~ N^2
- FWHM ~ $2\pi/N$
  - FWHM --> Size of crystal

Laue Function

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

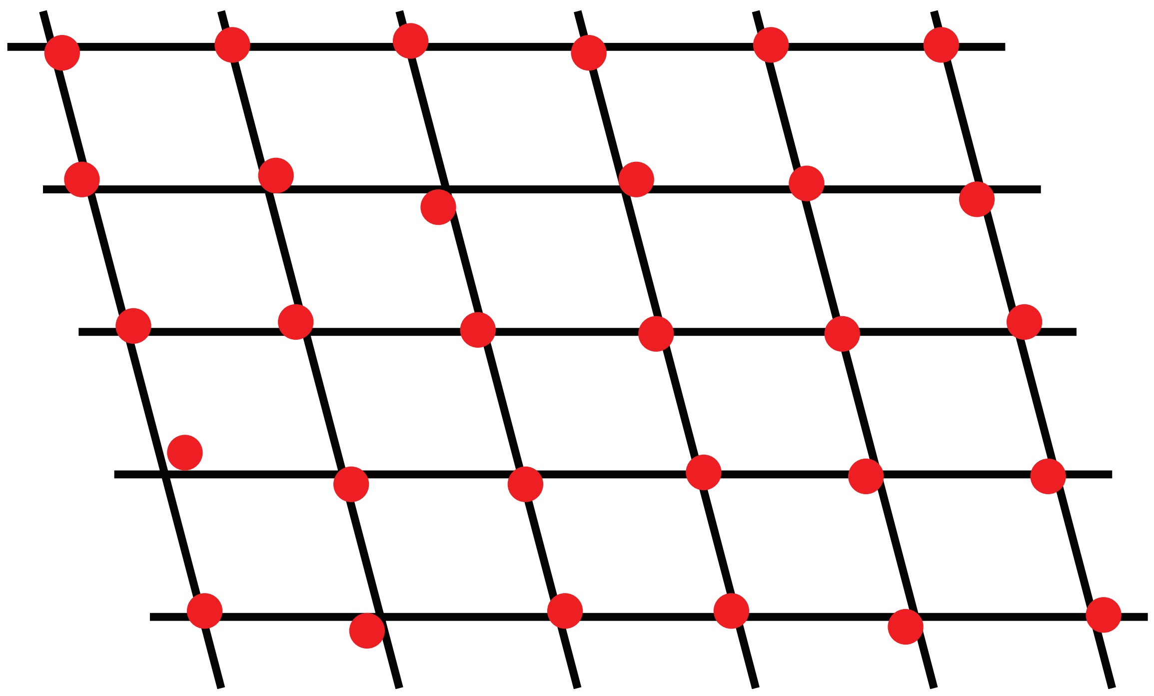
- Large crystal
  - High diffraction intensity
  - Narrow FWHM
- Soft matter (crystal size: small)
  - Low diffraction intensity
  - Wide FWHM

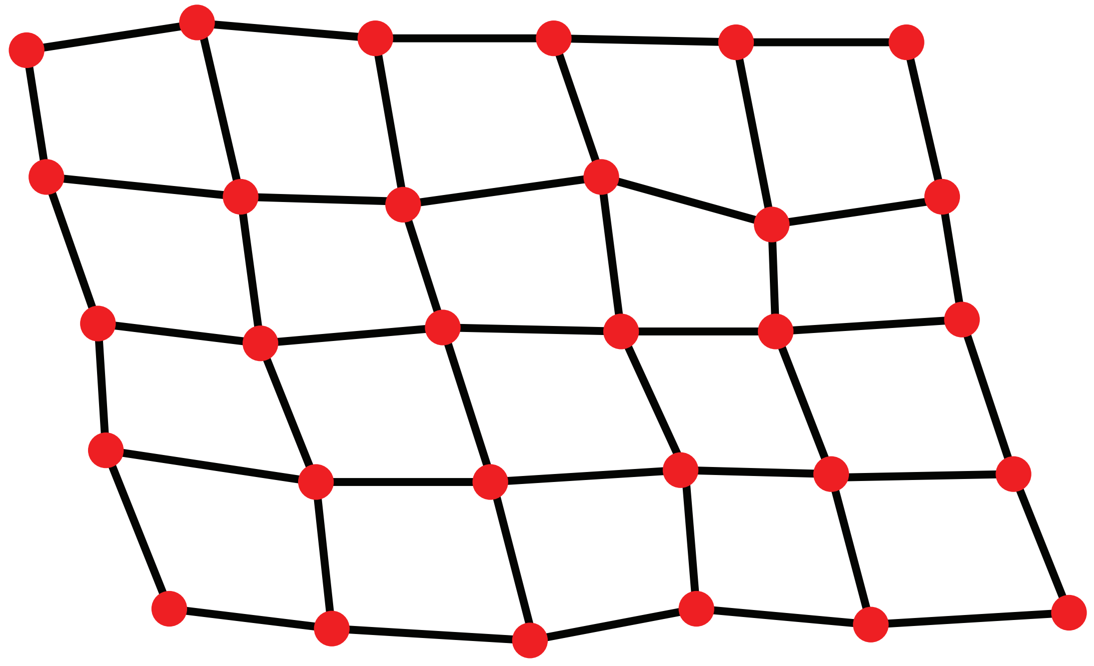
→ low S/N



Crystal size --> Intensity & FWHM of diffraction

Imperfection of crystal (2D)





Imperfection of 1st kind

Thermal fluctuation etc.

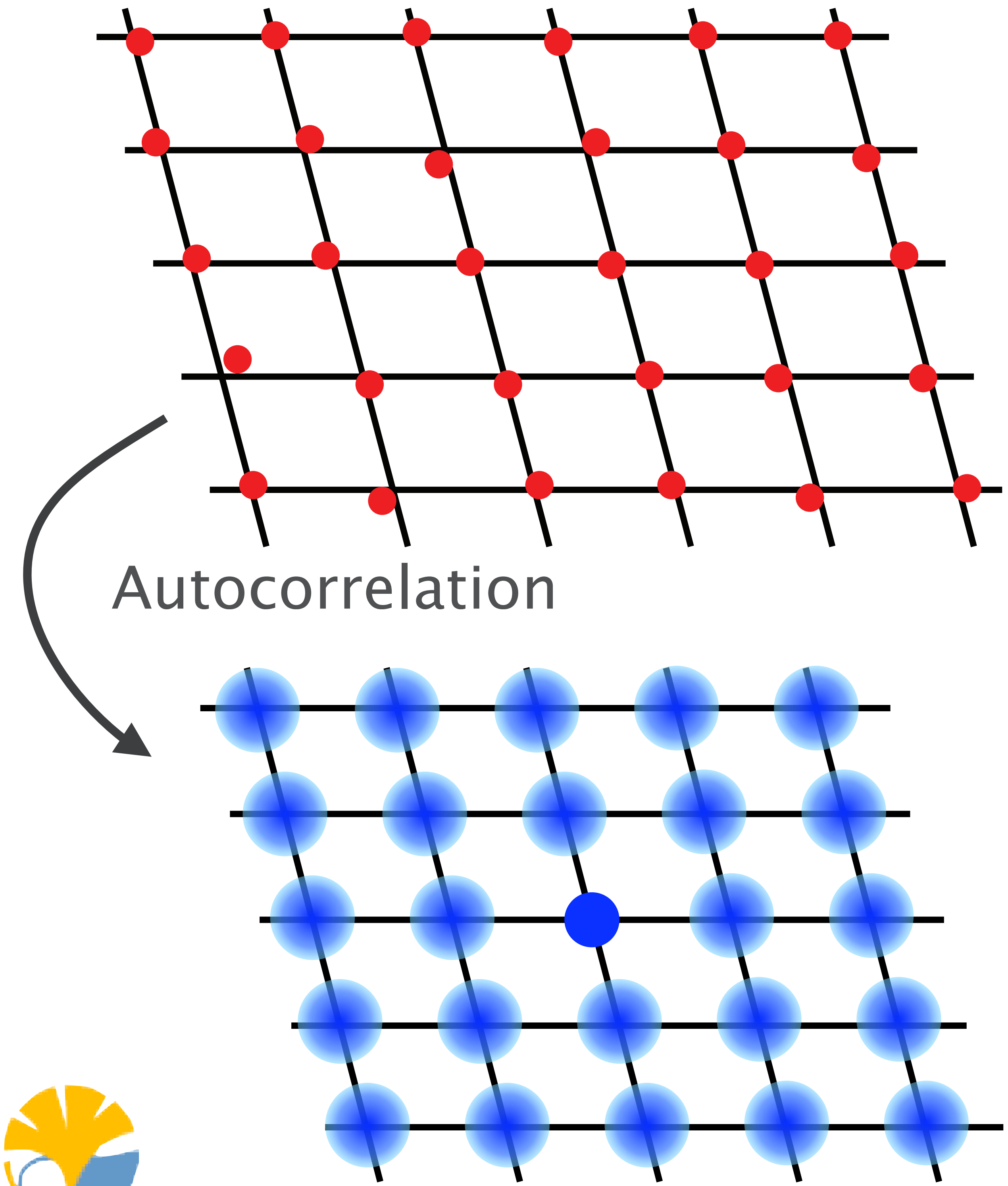
Imperfection of 2nd kind

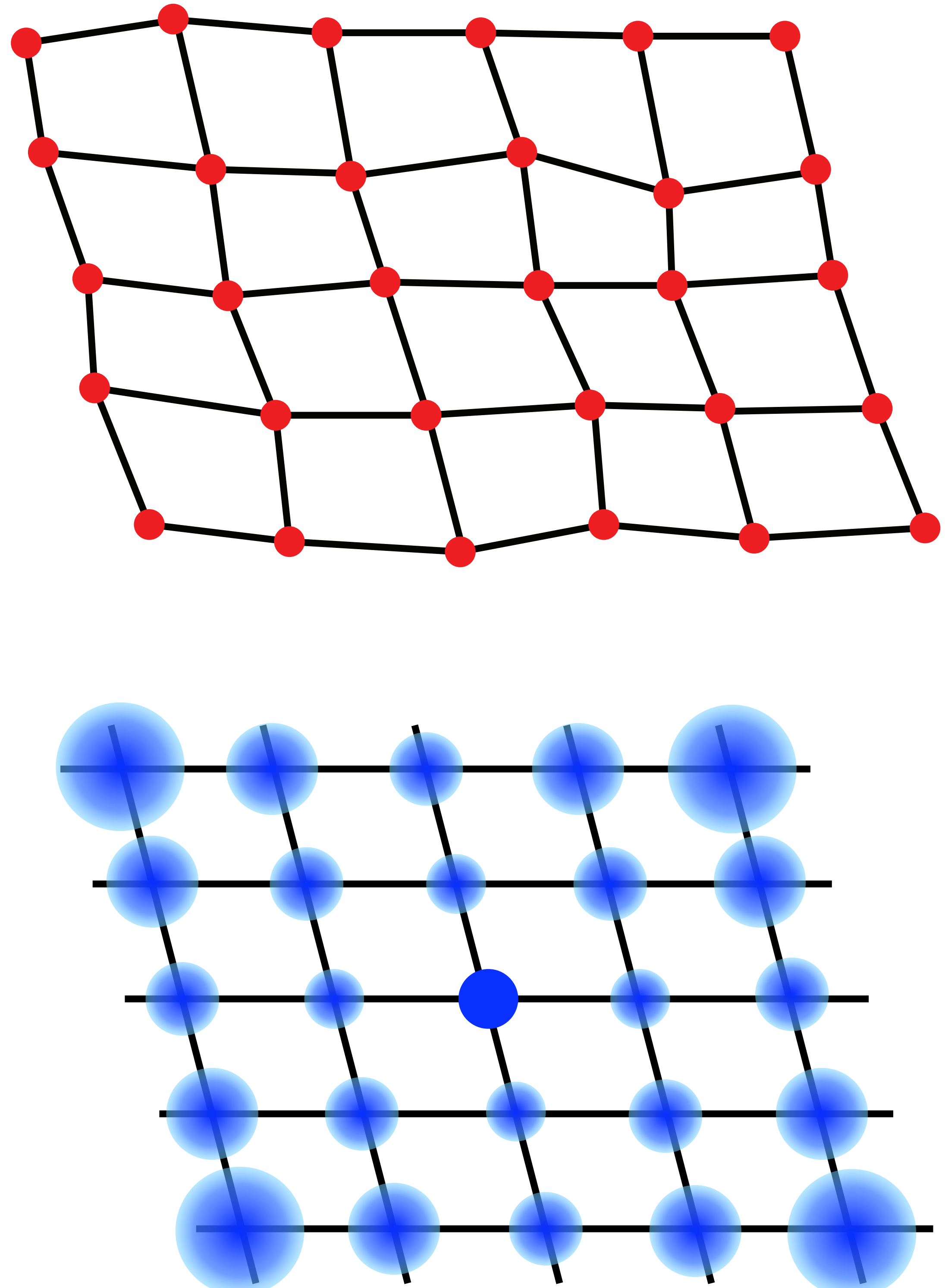
in the case of soft matter

Imperfection of crystal

Imperfection of 1st kind

Imperfection of 2nd kind



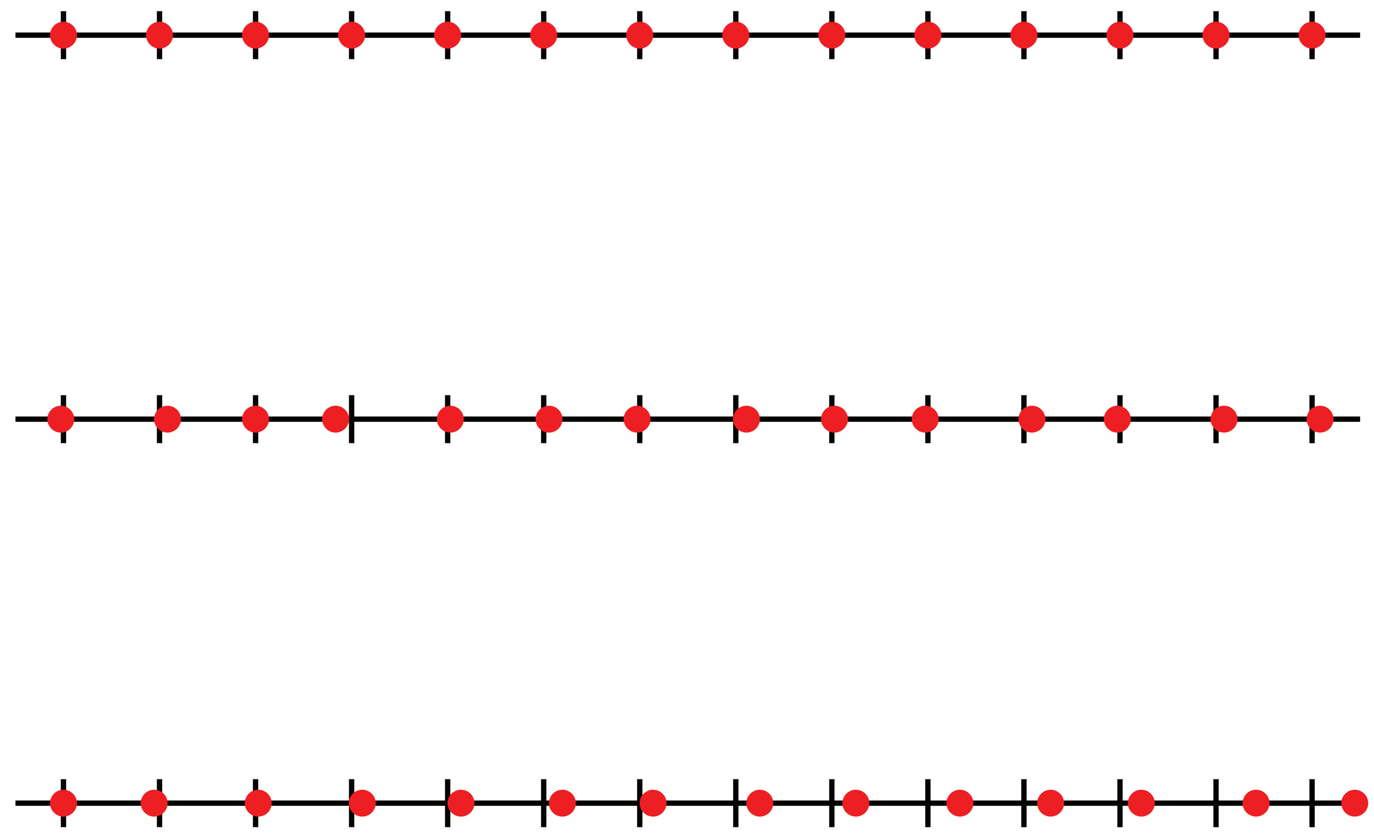


Imperfection of lattice (1D)

Perfect lattice

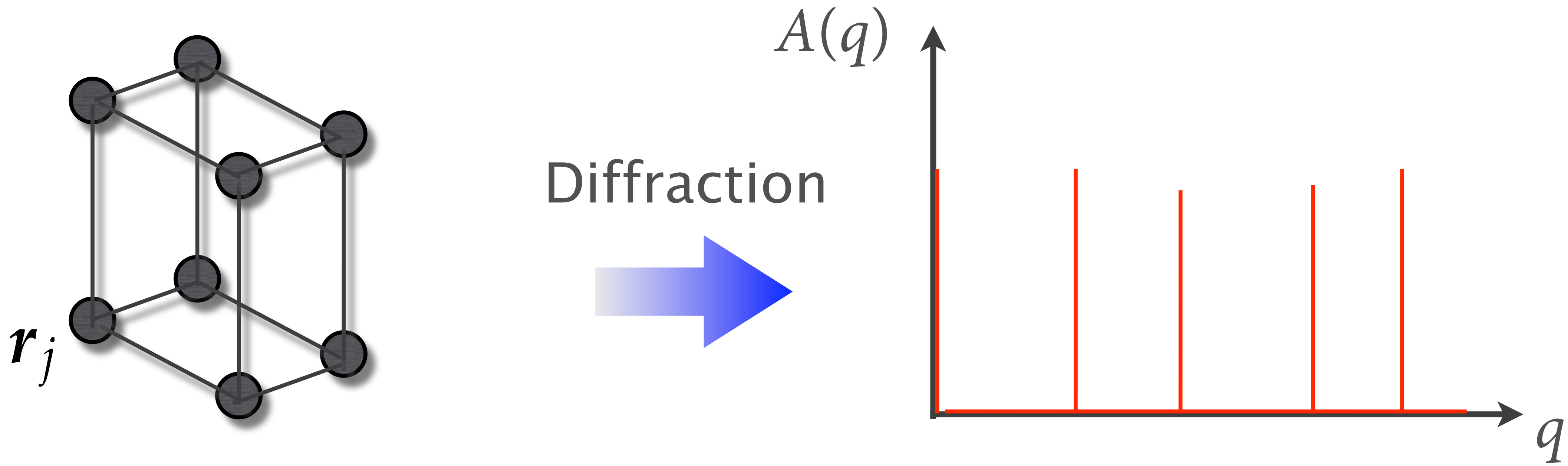
Imperfection of 1st kind

Imperfection of 2nd kind



- Effect of imperfections on diffraction ?

Diffraction from lattice-structure



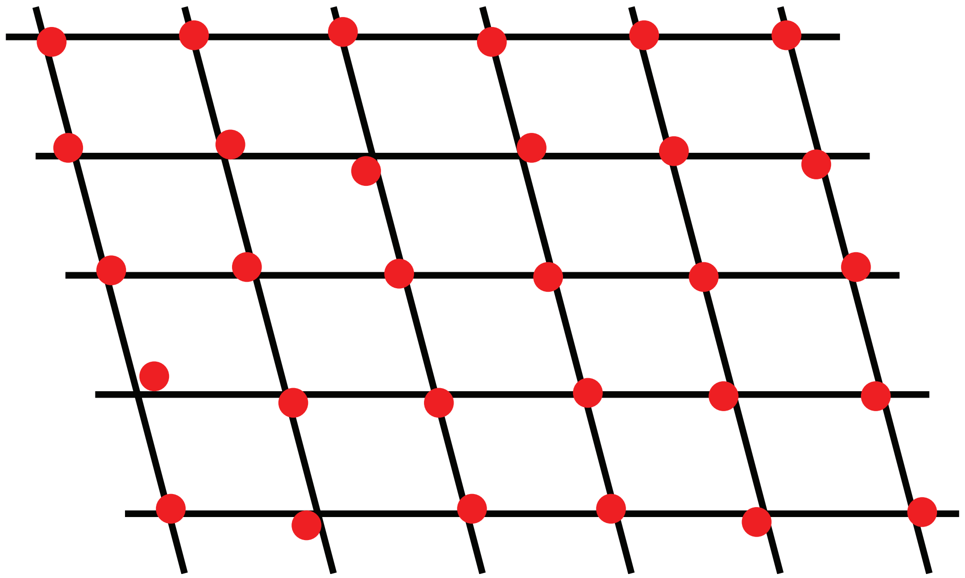
$$\rho(\boldsymbol{r}) = \rho_u(\boldsymbol{r}) * \underline{z(\boldsymbol{r})}$$

$$A(\boldsymbol{q}) = F(\boldsymbol{q}) \cdot \underline{Z(\boldsymbol{q})}$$

Form of lattice

$z(\boldsymbol{r})$ with imperfection ---> calculate $Z(\boldsymbol{q})$

Imperfection of 1st kind



$p(\boldsymbol{r})$: distribution function

$\xrightarrow{\text{Fourier trans.}}$ $P(\boldsymbol{q})$

Diffraction with imperfection: $$|Z(\boldsymbol{q})|^2 = N\left[1 - |P(\boldsymbol{q})|^2\right] + |P(\boldsymbol{q})|^2 Z_0(\boldsymbol{q})$$

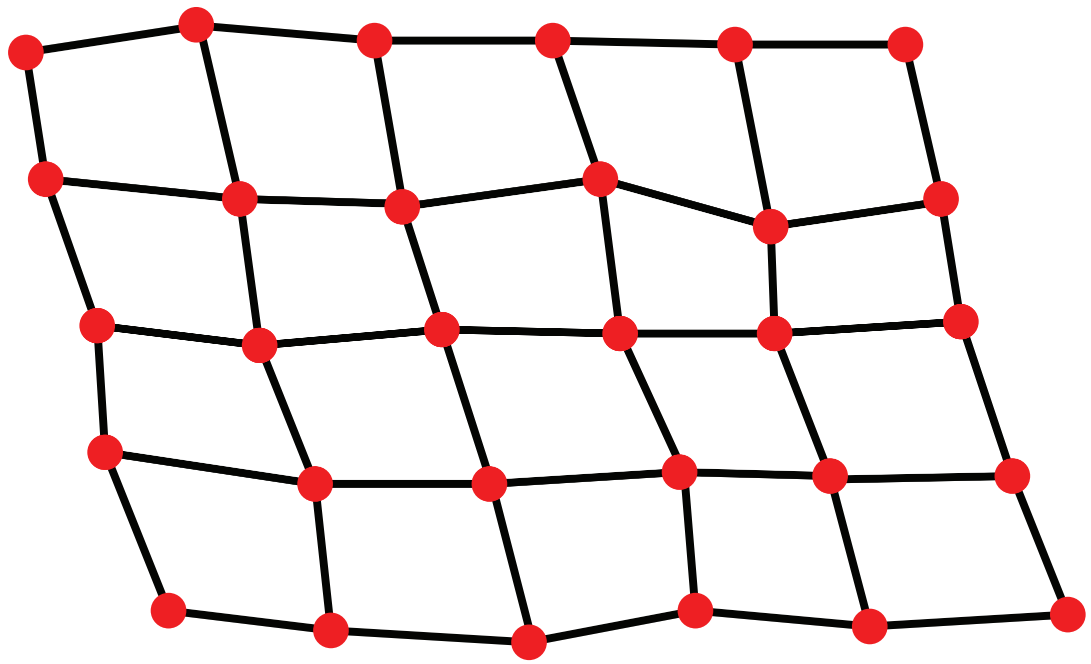
ideal lattice

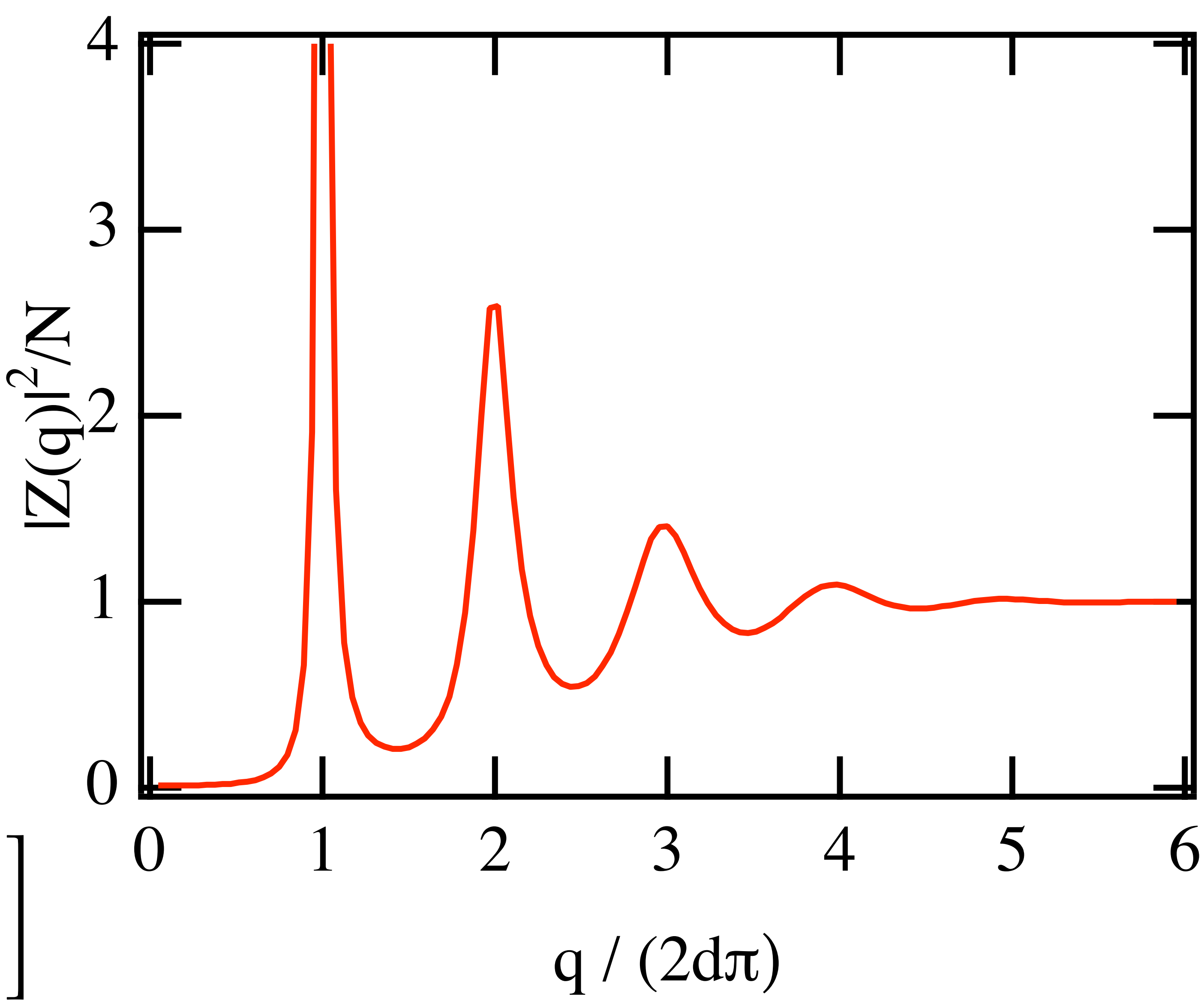
Thermal fluctuation (p(r): Gaussian)

Debye-Waller factor: $$\exp\left(-\frac{1}{3}\sigma^2 q^2\right)$$

- decrease diffraction intensity (no effect on FWHM)
- background at larger angle diffraction

Imperfection of 2nd kind





Paracrystal theory

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

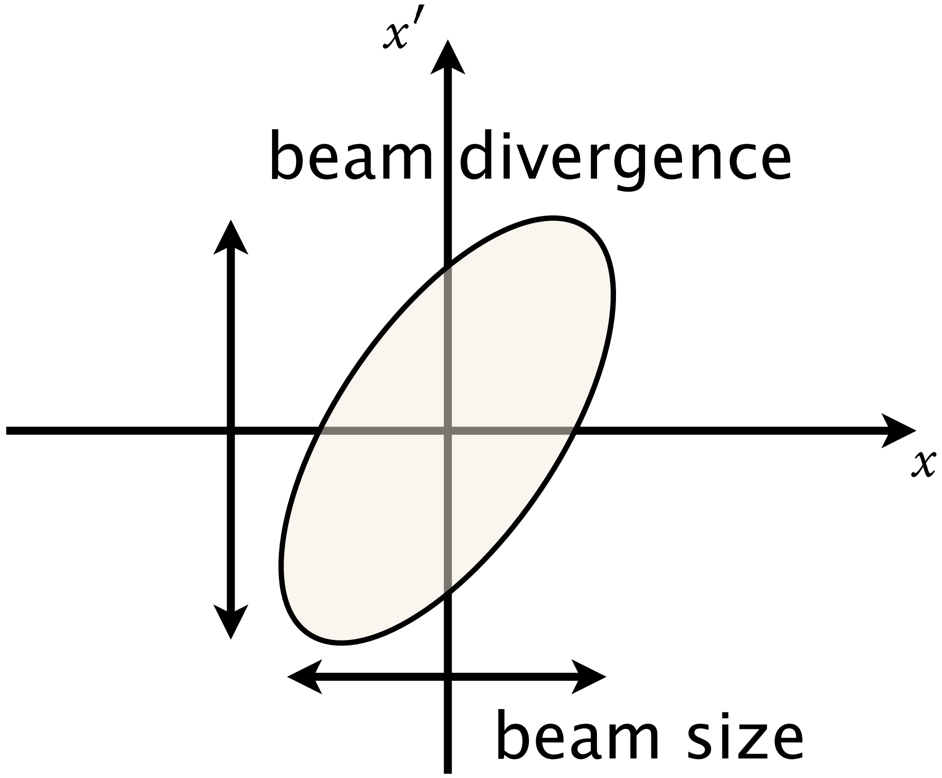
Decrease of diffraction intensity and
Increase of FWHM

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

X-ray Source for SAXS

Brilliance -- Product of size and divergence of beam

$$\text{Brilliance} = \frac{\mathrm{d}^4 N}{\mathrm{d}t \cdot \mathrm{d}\Omega \cdot \mathrm{d}S \cdot \mathrm{d}\lambda/\lambda}$$



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

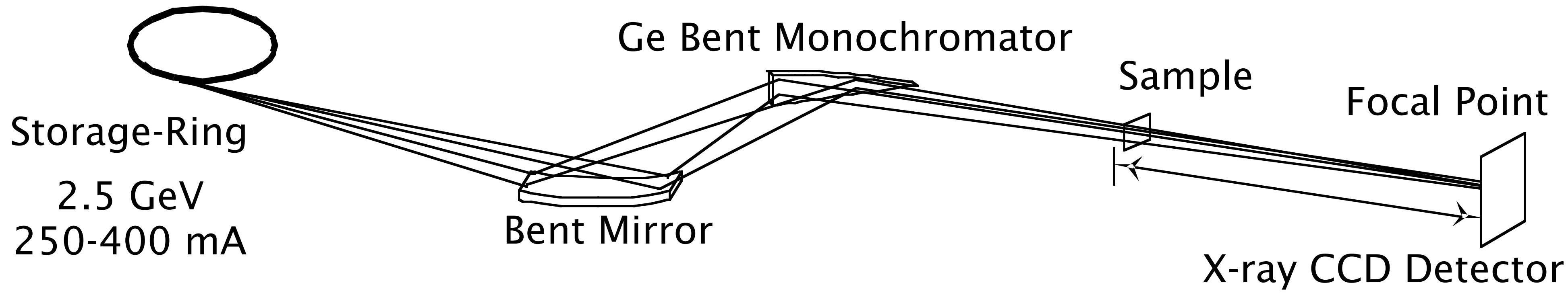
Brilliance is preserved (Liouville's theorem).

SAXS with a low divergence and small beam

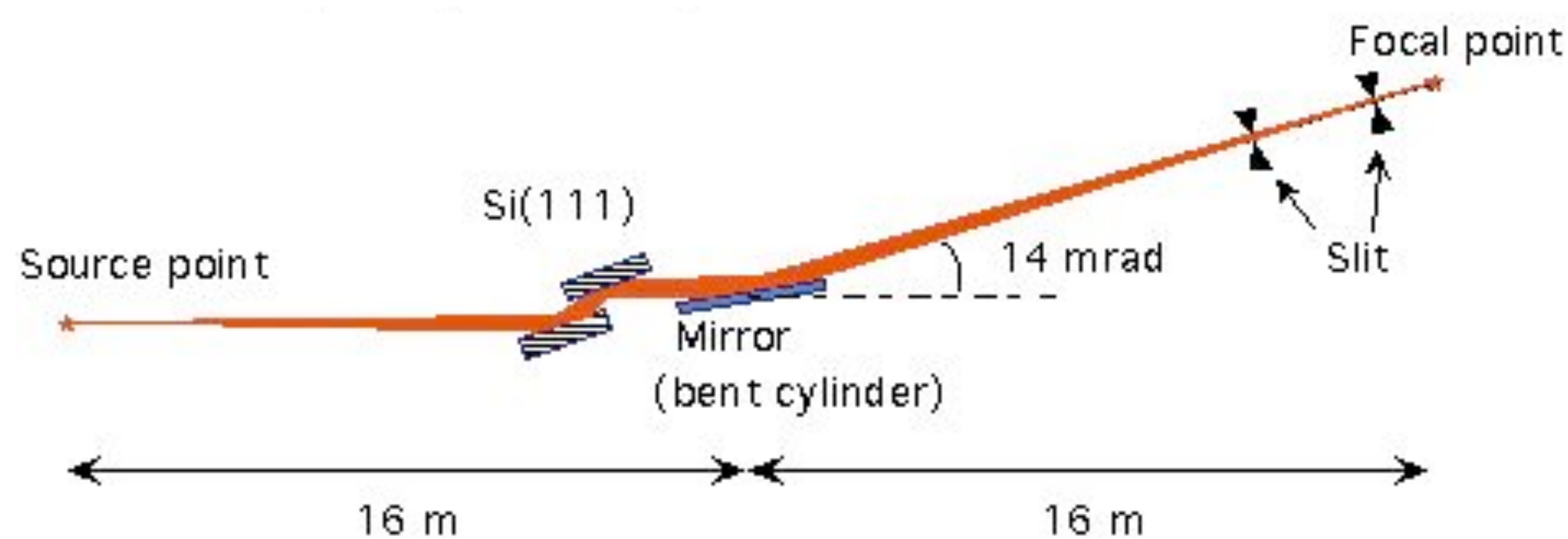
→ High brilliance beam is required !

SAXS Optics

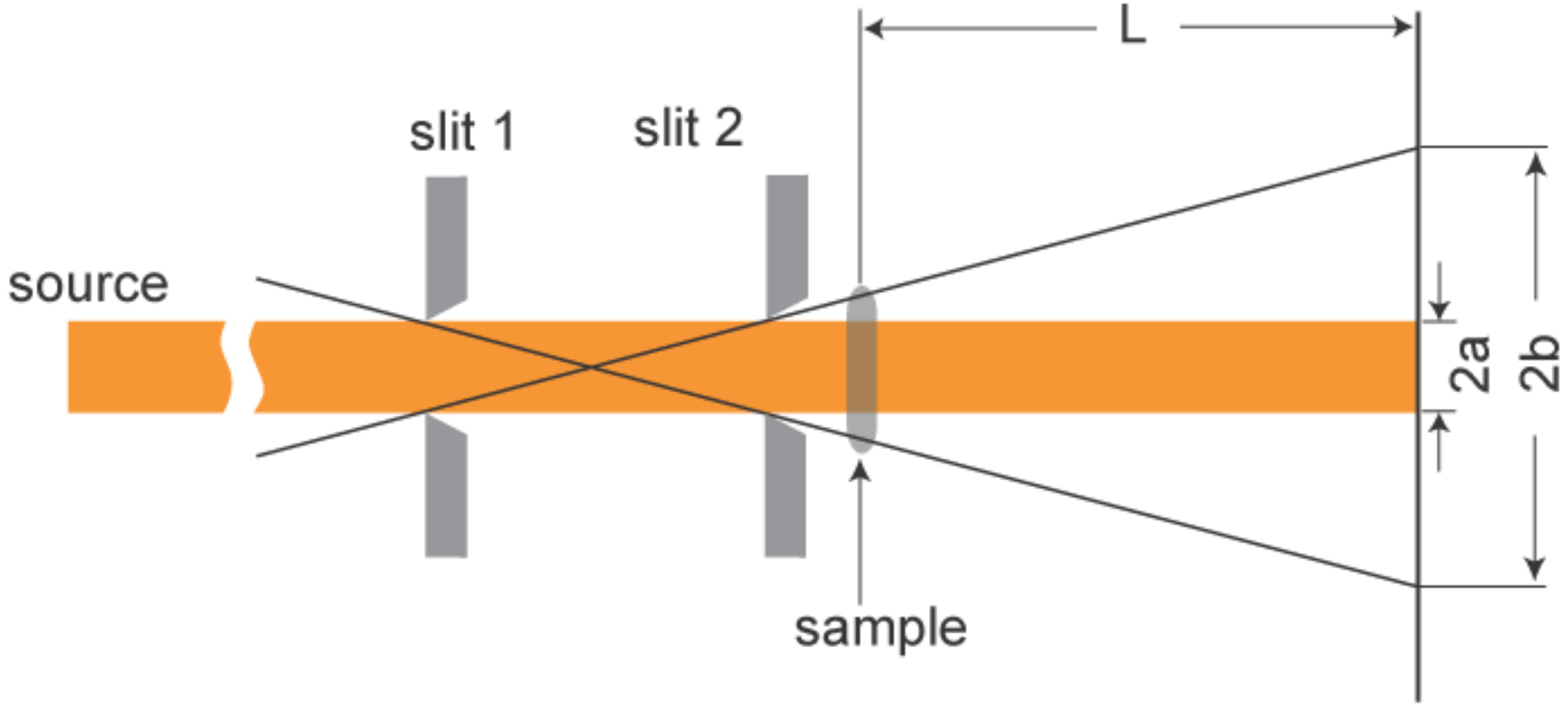
PF BL-15A



PF BL-10C



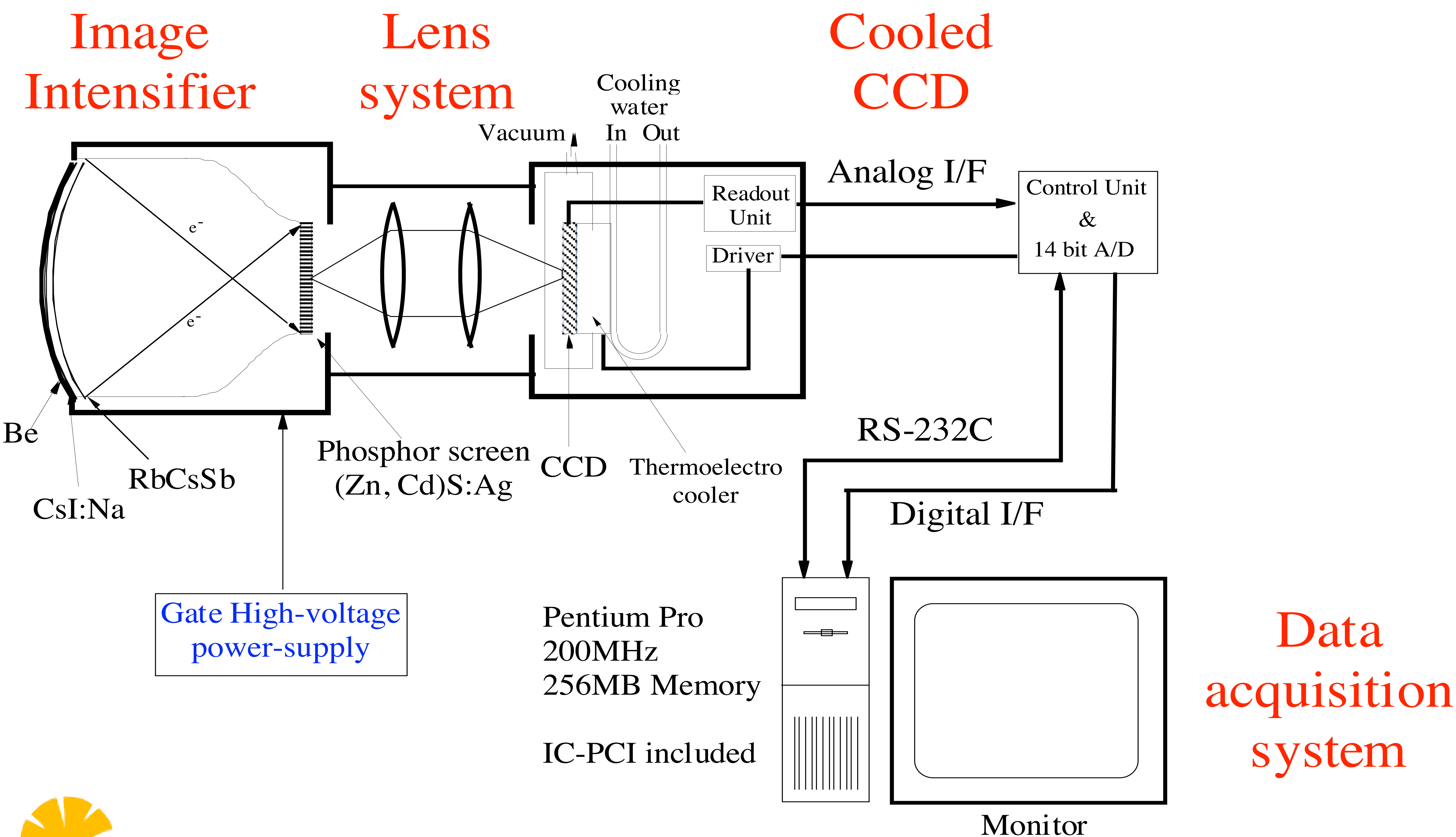
SAXS slits



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



Advanced SAXS

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

XPCS
- structural fluctuation
- dynamics

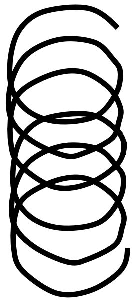
Combined measurement with DSC, viscoelasticity

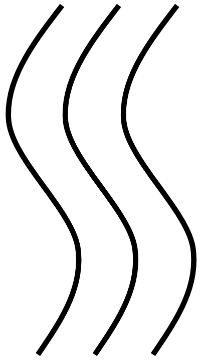
wide-q (USAXS-SAXS-WAXS)
- hierarchical structure

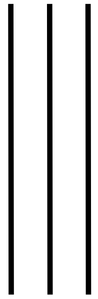
2D measurement
- anisotropic structure

Application of paracrystal theory

Collab. with Kao ltd.



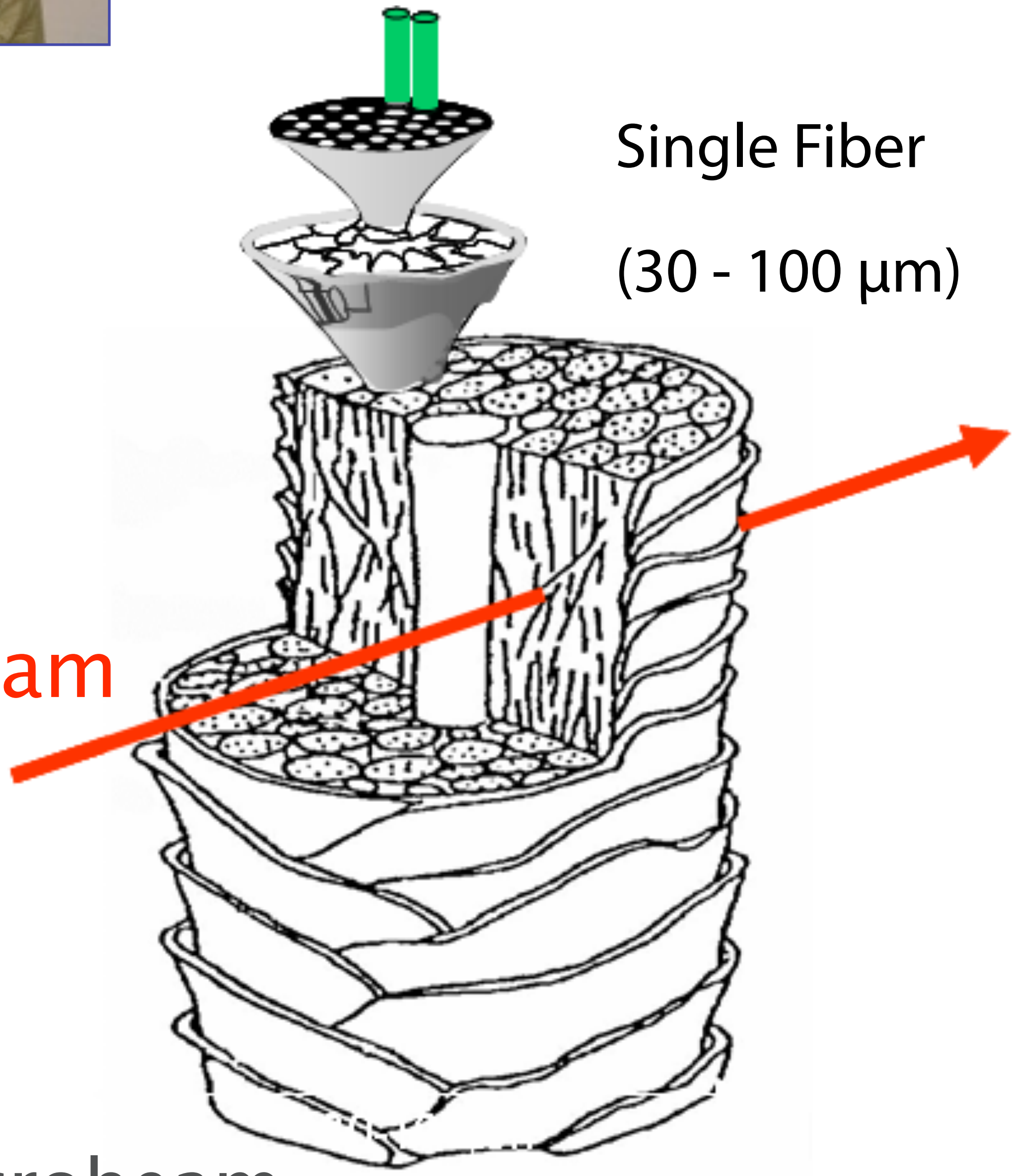




African

Caucasian

Asian

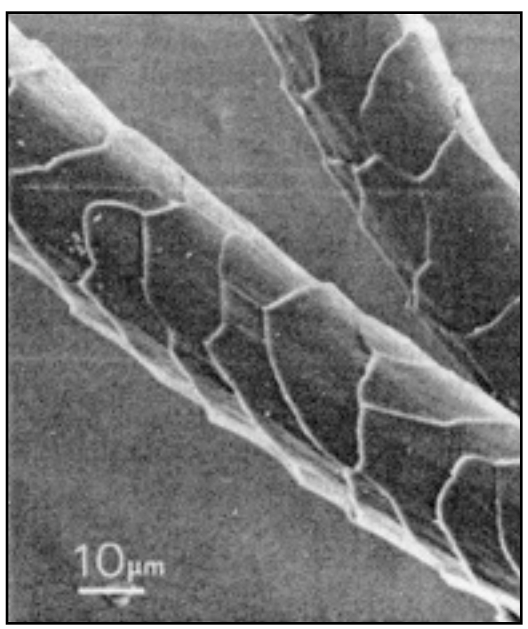


Relationship between macroscopic form and microscopic structure?

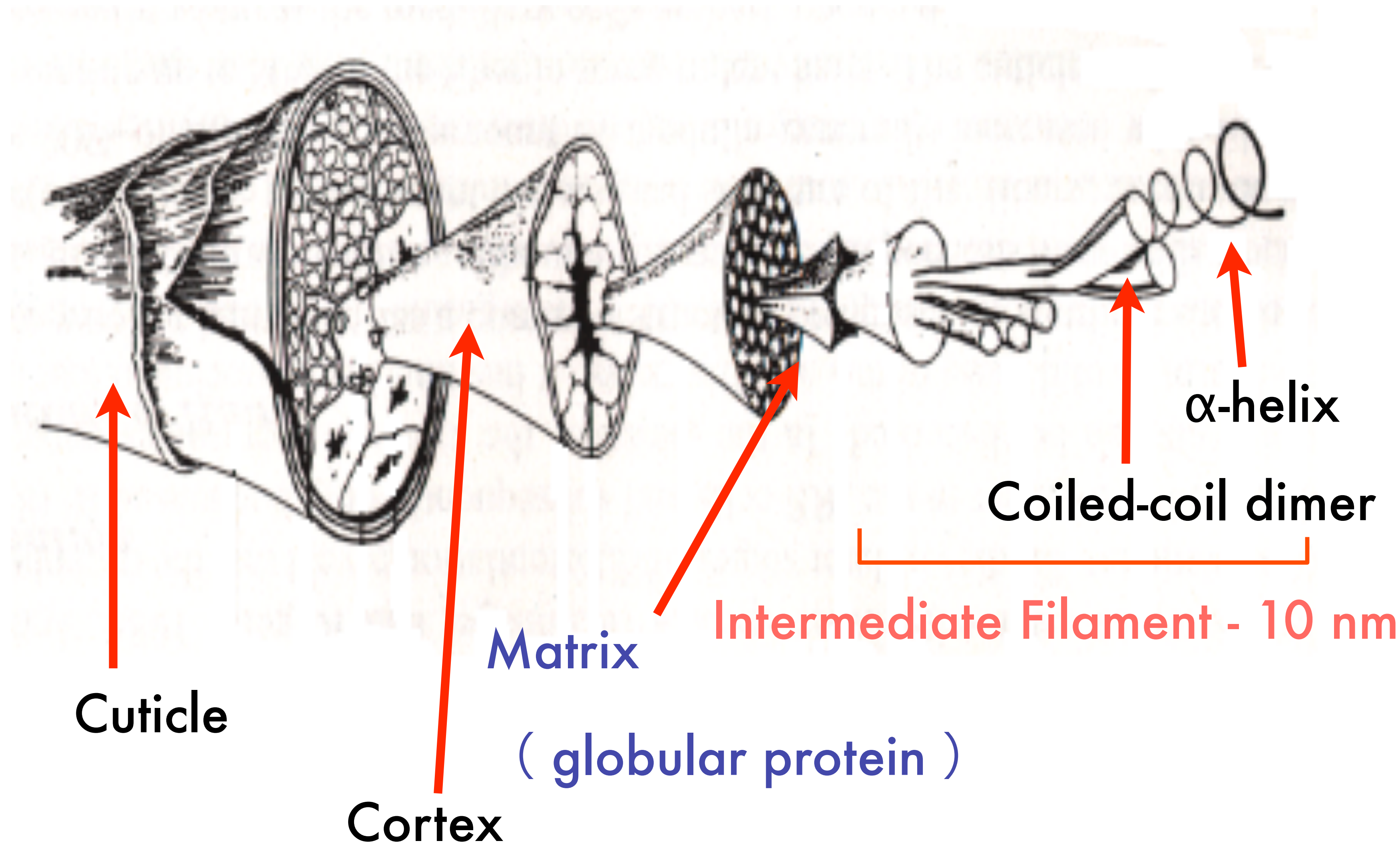
Local observation with an X-ray microbeam

Internal structure of wool

SEM 像



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

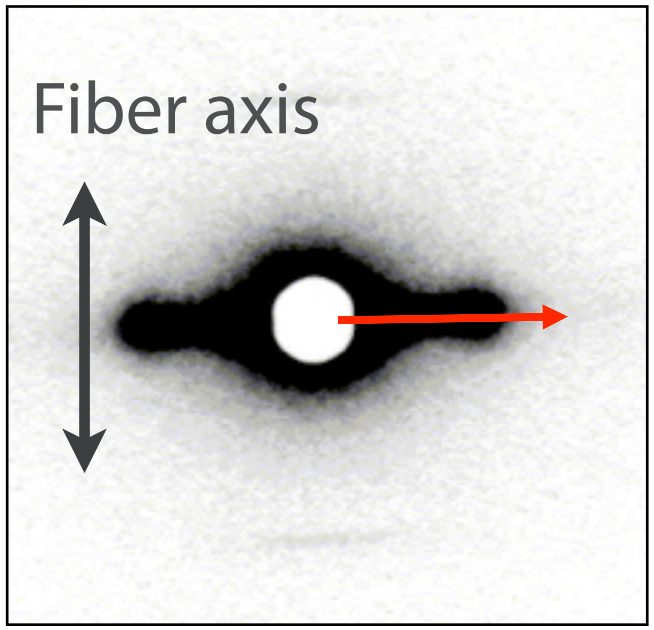


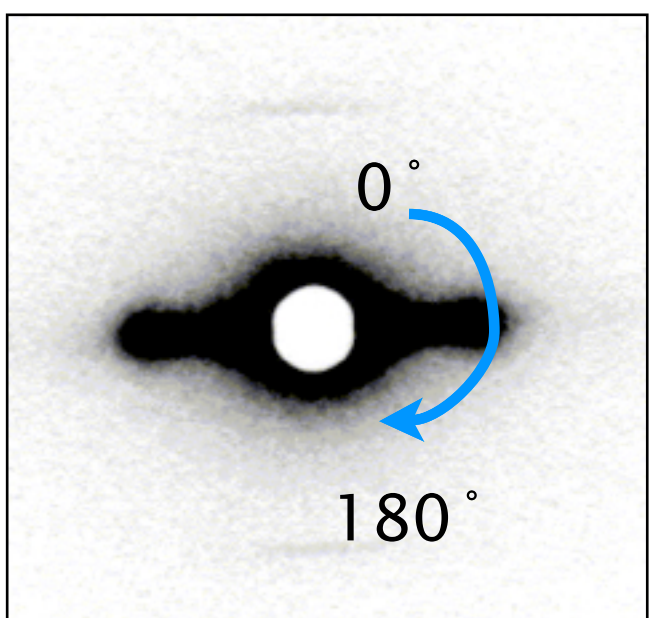
R. D. B. Fraser et al., Proc. Int. Wool Text. Res. Conf., Tokyo, II, **37**, (1985) partially changed.

Relationship between IF distribution and hair curlness?

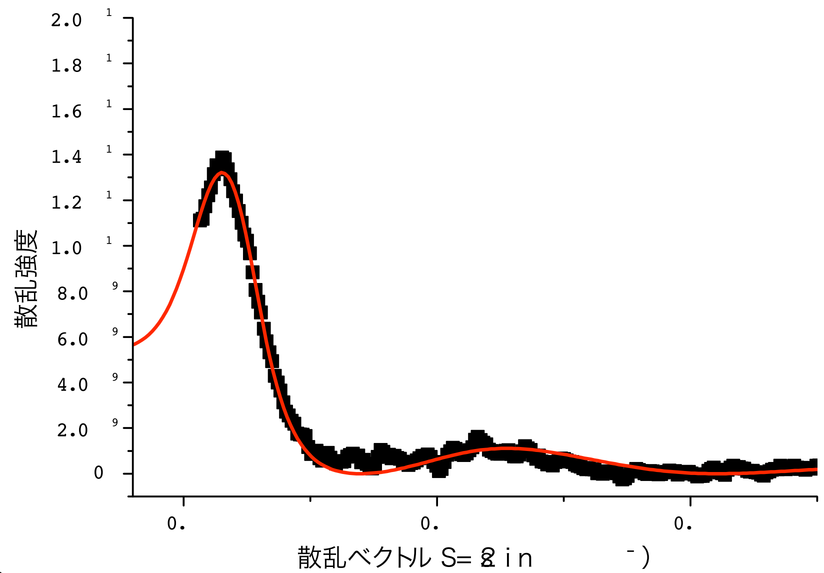
Structure of Intermediate Filament

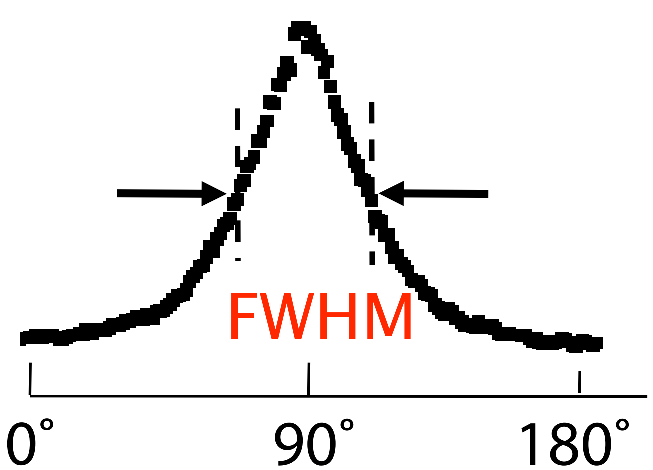
Scattering pattern



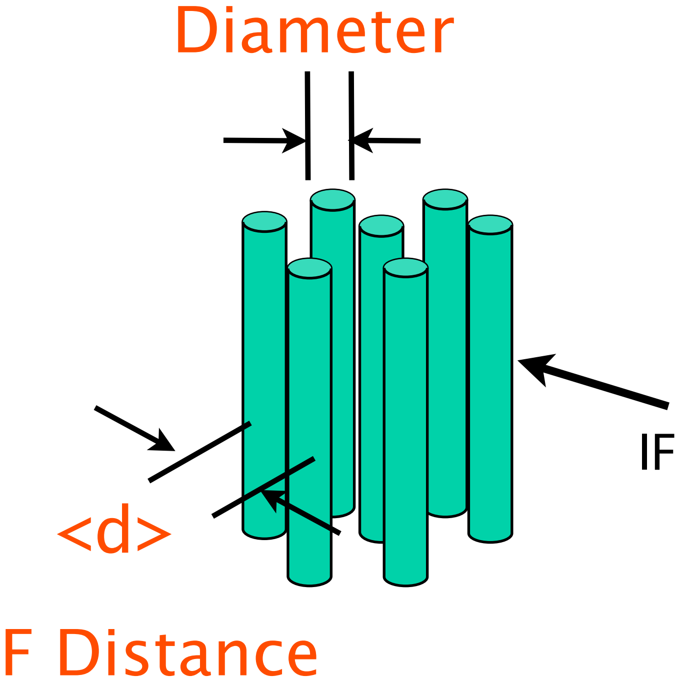


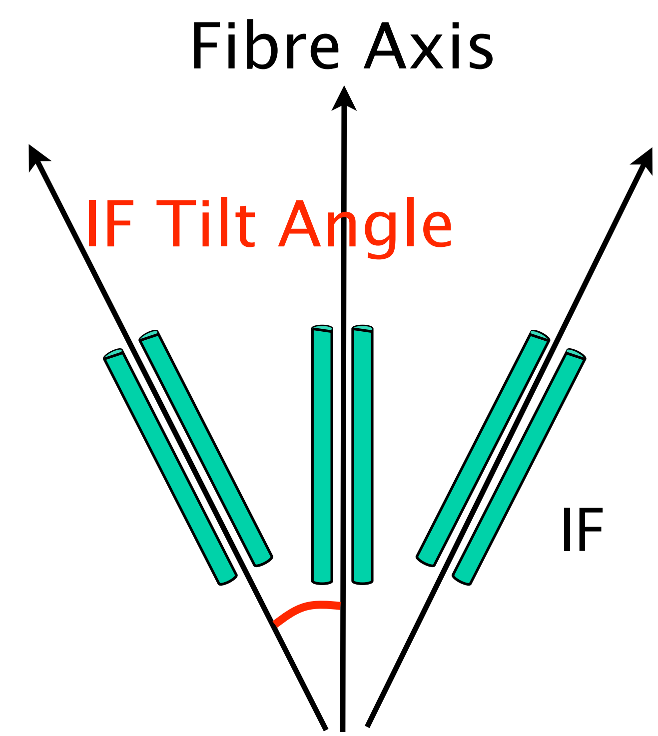
1D intensity profile



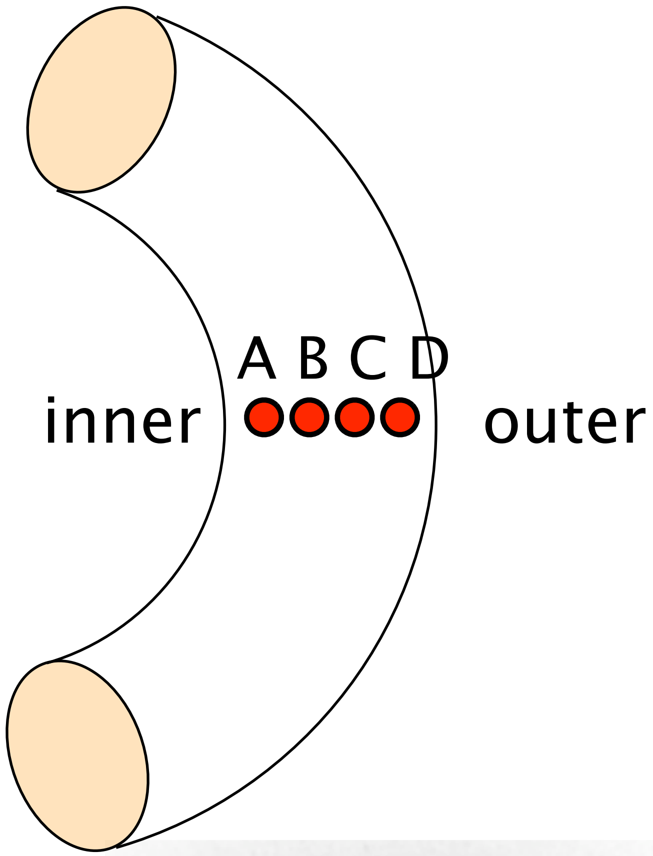


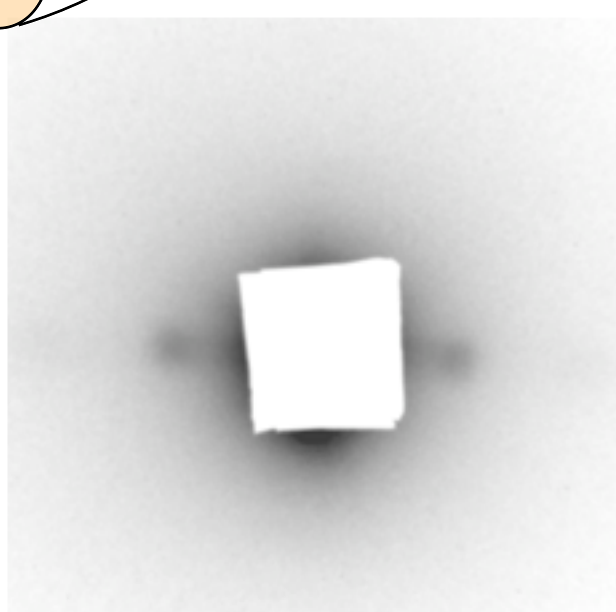
Real space structure

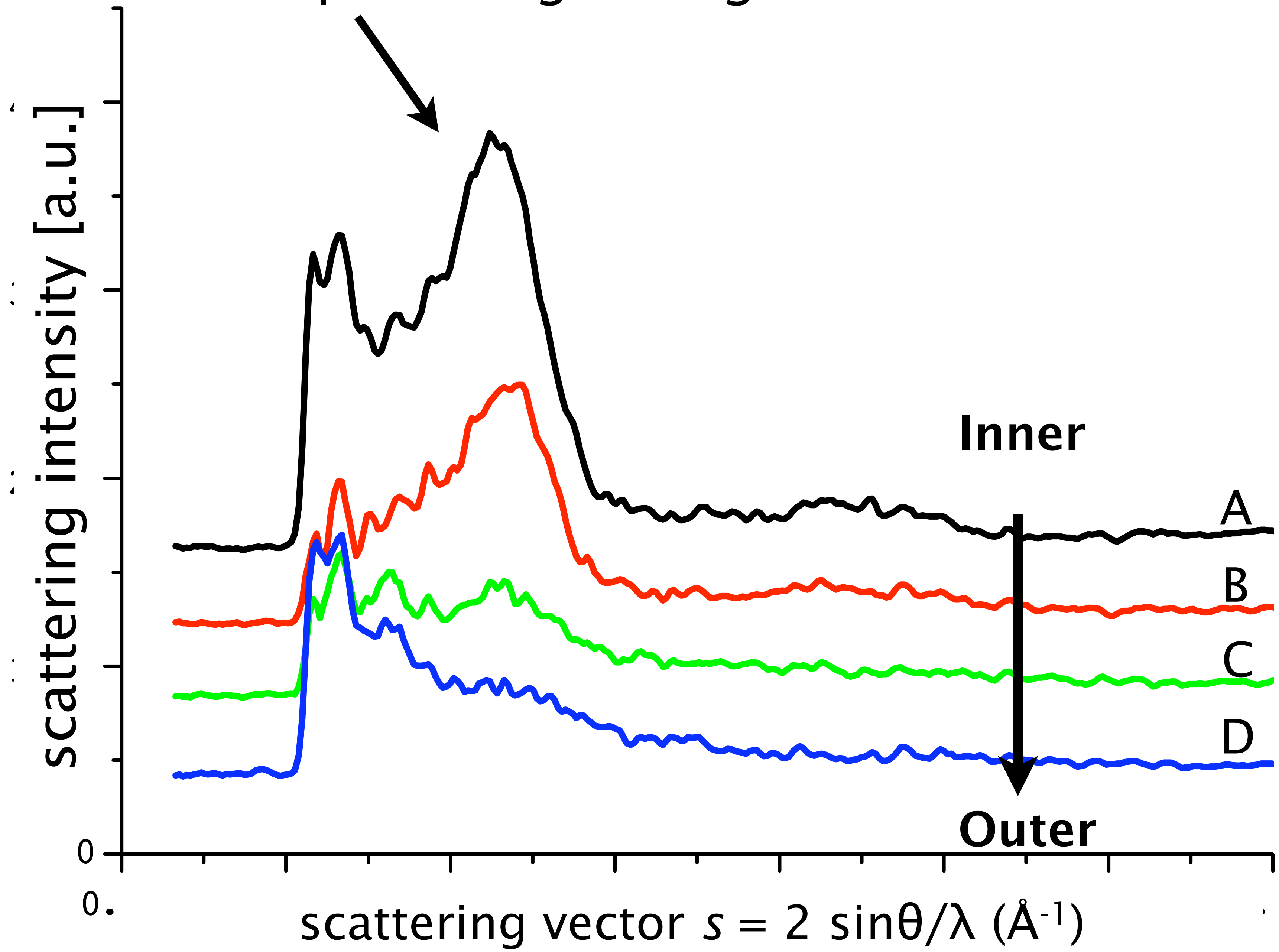




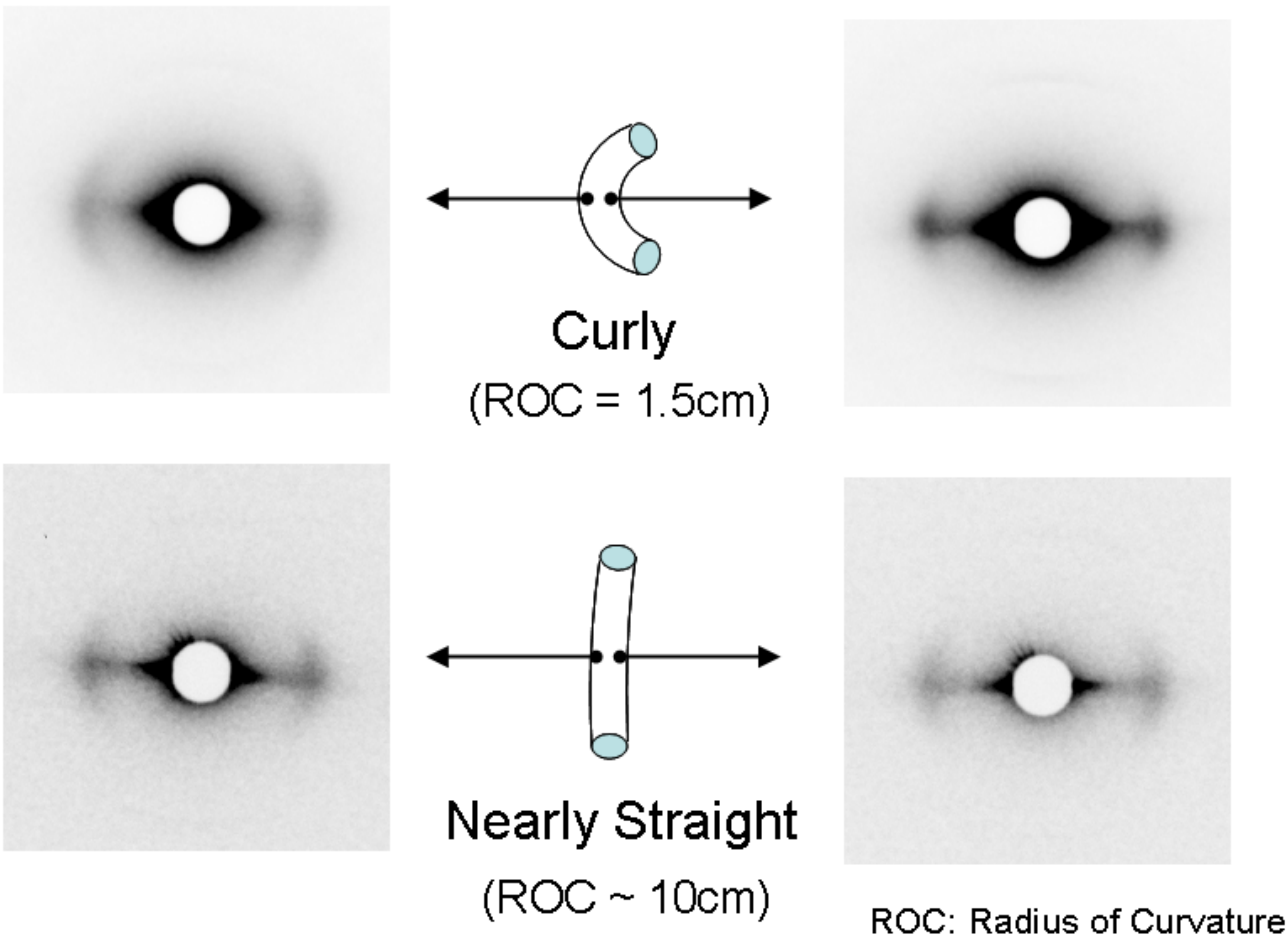
Diffraction intensity profiles



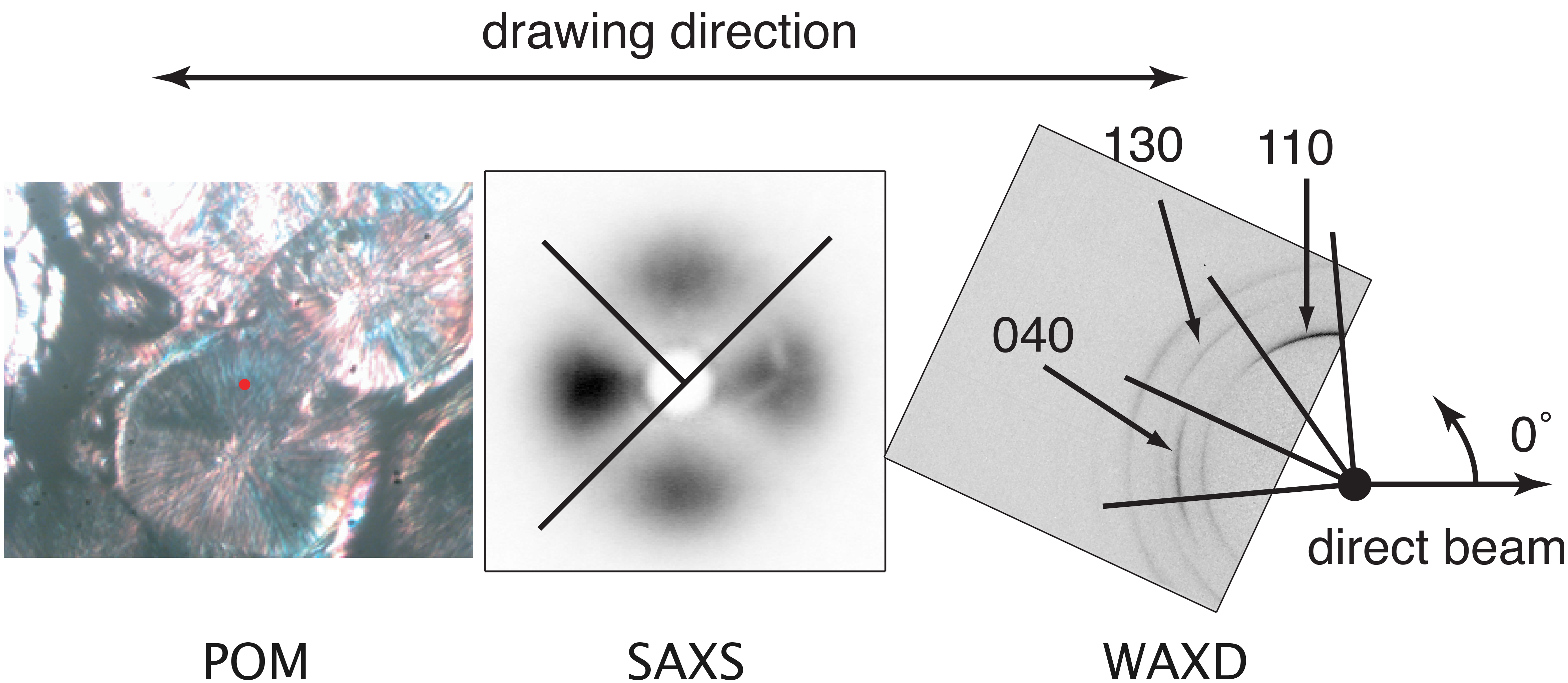




Difference in diffraction intensity
--> Structural difference in cortex.


Curly
(ROC = 1.5cm)
Nearly Straight
(ROC ~ 10cm)
ROC: Radius of Curvature

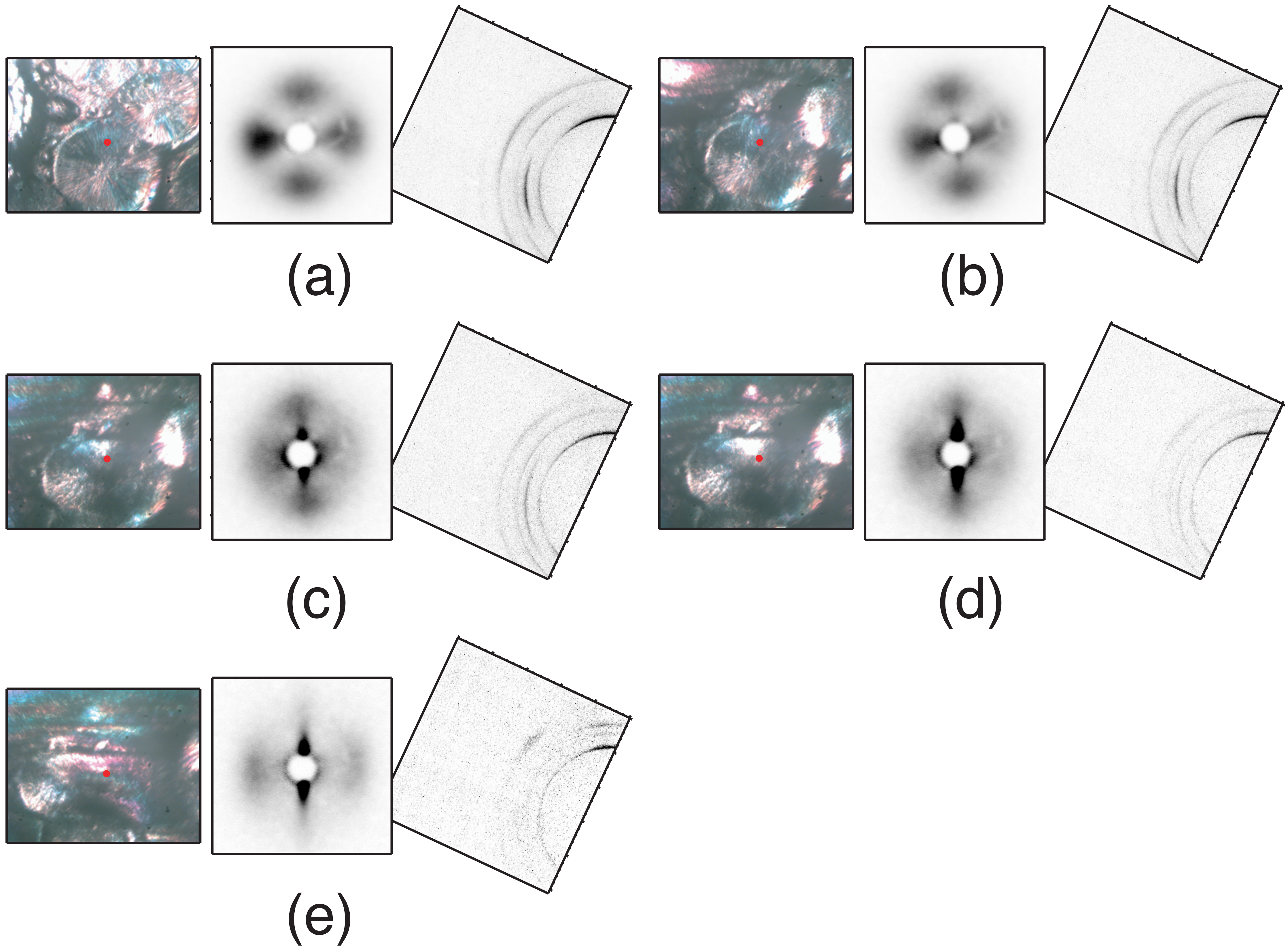
Deformation process of spherulite



BL40XU @ SPring-8

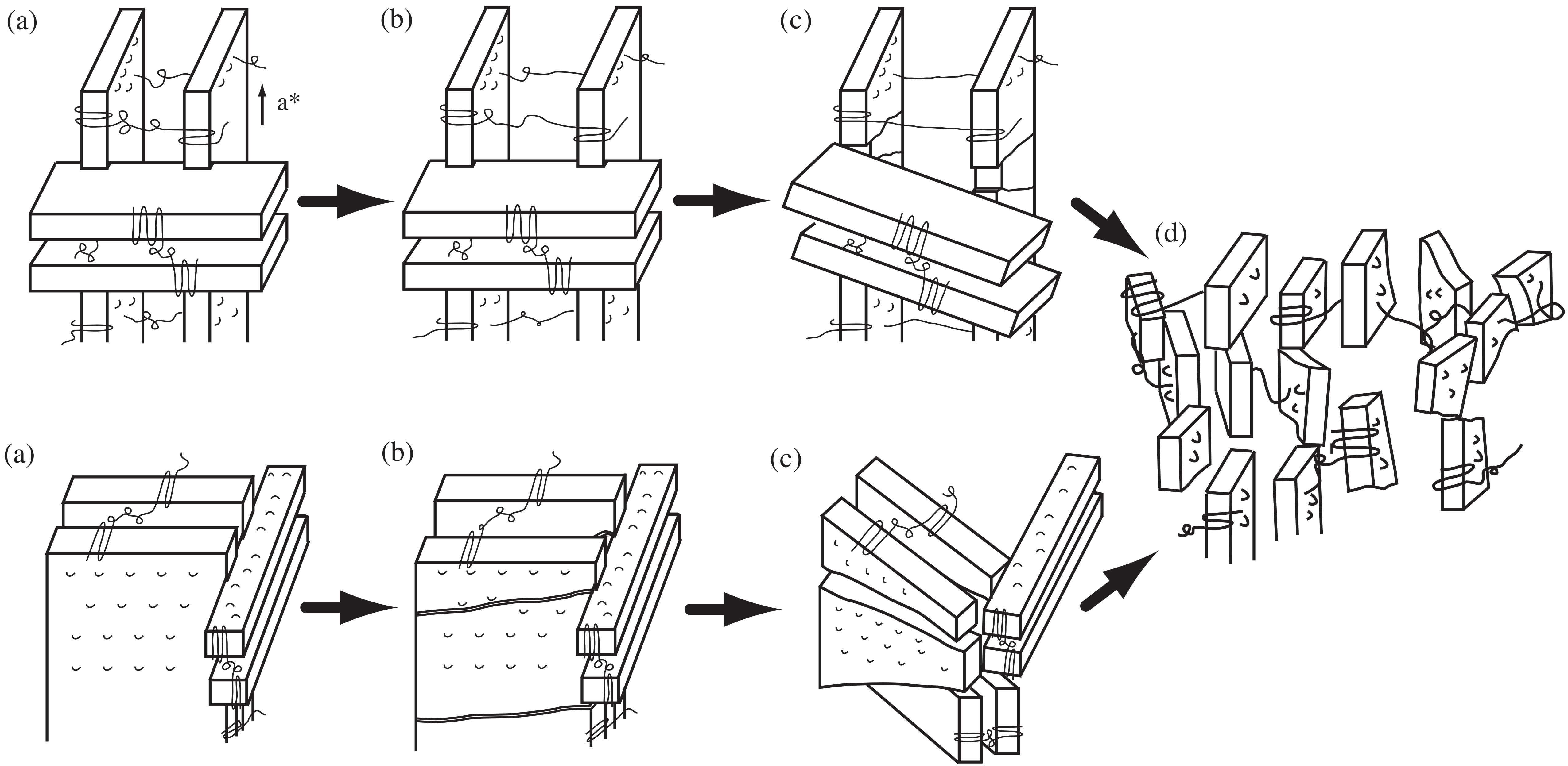
Local deformation manner of polypropylene during uniaxial elongation process

→ Combined measurement of polarized microscope and microbeam SAXS/WAXD.



(a)
(b)
(c)
(d)
(e)

Deformation model of PP



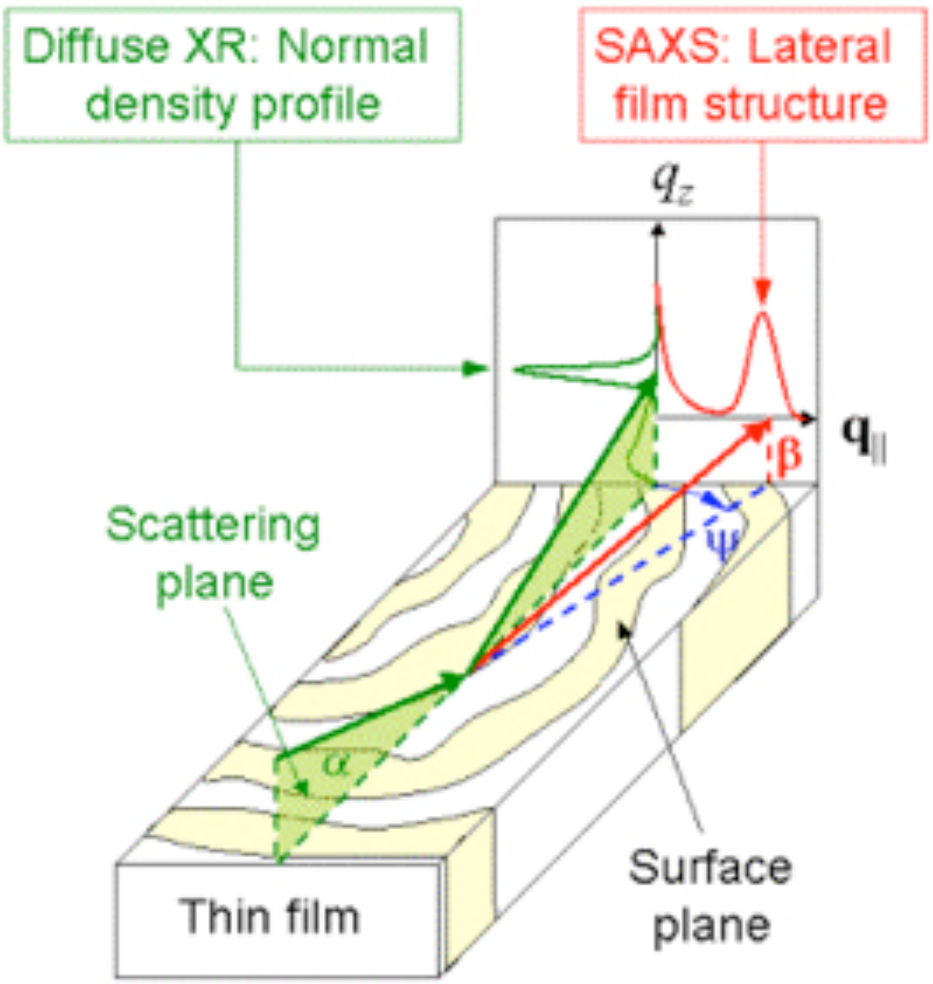
Y. Nozue, Y. Shinohara, Y. Ogawa et al., Macromolecules, **40**, 2036 (2007).

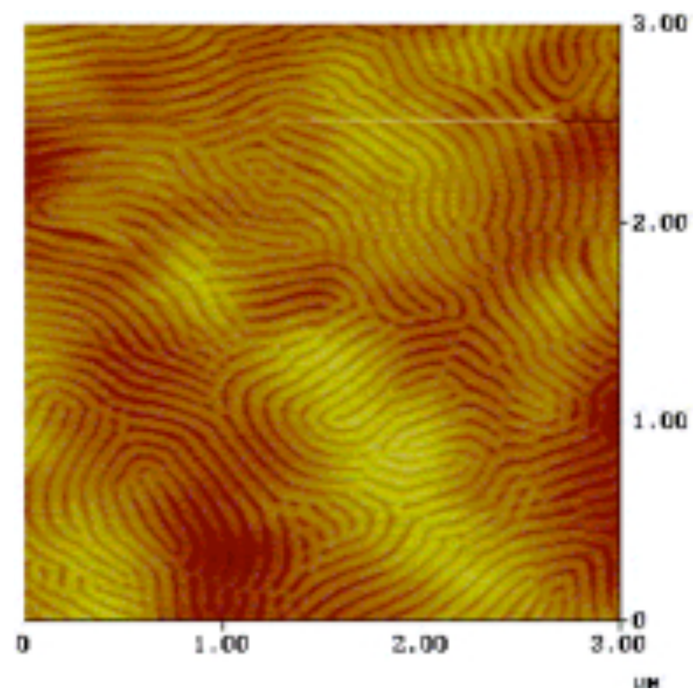
Grazing Incidence SAXS

Advantage

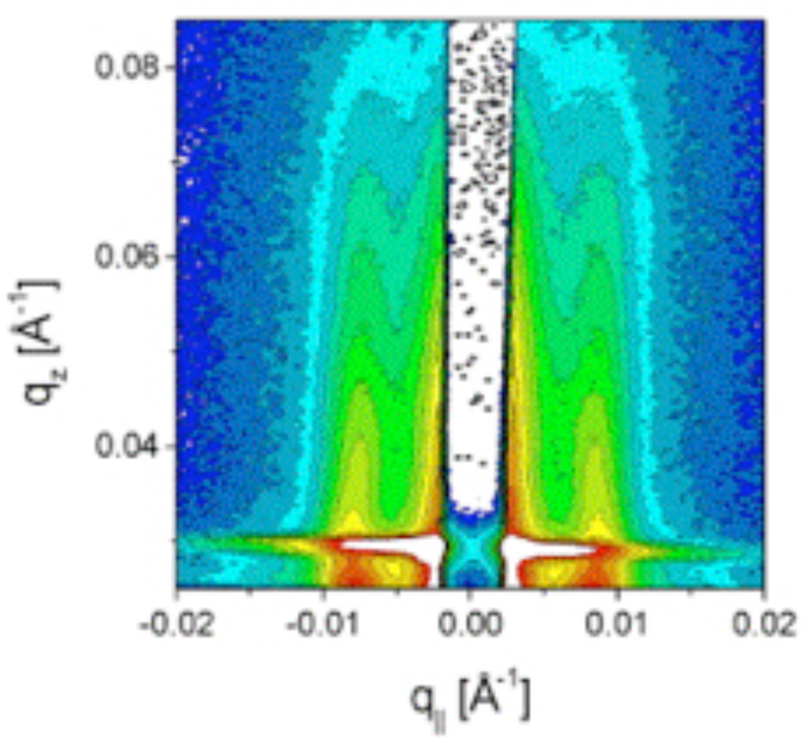
- Surface/interface sensitive (beam footprint).
- In-plane structure and out-of-plane structure can be separated.
- Thin film sample on substrate can be measured.

Ex: from Web page of Dr. Smiligies @ CHESS



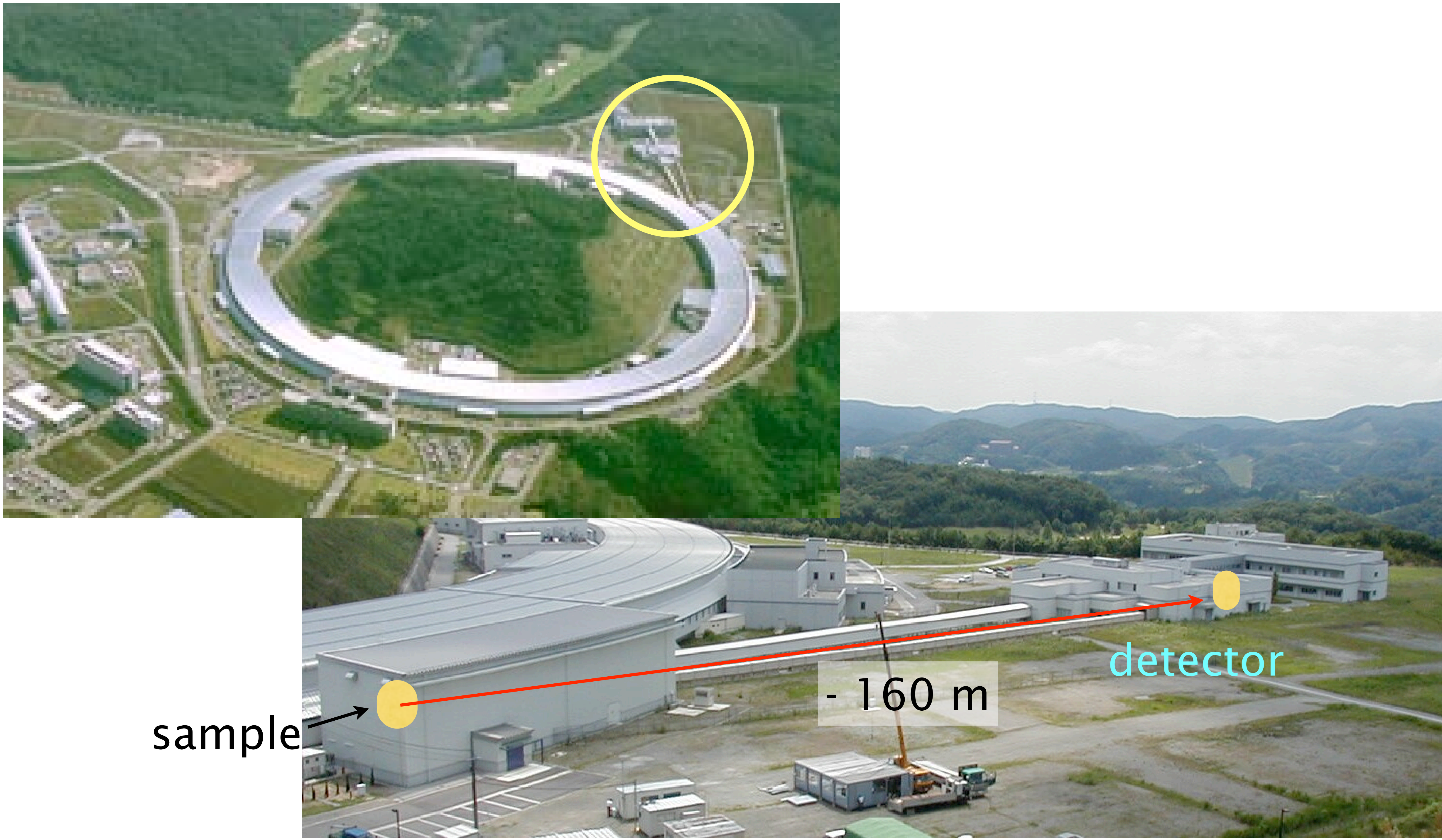


AFM image

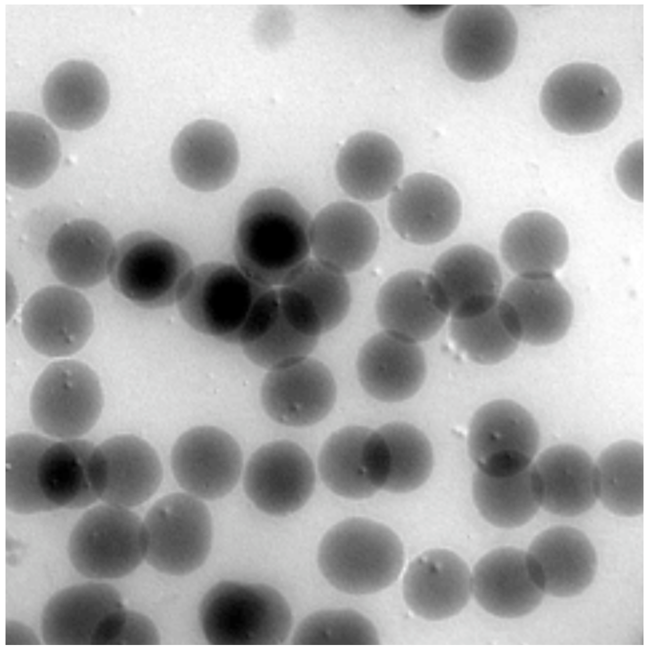


GI-SAXS image

USAXS using medium-length beamline

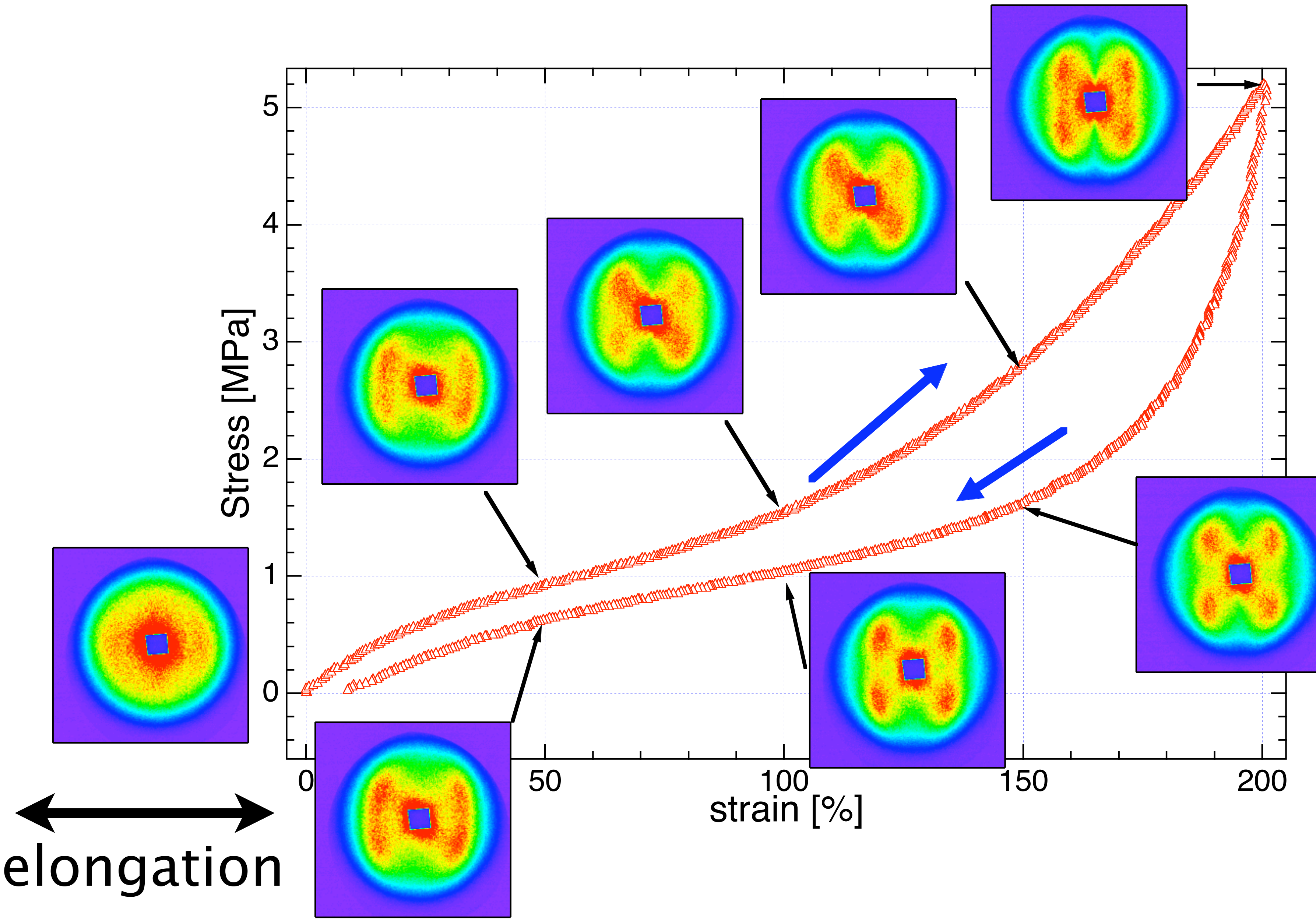


USAXS patterns from elongated rubber



TEM image

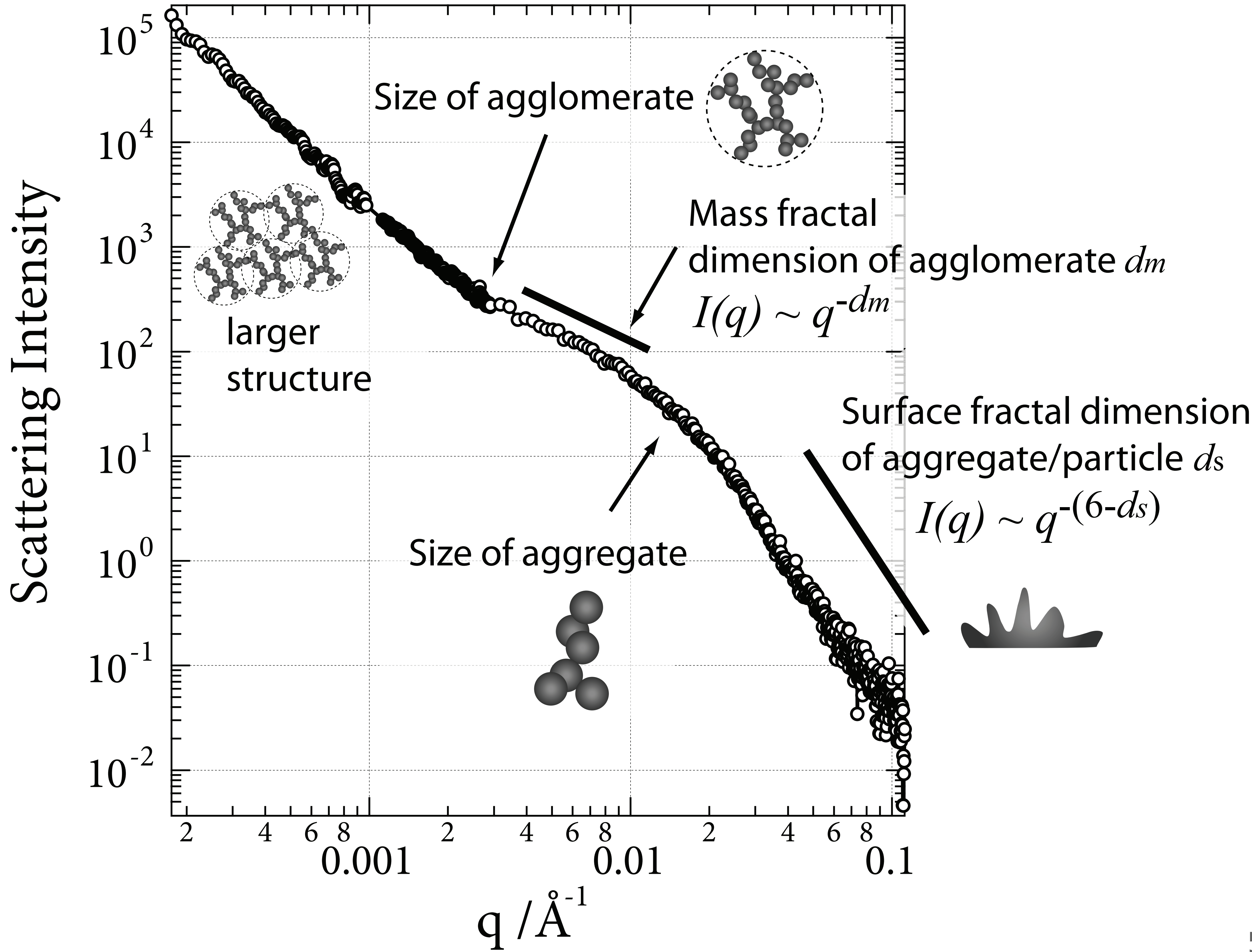
Rubber filled with spherical silica



Scattering pattern also shows hysteresis.

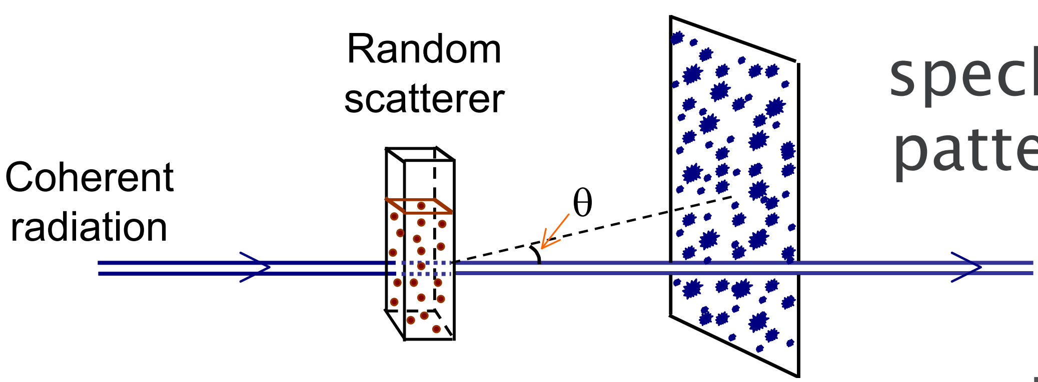
Y. Shinohara et al., J. Appl. Cryst., **40**, s397 (2007).

Structural information from USAXS



X-ray Photon Correlation Spectroscopy: XPCS

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

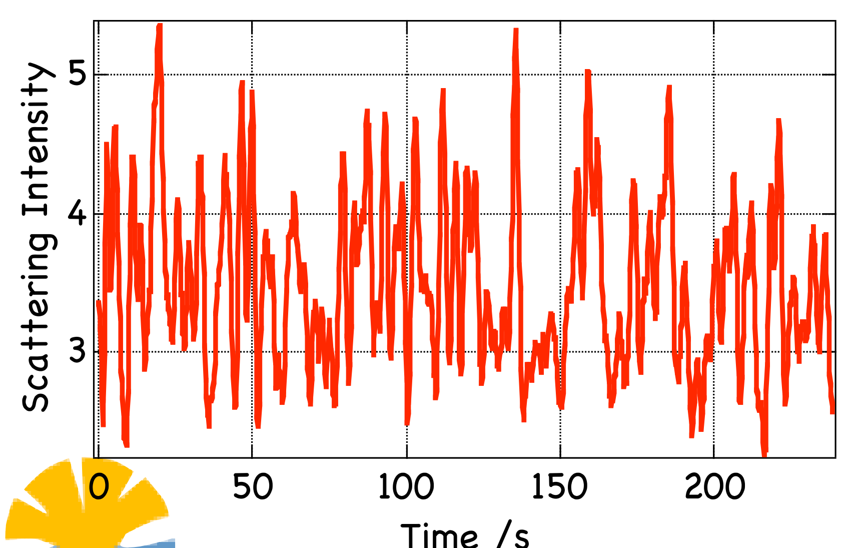


$$g^{(2)}(q,\ \tau) = \frac{\langle I(q,0)I^{*}(q,\ \tau)\rangle}{\langle I(q)\rangle^{2}}$$

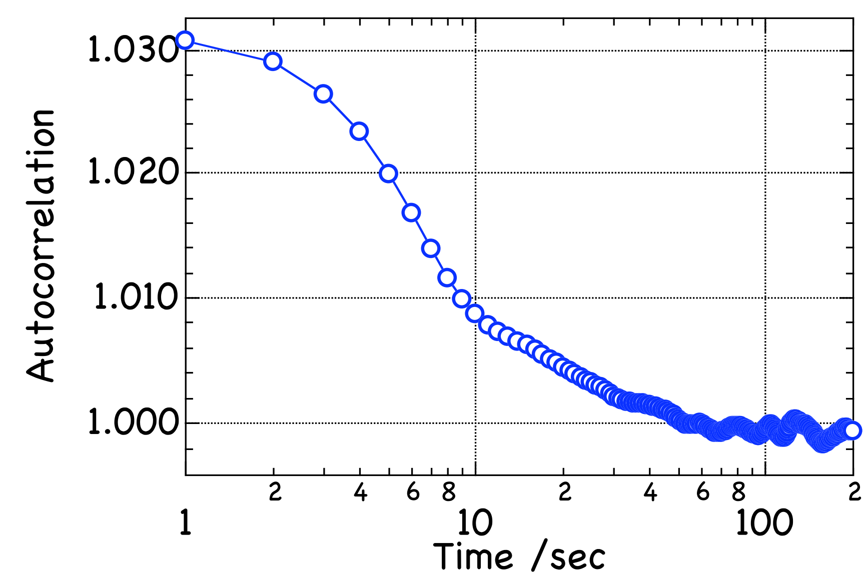
Time-resolved SAXS with coherent X-ray

Fluctuation of intensity

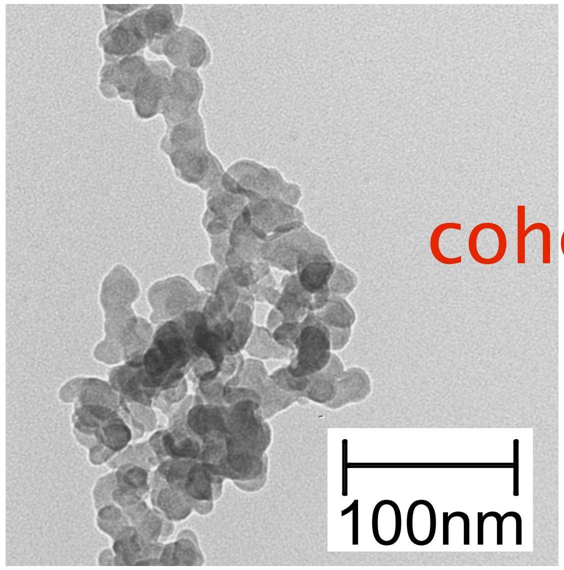
relaxation time in system



Autocorrelation

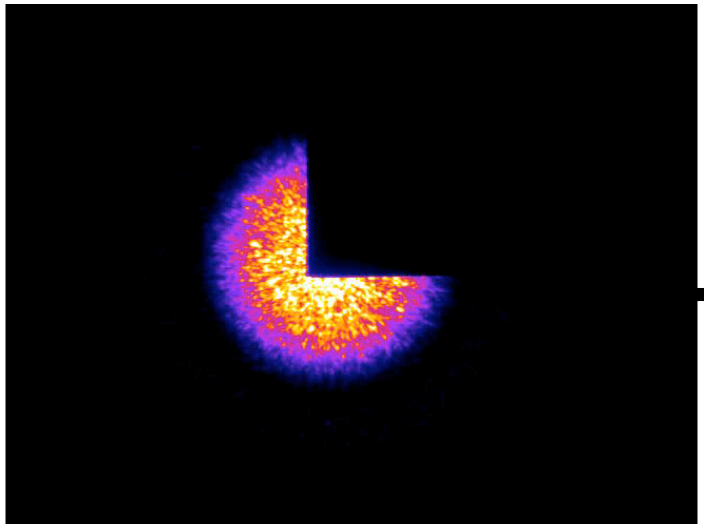


Dynamics of nanoparticles observed with XPCS

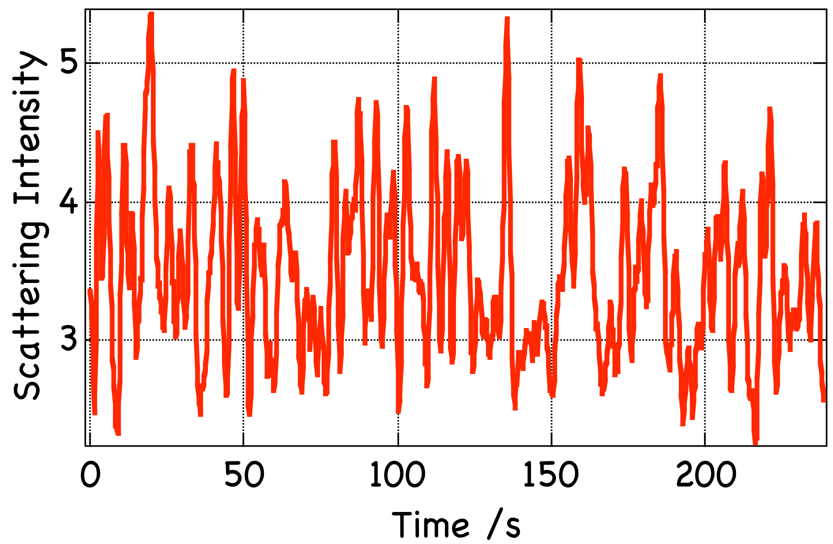


coherent x-ray

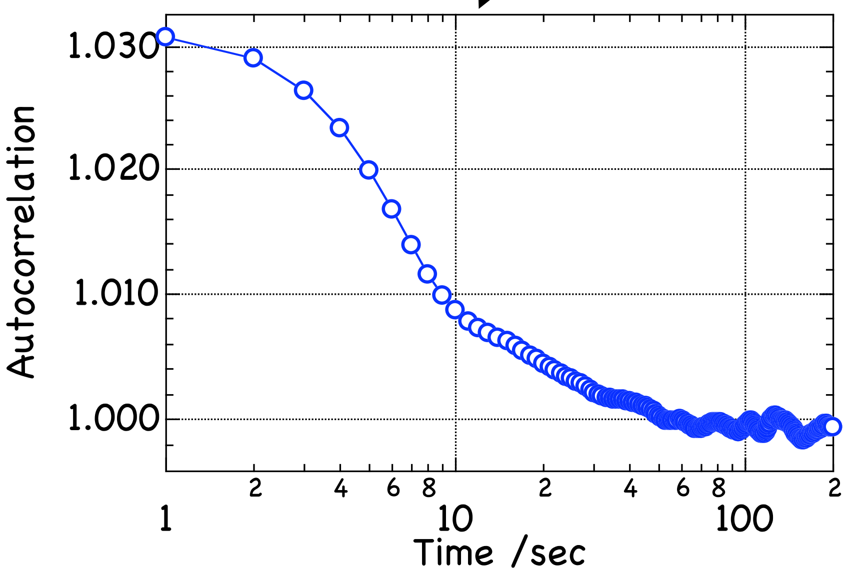
nano-particles in rubber



speckle pattern



fluctuation of scattering intensity

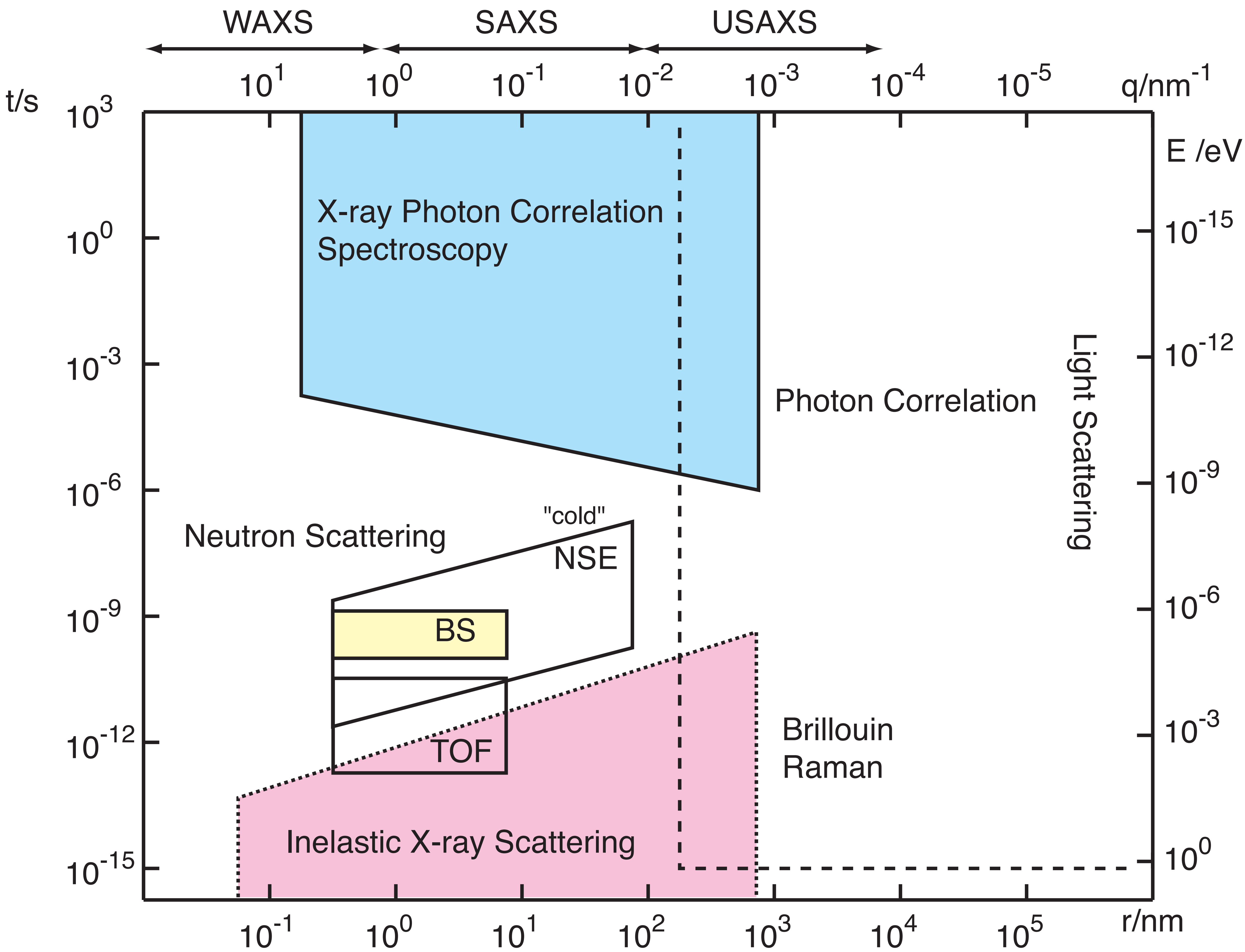


Dynamics of Filler in Rubber

Dependence of dynamics on...

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

etc.



WAXS
SAXS
USAXS
10^1 10^0 10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5} q/nm^{-1}
t/s
10^3
10^0
10^{-3}
10^{-6}
10^{-9}
10^{-12}
10^{-15}
E /eV
10^{-15}
10^{-12}
10^{-9}
10^{-6}
10^{-3}
10^0
X-ray Photon Correlation Spectroscopy
Photon Correlation
Light Scattering
Neutron Scattering
"cold"
NSE
BS
TOF
Brillouin
Raman
Inelastic X-ray Scattering
10^{-1} 10^0 10^1 10^2 10^3 10^4 10^5 r/nm

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