

One approach concerning teaching methods about diffraction and scattering of X-ray and visible light

Masaru Matsuo

*Dalian University of Technology,
Department of Polymer Science and Materials,
Dalian 116024, China*

Polychar 25

Kuala Lumpur October 9 – 13, 2017

The subjects in this note have been developed as one of the teaching programs to study polymer materials by X-ray together with Prof. Bin at Dalian University of Technology

This note is concerned with **diffraction and scattering** for **X-ray beam and visible light beam**.

The wavelength of X-ray beam is much shorter than that of visible light beam and then the **particle** nature is predominant in comparison with **wave** nature. Hence **X-ray beam and visible light beam provide different characteristics**. (Short course, POLYCHAR 24)

Difference between the two is related to the different fluctuations of system dependent upon the absolute values of scattered intensity. That is, X-ray scattering intensity is due to **mean square value of electron density fluctuation**, while **light scattering intensity, mean square value of refractive index**. **The both scattered intensities are given by Fourier transform of these fluctuations.**

The wavelengths (λ) of X-ray beam generated from Cu and Mo targets are 0.154 and 0.06198 nm, respectively, while the wavelength of He-Ne gas laser is ca. 650 nm. The large difference is **photon energy** (\mathcal{E}) between the two given generally by

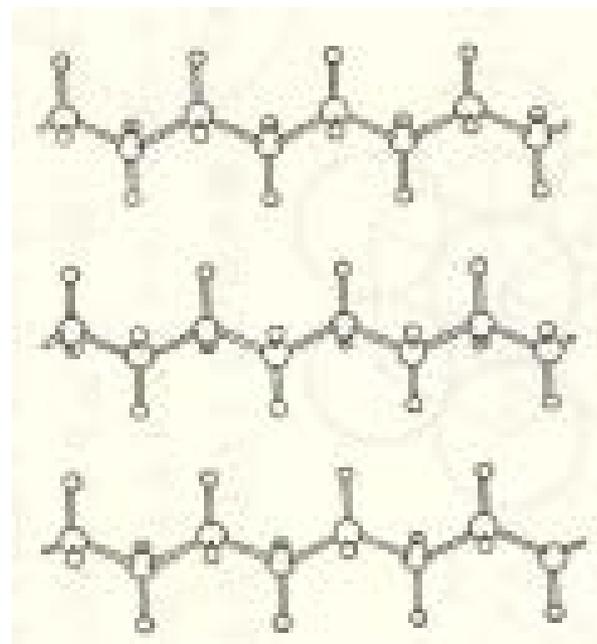
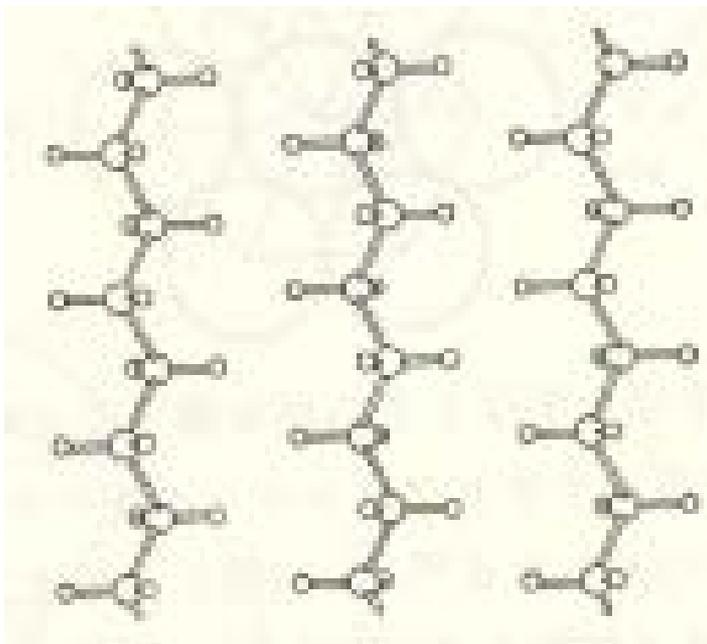
$$\mathcal{E} = \frac{hc}{\lambda} = h\nu$$

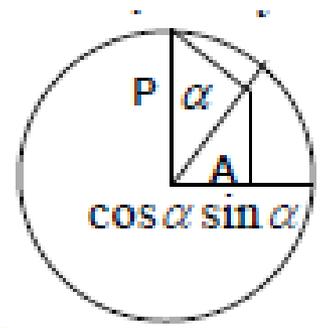
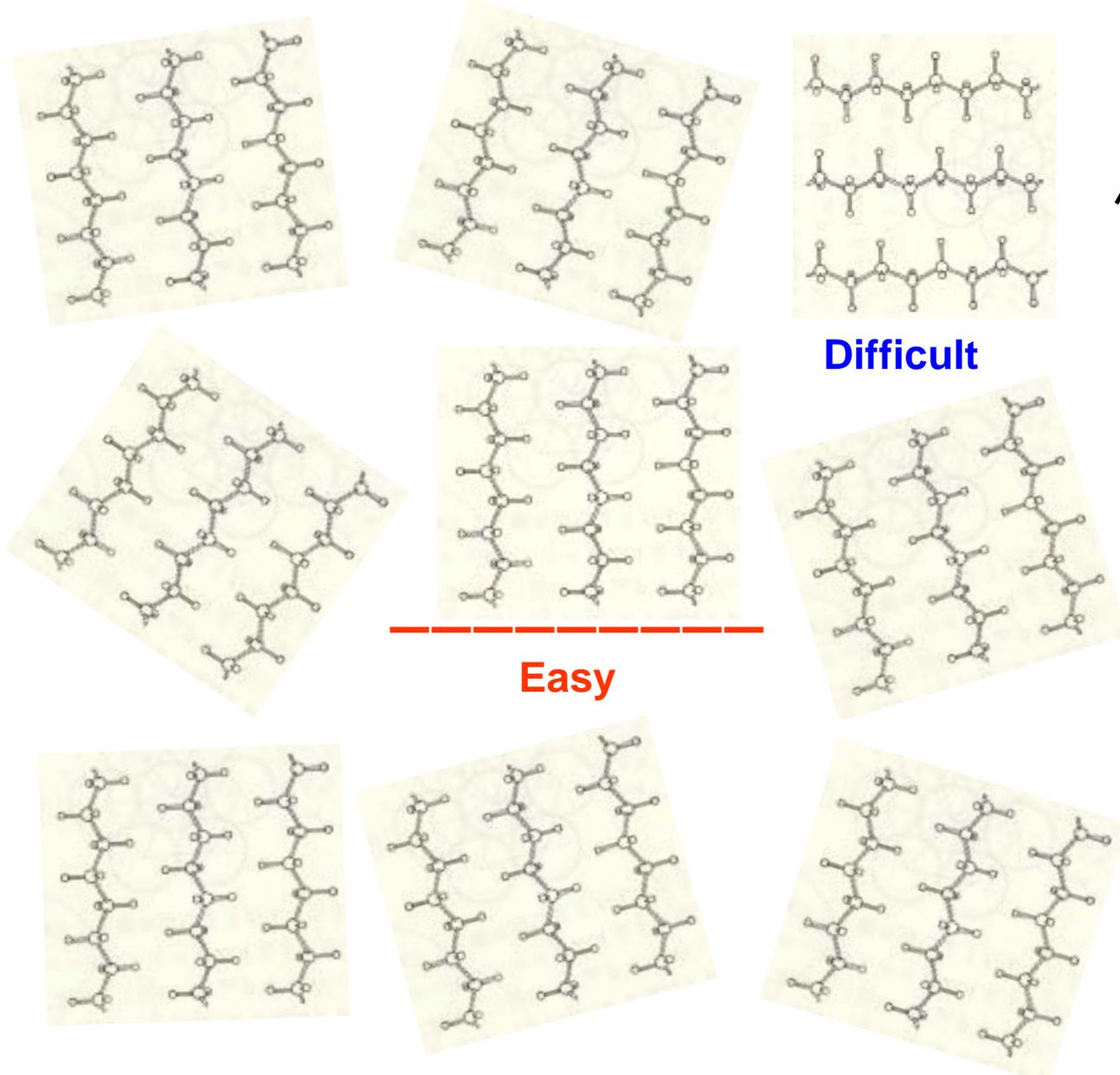
(c : velocity of light, ν : frequency, h : Planck's constant)

When an incident X-ray beam is entered, the **electrons in atoms** behave as **free electrons because of high photon energy.**

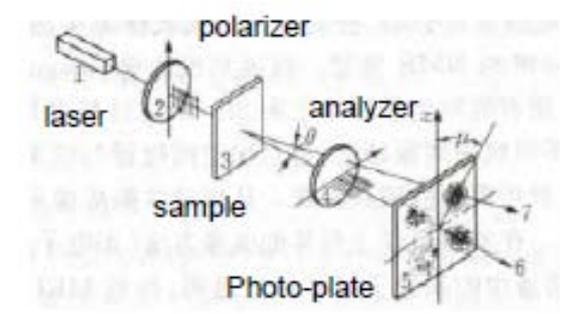
On the other hand, when visible light is entered, **electrons in atom** cause **vibration on bottom of the potential box.**

Considering vibrating dipole, **the potential field is not isotropic and electrons move easily along C-C polymer main chain axis** in comparison with the direction perpendicular to the C-C axis, when an incident wave interact with electrons belonging to C-C covalent bonds in main chains. That is, for an incident beam, **the vibrating dipole moment along C-C axis becomes larger than that perpendicular to the C-C axis.** Accordingly, scattered wave is sensitive to polarization condition of an incident beam.





$\alpha = 45^\circ$



Polarized light scattering (Hv pattern)

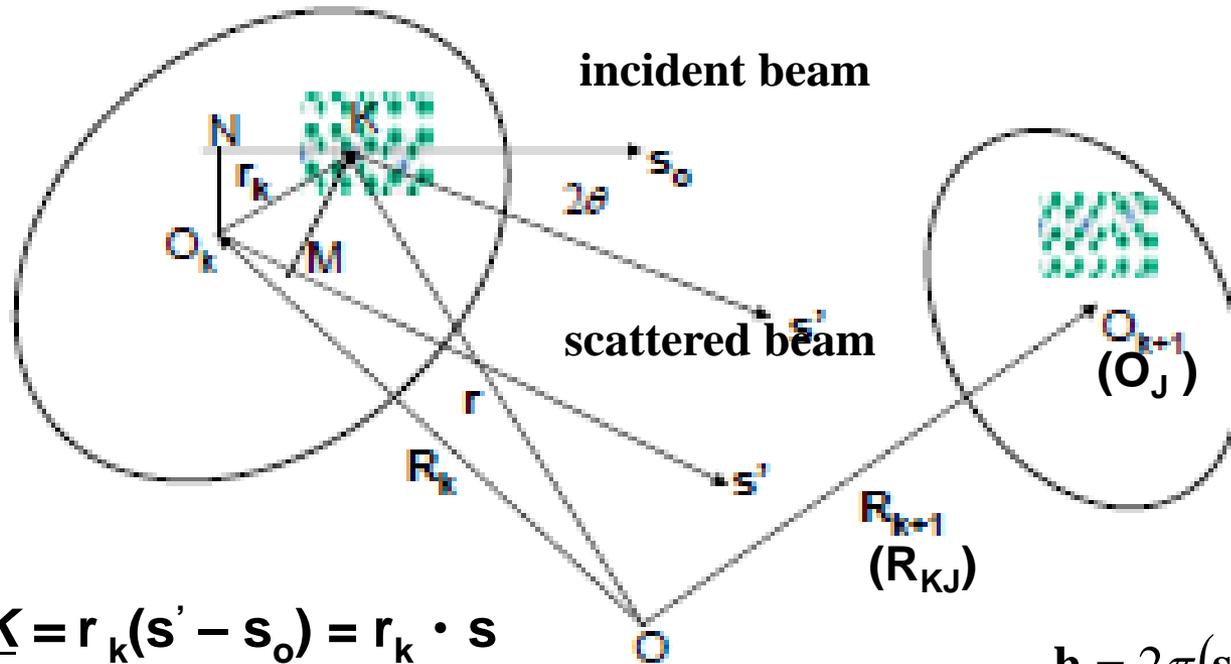
This short course is concerned with the difference between X-ray and visible light. The different points for fundamental equations between diffraction and scattering are not pointed out in their text books.

Because, each chapter for the diffraction and scattering have been written by different authors in most of textbooks. The unified understanding above concept is very important as the user.

First Chapter

X-ray scattering from atoms and the application to one polymeric molecule

For scattering of X-ray and visible light, the scattered intensity I is given by EE^* , in which E is the scattering amplitude and E^* is the conjugate complex. Of course, the X-ray diffraction intensity is given by the same equation $I = EE^*$.

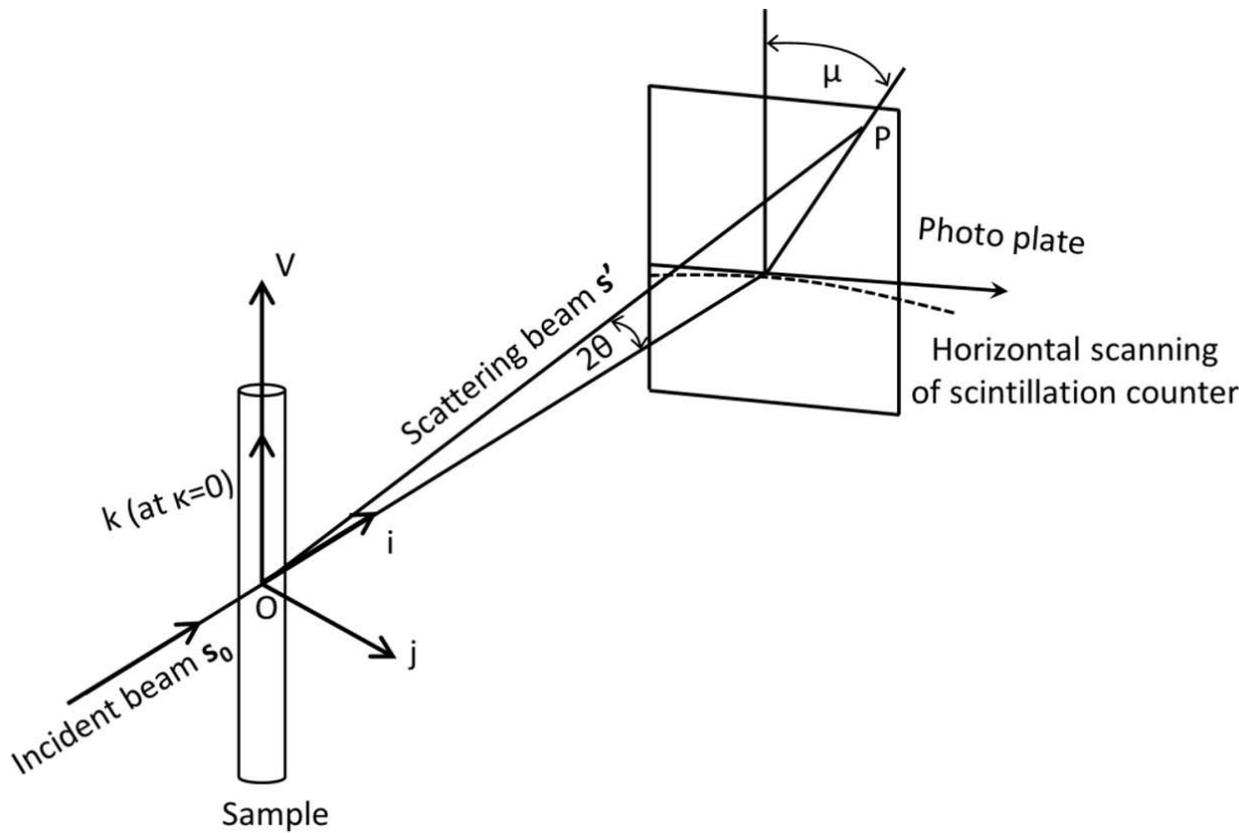


$$\underline{O_k M} - \underline{NK} = r_k (s' - s_0) = r_k \cdot s$$

$$h = 2\pi(s' - s_0)$$

$$E_k = \sum_{i=1}^K E_i \exp[2\pi i (s' - s_0) / \lambda \cdot (r_{ki} + \mathbf{R}_K)] = \exp(ih \cdot \mathbf{R}_K) \sum_{i=1}^K E_i \exp(ih \cdot \mathbf{r}_i)$$

$$= K \exp(ih \cdot \mathbf{R}_K) \int_{kth} \rho(\mathbf{r}_K) \exp(ih \cdot \mathbf{r}_K) d\mathbf{r}_K$$



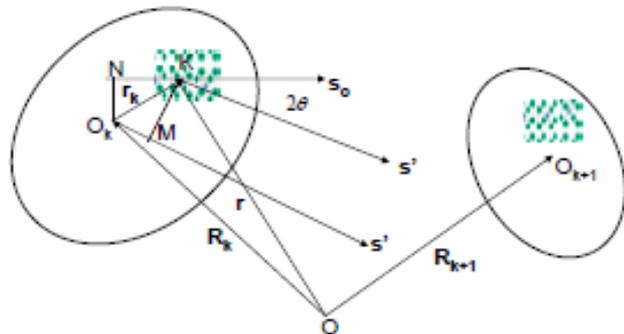
$$h = |\mathbf{h}| = (4\pi/\lambda)\sin\theta$$

2θ scattering angle

μ azimuthal angle

$$-(2\pi/\lambda)(\mathbf{s}' - \mathbf{s}_0) = (2\pi/\lambda)[(1 - \cos 2\theta)\mathbf{i} - \sin 2\theta \sin \mu \mathbf{j} - \sin 2\theta \cos \mu \mathbf{k}] = (4\pi/\lambda)\sin\theta \mathbf{h} = h\mathbf{h}$$

$$(4\pi/\lambda)\sin\theta[\sin\theta \mathbf{i} - \cos\theta \sin \mu \mathbf{j} - \cos\theta \cos \mu \mathbf{k}] = (4\pi/\lambda)\sin\theta \mathbf{v} = h\mathbf{v} = \mathbf{h}$$



$$\rho(\mathbf{r}) = (\rho_o - \rho_s)\sigma(\mathbf{r}) + \rho_s$$

$$\sigma(\mathbf{r}) = 1 \quad \text{within a particle}$$

$$\sigma(\mathbf{r}) = 0 \quad \text{without a particle}$$

General description about scattering for X-ray and visible light.

$$\rho(\mathbf{r}) = (\rho_o - \rho_s)\sigma(\mathbf{r}) + \rho_s \quad \rho_s = 0$$

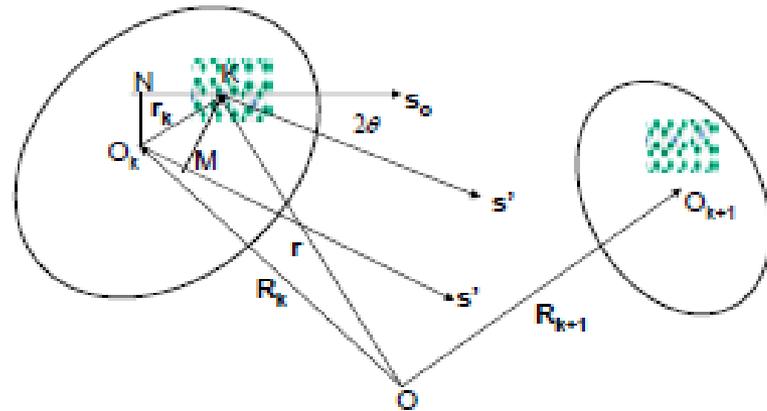
$$E_k(h) = K \exp(i\mathbf{h} \cdot \mathbf{R}_K) \int_{kth} \rho(\mathbf{r}_K) \exp[i\mathbf{h} \cdot \mathbf{r}_K] d\mathbf{r}_K$$

$$= K \exp(i\mathbf{h} \cdot \mathbf{R}_K) \int \rho_o \exp[i\mathbf{h} \cdot \mathbf{r}_K] d\mathbf{r}_k = K \exp(i\mathbf{h} \cdot \mathbf{R}_k) \int \rho_o \exp(i\mathbf{h} \cdot \mathbf{r}) d\mathbf{r}$$

$d\mathbf{r}_k$ is micro-volume element at position vector \mathbf{r}_k . $\int d\mathbf{r}_k$: volume integral

$$E = \sum_{k=1}^N E_k \quad E^* = \sum_{k=1}^N E_k^*$$

N is the number of particles.

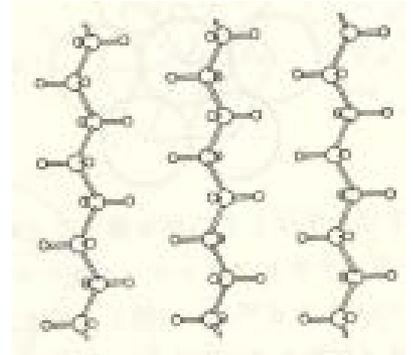


Scattering from an **isolated particle** reveals that \mathbf{R}_k becomes $\mathbf{0}$ and $\exp(i\mathbf{h} \cdot \mathbf{R}_k) = 1$

$$E_{iso} = K \int \rho(\mathbf{r}_k) \exp(i\mathbf{h} \cdot \mathbf{r}_k) d\mathbf{r}_k = K \int \rho(\mathbf{r}) \exp(i\mathbf{h} \cdot \mathbf{r}) d\mathbf{r} = K \rho_o \int \exp(i\mathbf{h} \cdot \mathbf{r}) d\mathbf{r}$$

For visible light beam, electrons of atom cause vibration on bottom of the potential box. Considering vibrating dipole, the potential field is not isotropic and electrons move easily along C-C main chain axis of polymer in comparison with the direction perpendicular to the C-C axis, when incident wave interact with electrons along C-C covalent bonds in main chains. That is, for incident beam, **the vibrating dipole moment along C-C axis becomes larger than that perpendicular to the C-C axis.**

Accordingly, scattered wave is sensitive to polarization condition of an incident beam.



ρ_o is not constant.

$$\begin{aligned}
 E_k &= \sum_{i=1}^K E_i \exp[2\pi i(\mathbf{s}' - \mathbf{s}_o) / \lambda \cdot (\mathbf{r}_i + \mathbf{R}_K)] = \exp(i\mathbf{h} \cdot \mathbf{R}_K) \sum_{i=1}^K E_i \exp(i\mathbf{h} \cdot \mathbf{r}_i) \\
 &= K \exp(i\mathbf{h} \cdot \mathbf{R}_K) \int \rho(\mathbf{r}) \exp[i\mathbf{h} \cdot \mathbf{r}_K] d\mathbf{r}_K = K \exp(i\mathbf{h} \cdot \mathbf{R}_K) \int (\mathbf{M}_k \cdot \mathbf{O}) \exp(i\mathbf{h} \cdot \mathbf{r}_k) d\mathbf{r}_k \\
 &= K \exp(i\mathbf{h} \cdot \mathbf{R}_K) \int (\mathbf{M} \cdot \mathbf{O}) \exp(i\mathbf{h} \cdot \mathbf{r}) d\mathbf{r}
 \end{aligned}$$

where M_k is dipole moment induced by k -th scattering element, and \mathbf{O} is unit vector along polarization direction of analyzer.

For scattering from an isolated particle, it can be written as follows:

$$E_{iso} = K \int \rho(\mathbf{r}_k) \exp(i\mathbf{h} \cdot \mathbf{r}_k) d\mathbf{r}_k = K \int \rho(\mathbf{r}) \exp(i\mathbf{h} \cdot \mathbf{r}) d\mathbf{r} = K \rho_o \int \exp(i\mathbf{h} \cdot \mathbf{r}) d\mathbf{r}$$

$$E = \sum_{i=1}^Z E_i \exp[2\pi i(\mathbf{s}' - \mathbf{s}_0) / \lambda \bullet \mathbf{r}_{ij}] = \sum_{i=1}^Z E_i \exp[i\mathbf{h} \bullet \mathbf{r}_{ij}]$$

$$I = I_e \left| \sum_{i=1}^Z E_i \exp[i\mathbf{h} \bullet \mathbf{r}_{ij}] \right|^2 = I_e \sum_{i=1}^Z \sum_{j=1}^Z \exp\{i\mathbf{h} \bullet (\mathbf{r}_i - \mathbf{r}_j)\}$$

$$= I_e \left[Z + \sum_{i \neq j} \sum_{j=1}^Z \exp[i\mathbf{h} \bullet \mathbf{r}_{ij}] \right]$$

$$I = I_e \left(Z + \left| \sum_{i=1}^Z f_i \right|^2 - \sum_{i=1}^Z |f_i|^2 \right)$$

$$f_i = \int \rho_i(\mathbf{r}) \exp(\mathbf{h} \bullet \mathbf{r}) dV$$

$\rho_i(\mathbf{r})$: density distribution of the i -th electron

f_i : electric structure factor,

dV : volume element

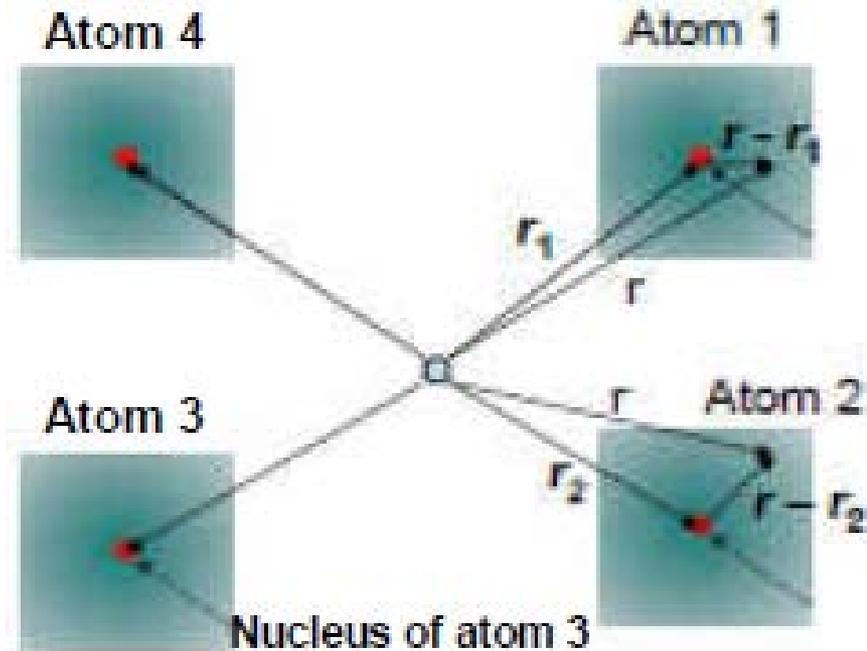
The average density distribution within an atom with atomic number Z is postulated as

$$\rho(\mathbf{r}) = \rho_1(\mathbf{r}) + \rho_2(\mathbf{r}) + \dots + \rho_z(\mathbf{r})$$

$$f = \sum_{i=1}^Z f_i = \int \rho(\mathbf{r}) \exp(\mathbf{h} \bullet \mathbf{r}) dV$$

f is termed as atomic structure factor for an atom with electron number Z .

Summation of electric structure factor f_i



$$I = I_e \left(Z + |f|^2 - \sum_{i=1}^Z |f_i|^2 \right)$$

When the electron density distribution is uniform within the atom, $I_e \sum_{i=1}^Z |f_i|^2$ is equal to $I_e Z$ denoting the summation of scattered intensity from Z electrons.

$$I = I_e |f|^2$$

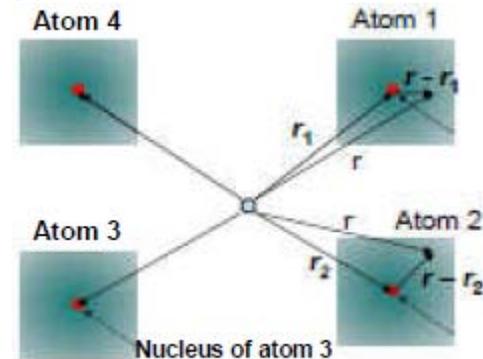
To discuss scattering from scale larger than an atom, the scattering from one molecule with multi-atoms shall be described. As like the scattered intensity from one atom with the atomic structure factor f , the scattered intensity I_m from one polyatomic molecule with the structure factor F_m in gas is given by neglecting molecular interference as follows:

$$I_m = I_e |F_m|^2$$

$$\rho_{mol}(\mathbf{r}) = \sum_{i=1}^{Z_1} \rho_1(\mathbf{r} - \mathbf{r}_i) + \sum_{i=1}^{Z_2} \rho_2(\mathbf{r} - \mathbf{r}_i) + \dots + \sum_{i=1}^{Z_N} \rho_N(\mathbf{r} - \mathbf{r}_i)$$

$$\sum_{i=1}^{Z_1} \rho_1(\mathbf{r} - \mathbf{r}_i) \quad \text{Electron density of 1st atom with } Z_1 \text{ electrons}$$

$$\sum_{i=1}^{Z_N} \rho_N(\mathbf{r} - \mathbf{r}_i) \quad \text{Electron density of the } N\text{-th atom with } Z_N \text{ electrons}$$



The structural factor of one polymeric molecule F_m is given by

$$\begin{aligned}
 F_m &= \int \exp[i\mathbf{h} \cdot \mathbf{r}] \left\{ \sum_{i=1}^{Z_1} \rho_1(\mathbf{r} - \mathbf{r}_i) d\nu_1 + \sum_{i=1}^{Z_2} \rho_2(\mathbf{r} - \mathbf{r}_i) d\nu_2 + \dots + \sum_{i=1}^{Z_N} \rho_N(\mathbf{r} - \mathbf{r}_i) d\nu_N \right\} \\
 &\approx \sum_{i=1} \exp[i\mathbf{h} \cdot \mathbf{r}_i] \left\{ \int \left\{ \sum_{i=1}^{Z_1} \rho_1(\mathbf{r} - \mathbf{r}_i) \exp[i\mathbf{h} \cdot (\mathbf{r} - \mathbf{r}_i)] d\nu_1 + \sum_{i=1}^{Z_2} \rho_2(\mathbf{r} - \mathbf{r}_i) \exp[i\mathbf{h} \cdot (\mathbf{r} - \mathbf{r}_i)] d\nu_2 + \right. \right. \\
 &\quad \left. \left. \dots + \sum_{i=1}^{Z_N} \rho_N(\mathbf{r} - \mathbf{r}_i) \exp[i\mathbf{h} \cdot (\mathbf{r} - \mathbf{r}_i)] d\nu_N \right\} \right\}
 \end{aligned}$$

Then the scattered intensity I_m from one polyatomic molecule is given by

$$F_m = \sum_i f_i^{at} \exp[i(\mathbf{h} \cdot \mathbf{r}_i)] = \sum_i f_i^{at} \exp[2\pi i(\mathbf{s}' - \mathbf{s}_0) / \lambda \cdot \mathbf{r}_i]$$

Each integration part corresponds to each atomic structure factor given by f_i^{at} for the i -th atom with Z_i electrons.

Thus, F_m is rewritten as

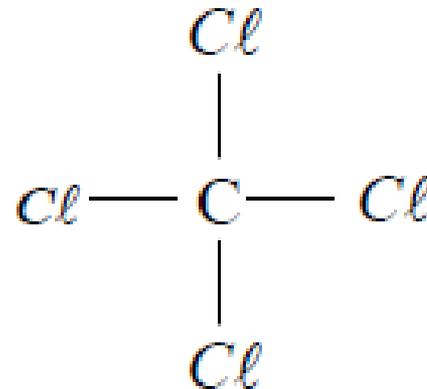
$$\begin{aligned}
 I_m &= I_e |F_m|^2 = I_e F_m F_m^* = I_e \sum_i \sum_j f_i^{at} f_j^{at} \exp[i\mathbf{h}(\mathbf{r}_i - \mathbf{r}_j)] \\
 &= I_e \sum_i \sum_j f_i^{at} f_j^{at} \exp[i(\mathbf{h} \cdot \mathbf{r}_{ij})] = I_e \sum_i \sum_j f_i^{at} f_j^{at} \exp[2\pi i(\mathbf{s}' - \mathbf{s}_0) / \lambda \cdot \mathbf{r}_{ij}]
 \end{aligned}$$

$$\begin{aligned}
 I_m &= I_e |F_m|^2 = I_e F_m F_m^* = I_e \sum_i \sum_j f_i^{at} f_j^{at} \exp[i\mathbf{h}(\mathbf{r}_i - \mathbf{r}_j)] \\
 &= I_e \sum_i \sum_j f_i^{at} f_j^{at} \exp[i(\mathbf{h} \cdot \mathbf{r}_{ij})] = I_e \sum_i \sum_j f_i^{at} f_j^{at} \exp[2\pi i (\mathbf{s}' - \mathbf{s}_o) / \lambda \cdot \mathbf{r}_{ij}]
 \end{aligned}$$

- The calculation of I_m must be carried out in two considerations:
- 1) interference effect between atoms existed in the molecule, and
 - 2) the equal existing probability in three-dimensional space.

Hence,

$$I_m = I_e \langle |F_m|^2 \rangle = I_e \sum_i \sum_j f_i^{at} f_j^{at} \frac{\sin(hr_{ij})}{hr_{ij}}$$



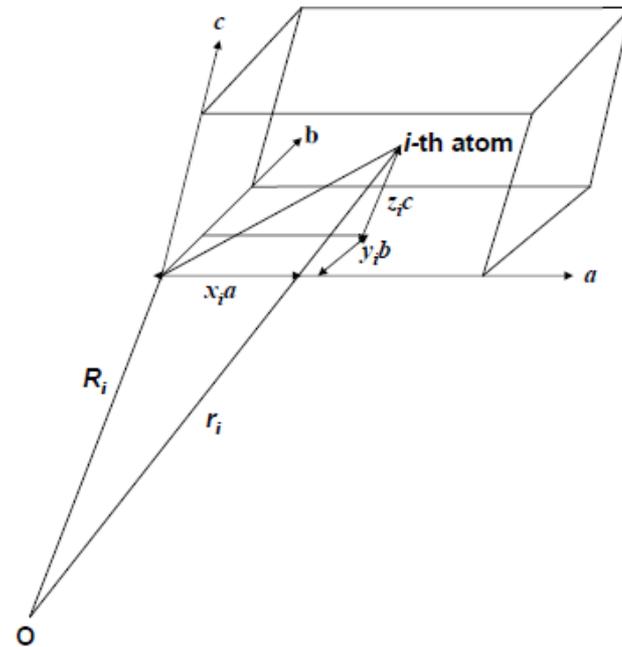
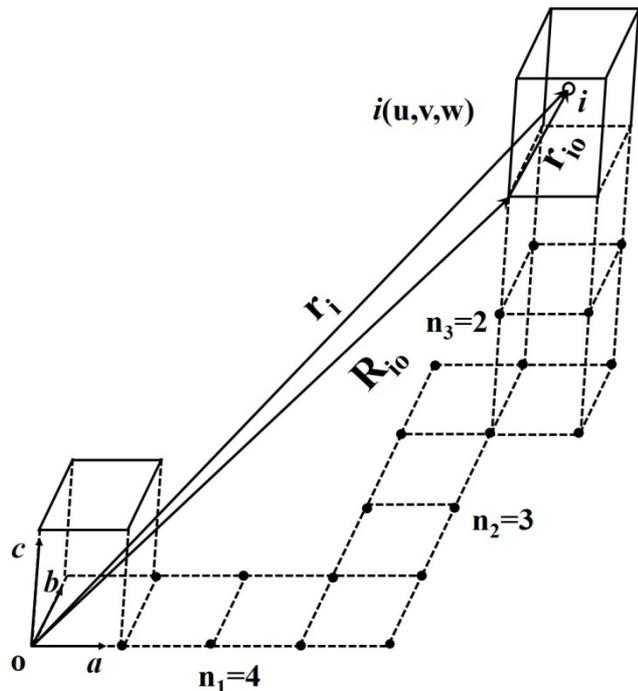
Let's represent the concrete example for isolated carbon tetrachloride

$$I_m = f_C^2 + 4f_{Cl}^2 + 8f_C f_{Cl} \frac{\sin[hr(C - Cl)]}{hr(C - Cl)} + 12f_{Cl}^2 \frac{\sin[hr(Cl - Cl)]}{hr(Cl - Cl)}$$

II-3. X-ray diffraction from crystallites

Let's consider X-ray diffraction by using Eq. (II-22) concretely.

For X-ray diffraction, a particle can be replaced with a crystallite and a crystallite consists of crystal units and the crystal units with regularity are arranged as shown in Figure 4. Then the probability function to find other units within the crystallite is defined to be unity and the intensity from a crystal unit becomes simple summation for intensities from atoms in the unit by neglecting the interference effect.



$$\mathbf{r}_i = \mathbf{R}_{i0} + \mathbf{r}_{i0} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} + x_i \mathbf{a} + y_i \mathbf{b} + z_i \mathbf{c}$$

$$\begin{aligned}
I_m &= I_e |F_m|^2 = I_e F_m F_m^* = I_e \sum_i \sum_j f_i^{at} f_j^{at} \exp[i\mathbf{h}(\mathbf{r}_i - \mathbf{r}_j)] \\
&= I_e \sum_i \sum_j f_i^{at} f_j^{at} \exp[i(\mathbf{h} \cdot \mathbf{r}_{ij})] = I_e \sum_i \sum_j f_i^{at} f_j^{at} \exp[2\pi i(\mathbf{s}' - \mathbf{s}_o)/\lambda \cdot \mathbf{r}_{ij}] \\
I &= I_e \left\{ \sum_i f_i^{at} \exp[2\pi i(\mathbf{s}' - \mathbf{s}_o)/\lambda \cdot \mathbf{r}_i] \right\}^2 = I_e \left\{ \sum_i f_i^{at} \exp[i\mathbf{h} \cdot \mathbf{r}_i] \right\}^2 = I_e |F_C|^2 \\
I &= I_e \left\{ \sum_i f_i \exp[2\pi i(\mathbf{s}' - \mathbf{s}_o)/\lambda \cdot \mathbf{r}_i] \right\}^2 = I_e \left\{ \sum_i f_i \exp[i\mathbf{h} \cdot \mathbf{r}_i] \right\}^2 = I_e |F_C|^2
\end{aligned}$$

$$\mathbf{r}_i = \mathbf{R}_{i0} + \mathbf{r}_{i0} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} + x_i \mathbf{a} + y_i \mathbf{b} + z_i \mathbf{c}$$

$$\begin{aligned}
I &= I_e \left[\sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} \exp[i\mathbf{h}(n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c})] \times \sum_i f_i \exp[i\mathbf{h}(x_i \mathbf{a} + y_i \mathbf{b} + z_i \mathbf{c})] \right]^2 \\
&= I_e LL^* \left| \sum_i f_i \exp[i\mathbf{h}(x_i \mathbf{a} + y_i \mathbf{b} + z_i \mathbf{c})] \right|^2 = I_e LL^* |F(S)|^2
\end{aligned}$$

$$L = \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} \exp[i\mathbf{h}(n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c})] = \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} \exp[2\pi i(\mathbf{s}' - \mathbf{s}_o)/\lambda \cdot (n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c})]$$

$$F(S) = \sum_i f_i \exp[i\mathbf{h}(x_i \mathbf{a} + y_i \mathbf{b} + z_i \mathbf{c})] = \sum_i f_i \exp[2\pi i\mathbf{S}(x_i \mathbf{a} + y_i \mathbf{b} + z_i \mathbf{c})] \quad \mathbf{h} = 2\pi\mathbf{S}$$

$$\begin{aligned}
L &= \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} \exp[2\pi i(n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}) \cdot \mathbf{S}] \\
&= \sum_{n_1=0}^{N_1-1} \exp[2\pi i n_1 (\mathbf{a} \cdot \mathbf{S})] \sum_{n_2=0}^{N_2-1} \exp[2\pi i n_2 (\mathbf{b} \cdot \mathbf{S})] \sum_{n_3=0}^{N_3-1} \exp[2\pi i n_3 (\mathbf{c} \cdot \mathbf{S})] \\
&= \sum_{n_1=0}^{N_1-1} \exp[2\pi i n_1 h] \sum_{n_2=0}^{N_2-1} \exp[2\pi i n_2 k] \sum_{n_3=0}^{N_3-1} \exp[2\pi i n_3 \ell] \\
LL^* &= \frac{\sin^2(\pi N_1 h) \sin^2(\pi N_2 k) \sin^2(\pi N_3 \ell)}{\sin^2(\pi h) \sin^2(\pi k) \sin^2(\pi \ell)}
\end{aligned}$$

Laue condition
Laue function

where L^* is complex conjugate of L .

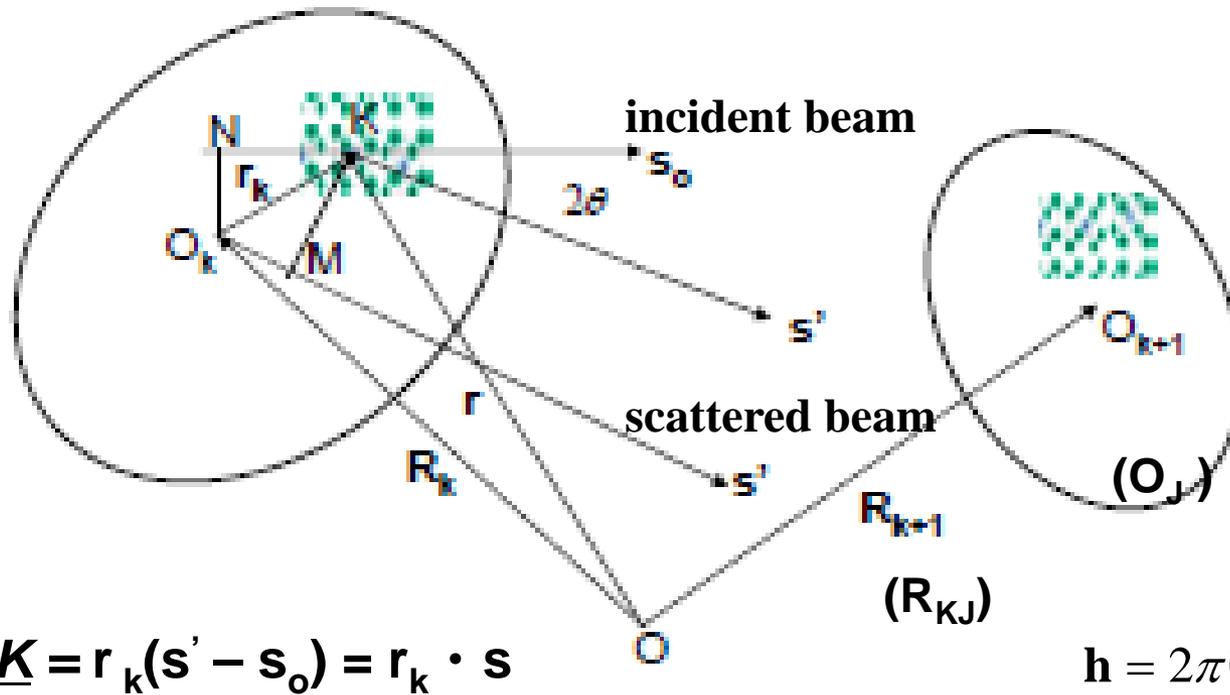
At $N_1, N_2, N_3 \gg 1$, the above eq. becomes a periodic function termed as Laue function, when the following eq. is satisfied, in which h, k , are well-known as Miller index. These are very important conditions to raise X-ray diffraction. The following eq. is also termed as Laue conditions, which is indispensable rule different from usual scattering.

$$\mathbf{S} \cdot \mathbf{a} = h, \quad \mathbf{S} \cdot \mathbf{b} = k, \quad \mathbf{S} \cdot \mathbf{c} = \ell \quad (h, k, \ell : \text{integer})$$

Many text books explain the reason why the above relationship is dispensable for X-ray diffraction.

However, LL^* is one of the special cases of X-ray scattering represented by the fundamental eq. generally.

The X-ray diffraction intensity is given by the same equation $I = EE^*$.



$$\underline{O_k M} - \underline{NK} = \mathbf{r}_k (\mathbf{s}' - \mathbf{s}_0) = \mathbf{r}_k \cdot \mathbf{s}$$

$$\mathbf{h} = 2\pi(\mathbf{s}' - \mathbf{s}_0)$$

Fundamental equation

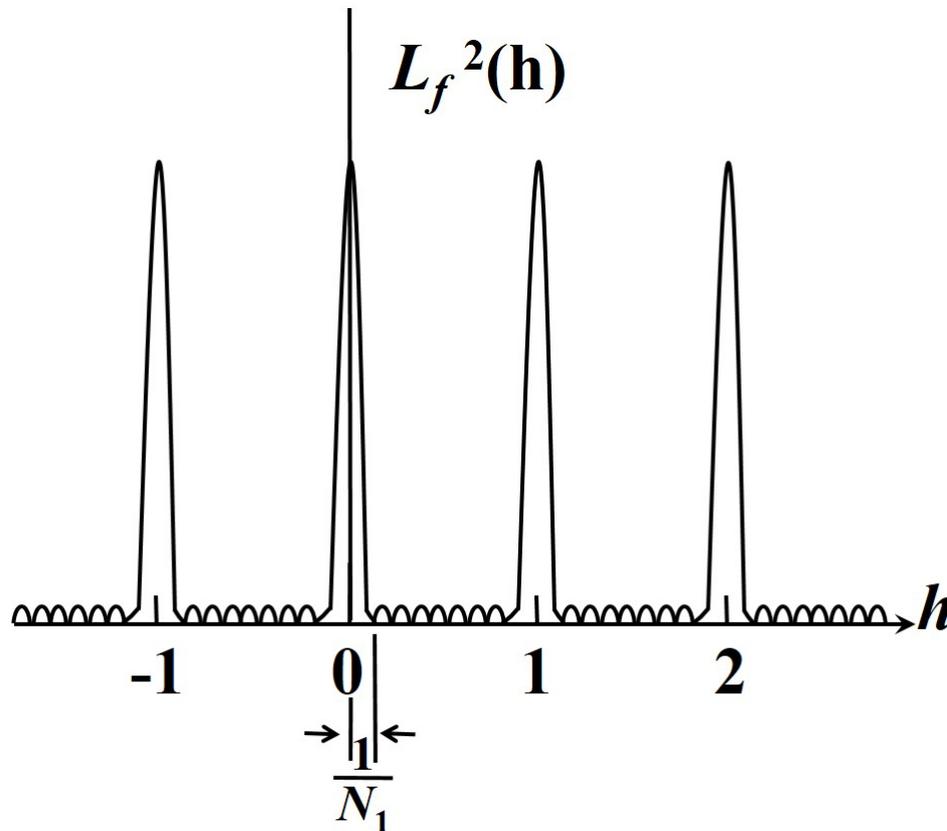
$$E_k = \sum_{i=1}^K E_i \exp[2\pi i (\mathbf{s}' - \mathbf{s}_0) / \lambda \cdot (\mathbf{r}_{ki} + \mathbf{R}_K)] = \exp(i\mathbf{h} \cdot \mathbf{R}_K) \sum_{i=1}^K E_i \exp(i\mathbf{h} \cdot \mathbf{r}_i)$$

$$= K \exp(i\mathbf{h} \cdot \mathbf{R}_K) \int_{kth} \rho(\mathbf{r}_K) \exp(i\mathbf{h} \cdot \mathbf{r}_K) d\mathbf{r}_K$$

Laue function LL^* in WAXD is in connection to crystal size and is also discontinuous part in X-ray scattering.

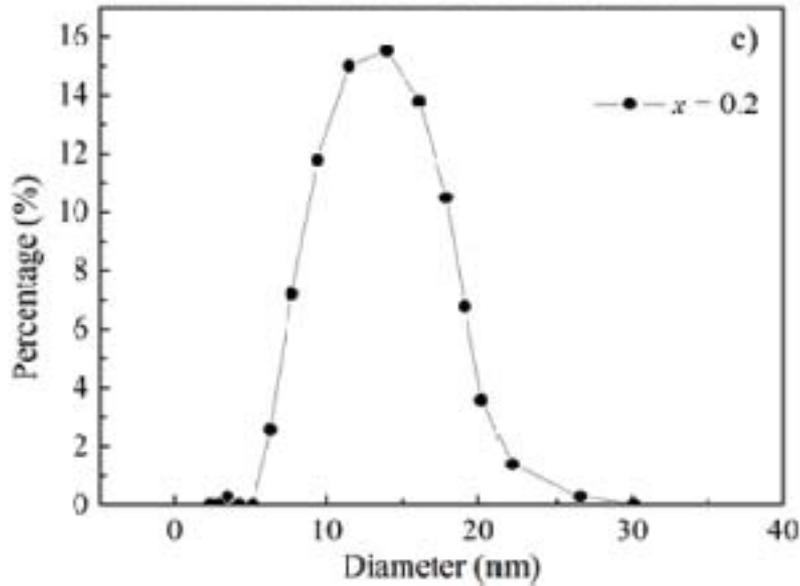
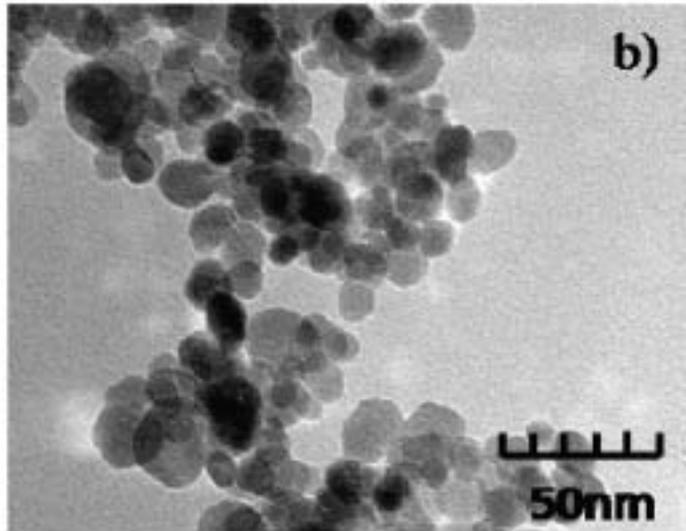
One dimensional case

$$L_1(h)L_1^*(h) = L_1^2(h) = \frac{\sin^2(\pi N_1 h)}{\sin^2(\pi h)}$$



$$I(2\theta) = KC^2 \frac{\sin^2 \left[\frac{2\pi}{\lambda} Nd \sin \theta \right]}{\sin^2 \left[\frac{2\pi}{\lambda} d \sin \theta \right]}$$

Zn_{0.2}Fe_{2.8}O₄ particles

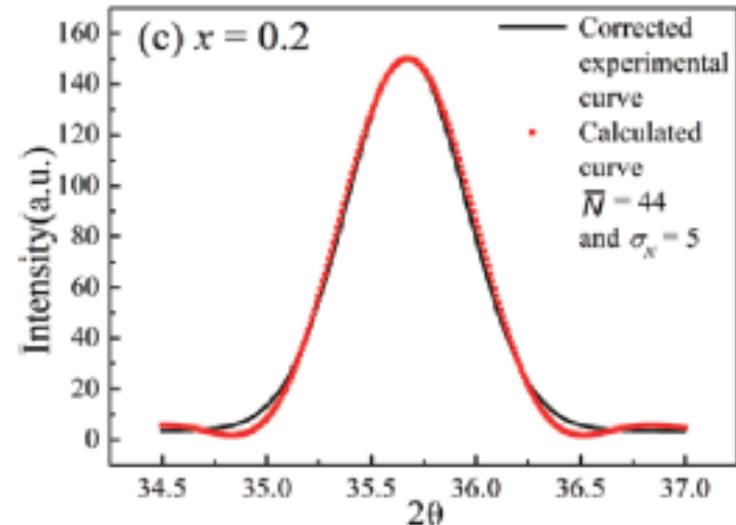


$$I(2\theta) = KC^2 \frac{\sin^2 \left[\frac{2\pi}{\lambda} Nd \sin \theta \right]}{\sin^2 \left[\frac{2\pi}{\lambda} d \sin \theta \right]}$$

$$P(N) = \frac{\exp \left[-\frac{(N - \bar{N})^2}{2\sigma_N^2} \right]}{\sum_{N=1}^{2\bar{N}-1} \exp \left[-\frac{(N - \bar{N})^2}{2\sigma_N^2} \right]}$$

$$\langle I(2\theta) \rangle = \sum_{N=1}^{2\bar{N}-1} P(N) I(2\theta)$$

$$I_{cal}(\theta) = \frac{\langle I(2\theta) \rangle}{\langle I_{top}(2\theta) \rangle} I_{exp}(2\theta)$$



$$F(S)F^*(S) = |F(S)|^2$$

Crystal structural factor is related to the scattering from the total atoms in a crystal unit. To satisfy Laue conditions, $(\mathbf{s}' - \mathbf{s}_0)/\lambda = \mathbf{S}$ must be represented by must be represented by reciprocal lattice vector \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* in a crystal unit, which is given by

$$\frac{\mathbf{s}' - \mathbf{s}_0}{\lambda} = \mathbf{S} = h\mathbf{a}^* + k\mathbf{b}^* + \ell\mathbf{c}^* \quad S = |\mathbf{S}| = \frac{2 \sin \theta}{\lambda} = \frac{1}{d} \quad (h, k, \ell : \text{integer})$$

Very important Eq. to pursue the mathematical treatment for WAXD

where

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{V} \quad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{V} \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{V} \quad (\mathbf{a}\mathbf{a}^* = \mathbf{b}\mathbf{b}^* = \mathbf{c}\mathbf{c}^* = 1, \text{ the others, zero})$$

V is the volume of a crystal unit.

$$F(S) = F(h, k, \ell) = \sum_i f_i \exp\{2\pi i(h\mathbf{a}^* + k\mathbf{b}^* + \ell\mathbf{c}^*)(x_i\mathbf{a} + y_i\mathbf{b} + z_i\mathbf{c})\}$$

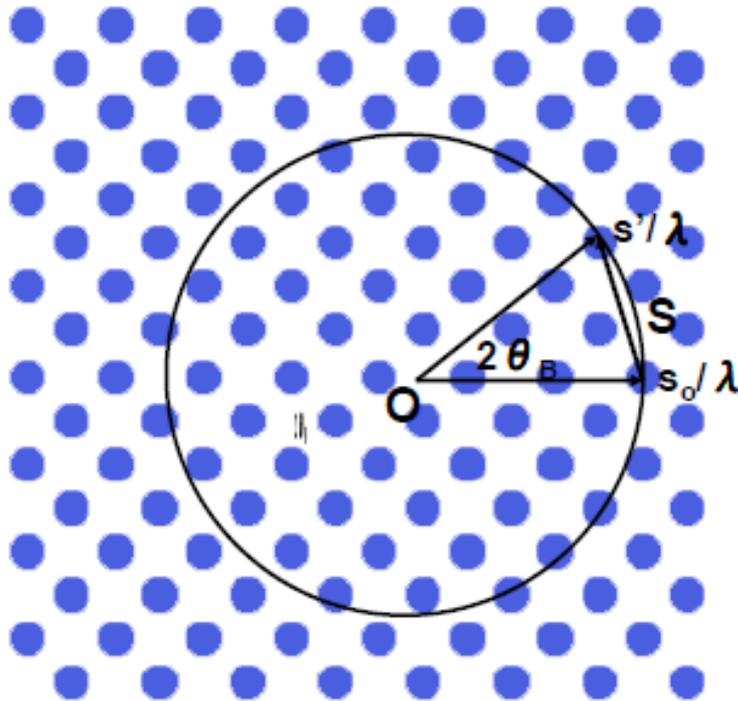
($\mathbf{a}\mathbf{a}^* = \mathbf{b}\mathbf{b}^* = \mathbf{c}\mathbf{c}^* = 1$, the others, zero)

$$F(h, k, \ell) = \sum_i f_i \exp[2\pi i(hx_i + ky_i + \ell z_i)]$$

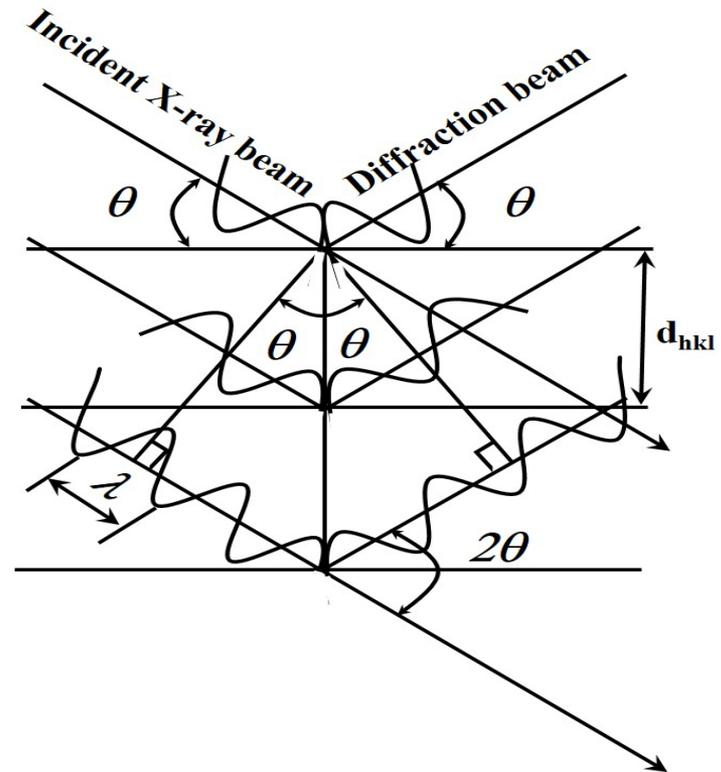
$$(\mathbf{s}' - \mathbf{s}_o) / \lambda = \mathbf{S}$$

$$S = |\mathbf{S}| = \frac{2 \sin \theta}{\lambda} = \frac{1}{d}$$

λ : 0.1542 nm for X-ray generated from Cu target



Ewald sphere representing Laue condition in reciprocal space.



Bragg equation representing X-ray diffraction in real space

$$2d \sin \theta_B = n\lambda \quad (n = 1, 2, \dots)$$

If there exist N atoms in a crystal unit, the coordinate of each atom can be given by:

Atom	1	2	3	-----	N
Coordinate	x_1, y_1, z_1	x_2, y_2, z_2	x_3, y_3, z_3		x_N, y_N, z_N
Atomic scattering factor	f_1	f_2	f_3		f_N

Thus, we have

$$F(h, k, \ell) = F_{hkl} = f_1 \exp\{2\pi i(hx_1 + ky_1 + \ell z_1)\} + f_2 \exp\{2\pi i(hx_2 + ky_2 + \ell z_2)\} + f_3 \exp\{2\pi i(hx_3 + ky_3 + \ell z_3)\} + \dots + f_N \exp\{2\pi i(hx_N + ky_N + \ell z_N)\}$$

$$|F_{hkl}|^2 = F_{hkl} F_{hkl}^* \quad I \propto |F_{hkl}|^2$$

Here every crystal plane is not related to the X-ray diffraction. Some crystal planes contribute to the reflection, but some do not contribute on the basis of extinction rule. The above Eq. is the fourth important thing to pursue the mathematical treatment for WAXD.

WAXD intensity $I(h, k, \ell) = I_e \frac{\sin^2(\pi N_1 h) \sin^2(\pi N_2 k) \sin^2(\pi N_3 \ell)}{\sin^2(\pi h) \sin^2(\pi k) \sin^2(\pi \ell)} |F_{hkl}|^2$

As the concrete examples,

Primitive lattice or simple lattice (Fig. III-7a)

1/8 atom x 8 = 1 atom

The center of coordinate **0, 0, 0**

$$F = f \exp[2\pi i(0)] = f \quad F^2 = f^2$$

Base centered lattice (Fig. III-7b)

Atom number in unit cell

1/8 atom x 8 + 1/2 atom x 2 = 2 atom

The center of coordinate **0, 0, 0** **1/2, 1/2, 0**

$$F = f \exp[2\pi i(0)] + f \exp[2\pi i\{h/2 + k/2\}]$$

$$= f \{1 + \exp[\pi i(h + k)]\}$$

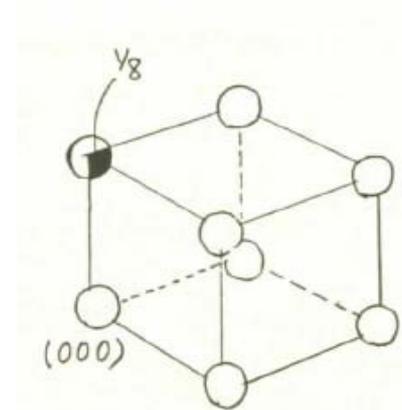
$$h+k \text{ even, } F = 2f \quad F^2 = 4f^2$$

h or k even or odd

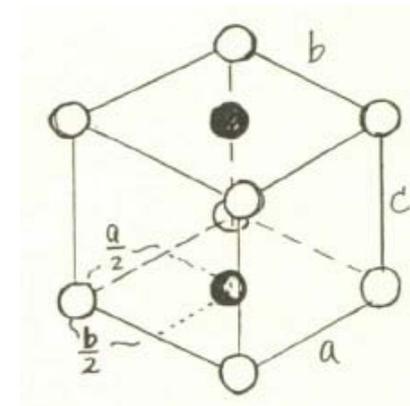
$h+k$ odd $F = 0$ Extinction rule

As for (1 1 1) (1 1 2) (1 1 3) (0 2 1) (0 2 0) (0 2 3) F values are the same.

As for (0 1 1) (0 1 2) (0 1 3) (1 0 1) $F = 0$ Extinction rule



(a) Primitive lattice



(b) Base centered lattice

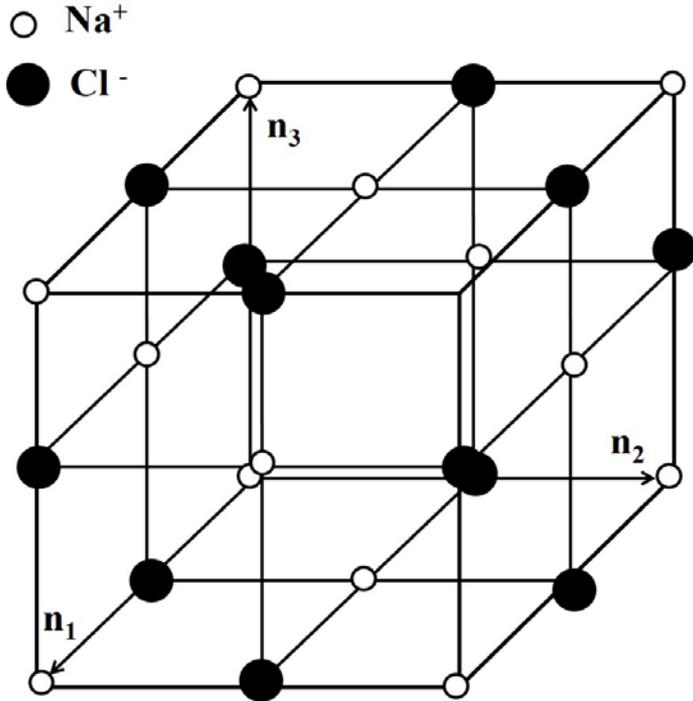
Extinction rule

Bravais lattice	Reflection	No reflection
Primitive	all	non
Base centered	h, k, ℓ all odd or all even	h, k, ℓ h or k odd (or even)
body centered	$(h+k+\ell)$ even	$(h+k+\ell)$ odd
face centered	h, k, ℓ all odd or all even	h, k, ℓ h, k, ℓ odd (or even)

A number of textbooks refer to the calculation procedures of $|F_{hkl}|^2$ concerning simple cubic lattice, base-centered orthorhombic lattice, body-centered cubic lattice and face-centered cubic lattice and then this paper does not describe the commentary. The example is shown for $NaCl$ unit.

Practice problem

Describe the structural factor of $NaCl$ unit and discuss extinction rule



Answer

The coordinate Na^+ and Cl^- are as follows:

Na^+

$$(0, 0, 0), \quad (0, \frac{1}{2}, \frac{1}{2}), \quad (\frac{1}{2}, 0, \frac{1}{2}), \quad (\frac{1}{2}, \frac{1}{2}, 0)$$

Cl^-

$$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \quad (\frac{1}{2}, 0, 0), \quad (0, \frac{1}{2}, 0), \quad (0, 0, \frac{1}{2})$$

$$F(hkl) = (f_{Na^+}) \{1 + \exp[\pi i(k + l)] + \exp[\pi i(h + l)] + \exp[\pi i(h + k)]\} \\ + (f_{Cl^-}) \exp(\pi i(h + k + l)) \{1 + \exp[-\pi i(k + l)] + \exp[-\pi i(h + l)] + \exp[-\pi i(h + k)]\}$$

$$F(h, k, \ell) = \begin{cases} 4(f_{Na^+} + f_{Cl^-}) \\ 4(f_{Na^+} - f_{Cl^-}) \\ 0 \end{cases}$$

k, h, ℓ , all even

k, h, ℓ , all odd

k, h, ℓ , even and odd mixing

For example

diffraction from the (111) plane

$$4(f_{Na^+} - f_{Cl^-})$$

diffraction from the (220) plane

$$4(f_{Na^+} + f_{Cl^-})$$

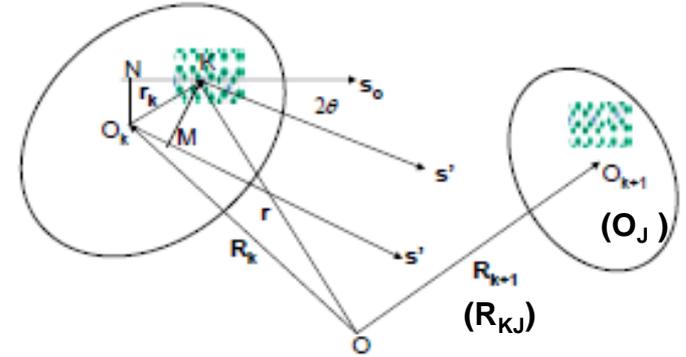
As supplementary explanation, let's consider the $F(h, k, \ell)$ for KCl with close atomic number $K(19)$ and $Cl(18)$. Different from $NaCl$, the difference between f_{K^+} and f_{Cl^-} are very small, since the number of electrons for K^+ and that for Cl^- are the same 18.

$$E_k(h) = K \int_{kth} \rho(\mathbf{r}) \exp[2\pi i(\mathbf{s}' - \mathbf{s}_0) / \lambda \cdot \mathbf{r}] d\mathbf{r} = K \int \rho(\mathbf{r}) \exp[i\mathbf{h} \cdot \mathbf{r}] d\mathbf{r}$$

$$= K \int \rho(\mathbf{r}_k) \exp[i\mathbf{h}(\mathbf{r}_k + \mathbf{R}_k)] d\mathbf{r}_k = K \exp(i\mathbf{h} \cdot \mathbf{R}_k) \int \rho(\mathbf{r}_k) \exp(i\mathbf{h} \cdot \mathbf{r}_k) d\mathbf{r}_k$$

IV Understandable explanation about SAXS

First of all, we shall consider N particles in the irradiated volume. Among N particles, we shall spot the K -th particle. As described already, the scattered intensity from K -th particle can be evaluated by using the above Eq. For SAXS, the Eq. is rewritten as follows:



$$E_K(h) = E_e \exp(i\mathbf{h} \cdot \mathbf{R}_K) \int \rho(\mathbf{r}_k) \exp[i(\mathbf{h} \cdot \mathbf{r}_k)] d\mathbf{r}_k \equiv E_e F_K(h) \exp(i\mathbf{h} \cdot \mathbf{R}_K)$$

$$F_K(h) = \int \rho(\mathbf{r}_k) \exp[i(\mathbf{h} \cdot \mathbf{r}_k)] d\mathbf{r}_k \quad E_e \text{ corresponds to } K \text{ and } I_e = E_e^2.$$

$F_K(h)$ is structural amplitude of K -particle and $\exp(i\mathbf{h} \cdot \mathbf{R}_K)$ is the phase factor for the center OK in K -particle based on the origin of the coordinate. Assuming that scattering wave is coherent, the total scattering amplitude E_s of the entire system is given by

$$E_s(h) = \sum_{K=1}^N E_K(h) = E_e \sum_{K=1}^N F_K(h) \exp(i\mathbf{h} \cdot \mathbf{R}_K)$$

Putting $\mathbf{R}_{KJ} = \mathbf{R}_J - \mathbf{R}_K$, the scattered intensity $I(h)$ becomes

$$\begin{aligned}
 I(h) &= I_e \sum_{K=1}^N \sum_{J=1}^N F_K(h) F_J^*(h) \exp(i\mathbf{h} \cdot \mathbf{R}_K) \exp(-i\mathbf{h} \cdot \mathbf{R}_J) \\
 &= I_e \sum_{K=1}^N \sum_{J=1}^N F_K(h) F_J^*(h) \exp(-i\mathbf{h} \cdot \mathbf{R}_{KJ}) \\
 &= I_e \left\{ \sum_{K=1}^N |F_K^2| + \sum_{K \neq J}^N \sum_{J=1}^N F_K(h) F_J^*(h) \exp(-i\mathbf{h} \cdot \mathbf{R}_{KJ}) \right\}
 \end{aligned}$$

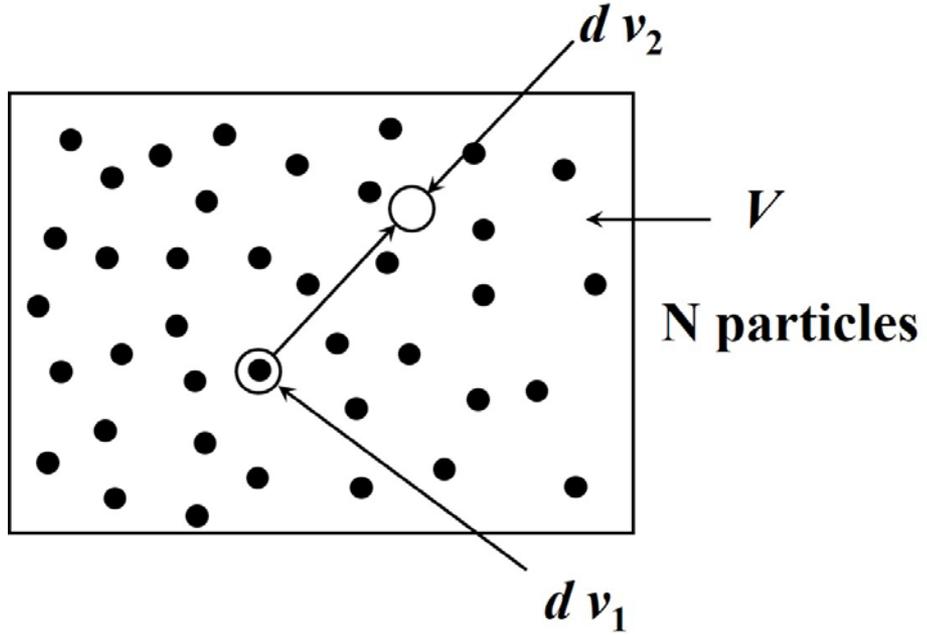
The first term means the total scattered intensity from each particle and the second term is related to inter-particle interference in the entire system. Here there is no orientation correlation between isotropic particles in the position of center of each particles, Eq. can be written as follows:

$$\begin{aligned}
 I(h) &= I_e \left\{ N \langle F^2 \rangle + \langle F \rangle^2 \sum_{K \neq J}^N \sum_{J=1}^N \exp(-i\mathbf{h} \cdot \mathbf{R}_{KJ}) \right\} \\
 &= I_e N \left[\langle F^2 \rangle - \langle F \rangle^2 \right] + I_e \langle F \rangle^2 \left[N + \sum_{K \neq J}^N \sum_{J=1}^N \exp(-i\mathbf{h} \cdot \mathbf{R}_{KJ}) \right]
 \end{aligned}$$

Generally, each particle is not spherically symmetry and then $\langle F^2 \rangle - \langle F \rangle^2$ termed as diffuse scattering is not zero. As shown in the previous Eq. , the significant term for SAXS is due to inter-particle interference effect. This effect is unnecessary to consider for WAXD as described in Session II.

Now, let's focus assembly of single atom as shown in Figure 12.

The existing possibility of other atom in dV separated with distance r from the center is $dP(r)$. In the volume V of the whole specimen, there exist N atoms. The average volume occupied by one atom becomes $V/N = v_1$. In this case, the possibility to find the first atom in dV is dV/v_1 . When the atoms are separated at enough distance each other, the finding possibility for the second atom at the pointed tip of r becomes always dV/v_1 .



N particles in volume V .

However, in dense atomic assembly as like liquid, the possibility at the small r region is dependent upon r by inter-atomic interaction and it can describe as $dP(r) = P(r)d\nu/\nu_1$. Accordingly, when two atoms are connected or r is shorter than twice distance of atom radius, $P(r)$ becomes zero. When r is much far than twice distance of atom radius, $P(r)$ become unity. If r is in the middle region, $P(r)$ becomes a function with fluctuation around unity. If $\{P(r) - 1\}$ has the fluctuation, the double summation in the below Eq. cannot be carried out by the same weight for pair of each two-atoms and the summation must be represented by weight $\frac{1}{\nu_1}\{P(r) - 1\}$.

$$I(h) = I_e \left\{ N \langle F^2 \rangle + \langle F \rangle^2 \sum_{K \neq J}^N \sum_J^N \exp(-ih \cdot \mathbf{R}_{KJ}) \right\}$$

$$= I_e N \left[\langle F^2 \rangle - \langle F \rangle^2 \right] + I_e \langle F \rangle^2 \left[N + \sum_{K \neq J}^N \sum_J^N \exp(-ih \cdot \mathbf{R}_{KJ}) \right]$$

Let's consider \mathbf{R}_{KJ} as continuous scale in statistical group, the integration can be done in stead of summation of

$$\sum_{K \neq J} \sum_J \exp(-ih \cdot \mathbf{R}_{KJ}) = \frac{1}{\nu_1} \int_0^\infty \{P(R_{KJ}) - 1\} \exp(-ih \cdot \mathbf{R}_{KJ}) d\nu$$

$$= \frac{4\pi}{\nu_1} \int_0^\infty \{P(R_{KJ}) - 1\} \frac{\sin(hR_{KJ})}{h} R_{KJ} dR_{KJ}$$

$$\begin{aligned}
I(h) &= I_e N \left[\langle F^2 \rangle - \langle F \rangle^2 \right] + I_e \langle F \rangle^2 \left[N + \sum_{K \neq J}^N \sum_J^N \exp(-ih \cdot \mathbf{R}_{KJ}) \right] \\
&= I_e N \left[\langle F^2 \rangle - \langle F \rangle^2 \right] + I_e \langle F \rangle^2 \left[N + \frac{4\pi}{v_1} \int_0^\infty \{P(R_{KJ}) - 1\} \frac{\sin(hR_{KJ})}{h} R_{KJ} dR_{KJ} \right] \\
&= I_e N \left[\langle F^2 \rangle - \langle F \rangle^2 \right] + I_e \langle F \rangle^2 \left[N + \frac{4\pi}{v_1} \int_0^\infty \{P(R) - 1\} \frac{\sin(hR)}{h} R dR \right] \\
&= I_e N \left[\langle F^2 \rangle - \langle F \rangle^2 \right] + I_e N \langle F \rangle^2 \left[1 + \frac{4\pi}{V} \int_0^\infty \{P(R) - 1\} \frac{\sin(hR)}{h} R dR \right]
\end{aligned}$$

When the system is isotropic and all the particles are the same shape with the same volume, $\langle F^2 \rangle$ is equal to $\langle F \rangle^2$.

Also, the density at R is $\rho(r) = P(r)/V$ and the average density is $\rho_o = 1/V$.

$$I(h) = I_e N \langle F \rangle^2 \left[1 + 4\pi \int_0^\infty \{\rho(R) - \rho_o\} \frac{\sin(hR)}{hR} R^2 dR \right]$$

Here, the above equation can be rewritten by using $P(R) = \rho(R) - \rho_o$

$$I(h) = I_e N \langle F \rangle^2 \left[1 + 4\pi \int_0^\infty P(R) \frac{\sin(hR)}{hR} R^2 dR \right] \quad \mathbf{P(R) : radial distribution function}$$

$$I(h) = I_e N \langle F \rangle^2 \left[1 + 4\pi \int_0^\infty P(R) \frac{\sin(hR)}{hR} R^2 dR \right] = I_o + I_o \int_0^\infty 4\pi R^2 P(R) \frac{\sin(hR)}{hR} dR$$

$$I'(h) = \frac{I(h) - I_o}{I_o} = \int_0^\infty 4\pi R^2 P(R) \frac{\sin(hR)}{hR} dR$$

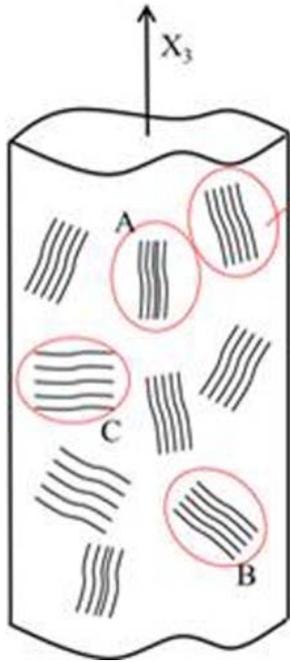
In most of textbooks, R is written by r .

$$I'(h) = \frac{I(h) - I_o}{I_o} = \int_0^\infty 4\pi r^2 P(r) \frac{\sin(hr)}{hr} dr$$

By Fourier transform

$$4\pi r P(r) = \frac{2}{\pi} \int_0^\infty h I'(h) \sin(hr) dh$$

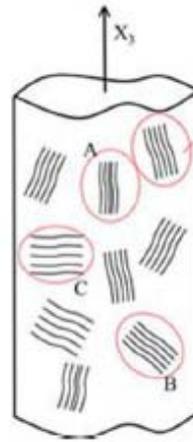
Weak inter-chain force



Amorphous chain arrangement

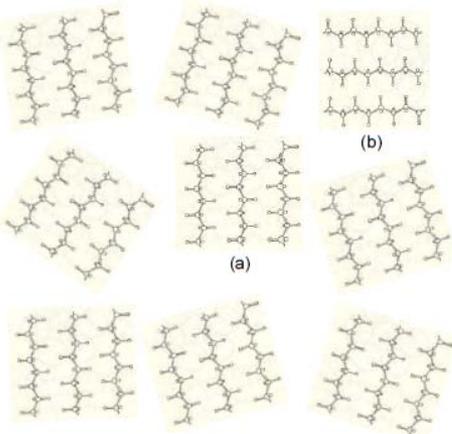
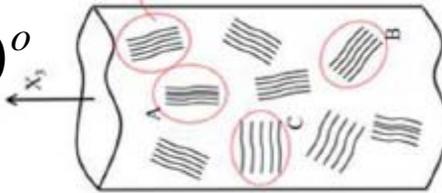
$$\kappa = 0^\circ$$

$$\alpha = 90^\circ$$

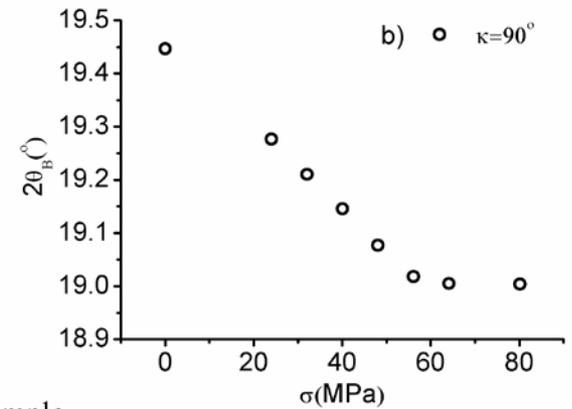
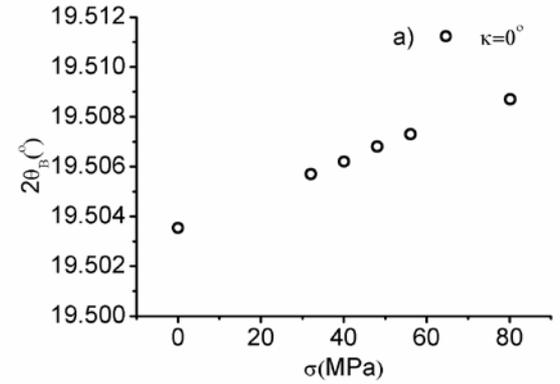
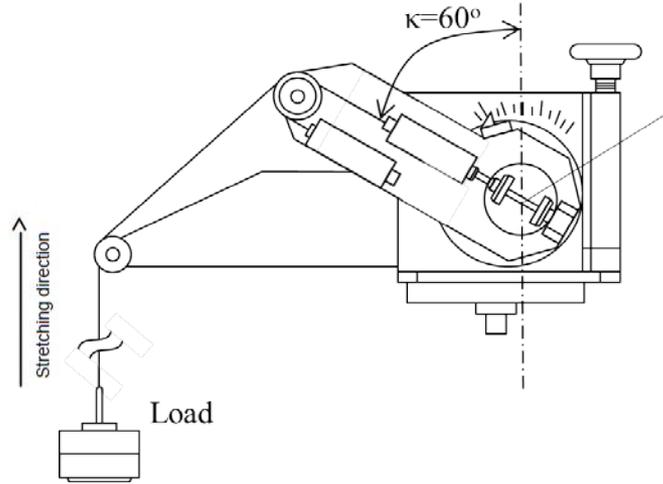


$$\kappa = 90^\circ$$

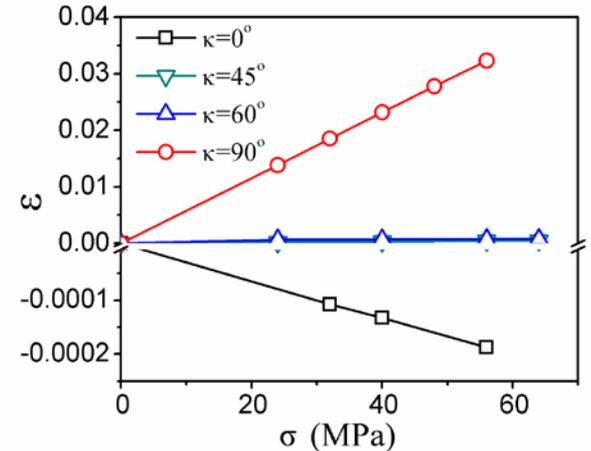
$$\alpha = 0^\circ$$

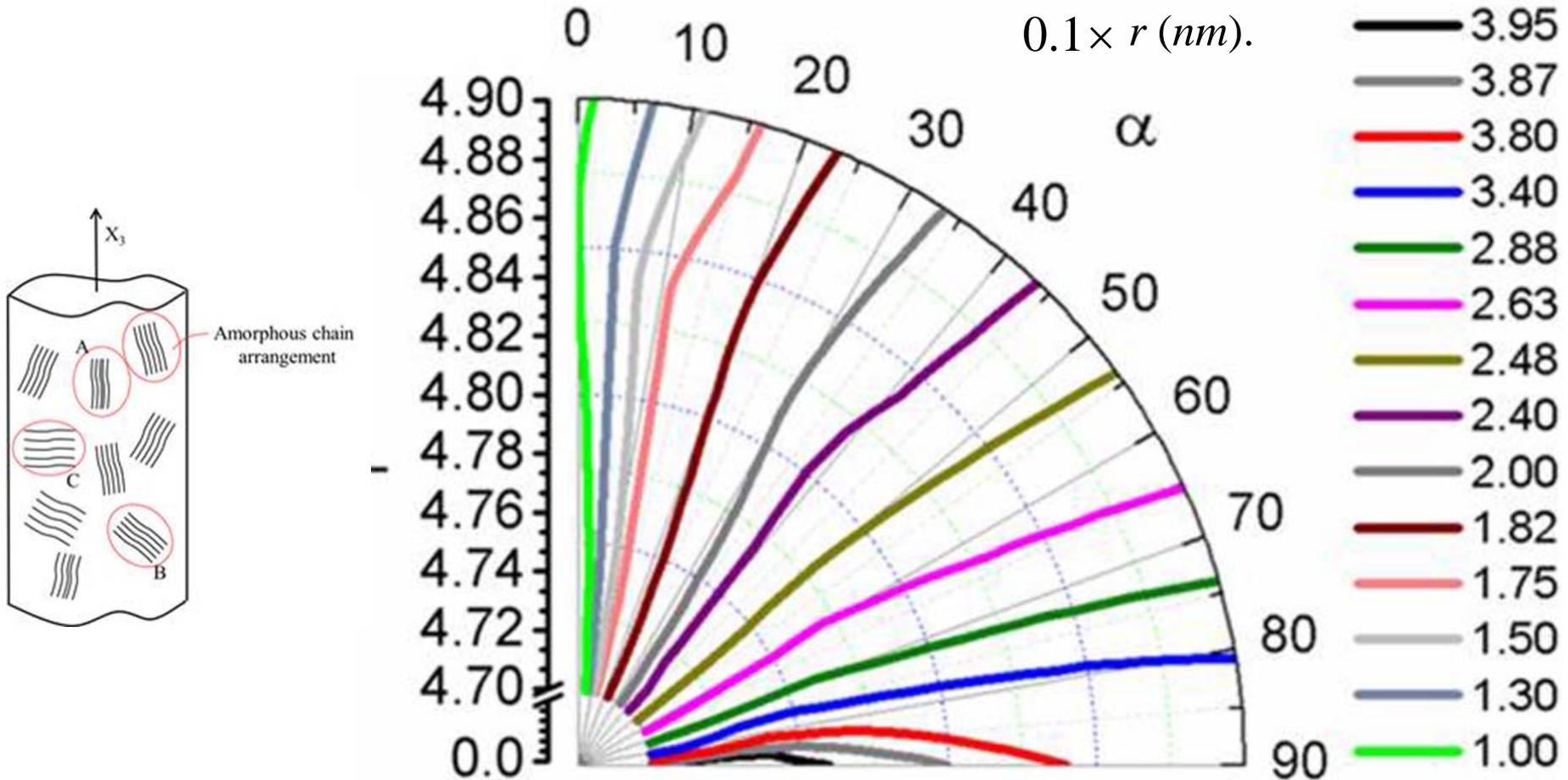


Orientation of polyethylene crystallites



Sample





Radial distribution function associated with electron density distribution for a PPEK fiber

The most probable distance r between adjacent chains
 0.486 nm at $\alpha = 0^\circ$, 0.473 nm at $\alpha = 90^\circ$

$$F_K(h) = \int \rho(\mathbf{r}_k) \exp[i(\mathbf{h} \cdot \mathbf{r}_k)] d\mathbf{r}_k$$

Let's consider for a sphere with radius a . From

$$\rho(r) = \rho_o \quad r \leq a/2$$

$$\rho(r) = 0 \quad r \geq a/2$$

$$F(h) = \int \rho(\mathbf{r}) \exp[i(\mathbf{h} \cdot \mathbf{r})] d\mathbf{r} = \rho_o \int_0^{2\pi} \int_0^\pi \int_0^a r^2 \cos[hr \cos \alpha] \sin \alpha dr d\alpha d\phi$$

$$= 3V(\sin U - U \cos U) / U^3$$

$$I(h) = I_e \rho_o |F(h)|^2$$

$$I(h) = 9I_e \rho_o V^2 (\sin U - U \cos U)^2 / U^6 = I(q)$$

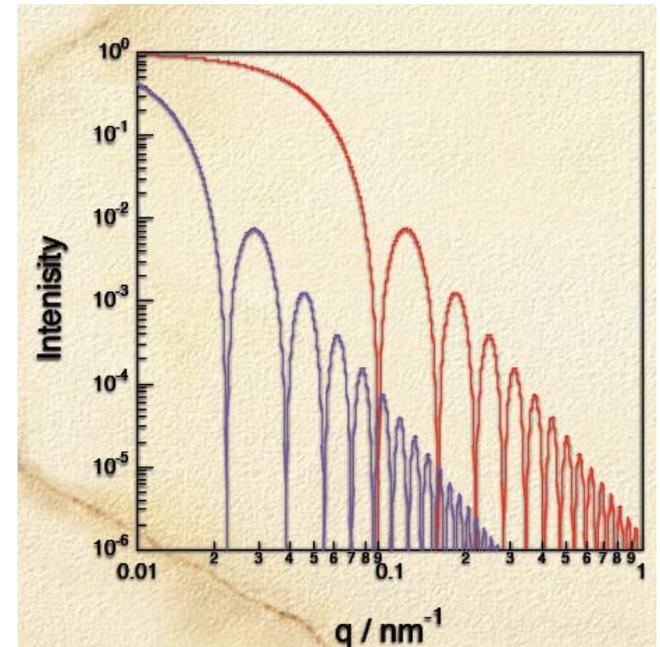
$$U = ha = (4\pi a / \lambda) \sin \theta = 2\pi qa \quad V = 4\pi a^3 / 3$$

Plotting $I(q)$ against q , many sharp peaks reflecting intra-particle effect appear in high range of q .

The decrease of peak top of $I(q)$ shows asymptotical behavior of q^{-4} , which is termed as - 4 rule (Porod rule).

Such many peaks can be observed in the system where the isolated uniform spheres with the same radius are dispersed in solution but the peaks become duller for the particles with different radius.

Of course, the many scattered peaks of $I(h)$ are independent of X-ray diffraction from crystal planes, even if the sphere composed of crystallites. The angle range concerning diffraction peaks is much wider than the small angle range discussed above.



$$I'(h) = \frac{I(h) - I_o}{I_o} = \int_0^\infty 4\pi r^2 P(r) \frac{\sin(hr)}{hr} dr$$

Guinier law

Now, let's consider Guinier law, since the law is very important for SAXS. For SAXS measurements for uniform dilute polymer solution or uniform particle dispersion, Guinier plots have been used to determine radius of inertia of polymer chain or that of particle in the dilute solution. Guinier plots can be induced by series expansion (Maclaurin) of $\sin(hr)$ around $hr = 0$ for the above Eq.

$$I'(h) = \frac{I(h) - I_o}{I_o} = \int_0^\infty 4\pi R^2 P(R) \frac{\sin(hR)}{hR} dR \quad \frac{\sin x}{x} = 1 - \frac{x^2}{6} + \frac{x^4}{120} - \dots$$

$$= 4\pi \left\{ \int_0^D P(R) R^2 dR - \frac{h^2}{6} \int_0^D P(R) R^4 dR + \frac{h^4}{120} \int_0^D P(R) R^6 dR - \dots \right\}$$

$$= 4\pi \int_0^D P(R) R^2 dR \left\{ 1 - \frac{h^2}{3} \left[\frac{\int_0^D P(R) R^4 dR}{2 \int_0^D P(R) R^2 dR} \right] + \dots \right\}$$

D is the point at $P(R) = 0$ and corresponds to the diameter for sphere. Here,

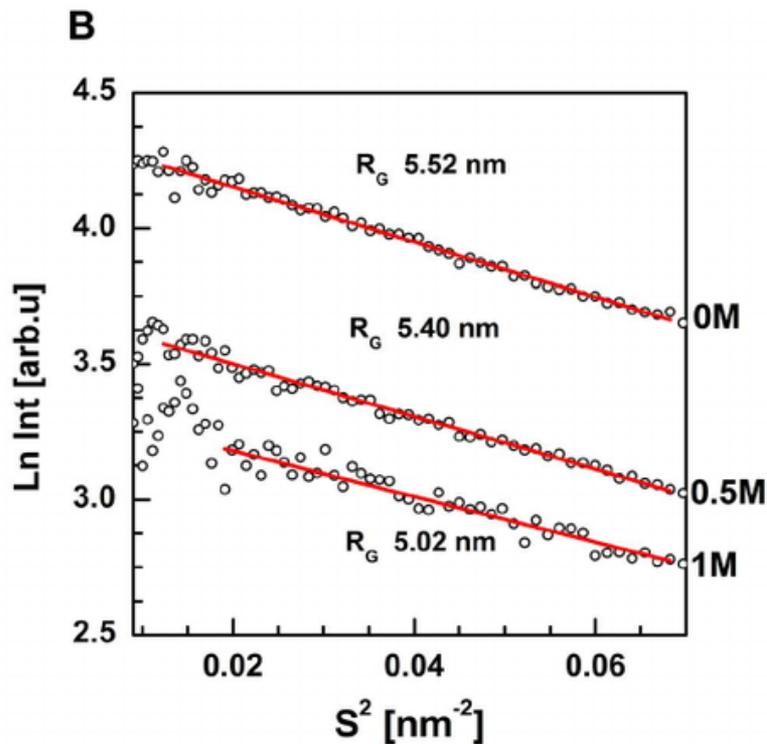
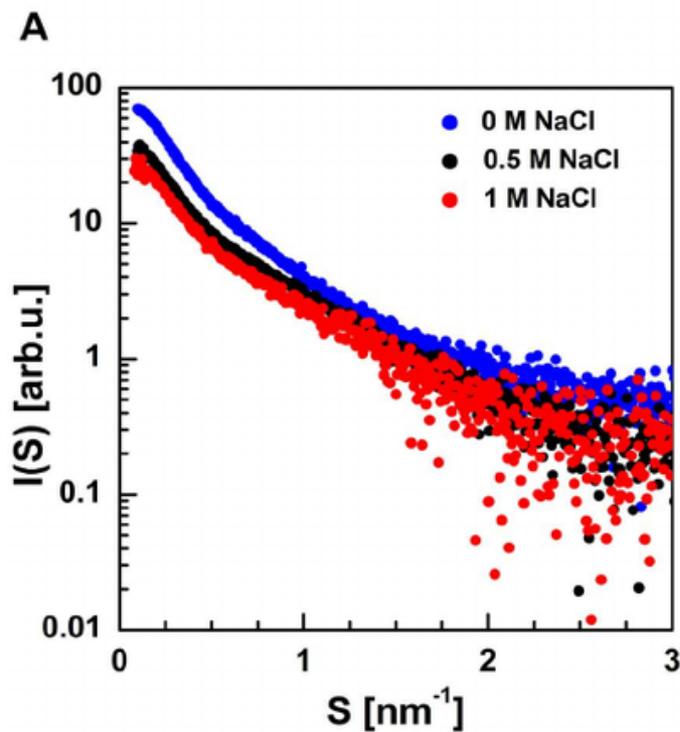
$$I(0) = 4\pi \int_0^D P(R)R^2 dr \quad R_g^2 = \frac{1}{2} \frac{\int_0^D P(R)R^4 dR}{\int_0^D P(R)R^2 dR}$$

$$I'(h) = I(0) \left\{ 1 - \frac{h^2}{3} R_g^2 + \frac{1}{2} \left(\frac{h^2}{3} R_g^2 \right)^2 - \dots \right\} \approx I(0) \exp\left(-\frac{h^2 R_g^2}{3}\right)$$

$$I'(s) = I(0) \exp\left[-\frac{(2\pi s)^2 R_g^2}{3}\right]$$

$$e^x = 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \dots$$

R_g is termed as radius gyration.



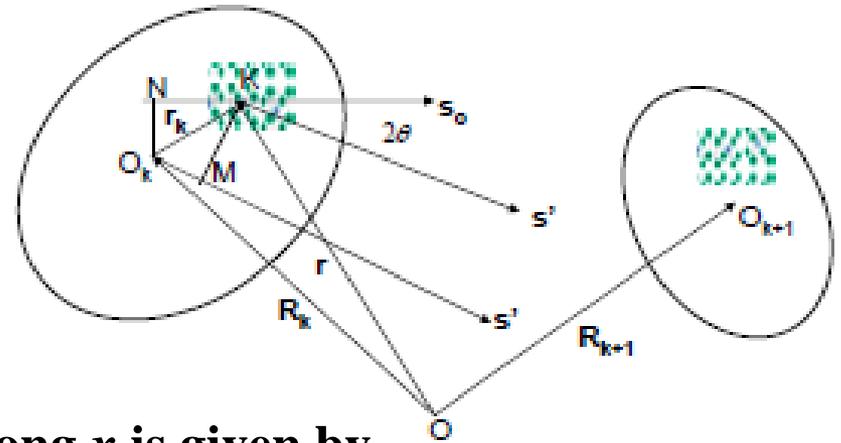
SAXS scattering profiles of the full-length barley SG-T1 protein in solution

The overlapped particles K and $K+1$ are separated and the separation for two spheres is shown below figure.

For a sphere with radius a , the correlation function $Q(r)$ can be induced as follows:

$$x^2 + y^2 = a^2$$

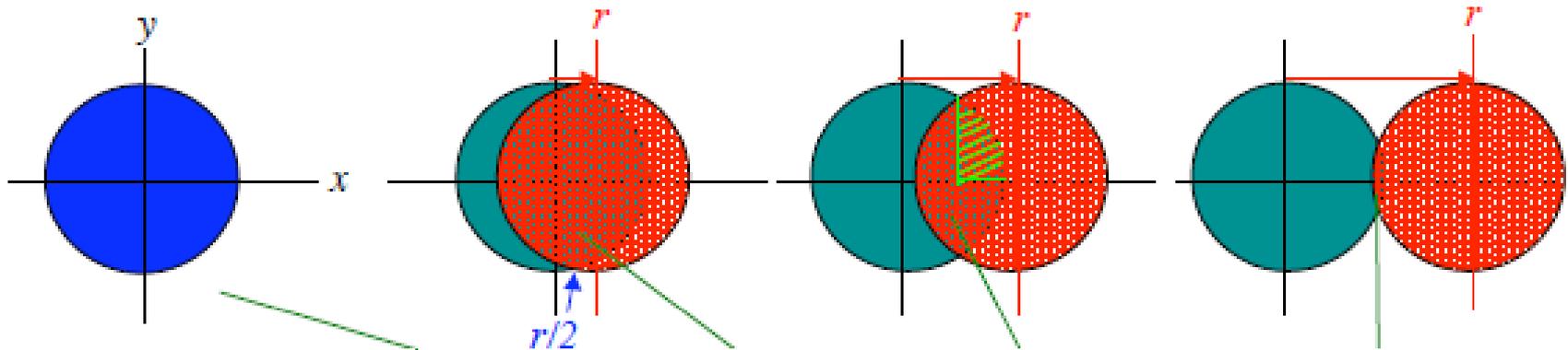
$$(x - a)^2 + y^2 = a^2$$



Evaluation for volume V of revolution along x is given by

$$V = \int_{r/2}^a 2\pi \left(\sqrt{a^2 - x^2} \right)^2 dx \quad r \rightarrow R \quad Q(R) = \rho^2 \frac{4\pi a^3}{3} \left[1 - \frac{3R}{4a} + \frac{1}{16} \left(\frac{R}{a} \right)^3 \right] = P(R)$$

$$R_g^2 = \frac{1 \int_0^{2a} Q(R) R^4 dR}{2 \int_0^{2a} Q(R) R^2 dR} = \frac{1 \int_0^{2a} Q(R) R^4 dR}{2 \int_0^{2a} Q(R) R^2 dR} = \frac{1}{2} \frac{2a^5/5}{a^3/3} = \frac{3a^2}{5} \quad R_g = \sqrt{\frac{3}{5}} a$$



Radius gyration (R_g) for several particles

Particle shape, size radius gyration (R_g)

Sphere with radius a $\left(\frac{3}{5}\right)^{1/2} a$

Spheroid (a, a, va) $a\left(\frac{2+v^2}{5}\right)^{1/2}$

Cylinder (2H: height, R: radius) $\left(\frac{R^2}{2} + \frac{H^2}{3}\right)^{1/2}$

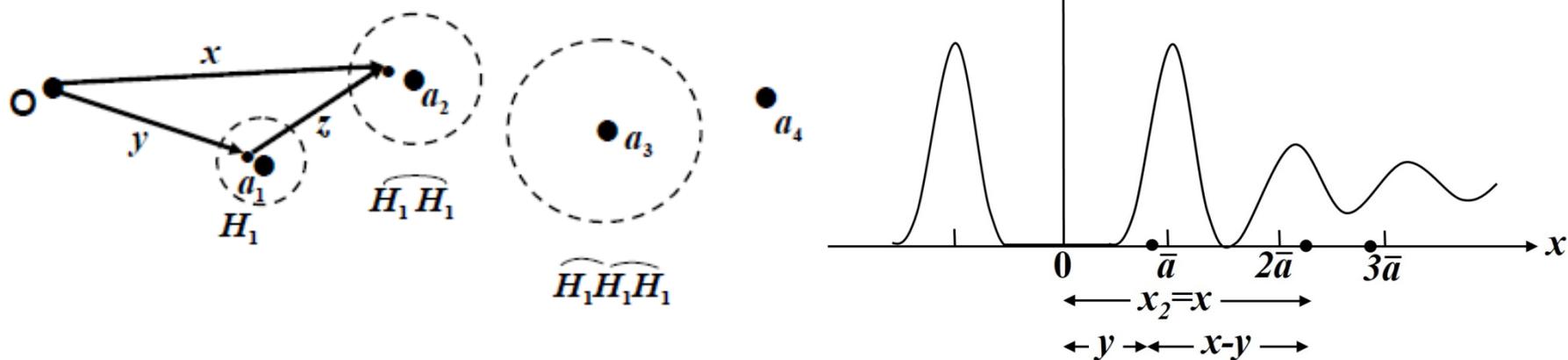
Very thin disk (R: radius) $\frac{R}{\sqrt{2}}$

Evaluation of inter-particle interference effect by convolution

This section is focused on the reason why the X-ray profile is strongly affected by the distance fluctuation between adjacent particles (lattices) and the intensity profile broadness is considerable as the fluctuation increases. Let's consider statistical treatment about inter-particle interference effect.

As shown in Fig. , there exist lattice points a_1, a_2, a_3, \dots ,
 When existence probability of a_1 at the tip of vector y from origin O is $H_1(y)$,
 the possibility of a_2 at the tip of vector z from a_1 is $H_1(y)H_1(z)$. In this case,
 the possibility of a_2 at the tip of vector $x (= y + z)$ from O is not $H_1(y) H_1(z)$

but
$$\int H_1(y)H_1(x - y)dy$$



The lattice points a_1, a_2, a_3, \dots exist on vector x

That is, the existence possibility of the tip of vector \mathbf{x} at a_2 is given by

$$H_2(\mathbf{x}) = \int H(\mathbf{y})H(\mathbf{x} - \mathbf{y})d\mathbf{y} = H \wedge H$$

Hence the possibility for the n -th lattice point is as follows:

$$H_k(\mathbf{x}) = H_1 \wedge H_1 \wedge H_1 \wedge \dots = H \wedge H \wedge H \wedge \dots \quad (\text{convolution of } (n - 1) \text{ times})$$

$H(x)$ is probability function between x and $x + dx$, when x is the closest distance between two points. Of course, $H(x)$ must be normalized as follows:

$$\int_0^{\infty} H(\mathbf{x})d\mathbf{x} = 1$$

The lattice points a_1, a_2, a_3, \dots exist on vector \mathbf{x} and then $H(\mathbf{x})$ may be replaced on scalar $H(x)$. The average value \bar{a} for the closest distance is

$$\bar{a} = \int_0^{\infty} xH_1(x)dx$$

Similarly, when $H_2(x)$ is the probability for finding the second closest distance,

$$2\bar{a} = \int_0^{\infty} xH_2(x)dx$$

When the origin of coordinate corresponds to the center of the coordinate, the summation in the positive and negative directions can be represented easily. In one-dimensional case, statistical distance $z(x)$ concerning the existence possibility of the point distances along the disordered point sequence is given by

$$z(x) = \delta(x - 0) + \sum_{n=1}^{\infty} H_n(x) + \sum_{n=1}^{\infty} H_n(-x)$$

Considering Fourier transformation $Z(X)$ of $z(x)$, $Z(X)$ becomes diffraction intensity from point sequence corresponding to one-dimensional disordered lattice factor. By using mathematical treatment that Fourier transformation of convolution becomes product of each Fourier transformation, Fourier transformations $[F(X)]^n$ of $H_n(x)$ and $[F^*(X)]^n$ of $H_n(-x)$ are given by

$$F(X) = \int_0^{\infty} H(x) \exp[i\mathbf{h} \cdot \mathbf{x}] dx \quad [F(X)]^n = \int_0^{\infty} H_n(x) \exp[i\mathbf{h} \cdot \mathbf{x}] dx$$

$$F^*(X) = \int_0^{\infty} H(-x) \exp[-i\mathbf{h} \cdot \mathbf{x}] dx \quad [F^*(X)]^n = \int_0^{\infty} H_n(-x) \exp[-i\mathbf{h} \cdot \mathbf{x}] dx$$

$$1 = \int_{0^-}^{0^+} \delta(x - 0) \exp[i\mathbf{h} \cdot \mathbf{x}] dx$$

As described above, $Z(X)$ is Fourier transformation of $z(x)$ and is given as follows:

$$\begin{aligned}
 Z(X) &= 1 + F(X) + F^2(X) + \dots + F^*(X) + [F^*(X)]^2 + \dots \\
 &= 1 + \frac{F(X)}{1 - F(X)} + \frac{F^*(X)}{1 - F^*(X)} = \operatorname{Re} \left[\frac{1 + F(X)}{1 - F(X)} \right] = \frac{1 - |F|^2}{1 + |F|^2 - 2|F| \cos(\mathbf{h} \cdot \bar{\mathbf{a}})}
 \end{aligned}$$

When lattice points a_1, a_2, a_3, \dots are set on vector \mathbf{h} , $\bar{\mathbf{a}}$ is written as vector.

$$F(X) = |F| \cos(\mathbf{h} \cdot \bar{\mathbf{a}}) = |F| \cos(h\bar{a})$$

The above Eq. is scattered (or diffraction) intensity profile from lattice factors along point sequence. ($n \rightarrow \infty$)

Assuming $H(x)$ to be Gauss function at the center \bar{a}

$$H(x) = \frac{1}{\sqrt{2\pi\sigma}} \exp \left\{ -\frac{(x - \bar{a})^2}{2\sigma^2} \right\}$$

$$F(X) = \exp[2\pi i X \bar{a}] \int_{-\infty}^{\infty} H(x) \exp[2\pi i X (x - \bar{a})] dx = \exp[2\pi i X \bar{a}] \exp[-2\pi^2 X^2 \sigma^2]$$

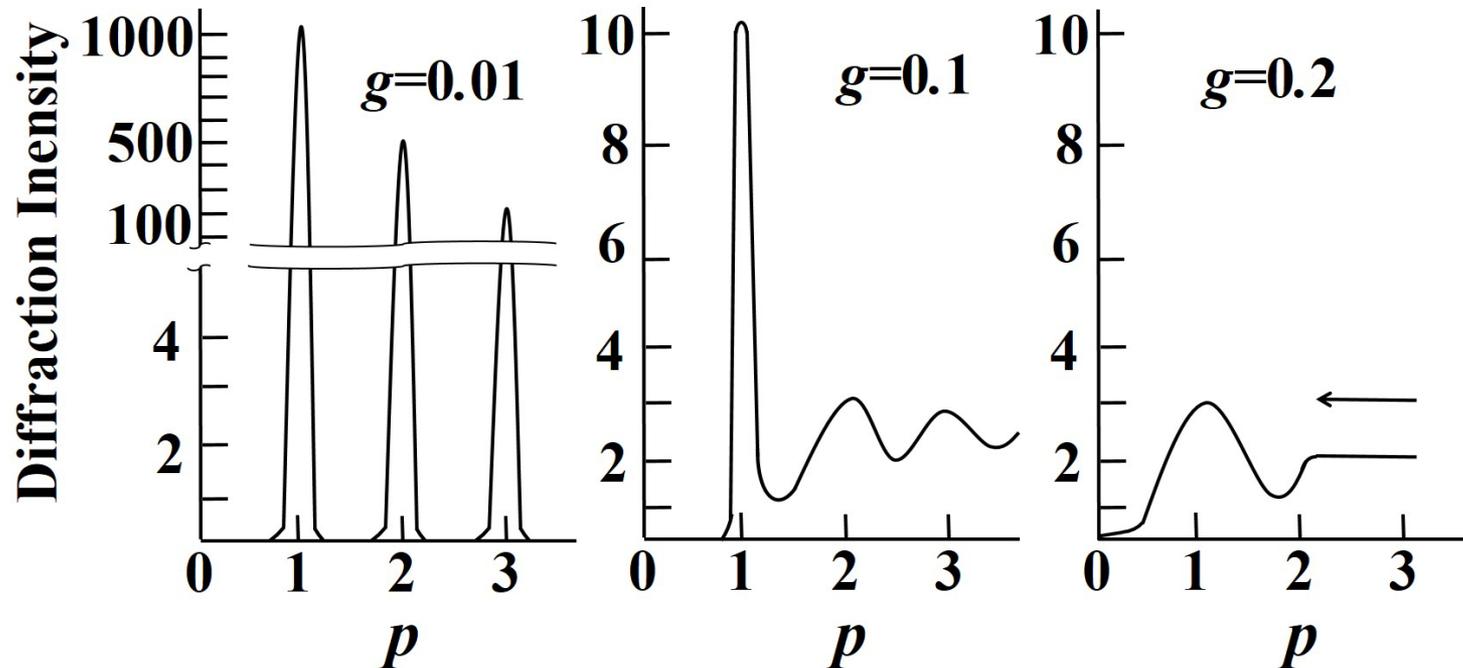
By using variable $g (= \sigma / \bar{a})$ denoting the fluctuation and reciprocal space coordinate X representing as $X (= p / \bar{a})$

$$|F| = \exp[-2\pi^2 X^2 \sigma^2] = \exp[-2\pi^2 g^2 p^2]$$

Hence $Z(h)$ can be represented as follows:

$$Z(h) = \frac{1 - \exp[-4\pi^2 g^2 p^2]}{[1 - \exp\{-2\pi^2 g^2 p^2\}]^2 + 4 \sin^2(\pi p) \exp\{-2\pi^2 g^2 p^2\}}$$

Fig. shows that the scattered peaks (or diffraction peaks) becomes smaller and broader as the fluctuation g becomes larger.



The diffraction intensity as a function of p at the indicated fluctuation given as g .

The above concept for lattice sequence in one-dimensional direction can be applied to particle sequence. The application shall be induced by using more reasonable treatment. Returning to the following Eq. , the lattice points $a_1, a_2, a_3 \dots a_n$ in Fig. can be replaced by the center of gravity of each scattering element. Hence the last term in Eq. is given by

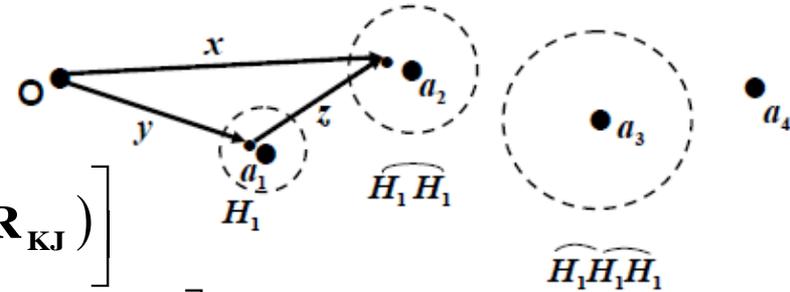
$$I(h) = I_e \left\{ N \langle F^2 \rangle + \langle F \rangle^2 \sum_{K \neq J}^N \sum_J^N \exp(-i\mathbf{h} \cdot \mathbf{R}_{\mathbf{KJ}}) \right\}$$

$$= I_e N \left[\langle F^2 \rangle - \langle F \rangle^2 \right] + I_e \langle F \rangle^2 \left[N + \sum_{K \neq J}^N \sum_J^N \exp(-i\mathbf{h} \cdot \mathbf{R}_{\mathbf{KJ}}) \right]$$

$$I(h) = I_e N \left[\langle F^2 \rangle - \langle F \rangle^2 \right] + I_e \langle F \rangle^2 \left[N + \sum_{K \neq J}^N \sum_J^N \exp(-i\mathbf{h} \cdot \mathbf{R}_{\mathbf{KJ}}) \right]$$

$$= I_e N \left[\langle f^2 \rangle - \langle f \rangle^2 \right] + I_e \langle f \rangle^2 \left[N + \sum_{K \neq J}^N \sum_J^N \exp(-i\mathbf{h} \cdot \mathbf{R}_{\mathbf{KJ}}) \right]$$

$$= I_e N \left[\langle f^2 \rangle - \langle f \rangle^2 \right] + I_e N \langle f \rangle^2 \left[\frac{1+F}{1-F} + \frac{2F(1-F^N)}{N(1-F)^2} \right]$$



As one example, numerical calculation by using Eq. is carried out for carbon fiber (CF) with ellipsoidal voids on the basis of Babinet's reciprocity theorem. This example indicates that the scattering from voids provides SAXS patterns with intensity maxima like scattering from particles.

The calculation was carried out in accordance with Babonet's reciprocity theorem.

$$\rho(\mathbf{r}) = (\rho_s - \rho_o)\sigma(\mathbf{r}) + \rho_o = \rho_s\sigma(\mathbf{r})$$

$$\rho_o = 0 \quad \bar{d} : \text{the average distance}$$

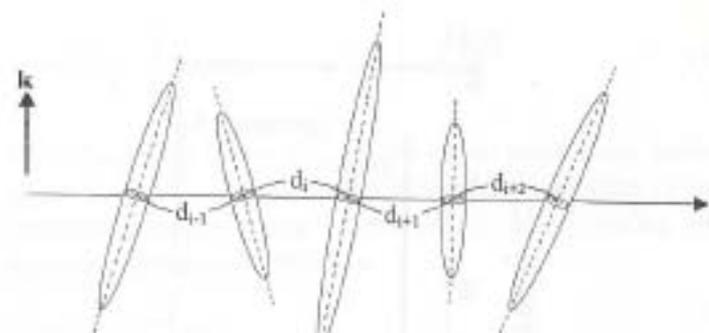
To analyze SAXS pattern from ellipsoidal voids.

The ellipsoidal void shape is related to b/a , in which b and a are the long and short axes of the void, respectively. The center of gravity of each void is arranged in the one direction (j -axis) and the distance between adjacent voids was given as like d_{i-1} , d_i , d_{i+1} .

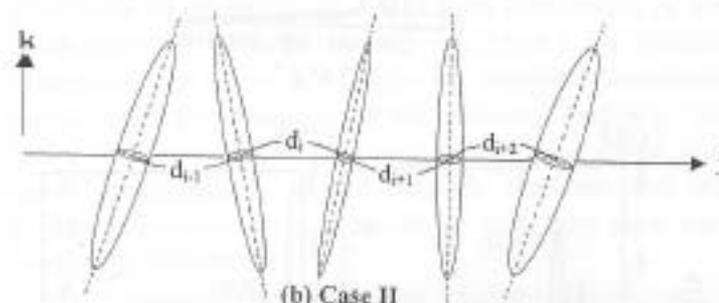
In Case I, b/a ($= P$) is variable
 a/λ ($= Q$) is constant

In Case II, P is constant
 Q is variable

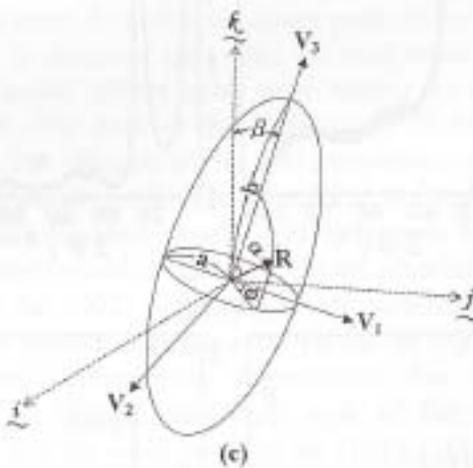
$$p(\beta) = \exp(-\sigma_\beta^2 \sin^2 \beta)$$



(a) Case I



(b) Case II



(c)

Case I

$$N(P) = \frac{\exp\left[-\frac{(P - \bar{P})^2}{2\sigma_P^2}\right]}{\sum_{P=1}^{2\bar{P}-1} \exp\left[-\frac{(P - \bar{P})^2}{2\sigma_P^2}\right]}$$

$$\langle I_P(h) \rangle_{av} = \sum_{P=1}^{2\bar{P}-1} N(P) I_P(h)$$

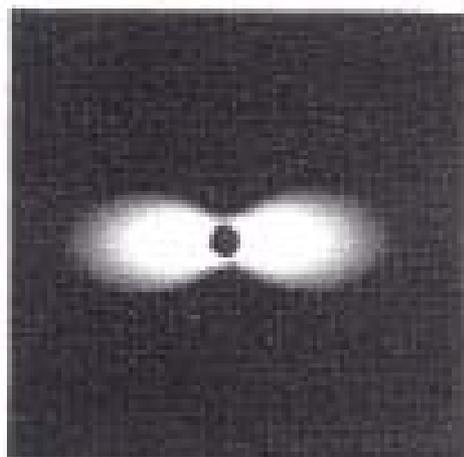
Case II

$$N(q) = \frac{\exp\left[-\frac{(\frac{q}{2} - \bar{q})^2}{2\sigma_q^2}\right]}{\sum_{q=1}^{4\bar{q}-1} \exp\left[-\frac{(\frac{q}{2} - \bar{q})^2}{2\sigma_q^2}\right]}$$

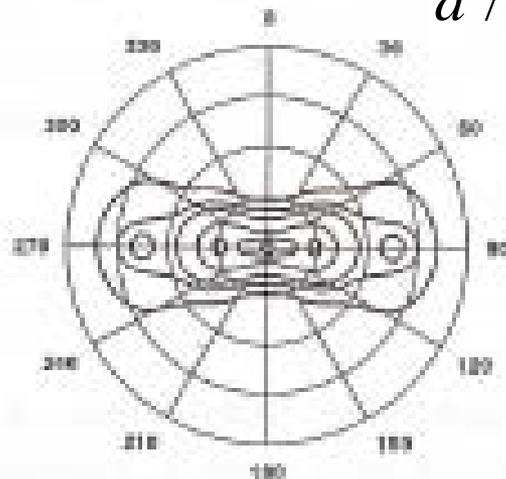
$$\langle I_q(h) \rangle_{av} = \sum_{q=1}^{4\bar{q}-1} N(q) I_q(h)$$

$$p(\beta) = \exp(-\sigma_\beta^2 \sin^2 \beta)$$

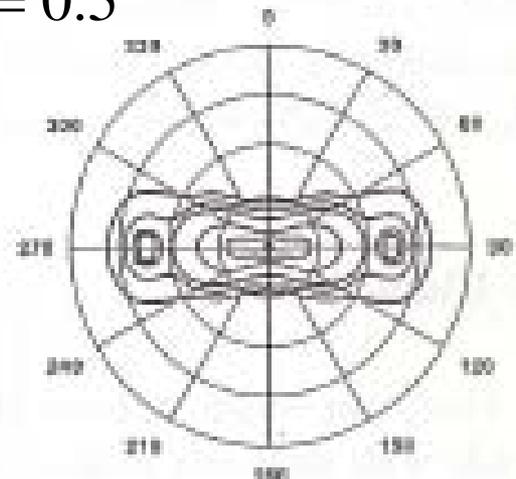
Case II $\bar{d}/a = 0.5$



Observed SAXS pattern

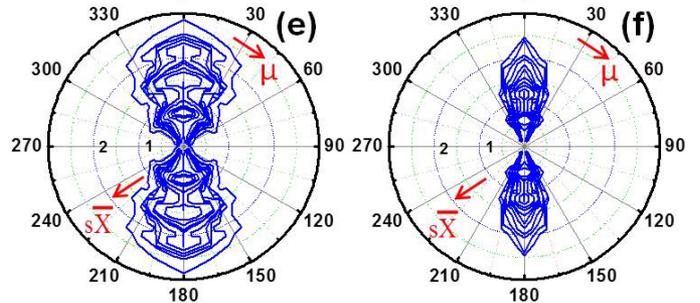
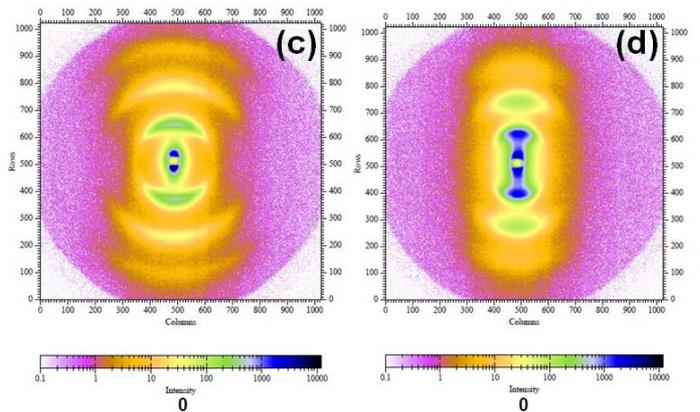
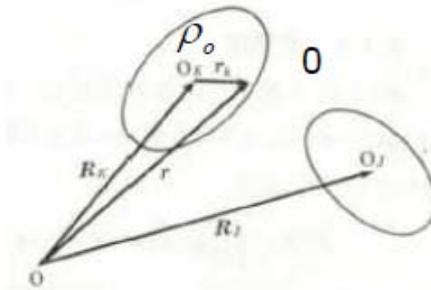
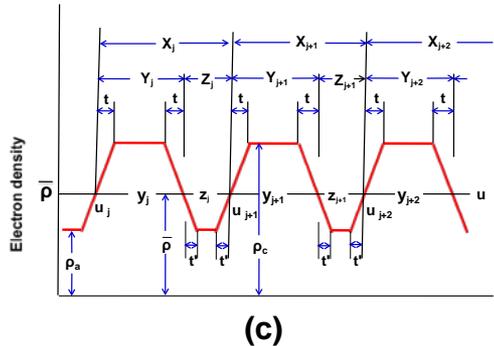
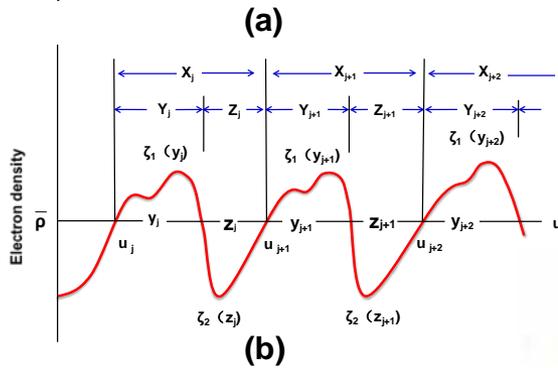
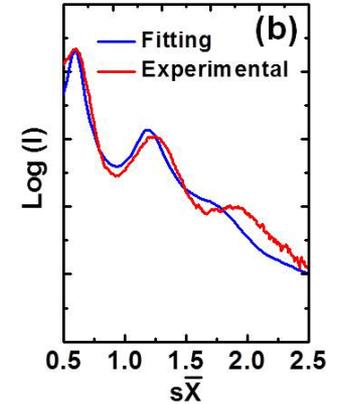
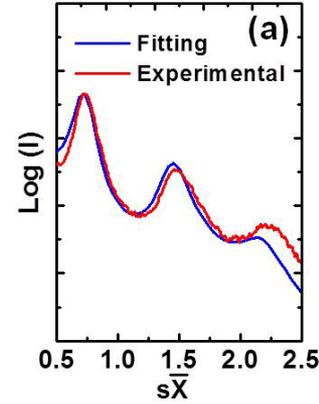
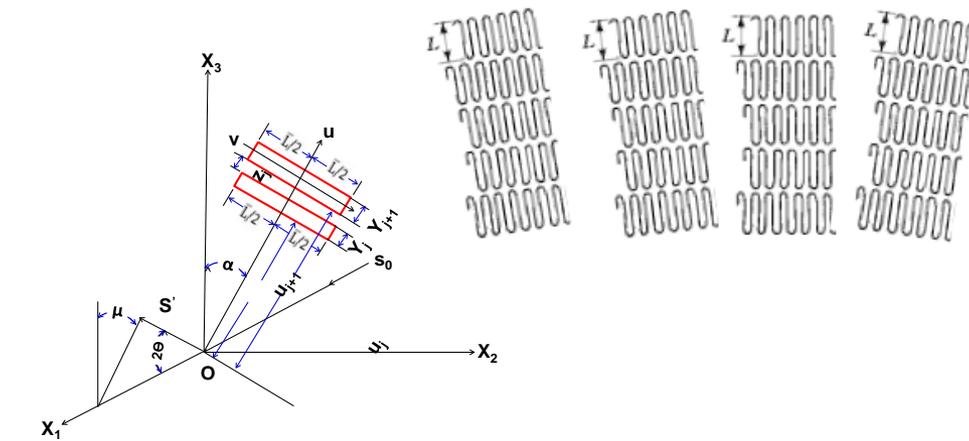


$$\sigma / \bar{d} = 0.01$$



$$\sigma / \bar{d} = 0.5$$

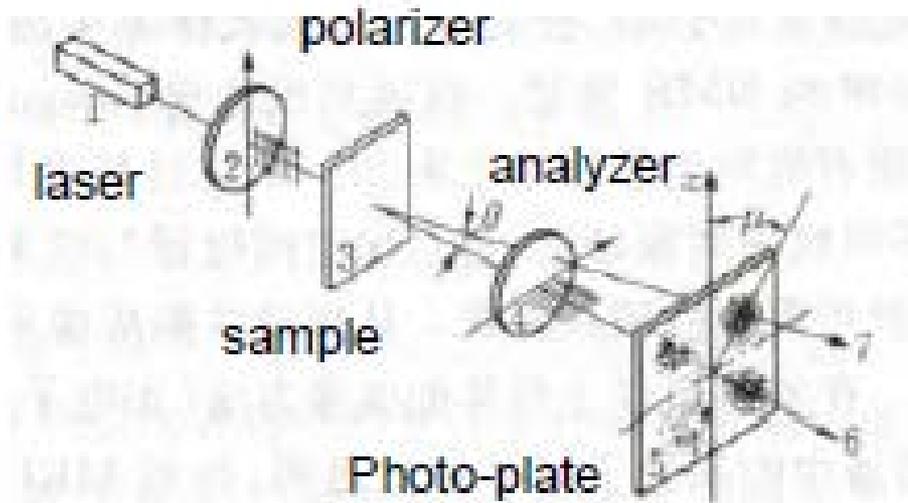
The reasonable approach to analyze SAXS intensity distribution is that the electron density fluctuation must be evaluated on the average density $\bar{\rho}$ of the specimen.



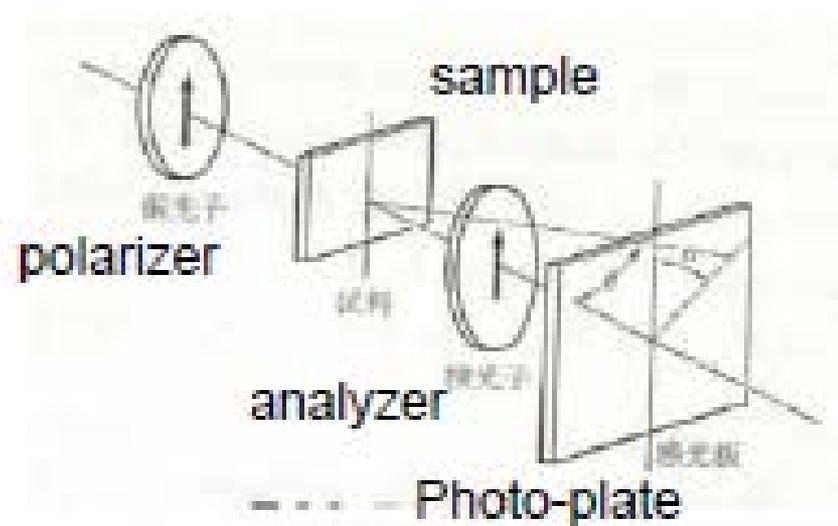
Understandable explanation about small angle light scattering (SALS) under polarization

As described in Introduction, the different characteristics between X-ray beam and visible light beam are due to the different wavelengths associated with the difference of photon energy. Therefore the electrons in atoms by an incident X-ray beam behave as free electrons because of high photon energy, while electrons of atom by visible light cause vibration on bottom of the potential box. Surely, polarized incident X-ray surely provides strong intensity. The scattered X-ray beam, however, is independent of the polarization direction of the beam. On the other hand, the scattered visible light intensity strongly depends on the polarization direction of the incident beam.

Figs. 21(a) and (b) show the arrangement of polarizer and analyzer under Hv and Vv scatterings, respectively.



(a) Hv scattering



(b) Vv scattering

- polarizer-vertical and analyzer-horizontal Hv
- polarizer-vertical and analyzer-vertical Vv
- polarizer-horizontal and analyzer-horizontal Hh
- polarizer-horizontal and analyzer-vertical Vh

Scattering angle for PALS is represented as θ in stead of 2θ for SXAS.

Different from X-ray scattering, visible light scattering is associated with refractive index fluctuation. The total scattering amplitude from scattering elements is given by

$$\begin{aligned}
 E_s(h) &= \sum_{i=1}^K E_i \exp[i(\mathbf{h} \cdot \mathbf{r}_i)] \\
 &= (4\pi^2 / R_o^2 \lambda_o^2) \sum_i (\mathbf{M}_i \cdot \mathbf{O}) \exp[i(\mathbf{h} \cdot \mathbf{r}_i)] = K \int (\mathbf{M} \cdot \mathbf{O}) \exp[ik(\mathbf{h} \cdot \mathbf{r})] d\mathbf{r}
 \end{aligned}$$

For visible light, E_i is the scattering amplitude given as $E_i = (4\pi^2 / R_o^2 \lambda_o^2) M_i \sin \gamma_i$, in which $M_i \sin \gamma_i$ is the characteristic term of visible light different from X-ray. M_i is induced dipole moment of i -th scattering element and γ_i is interior angle between M_i and R_i vectors. M_i is given by $\alpha_i E_o$, in which α_i is tensor for polarizability and E_o is electric vector. Accordingly, γ_i is dependent upon polarizability ellipsoid and the orientation. On observation of scattering beam through analyzer as shown in **Figure 21**, the polarization direction of analyzer denoting as unit vector \mathbf{O} can be detected among the tangential component of M_i for R_i . Eventually, $M_i \sin \gamma$ is replaced as $(\mathbf{M} \cdot \mathbf{O})$.

$d\mathbf{r}_j$ is micro-volume element at position vector \mathbf{r}_j . $\int d\mathbf{r}_j$ denotes volume integral.

$$\mathbf{s} = \mathbf{s}_o - \mathbf{s}'$$

$$k = 2\pi / \lambda$$

$$|s| = 2k \sin(\theta / 2)$$

For polymers, the refractive index difference between spherulite (or rod) index and the medium index is much less than unity and the phase shift of light passed through particles and medium becomes generally very small. The normal spherulite and rod sizes are less than 100 times in comparison with wavelength of He-Ne gas laser, which allows the evaluation for the scattering pattern by Rayleigh-Gans scattering. According to the concept by Rayleigh-Gans, scattered intensity for SALS is given by

$$\begin{aligned} I &= K^2 \int \int (\mathbf{M}_i \cdot \mathbf{O})(\mathbf{M}_j \cdot \mathbf{O}) \exp[-ik(\mathbf{r}_i \cdot \mathbf{s})] \exp[ik(\mathbf{r}_j \cdot \mathbf{s})] d\mathbf{r}_i d\mathbf{r}_j \\ &= K^2 \int \int (\mathbf{M}_i \cdot \mathbf{O})(\mathbf{M}_j \cdot \mathbf{O}) \exp[ik(\mathbf{r}_{ij} \cdot \mathbf{s})] d\mathbf{r}_i d\mathbf{r}_j \\ &= K^2 \int \int (\mathbf{M}_i \cdot \mathbf{O})(\mathbf{M}_j \cdot \mathbf{O}) \{ \cos[k(\mathbf{r} \cdot \mathbf{s})] + i \sin[k(\mathbf{r} \cdot \mathbf{s})] \} d\mathbf{r}_i d\mathbf{r}_j \\ &= K^2 \int \int (\mathbf{M}_i \cdot \mathbf{O})(\mathbf{M}_j \cdot \mathbf{O}) \cos[k(\mathbf{r} \cdot \mathbf{s})] d\mathbf{r}_i d\mathbf{r}_j \\ &= K^2 \int \left\{ \int (\mathbf{M}_i \cdot \mathbf{O})(\mathbf{M}_j \cdot \mathbf{O}) d\mathbf{r}_i \right\} \cos[k(\mathbf{r} \cdot \mathbf{s})] d\mathbf{r} \\ &= K^2 V \int \langle (\mathbf{M}_i \cdot \mathbf{O})(\mathbf{M}_j \cdot \mathbf{O}) \rangle_r \cos[k(\mathbf{r} \cdot \mathbf{s})] d\mathbf{r} \quad \mathbf{r} = \mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i \end{aligned}$$

Center of coordinate must be set in the center of particle. In this case, sin term disappears.

$$I = K^2 V \int \langle (\mathbf{M}_i \cdot \mathbf{O})(\mathbf{M}_j \cdot \mathbf{O}) \rangle_r \cos[k(\mathbf{r} \cdot \mathbf{s})] d\mathbf{r}$$

where $\mathbf{r} = \mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ and $\langle \rangle_r$ is the average of the product of scattering elements with separation distance r , depending upon optical density, anisotropy and orientation fluctuation. V is an irradiated volume.

M_i (dipole moment induced by i -th scattering element) is generally given by

$$M_i = E_o \left\{ \delta_i (\mathbf{t}_p \cdot \mathbf{a}_i) \mathbf{a}_i + (b_t)_i \mathbf{t}_p \right\}$$

where \mathbf{a}_i is the vector along the i -th optical axis and \mathbf{t}_p is unit vector denoting polarization direction of an incident beam,

$$\delta_i = (\alpha_{//})_i - (\alpha_{\perp})_i \quad (b_t)_i = (\alpha_{\perp})_i - \alpha_s$$

$(\alpha_{//})_i$ and $(\alpha_{\perp})_i$ polarizabilities parallel and perpendicular to optical axis (the unit vector \mathbf{a}_i), respectively. α_s is the polarizability of the medium. \mathbf{t}_p depends on the polarization components of scattering light; $\mathbf{t}_p = \mathbf{k}$ for vertical polarization direction and $\mathbf{t}_p = \mathbf{j}$ for horizontal polarization direction. Normally, $\mathbf{t}_p = \mathbf{k}$.

As for the observation of vertical and horizontal components of scattered intensity, $\mathbf{O}_V = \mathbf{k}$ and $\mathbf{O}_H = \mathbf{j}$ can be constructed approximately. Hence,

$$(\mathbf{M} \cdot \mathbf{O})_{H_V} = (\mathbf{M} \cdot \mathbf{O})_{V_h} = E_o \delta_i (\mathbf{a}_j \cdot \mathbf{j})(\mathbf{a}_i \cdot \mathbf{k})$$

$$(\mathbf{M} \cdot \mathbf{O})_{V_v} = E_o \left\{ \delta_i (\mathbf{a}_i \cdot \mathbf{k})^2 + (b_t)_i \right\}$$

$$(\mathbf{M} \cdot \mathbf{O})_{H_h} = E_o \left\{ \delta_i (\mathbf{a}_i \cdot \mathbf{j})^2 + (b_t)_i \right\}$$

SALS under polarization

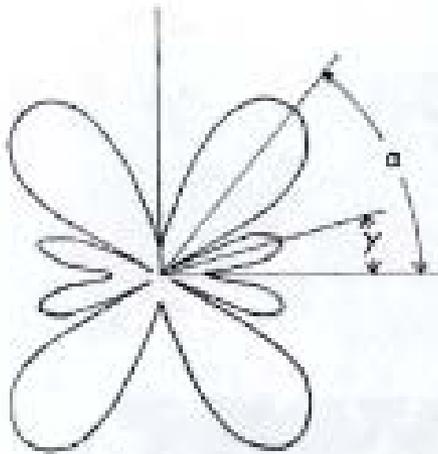
$$I = K^2 V \int \left\langle (\mathbf{M}_i \cdot \mathbf{O})(\mathbf{M}_j \cdot \mathbf{O}) \right\rangle_r \cos[k(\mathbf{r} \cdot \mathbf{s})] d\mathbf{r}$$

SAXS

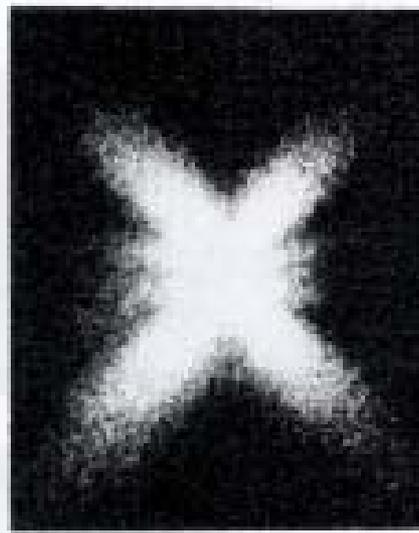
$$I \propto |F(\mathbf{h})|^2 = \int Q(\mathbf{r}) \exp[i(\mathbf{h} \cdot \mathbf{r})] d\mathbf{r}$$

$$Q(\mathbf{r}) = \int \rho(\mathbf{r}_j) \rho(\mathbf{r}_j - \mathbf{r}) d\mathbf{r}_j$$

$Q(\mathbf{r})$ for isolated particles can be evaluated roughly by Guinier plots as discussed already. However, for polarized light scattering, it is impossible to pull out information directly from complicated $\left\langle (\mathbf{M}_i \cdot \mathbf{O})(\mathbf{M}_j \cdot \mathbf{O}) \right\rangle_r$.



(a)



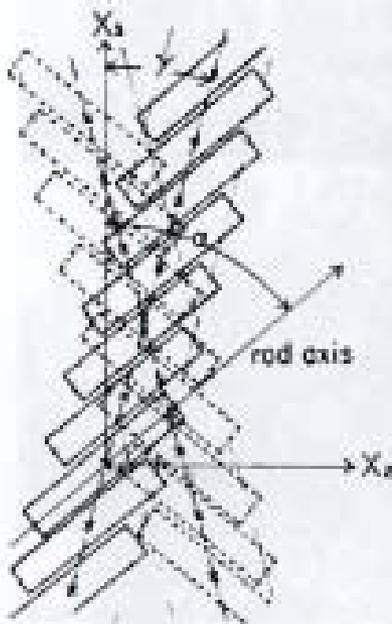
(c)

The SALS profile provides X-type for rods and four-leaves clover type for spherulites. Many reports have been published.

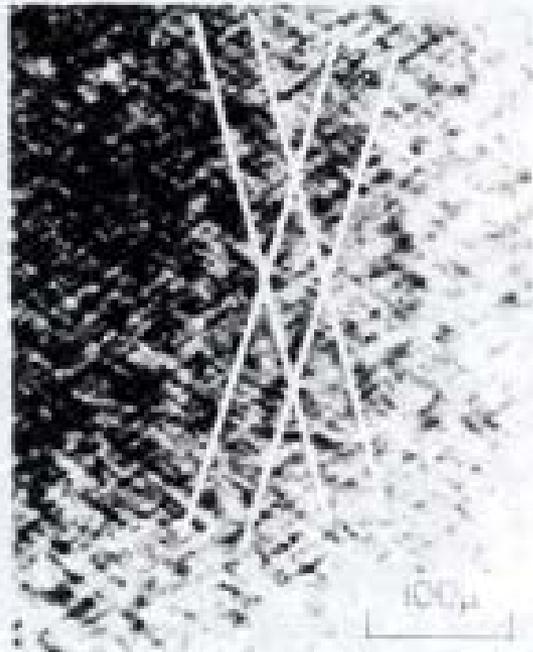
What is the sharp streaks in addition to the four lobes?

The POM indicates the ordered arrangement of rods.

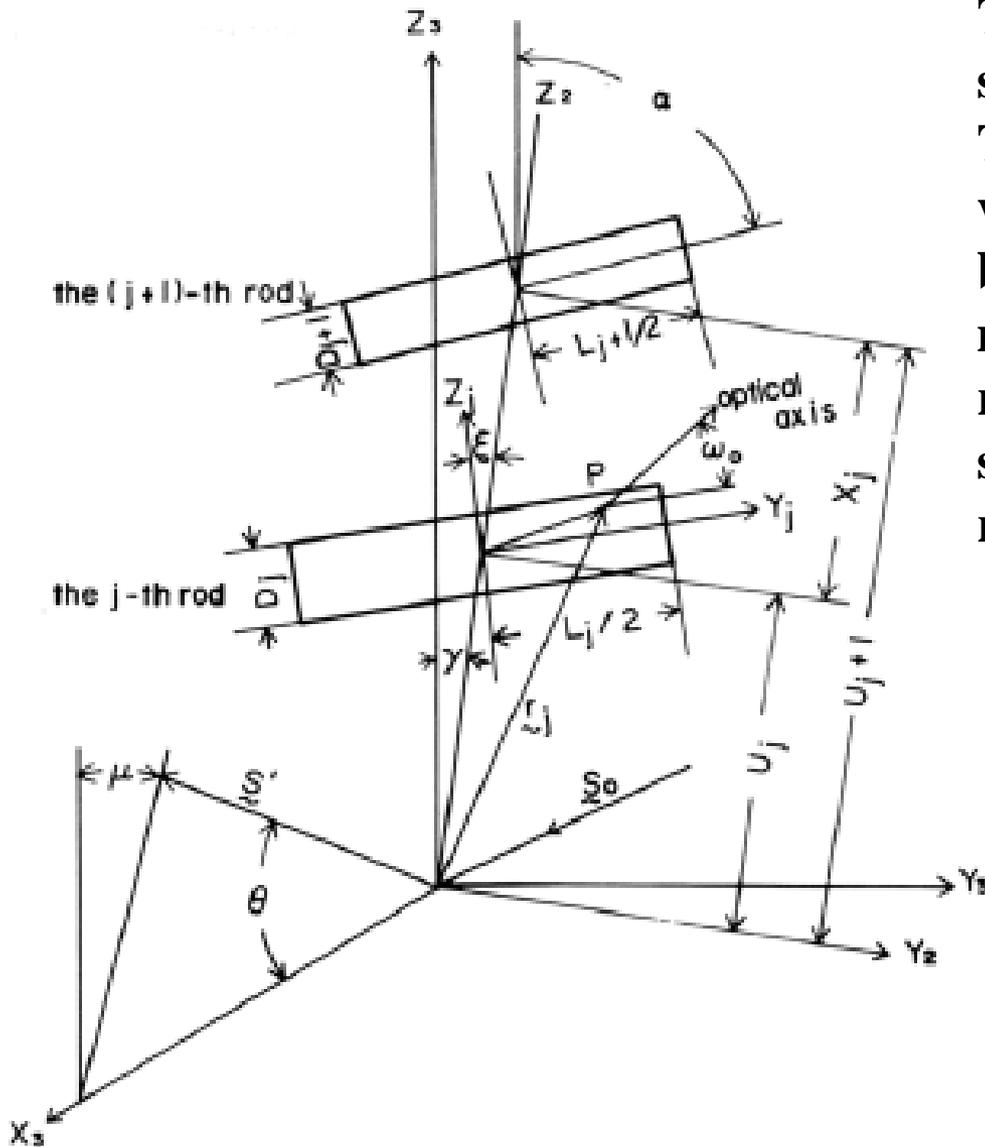
For theoretical calculation, the emphasized point is due to the fact that the difference between inter-particle interference between SAXS and SALS can be represented easily, when the particles are arranged in the one-dimensional direction on the two-dimensional plane.



(b)



(d)



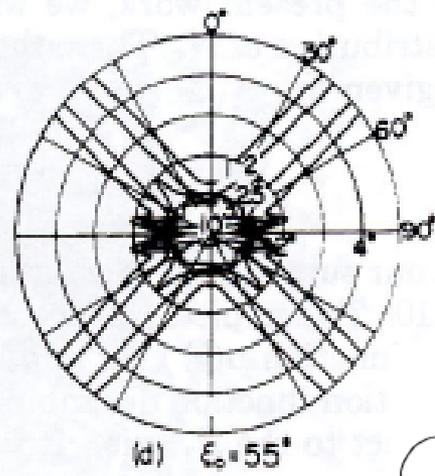
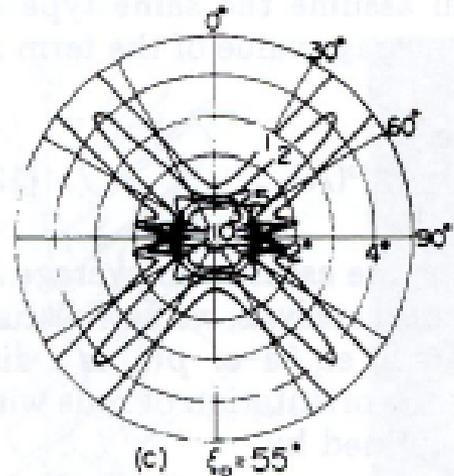
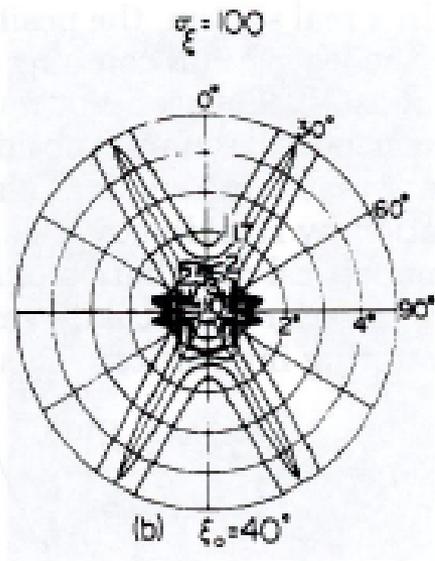
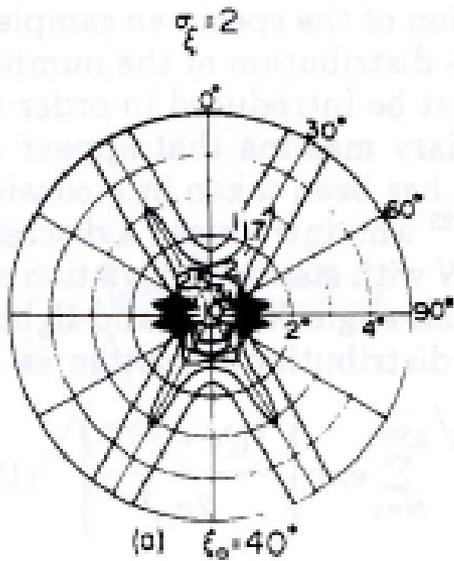
The scattered intensity provides the same style as Eq. (IV-24) for SAXS. The variations of the length L_j , the width D_j and the adjacent distance X_j between j -th and $(j+1)$ -th rods have no correlation each other and are represented by the following symmetrical functions with the respective mean lengths, \bar{L} , \bar{D} , \bar{X}

$$h(L_j) = \frac{1}{\sqrt{2\pi\sigma_\ell^2}} \exp\left\{-\frac{(L_j - \bar{L})^2}{2\sigma_\ell^2}\right\}$$

$$M(D_j) = \frac{1}{\sqrt{2\pi\sigma_d^2}} \exp\left\{-\frac{(D_j - \bar{D})^2}{2\sigma_d^2}\right\}$$

$$H(X_j) = \frac{1}{\sqrt{2\pi\sigma_x^2}} \exp\left\{-\frac{(X_j - \bar{X})^2}{2\sigma_x^2}\right\}$$

$$p(\xi) = \exp\left[-\sigma_\xi^2 \sin^2(\xi - \xi_0)\right] \quad P(N) = \exp\left\{-\frac{(N - \bar{N})^2}{2\sigma_N^2}\right\} / \sum_{N=1}^{2\bar{N}-1} \exp\left\{-\frac{(N - \bar{N})^2}{2\sigma_N^2}\right\}$$



γ is fixed to be 10° .

$$\alpha = 60^\circ$$

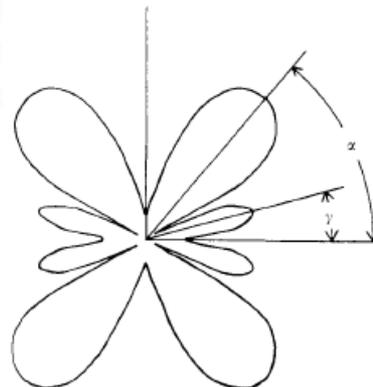
$$\xi_0 = 40^\circ$$

$$(\alpha = -\xi_0 + \gamma + 90^\circ)$$

$$\alpha = -60^\circ$$

$$\xi_0 = 40^\circ$$

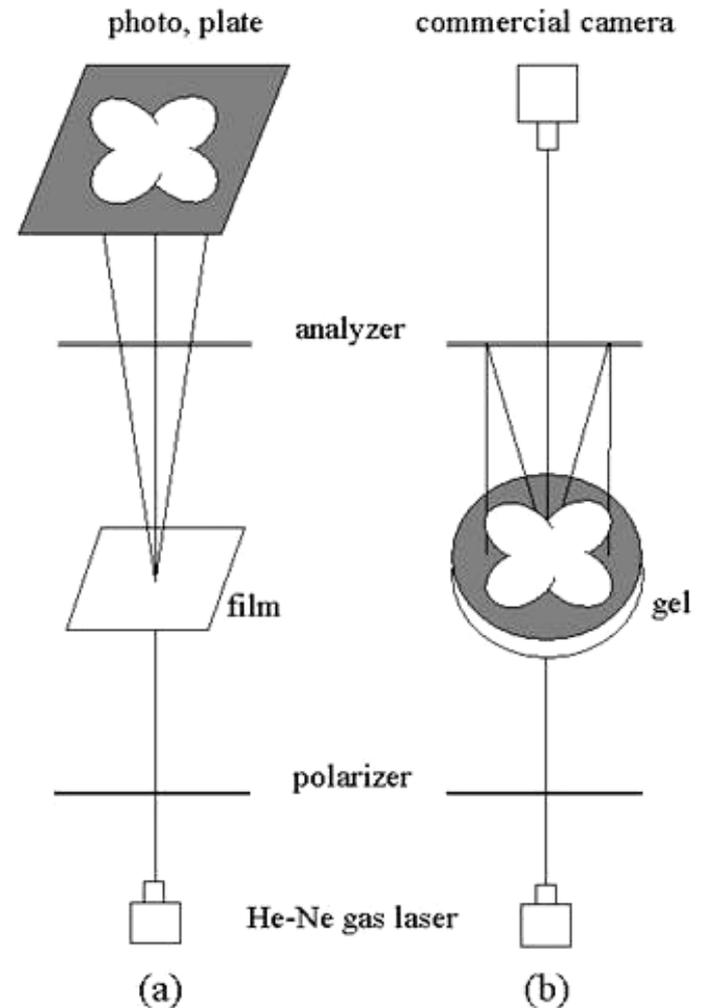
$$(\alpha = \xi_0 - \gamma - 90^\circ)$$

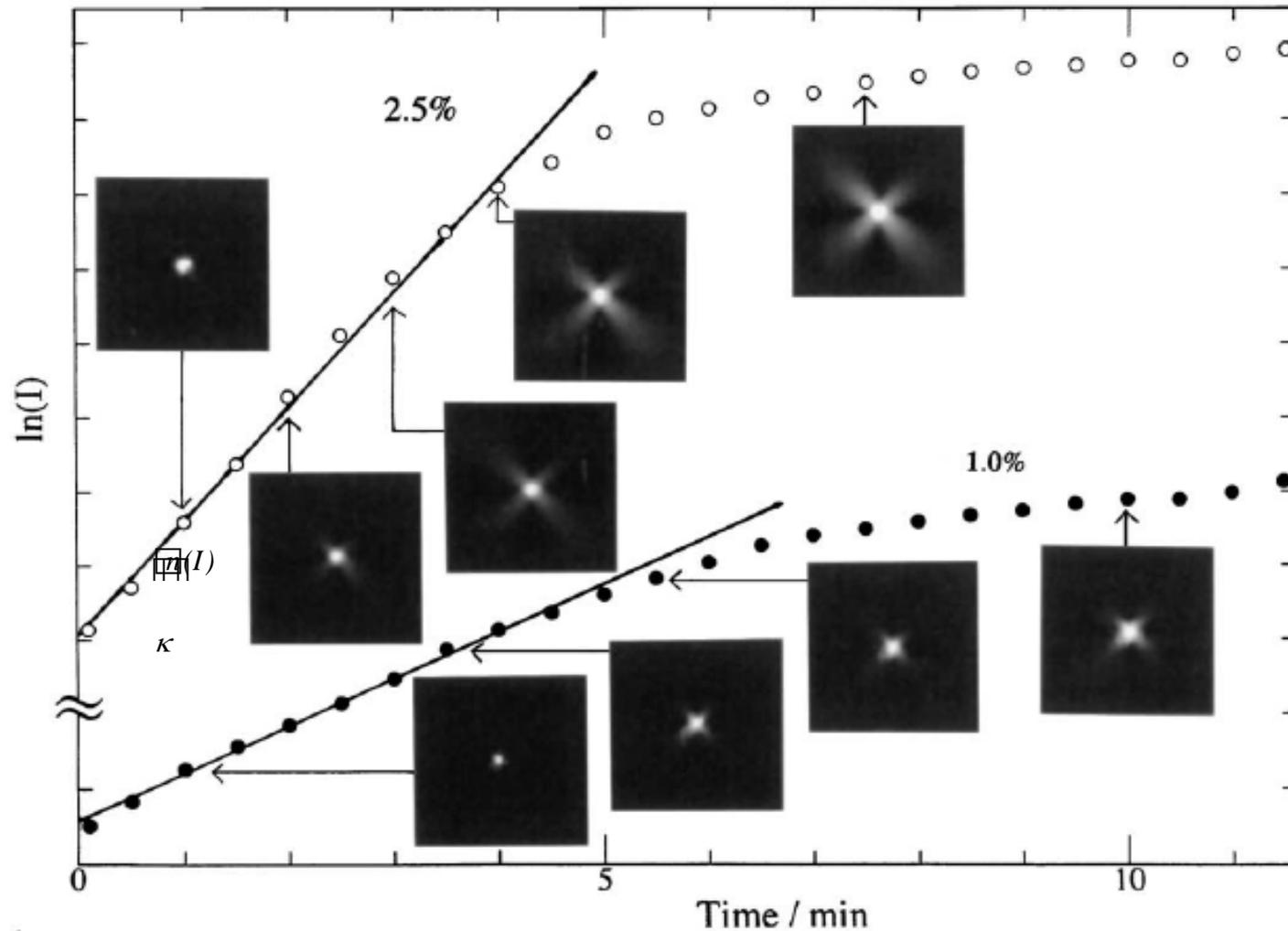


$\pm 10^\circ$

Statistical approach model

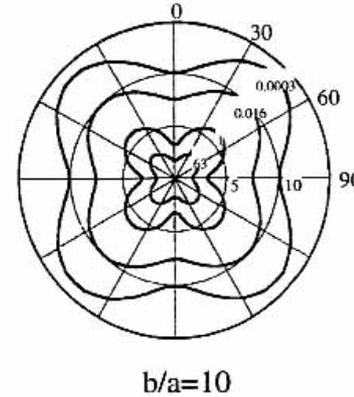
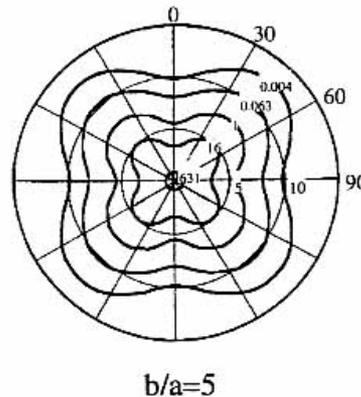
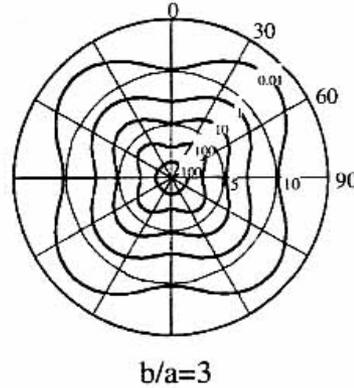
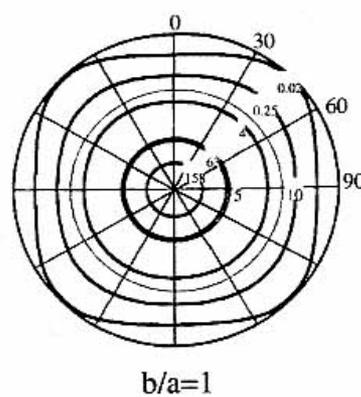
This method is useful for the system where the morphology observed by polarized microscopy provides unclear and dark structure. The statistical approach has been adopted for scattering from gels and amorphous films. When there exist many small assemblies with disordered chain arrangement in polymer film or gel, the assemblies can be considered as optical elements. In such case, Hv scattering pattern becomes very weak and the pattern could not be observed on the photo screen (frosted glass) (see Fig.), since the very weak light scattered from the gels could not pass through the analyzer. The pattern was observed on the sample surface by the reflection from analyzer, and then photographs were taken using a commercial camera.





Change of $\ln(I)$ at $\theta = 15^\circ$ and Hv patterns with respect to time measured for the 1.0 and 2.5% κ -carrageenan aqueous solutions after quenching at 30°C .

$$I_{Hv} = K \delta^2 \int_0^\pi \int_0^\infty \mu(r) \left\{ \frac{1}{15} f(r) + g(r)(1 - f(r)) \right. \\ \times \left[\frac{1}{720} (5 \cos^4 \alpha + 30 \cos^2 \alpha - 11) - \frac{1}{144} \cos^2 \frac{\theta}{2} (5 \cos^4 \alpha + 6 \cos^2 \alpha - 3) \right. \\ \left. \left. + \frac{1}{576} \cos^4 \frac{\theta}{2} \sin^2 2\mu (35 \cos^4 \alpha - 30 \cos^2 \alpha + 3) \right] \right\} \cos[hr \cos \alpha] r^2 \sin \alpha dr d\alpha$$



$$f(r) = \left\langle \frac{3 \cos^2 \omega_{ij} - 1}{2} \right\rangle_r$$

$$f(r) = \exp\left(-\frac{r^2}{a^2}\right)$$

$$g(r) = \left\langle 2 \cos^2 \phi_{ij} - 1 \right\rangle_r$$

$$g(r) = \exp\left(-\frac{r^2}{b^2}\right)$$

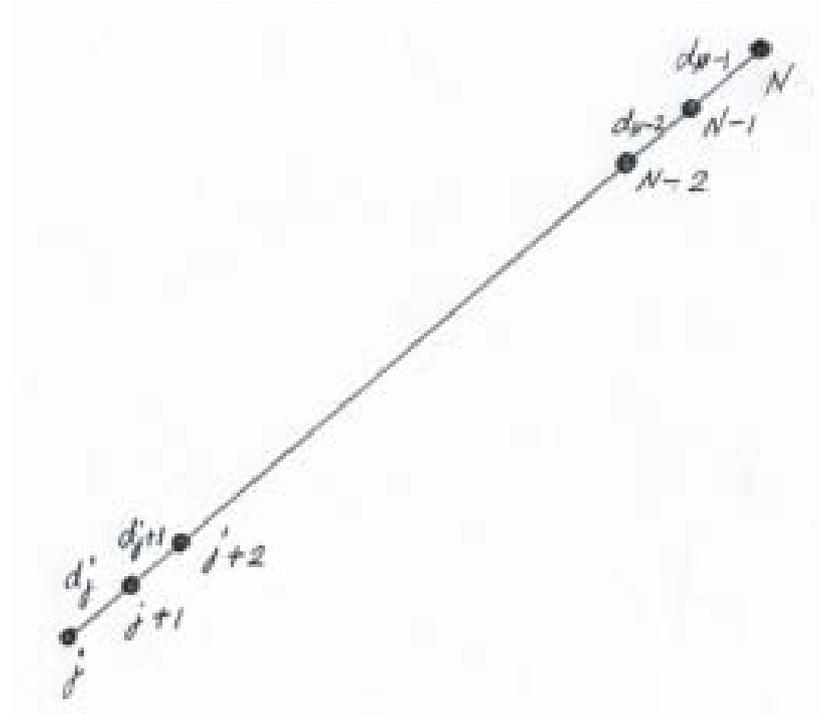
Summary

In the course, the application examples for WAXD, SAXS and SALS were described in comparison with more detailed observed and theoretical results. When an incident X-ray beam is entered in the polymer material, electrons in atoms behave as free electrons because of high photon energy. On the other hand, when visible light with low photon energy is entered, electrons of atom cause vibration on bottom of the potential box. Accordingly, SAXS and SALS scattered intensity distributions are given by Fourier transform of mean square value of electron density fluctuation and mean square value of refractive index, respectively. The WAXD and SAXS are written by the same fundamental equation EE^* (E : amplitude, E^* : the conjugate complex). WAXD can neglect inter-particle interference effect between crystallites and then the probability function to find other unit within the crystallite is defined to be unity and the intensity from a crystal unit becomes simple summation for intensities from atoms in the unit. However, under calculation of the magnitude, Laue condition must be satisfied for crystal units in each crystallite. Except scattered intensity from isolated particles evaluating Guinier law, SAXS patterns from materials must be analyzed by considering inter-particle interference effect.

$$Z(X) = 1 + F(X) + F^2(X) + \dots + F^*(X) + [F^*(X)]^2 + \dots$$

$$= 1 + \frac{F(X)}{1 - F(X)} + \frac{F^*(X)}{1 - F^*(X)} = \frac{1 - |F(X)|^2}{1 + |F(X)|^2 - 2|F(X)| \cos 2\pi\chi} \quad (\text{III-19})$$

Inter-particle interference effect can be calculated exactly by using the following method. Compare with Eq. (III-19)



$$\sum_{j,k} \langle \exp(-i\mathbf{h} \cdot \mathbf{z}_{jk}) \rangle = \sum_{j=1}^N \left[\sum_{k=1}^{j-1} \langle \exp(-i\mathbf{h} \cdot \mathbf{z}_{jk}) \rangle + \sum_{k=j+1}^N \langle \exp(-i\mathbf{h} \cdot \mathbf{z}_{jk}) \rangle \right]$$

$$\sum_{j,k} \langle \exp(-i\mathbf{h} \cdot \mathbf{z}_{jk}) \rangle = \sum_{j=1}^N \left[\sum_{k=1}^{j-1} \langle \exp(-i\mathbf{h} \cdot \mathbf{z}_{jk}) \rangle + \sum_{k=j+1}^N \langle \exp(-i\mathbf{h} \cdot \mathbf{z}_{jk}) \rangle \right]$$

$$\sum_{k=1}^{j-1} \langle \exp(-i\mathbf{h} \cdot \mathbf{z}_{jk}) \rangle$$

$$k = 1$$

$$\begin{aligned} \exp(-i\mathbf{h} \cdot \mathbf{z}_{j1}) &= \exp[-i\mathbf{h} \cdot (\mathbf{d}_1 + \mathbf{d}_2 + \mathbf{d}_3 + \text{-----} + \mathbf{d}_{j-1})] \\ &= \exp\{-i(\mathbf{h} \cdot \mathbf{d}_1)\} \exp\{-i(\mathbf{h} \cdot \mathbf{d}_2)\} \exp\{-i(\mathbf{h} \cdot \mathbf{d}_3)\} \text{-----} \exp\{-i(\mathbf{h} \cdot \mathbf{d}_{j-1})\} \\ &= \prod_{i=1}^{j-1} \exp\{-i(\mathbf{h} \cdot \mathbf{d}_i)\} \end{aligned}$$

$$k = 2$$

$$\begin{aligned} \exp(-i\mathbf{h} \cdot \mathbf{z}_{j2}) &= \exp[-i\mathbf{h} \cdot (\mathbf{d}_2 + \mathbf{d}_3 + \text{-----} + \mathbf{d}_{j-1})] \\ &= \exp\{-i(\mathbf{h} \cdot \mathbf{d}_2)\} \exp\{-i(\mathbf{h} \cdot \mathbf{d}_3)\} \text{-----} \exp\{-i(\mathbf{h} \cdot \mathbf{d}_{j-1})\} \\ &= \prod_{i=2}^{j-1} \exp\{-i(\mathbf{h} \cdot \mathbf{d}_i)\} \end{aligned}$$

$$\mathbf{k} = \mathbf{k}$$

$$\begin{aligned} \exp(-i\mathbf{h} \cdot \mathbf{z}_{jk}) &= \exp[-i\mathbf{h} \cdot (\mathbf{d}_k + \mathbf{d}_{k+1} + \dots + \mathbf{d}_{j-1})] \\ &= \prod_{i=k}^{j-1} \exp\{-i(\mathbf{h} \cdot \mathbf{d}_i)\} \end{aligned}$$

$$\sum_{j=1}^N \left[\sum_{k=1}^{j-1} \langle \exp\{-i(\mathbf{h} \cdot \mathbf{z}_{jk})\} \rangle \right] = \sum_{j=1}^N \sum_{k=1}^{j-1} \prod_{i=k}^{j-1} \exp[-i(\mathbf{h} \cdot \mathbf{d}_i)] = \sum_{j=1}^N \sum_{k=1}^{j-1} \prod_{i=k}^{j-1} F$$

$$\prod_{i=k}^{j-1} F = F \cdot F \cdot \dots \cdot F^{j-1-(k-1)} = F^{j-k}$$

$$\begin{aligned} \sum_{k=1}^{j-1} F^{j-k} &= F^{j-1} + F^{j-2} + F^{j-3} + \dots + F^2 + F \\ &= F(1 + F + F^2 + \dots + F^{j-2}) \\ &= F \left\{ \frac{1 - F^{j-2+1}}{1 - F} \right\} = F \left\{ \frac{1 - F^{j-1}}{1 - F} \right\} = \frac{F - F^j}{1 - F} \end{aligned}$$

$$\sum_{j=1}^N \frac{F - F^j}{1 - F}$$

$$\begin{aligned} \sum_{j=1}^N \frac{F - F^j}{1 - F} &= \frac{F - F}{1 - F} + \frac{1 - F^2}{1 - F} + \frac{1 - F^3}{1 - F} + \dots + \frac{1 - F^N}{1 - F} \\ &= \frac{NF}{1 - F} - \frac{F}{1 - F} \left\{ 1 + F + F^2 + \dots + F^{N-1} \right\} \\ &= \frac{NF}{1 - F} - \frac{F}{1 - F} \left\{ \frac{1 - F^N}{1 - F} \right\} = \frac{NF}{1 - F} - \frac{N(1 - F^N)}{(1 - F)^2} \end{aligned}$$

$$\sum_{k=j+1}^N \langle \exp(-i\mathbf{h} \cdot \mathbf{z}_{jk}) \rangle$$

$$k = j + 1 \quad \langle \exp(-i\mathbf{h} \cdot \mathbf{z}_{jj+1}) \rangle = \langle \exp\{-ih \cdot d_j\} \rangle$$

$$k = j + 2$$

$$\langle \exp(-i\mathbf{h} \cdot \mathbf{z}_{jj+2}) \rangle = \langle \exp\{-ih \cdot (d_j + d_{j+1})\} \rangle = \langle \exp\{-ih \cdot d_j\} \rangle \langle \exp\{-ih \cdot d_{j+1}\} \rangle$$

$$= \prod_{i=j}^{j+1} \langle \exp\{-ih \cdot d_i\} \rangle$$

$$k = N$$

$$\sum_{k=j+1}^N \langle \exp(-i\mathbf{h} \cdot \mathbf{z}_{jN}) \rangle = \exp\{-ih(d_j + d_{j+1} + d_{j+2} + \dots + d_{N-1})\}$$

$$= \prod_{i=j}^{N-1} \langle \exp\{-ih \cdot \mathbf{d}_i\} \rangle$$

$$\prod_{i=j}^{k-1} \langle \exp\{-ih \cdot \mathbf{d}_i\} \rangle = \prod_{i=j}^{k-1} F^* = F^{*k-j}$$

$$\sum_{k=j+1}^N (F^*)^{k-j} = F^* + F^{*2} + \dots + F^{*N-j} = \frac{F^* - F^{*N-j+1}}{1 - F^*}$$

$$\begin{aligned}
\sum_{j=1}^N \frac{F^* - F^{N-j+1}}{1 - F^*} &= \frac{F^* - F^{*N}}{1 - F^*} + \frac{F^* - F^{*N-1}}{1 - F^*} + \frac{1 - F^{*N-2}}{1 - F^*} + \dots + \frac{1 - F^{*2}}{1 - F^*} + \frac{1 - F^*}{1 - F^*} \\
&= \frac{NF^*}{1 - F^*} - \frac{F^*}{1 - F^*} \left\{ 1 + F^* + F^{*2} + \dots + F^{*N-1} \right\} \\
&= \frac{NF^*}{1 - F^*} - \frac{F^*}{1 - F^*} \left\{ \frac{1 - F^{*N}}{1 - F^*} \right\} = \frac{NF^*}{1 - F^*} - \frac{N(1 - F^{*N})}{(1 - F^*)^2}
\end{aligned}$$

$$\sum_{j=1}^N \frac{F - F^j}{1 - F} = \frac{NF}{1 - F} - \frac{F(1 - F^N)}{(1 - F)^2}$$

$$\sum_{j=1}^N \frac{F^* - F^{*N-j+1}}{1 - F^*} = \frac{NF^*}{1 - F^*} - \frac{F^*(1 - F^{*N})}{(1 - F^*)^2}$$

Summation of real part

$$\begin{aligned} & \operatorname{Re} \left[\frac{NF}{1 - F} - \frac{F(1 - F^N)}{(1 - F)^2} + \frac{NF}{1 - F} - \frac{F(1 - F^N)}{(1 - F)^2} \right] \\ &= 2 \operatorname{Re} \left[\frac{NF}{1 - F} - \frac{F(1 - F^N)}{(1 - F)^2} \right] \end{aligned}$$

$$\begin{aligned} & N + \frac{2NF}{1 - F} - \frac{2F(1 - F^N)}{(1 - F)^2} \\ &= \operatorname{Re} \left[\frac{N(1 + F)}{1 - F} \right] - \operatorname{Re} \left[\frac{2F(1 - F^N)}{(1 - F)^2} \right] \end{aligned}$$

$$\begin{aligned}
\frac{1+F}{1-F} &= \frac{1+|F|\exp(-i\mathbf{h}\cdot\bar{\mathbf{d}})}{1-|F|\exp(-i\mathbf{h}\cdot\bar{\mathbf{d}})} = \frac{\{1+|F|\exp(-i\mathbf{h}\cdot\bar{\mathbf{d}})\}\{1-|F|\exp(i\mathbf{h}\cdot\bar{\mathbf{d}})\}}{\{1-|F|\exp(-i\mathbf{h}\cdot\bar{\mathbf{d}})\}\{1-|F|\exp(i\mathbf{h}\cdot\bar{\mathbf{d}})\}} \\
&= \frac{1-|F|\exp(i\mathbf{h}\cdot\bar{\mathbf{d}})+|F|\exp(i\mathbf{h}\cdot\bar{\mathbf{d}})-|F|^2}{1-|F|\exp(i\mathbf{h}\cdot\bar{\mathbf{d}})+-|F|\exp(-i\mathbf{h}\cdot\bar{\mathbf{d}})-|F|^2} = \frac{1-|F|^2}{1-2|F|\cos(\mathbf{h}\cdot\bar{\mathbf{d}})+|F|^2}
\end{aligned}$$

$$\begin{aligned}
\frac{F(1-F^N)}{(1-F)^2} & \quad F(\mathbf{h}) = |F(\mathbf{h})|\exp\{-i\mathbf{h}\cdot\bar{\mathbf{d}}\} \\
&= \frac{2|F|\left\{\left(1+|F|^2\right)\cos(\mathbf{h}\cdot\bar{\mathbf{d}})-2|F|-|F|^N\cos[(N+1)(\mathbf{h}\cdot\bar{\mathbf{d}})]\right\}+2|F|^{N+1}\cos[N(\mathbf{h}\cdot\bar{\mathbf{d}})]-|F|^{N+2}\cos[(N-1)(\mathbf{h}\cdot\bar{\mathbf{d}})]}{\left\{1-2|F|\cos(\mathbf{h}\cdot\bar{\mathbf{d}})+|F|^2\right\}^2}
\end{aligned}$$

Equation (III-19) by convolution method corresponds to Eq. (A-1-1). By normalization, they are independent of N . On the other hand, Eq. (A-1-2) remains N and it is very important to smooth the intensity distribution. For curve fitting between experimental and theoretical results, Eq. (A-1) is reasonable.

Here, we have the average of $\exp(-i\mathbf{h} \cdot \mathbf{z})$ in accordance with H-function introduced by Hoseman

$$\langle \exp(-i\mathbf{h} \cdot \mathbf{z}) \rangle$$

$$H_1(z) = \frac{1}{\sqrt{2\pi\Delta d_{zz}^2}} \int_{-\infty}^{\infty} \exp\left[\frac{-(z - \bar{d})^2}{2\Delta d_{zz}^2}\right]$$

where \bar{d} is the average distance between adjacent particles and d_{zz} is the standard deviation along z-axis.

$$\begin{aligned} \langle \exp(-i\mathbf{h} \cdot \mathbf{z}) \rangle &= \int_{-\infty}^{\infty} H_1(z) \exp(-i\mathbf{h} \cdot \mathbf{z}) dz \\ &= \frac{1}{\sqrt{2\pi\Delta d_{zz}^2}} \int_{-\infty}^{\infty} \exp\left[\frac{-(z - \bar{d})^2}{2\Delta d_{zz}^2}\right] \exp\{-i(\mathbf{h} \cdot \mathbf{p})z\} dz = \frac{1}{\sqrt{2\pi\Delta d_{zz}^2}} \int_{-\infty}^{\infty} \exp\left[\frac{-(z - \bar{d})^2}{2\Delta d_{zz}^2}\right] \exp\{-iAz\} dz \\ &= \frac{1}{\sqrt{2\pi\Delta d_{zz}^2}} \int_{-\infty}^{\infty} \exp\left[\frac{-u^2}{2\Delta d_{zz}^2}\right] \exp\{-iA(u + \bar{d})\} du \quad z - \bar{d} = u \\ &\exp\{-iA(u + \bar{d})\} = \cos\{A(u + \bar{d})\} - i \sin\{A(u + \bar{d})\} \\ &= \cos Au \cos A\bar{d} - \sin Au \cos A\bar{d} - i \sin Au \cos A\bar{d} - i \cos Au \sin A\bar{d} \\ &= \cos Au \cos A\bar{d} - i \cos Au \sin A\bar{d} \end{aligned}$$

$$\begin{aligned}
& \frac{1}{\sqrt{2\pi\Delta d_{zz}^2}} \int_{-\infty}^{\infty} \exp\left[\frac{-u^2}{2\Delta d_{zz}^2}\right] \exp\{-iA(u + \bar{d})\} dz \\
&= \frac{1}{\sqrt{2\pi\Delta d_{zz}^2}} \cos A\bar{d} \int_{-\infty}^{\infty} \exp\left[\frac{-u^2}{2\Delta d_{zz}^2}\right] \cos Audu \\
&\quad - i \frac{1}{\sqrt{2\pi\Delta d_{zz}^2}} \sin A\bar{d} \int_{-\infty}^{\infty} \exp\left[\frac{-u^2}{2\Delta d_{zz}^2}\right] \cos Audu \\
&= \left[\frac{1}{\sqrt{2\pi\Delta d_{zz}^2}} \cos A\bar{d} - i \frac{1}{\sqrt{2\pi\Delta d_{zz}^2}} \sin A\bar{d} \right] \int_{-\infty}^{\infty} \exp\left[\frac{-u^2}{2\Delta d_{zz}^2}\right] \cos Audu \\
&= \frac{1}{\sqrt{2\pi\Delta d_{zz}^2}} \{\cos A\bar{d} - i \sin A\bar{d}\} \int_{-\infty}^{\infty} \exp\left[\frac{-u^2}{2\Delta d_{zz}^2}\right] \cos Audu \\
&\frac{1}{\sqrt{2\pi\Delta d_{zz}^2}} \{\cos A\bar{d}\} \int_{-\infty}^{\infty} \exp\left[\frac{-u^2}{2\Delta d_{zz}^2}\right] \cos Audu \\
\int_{-\infty}^{\infty} \exp\left[\frac{-u^2}{2\Delta d_{zz}^2}\right] \cos Audu &= \frac{2\sqrt{\pi}}{2\sqrt{\frac{1}{2\Delta d_{zz}^2}}} \exp\left\{-\frac{A^2}{4 \times \left(\frac{1}{2\Delta d_{zz}^2}\right)}\right\} = 2\sqrt{\frac{\pi}{2}} \Delta d_{zz} \exp\left(-\frac{\Delta d_{zz}^2 A^2}{2}\right)
\end{aligned}$$

$$\int_{-\infty}^{\infty} \exp\left[\frac{-u^2}{2\Delta d_{zz}^2}\right] \cos Audu = \frac{2\sqrt{\pi}}{2\sqrt{\frac{1}{2\Delta d_{zz}^2}}} \exp\left\{-\frac{A^2}{4 \times \left(\frac{1}{2\Delta d_{zz}^2}\right)}\right\} = 2\sqrt{\frac{\pi}{2}} \Delta d_{zz} \exp\left(-\frac{\Delta d_{zz}^2 A^2}{2}\right)$$

$$\frac{1}{\sqrt{2\pi\Delta d_{zz}^2}} \left\{ \cos A\bar{d} - i \sin A\bar{d} \right\} \int_{-\infty}^{\infty} \exp\left[\frac{-u^2}{2\Delta d_{zz}^2}\right] \cos Audu = \exp(-i\bar{A}d) \exp\left(-\frac{1}{2}\Delta d_{zz}^2 A^2\right)$$

$$\mathbf{A} = \mathbf{h} \bullet \mathbf{p} = h_z$$

$$A^2 = h_z^2$$

$$-A\bar{d} = \mathbf{h} \bullet \mathbf{p} \bullet \bar{\mathbf{d}} = \mathbf{h} \bullet \bar{\mathbf{d}}$$

$$\exp(-i\mathbf{h} \bullet \bar{\mathbf{d}}) \exp\left(-\frac{1}{2} h_z^2 \Delta d_{zz}^2\right)$$

$$F(\mathbf{h}) = |F(\mathbf{h})| \exp\{-i\mathbf{h} \bullet \bar{\mathbf{d}}\}$$

$$|F(\mathbf{h})| \exp\left\{-\frac{1}{2} h_z^2 \Delta d_{zz}^2\right\}$$

