One approach concerning teaching methods about diffraction and scattering of X-ray and visible light beams for graduate students studying material science

#### Masaru Matsuo

<sup>1</sup>Department of Polymer Science and Materials, Dalian University of Technology, Dalian 116024, P. R. China

#### Abstract

In attempt to pursue easy understanding 1) wide angle X-ray diffraction (WAXD), 2) small angle X-ray scattering SAXS) and 3) small angle light scattering (SALS) under polarization, teaching approaches about the three are focused on the different developments from the unified explanation given by the fundamental equation  $EE^*$  (E: scattering amplitude,  $E^*$ : the conjugate complex). The graduate students studying material science can understand the different developments based on mathematical knowledge in educational curriculum of undergraduate students. This approach refers to two important points. The first is the different wave lengths between X-ray and visible light associated with photon energy. 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. These different electron behaviors emphasize to provide the different scattering modes of X-ray and visible light in terms of photon energy. The second is the branch point associated with the different developments concerning X-ray diffraction and scattering. This is explained in terms of the focusing element scales. The diffraction and scattering in most of the textbooks have been described individually by different authors and then the descriptions have been never focused on the branch point. In addition to the above fundamental knowledge, serious defect for the recent instrument termed as simultaneous SAXS and WAXD measuring instrument" is pointed out in terms of the problem on evaluating radial distribution function of amorphous chains because of difficulty in estimating the incoherent intensity up to wide angle  $2\theta > 120^{\circ}$ .

#### Introduction

This paper is a short example to facilitate understanding of wide angle X-ray diffraction (WAXD), small angle X-ray scattering (SAXS) and small angle light scattering (SALS) systematically for graduate students studying polymer material science. For the facile understanding, mathematical knowledge beyond educational curriculum of undergraduate is unnecessary. A lot of efforts have been done to avoid abstract description and to focus on the concrete analysis for experimental results. Under the repeated teaching process, authors tried to the improvement that most of students can understand easily the morphology of polymer materials through WAXD, SAXS and SALS results. The students who observed unusual experimental results, have been obliged to pursue their analyses based on the well-known reports, while feeling the uncertainty. If they understood slightly the fundamental knowledge about WAXD, SAXS and SALS, they shall try to carry out the theoretical calculation in accordance with their own concept coming into their mind.

This paper aims to support theorization of their thinking ideas constructed. The paper focuses on three concepts; (1) Wavelength difference between X-ray and visible light; (2) The branch point of the same fundamental equation about WAXD and SAXS.

The important point (1) is the fact that the wavelength of X-ray beam is much shorter than that of visible light beam, and then X-ray and visible light beams provide different characteristics for polymer materials. (3) Fatal defect of recent X-ray machines termed as "simultaneous measurement instrument of WAXD and SAXS.

The wavelengths ( $\lambda$ ) 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 650 nm. The large difference is photon energy ( $\varepsilon$ ) between the two given by

 $\varepsilon = \frac{hc}{\lambda} = hv$  (I-1) (c: velocity of light, v: 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 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 polymer main chain axis in comparison with the direction perpendicular to the C-C axis. Hence incident wave interact with electrons belonging to C-C covalent bonds in main chains and scattered wave is sensitive to polarization condition of an incident beam. The basic concepts are described repeatedly in II and IV.

The important point (2) is the different developments for the fundamental equation

 $EE^*$  (E : scattering amplitude,  $E^*$  : the conjugate complex) associated with X-ray intensity. WAXD is unnecessary to consider the inter-particle interference effect between crystallites, since the diffraction peaks associated with the distance between crystal planes, the distance being generally much shorter than the distance between crystallite gains, appear in wide angle (twice the Bragg angle  $2\theta_{\rm B}$ ) range beyond 5°. On the other hand, for SAXS, the inter-particle interference between particles is important in addition to the scattering from an isolated particle. Namely, the inter-particle effect appeared in small angle region is hardly affected by atomic arrangement within each particle appeared in wide angle region. The analyses are described in II and IV. The important point (3) is the fact that young scientists must notice a serious defect of recent X-ray instrument termed as simultaneous measurement instrument for WAXD and SAXS, since the sample stage of the instrument is fixed. The instrument by imaging plate is certainly very effective to detect several SAXS peaks from ordered arrangement of large particles. High brightness of X-ray improves the scattering intensity distribution up to the high order peaks. However, the application of the instrument to WAXD measurement contains serious problem because of difficulty in evaluating inelastic scattering enhanced at wide angle region of  $2\theta_B$  and WAXD intensity from crystal planes oriented parallel to the film surface. The detailed explanation is described in V.

## II. Better understanding among fundamental WAXD, SAXS and SALS concepts

### II-1. General description about scattering for X-ray and visible light.

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. [1-3] Of course, the X-ray diffraction intensity is given by the same equation  $I = EE^*$ .

As shown in Figure 1, scattering amplitude from the k-th particle with K electrons, for example, is given in textbooks as follows:

$$E_{k} = \sum_{i=1}^{K} E_{i} \exp\left[2\pi i (\mathbf{s}' - \mathbf{s}_{o})/\lambda \bullet (\mathbf{r}_{ki} + \mathbf{R}_{K})\right] = \exp(i\mathbf{h} \bullet \mathbf{R}_{K}) \sum_{i=1}^{K} E_{i} \exp(i\mathbf{h} \bullet \mathbf{r}_{i})$$

$$= K \exp(i\mathbf{h} \bullet \mathbf{R}_{K}) \int_{kih} \rho(\mathbf{r}_{K}) \exp(i\mathbf{h} \bullet \mathbf{r}_{K}) d\mathbf{r}_{K}$$
(II-1)

where  $\lambda$  is the wavelength in vacuum. In Eq. (II-2),  $s_0$  and s' are the unit vectors along an incident beam and a scattered beam, respectively. **h** is  $2\pi (\mathbf{s'}-\mathbf{s}_0)/\lambda$ .



Figure 1. Geometrical arrangement to describe the fundamental equation for diffraction and scattering, in which  $O_{k+1}$  is neighbor particle. When  $O_{k+1}$  is not neighbor particles, the center is represented as  $O_j$ , as described later (IV).

For example,  $\exp(i\mathbf{h} \cdot \mathbf{r}_k)$  in Eq. (II-1) means the phase of *k*-th scattering element against the original coordinate for SAXS. That is,  $\underline{O_k M} - \underline{NK} = \mathbf{r}_k (\mathbf{s}' - \mathbf{s}_0) = \mathbf{r}_k \cdot \mathbf{s}$ .

The optical coordinate for the scattering system is shown in Figure 2.

$$\mathbf{h} = (2\pi/\lambda)(\mathbf{s'} - \mathbf{s_o}) \equiv (2\pi/\lambda)\mathbf{s} \qquad h = |\mathbf{h}| = (4\pi/\lambda)\sin\theta$$
  
where

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

In Eq. (II-2),  $2\theta$  is scattering angle and  $\mu$  is azimuthal angle.



Figure 2. General representation of optical coordinate. The scattering angle is given as  $2\theta_B$  for WAXD,  $2\theta$  for SAXS and  $\theta$  for SALS customarily.  $\mu$  is azimuthal angle.

To carry out theoretical calculation for SAXS and SALS patterns, the vector  $\mathbf{h} (= s' - s_0)$  in Eq. (II-2) can be selected as a reference axis in random system, while the vector  $\mathbf{v}$  must be selected in non-random system. Studies on this treatment are important for students. In Eq. (II-2),  $2\theta$  is scattering angle and  $\mu$  is azimuthal angle.

In Eq. (II-1), a uniform particle with electron density  $\rho_o$  exists in a medium with uniform density  $\rho_s$  and  $\rho(\mathbf{r})$  is given by using shape function  $\sigma(\mathbf{r})$ 

$$\rho(\mathbf{r}) = \left(\rho_o - \rho_s\right)\sigma(\mathbf{r}) + \rho_s \tag{II-3}$$

Generally, it may be described as  $\sigma(\mathbf{r}) = 1$  within a particle and  $\sigma(\mathbf{r}) = 0$  without a particle. Accordingly, at Eq. (II-3),  $\rho_s = 0$ . Hence Eq. (II-1) is given by

$$E_{k}(h) = K \int_{kth} \rho(\mathbf{r}) \exp[2\pi i (\mathbf{s}' - \mathbf{s}_{o})/\lambda \bullet \mathbf{r}] d\mathbf{r} = K \int_{kth} \rho(\mathbf{r}) \exp[i\mathbf{h} \bullet \mathbf{r}] d\mathbf{r}$$
$$= K \int \rho(\mathbf{r}_{k}) \exp[i\mathbf{h}(\mathbf{r}_{k} + \mathbf{R}_{k})] d\mathbf{r}_{k} = K \exp(i\mathbf{h} \bullet \mathbf{R}_{k}) \int \rho(\mathbf{r}_{k}) \exp(i\mathbf{h} \bullet \mathbf{r}_{k}) d\mathbf{r}_{k} \quad (\text{II-4})$$

 $d\mathbf{r}_{\mathbf{k}}$  is micro-volume element at position vector  $\mathbf{r}_{k}$ .  $\int d\mathbf{r}_{k}$  denotes volume integral. Since  $\mathbf{r} = \mathbf{r}_{\mathbf{k}} + \mathbf{R}_{\mathbf{k}}$  in Eq. (II-2),  $d\mathbf{r} = d\mathbf{r}_{\mathbf{k}}$  assuming that  $\mathbf{R}_{\mathbf{k}}$  is constant. Of course,  $E = \sum_{k=1}^{N} E_{k}$  and  $E^{*} = \sum_{k=1}^{N} E_{k}^{*}$ , where *N* is the number of particles. Eq. (II-4) is general representation about scattering and diffraction for X-ray and light beams. However, the different representation between X-ray and visible light scattering magnitudes is attributed to the different physical meanings of  $\rho(\mathbf{r})$ .

As discussed above, the intensity for X-ray is related to mean square value of electron density fluctuation. When the electron density within each particle is uniform,  $\rho(\mathbf{r})$  is given by  $\rho_o$ . The scattering from an isolated particle reveals  $\mathbf{R}_{\mathbf{k}} = 0$  and  $\exp(ih\mathbf{R}_{\mathbf{k}}) = 1$ . Then,

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

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. 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. Hence,  $\rho_o$  is not constant.

$$E_{k} = \sum_{i=1}^{K} E_{i} \exp[2\pi i (\mathbf{s}^{\prime} - \mathbf{s}_{o})/\lambda \bullet (\mathbf{r}_{i} + \mathbf{R}_{K})] = \exp(i\mathbf{h} \bullet \mathbf{R}_{K}) \sum_{i=1}^{K} E_{i} \exp(i\mathbf{h} \bullet \mathbf{r}_{i})$$
  
=  $K \exp(i\mathbf{h} \bullet \mathbf{R}_{K}) \int \rho(\mathbf{r}) \exp[i\mathbf{h} \bullet \mathbf{r}_{K}] d\mathbf{r}_{K} = K \exp(i\mathbf{h} \bullet \mathbf{R}_{k}) \int (\mathbf{M}_{k} \bullet \mathbf{O}) \exp(i\mathbf{h} \bullet \mathbf{r}_{k}) d\mathbf{r}_{k}$  (II-6)  
=  $K \exp(i\mathbf{h} \bullet \mathbf{R}_{k}) \int (\mathbf{M} \bullet \mathbf{O}) \exp(i\mathbf{h} \bullet \mathbf{r}) d\mathbf{r}$ 

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

For scattering from an isolated particle ( $\mathbf{R}_{\mathbf{k}} = 0$ ), it can be written as follows:

$$E_{iso} = K \int (\mathbf{M} \bullet \mathbf{O}) \exp(i\mathbf{h} \bullet \mathbf{r}) d\mathbf{r}$$
(II-7)

## II-2 X-ray scattering from atoms and the application to one polymeric molecule

X-ray diffraction is associated with the reflection from atomic arrangement plates termed as crystal planes. A particle corresponds to a crystallite constructing crystal units and the scattering element corresponds to one electron. The mathematical treatment in wide angle range can neglect interference effect due to a plurality of crystallites and then the coordinate for theoretical calculation can be limited to atomic arrangement within a particle. Before then, we shall start the scattering from an isolated atom as primitive phenomenon before starting diffraction from crystal units within a crystallite. Automatically, the representation for  $\mathbf{R}_{\mathbf{k}}$  is neglected and Figure 1 shall be replaced as Figure 3 simply. In Figure 3(a), the center  $O_k$  of the coordinate is represented as O by abbreviating suffix *k*.



Figure 3. (a) Optical coordinate to calculate scattered intensity from an atom using the phase difference between *i*-th and *j*-th electrons. (b) Simple coordinate to calculate scattered intensity from atoms, in which four atoms (Atom  $1 \sim Atom 4$ ) are shown as an example. The center of each atom is position of nucleus and existing probability of electrons is shown by blue zone around the each nucleus (red ink).

The X-ray scattering intensity is attributed to square of the amplitude from one atom with Z electrons (atomic number Z), in which interference effect (phase relation) between each scattered waves must be considered. From the phase difference  $[jm - ni = (\mathbf{s}' - \mathbf{s}_0) \cdot \mathbf{r}_{ij}]$  of scattered waves between *i* and *j* electrons in Figure 3(a), Eq. (II-1) can be written as follows:

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

$$E^{*} = \sum_{i=1}^{Z} E_{i} \exp\left[-2\pi i (\mathbf{s}' - \mathbf{s}_{o})/\lambda \bullet \mathbf{r}_{j}\right] = \sum_{i=1}^{Z} E_{i} \exp\left[-i\mathbf{h} \bullet \mathbf{r}_{j}\right]$$
(II-8)
(II-8)

The scattered intensity is give by

$$I = EE^* = I_e \sum_{i=1}^{Z} \sum_{j=1}^{Z} \exp\{i\mathbf{h} \bullet (\mathbf{r_i} - \mathbf{r_j})\} = I_e \left[Z + \sum_{i\neq}^{Z} \sum_{j=1}^{Z} \exp[i\mathbf{h} \bullet \mathbf{r_{ij}}]\right]$$
(II-9)

where  $I_e$  is the scattered intensity from one electron. Under no polarization,  $I_e$  is given by [1]

$$I_{e} = I_{o} \frac{1}{R^{2}} \left(\frac{e^{2}}{mc^{2}}\right)^{2} \frac{1 + \cos^{2} 2\theta}{2}$$

 $I_o$  is intensity of incident beam in which *c* is speed of light, *m* is electron mass and *e* is electron density, respectively.  $e^2/mc^2$  corresponds to radius of Bohr's classical model.  $I_e$  corresponds to  $K^2$  given as general description in Eq. (II-1). Considering polarization factor represented by  $(1 + \cos^2 2\theta)/2$ ,  $I_e$  becomes maximum at  $\theta = 0^\circ$ . Then, the polarized X-ray is useful only to increase  $I_e$ . Based on Eq. (II-9), the intensity from an atom with Z electrons is written as follows:

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

where

$$f_i = \int \rho_i(\mathbf{r}) \exp(\mathbf{h} \cdot \mathbf{r}) d\upsilon \qquad \text{(II-11)}$$

where  $f_i$  is termed as electric structure factor, and volume element is represented as dv in stead of dr (in Eqs. II-4 ~ II-7).  $\rho_i(\mathbf{r})$  is density distribution of the *i*-th electron.

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

$$\rho(\mathbf{r}) = \rho_1(\mathbf{r}) + \rho_2(\mathbf{r}) + \dots + \rho_z(\mathbf{r}) \quad \text{(II-12)}$$
where

where

is rewritten as

$$f = \sum_{i=1}^{Z} f_i = \int \rho(\mathbf{r}) \exp(\mathbf{h} \cdot \mathbf{r}) d\upsilon$$
 (II-13)

f is termed as atomic structure factor for an atom with electron number Z. Thus, Eq. (II-10) is rewritten as follows:

$$I = I_e \left( Z + \left| f \right|^2 - \sum_{i=1}^{Z} \left| f_i \right|^2 \right)$$
(II-14)

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, and then Eq. (II-14)

8

$$I = I_e \left| f \right|^2 \tag{II-15}$$

Incidentally, Eq. (II-10) represents the elastic scattering based on the assumption that the wave length of incident beam is equal to that of scattered beam.

Assuming that electron density distribution around the nucleus is spherically symmetry, Eq. (II-15) can be given by

$$I = I_e \left[ \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \rho(r) \frac{\cos(hr\cos\alpha)}{hr} r^2 \sin\alpha dr d\alpha d\beta \right]^2 = I_e \left[ 4\pi \int_0^{\infty} \rho(r) \frac{\sin(hr)}{hr} r^2 dr \right]^2$$
(II.16)

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:

$$I_m = I_e \left| F_m \right|^2 \qquad \text{(II-17)}$$

where

$$F_m = \int \rho_{mol}(\mathbf{r}) \exp[2\pi i (\mathbf{s}' - \mathbf{s}_o) / \lambda \bullet \mathbf{r}] d\upsilon = \int \rho_{mol}(\mathbf{r}) \exp[i\mathbf{h} \bullet \mathbf{r}] d\upsilon \qquad (\text{II-18})$$

Figure 3(b) shows the optical coordinate as an example for four atoms in one molecule. When one molecule consist of N number of atoms, the density of one molecule is generally given by the summation of electron density around nucleus

$$\rho_{mol}(\mathbf{r}) = \sum_{i=1}^{Z_1} \rho_1(\mathbf{r} - \mathbf{r}_i) + \sum_{i=1}^{Z_2} \rho_2(\mathbf{r} - \mathbf{r}_i) + \dots + \sum_{i=1}^{Z_N} \rho_N(\mathbf{r} - \mathbf{r}_i)$$
(II-19)

where  $\mathbf{r}_i$  is the position of the *i*-th nucleus.  $\sum_{i=1}^{Z_1} \rho_1(\mathbf{r} - \mathbf{r}_i)$  and  $\sum_{i=1}^{Z_N} \rho_N(\mathbf{r} - \mathbf{r}_i)$  are the

electron density of  $1^{st}$  atom with  $Z_1$  electrons and that of the *N*-th atom with  $Z_N$  electrons, respectively.

Substituting Eq. (II-19) into Eq. (II-18), the structural factor of one polymeric molecule  $F_m$  is given by

$$F_{m} = \int \exp[i\mathbf{h} \cdot \mathbf{r}] \left\{ \sum_{i=1}^{Z_{1}} \rho_{1}(\mathbf{r} - \mathbf{r}_{i}) d\upsilon_{1} + \sum_{i=1}^{Z_{2}} \rho_{2}(\mathbf{r} - \mathbf{r}_{i}) d\upsilon_{2} + \dots + \sum_{i=1}^{Z_{N}} \rho_{N}(\mathbf{r} - \mathbf{r}_{i}) d\upsilon_{N} \right\}$$

$$\approx \sum_{i=1}^{Z_{N}} \exp[i\mathbf{h} \cdot \mathbf{r}_{i}] \left\{ \int \left\{ \sum_{i=1}^{Z_{1}} \rho_{1}(\mathbf{r} - \mathbf{r}_{i}) \exp[i\mathbf{h} \cdot (\mathbf{r} - \mathbf{r}_{i})] d\upsilon_{1} + \sum_{i=1}^{Z_{2}} \rho_{2}(\mathbf{r} - \mathbf{r}_{i}) \exp[i\mathbf{h} \cdot (\mathbf{r} - \mathbf{r}_{i})] d\upsilon_{2} + \dots + \sum_{i=1}^{Z_{N}} \rho_{N}(\mathbf{r} - \mathbf{r}_{i}) \exp[i\mathbf{h} \cdot (\mathbf{r} - \mathbf{r}_{i})] d\upsilon_{N} \right\}$$

(II-20)

Comparing with Eq. (II-13), each integration part in Eq. (II-20) 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

$$F_m = \sum_i f_i^{at} \exp[i(\mathbf{h} \bullet \mathbf{r}_i)] = \sum_i f_i^{at} \exp[2\pi i \left(\mathbf{s'} - \mathbf{s}_o\right) / \lambda \bullet \mathbf{r}_i] \qquad (II-21)$$

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

$$I_{m} = I_{e} |F_{m}|^{2} = I_{e} F_{m} F_{m}^{*} = I_{e} \sum_{i} \sum_{j} f_{i}^{at} f_{j}^{at} \exp[i\mathbf{h}(\mathbf{r_{i}} - \mathbf{r_{j}})]$$
  
$$= I_{e} \sum_{i} \sum_{j} f_{i}^{at} f_{j}^{at} \exp[i(\mathbf{h} \cdot \mathbf{r_{ij}})] = I_{e} \sum_{i} \sum_{j} f_{i}^{at} f_{j}^{at} \exp[2\pi i (\mathbf{s'} - \mathbf{s_{o}})/\lambda \cdot \mathbf{r_{ij}}]$$
(II-22)

The  $I_m$  must be evaluated by considering: 1) interference effect between atoms in the molecule, and 2) the equal existing probability in three-dimensional space. Thus the intensity from N atoms in irradiated volume is given by

$$I_{m} = I_{e} \left\langle \left| Fm \right|^{2} \right\rangle = I_{e} \sum_{i=1}^{N} \sum_{j=1}^{N} f_{i}^{at} f_{j}^{at} \frac{\sin(hr_{ij})}{hr_{ij}} \qquad \text{(II-23)}$$

Let's represent the concrete example for isolated carbon tetrachloride (CC  $\ell_4$ ). [3]

$$I_{m} = f_{C}^{2} + 4f_{C\ell}^{2} + 8f_{C}f_{C\ell}\frac{\sin[hr(C - C\ell)]}{hr(C - C\ell)} + 12f_{C\ell^{2}}\frac{\sin[hr(C\ell - C\ell)]}{hr(C\ell - C\ell)}$$
(II-24)

The intensity  $I_m$  is usually given as a function of  $\sin \theta / \lambda \ (= h/4\pi)$ .

#### II-3. X-ray diffraction from crystallites

((

Let's consider X-ray diffraction intensity 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 are arranged regularly 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. Accordingly, Eq. (II-22) can be written as follows:

$$I = I_e \left\{ \sum_i f_i^{at} \exp[2\pi i \left(\mathbf{s'} - \mathbf{s_o}\right) / \lambda \bullet \mathbf{r_i}] \right\}^2 = I_e \left\{ \sum_i f_i^{at} \exp[i\mathbf{h} \bullet \mathbf{r_i}] \right\}^2 = I_e |F_c|^2 \quad (\text{II-25})$$

For X-ray diffraction, the atomic structure factors  $f_i^{at}$  is usually represented as  $f_i$ , since X-ray diffraction and scattering have been written by different authors in most of the textbooks.[1, 3] The values of the atomic structural factors as a function of  $\sin \theta / \lambda$  are given as table to calculate crystal structural factor. Replacing  $f_i^{at}$  to  $f_i$ , Eq. (II-25) is rewritten as follows:



Figure 4. (a) Geometrical arrangement for the crystal units. (b) Atoms in the unit.[2]

Eq. (II-25) is the first important thing to pursue the mathematical treatment for WAXD.

When the number of units along x, y and z directions is  $N_1$ ,  $N_2$  and  $N_3$ , respectively, the total number of the units is  $N_1N_2N_3$ . As a simple example, the representation in Figure 4 is adopted as geometrical arrangement to determine the position i(u,v,w) of *i*-th atom in a selected crystal unit, in which  $u=(4+x_i)a$ ,  $v=(3+y_i)b$ ,  $w=(2+z_i)c$ . Considering periodicity of the atomic arrangement, the vector  $\mathbf{r}_i$  is generally given by 26) (51)

$$\mathbf{r}_{\mathbf{i}} = \mathbf{R}_{\mathbf{i}\mathbf{o}} + \mathbf{r}_{\mathbf{i}\mathbf{o}} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} + x_{\mathbf{i}} \mathbf{a} + y_{\mathbf{i}} \mathbf{b} + z_{\mathbf{i}} \mathbf{c} \qquad (n_1, n_2, n_3: \text{ integer}) \qquad (\text{II-2})$$

Substituting Eq. (II-26) into Eq. (II-25), Eq. (II-25) can be written by

$$I = I_{e} \left[ \sum_{n_{1}=0}^{N_{1}-1} \sum_{n_{2}=0}^{N_{2}-1N_{3}-1} \exp[i\mathbf{h}(n_{1}\mathbf{a} + n_{2}\mathbf{b} + n_{3}\mathbf{c})] \times \sum_{i} f_{i} \exp[i\mathbf{h}(x_{i}\mathbf{a} + y_{i}\mathbf{b} + z_{i}\mathbf{c})] \right]^{2}$$

$$= I_{e}LL * \left| \sum_{i} f_{i} \exp[i\mathbf{h}(x_{i}\mathbf{a} + y_{i}\mathbf{b} + z_{i}\mathbf{c})] \right|^{2} = I_{e}LL * |F(S)|^{2}$$
(II-27)

where

$$L = \sum_{n_{1=}=0}^{N_{1}-1} \sum_{n_{2}=0}^{N_{2}-1N_{3}-1} \exp[i\mathbf{h}(n_{1}\mathbf{a}+n_{2}\mathbf{b}+n_{3}\mathbf{c})] = \sum_{n_{1=}=0}^{N_{1}-1} \sum_{n_{2}=0}^{N_{2}-1N_{3}-1} \exp[2\pi i(\mathbf{s}'-\mathbf{s}_{o})/\lambda \bullet (n_{1}\mathbf{a}+n_{2}\mathbf{b}+n_{3}\mathbf{c})]$$
(II-28)

and **h** is represented as  $2\pi S$  for X-ray diffraction in many textbooks.

$$F(S) = \sum_{i} f_{i} \exp[i\mathbf{h}(x_{i}\mathbf{a} + y_{i}\mathbf{b} + z_{i}\mathbf{c})] = \sum_{i} f_{i} \exp[2\pi i\mathbf{S}(x_{i}\mathbf{a} + y_{i}\mathbf{b} + z_{i}\mathbf{c})]$$
(II-29)

F(S) is termed as crystal structural factor and corresponds to the structural factor  $F_m$  of one polymeric molecule in Eq. (II-21), which is related to the scattered intensity  $I_m$  from one polyatomic molecule in gas neglecting molecular interference.

Similar to **h** used for scattering, **S** is used for X-ray diffraction routinely.

$$(\mathbf{s'}-\mathbf{s}_{o})/\lambda = \mathbf{S}, \qquad S = |\mathbf{S}| = \frac{2\sin\theta}{\lambda}, \qquad h = |\mathbf{h}| = \frac{4\pi\sin\theta}{\lambda} = 2\pi|\mathbf{S}| = 2\pi S$$
(II-30)

Hence *L* is simplified as follows:

$$L = \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1N_3-1} \exp[2\pi i (n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}) \mathbf{S}]$$
  
=  $\sum_{n_2=0}^{N_1-1} \exp[2\pi i n_1 (\mathbf{a} \bullet \mathbf{S})] \sum_{n_2=0}^{N_2-1} \exp[2\pi i n_2 (\mathbf{b} \bullet \mathbf{S})] \sum_{n_3=0}^{N_3-1} \exp[2\pi i n_3 (\mathbf{c} \bullet \mathbf{S})]$   
=  $\sum_{n_2=0}^{N_1-1} \exp[2\pi i n_1 h] \sum_{n_2=0}^{N_2-1} \exp[2\pi i n_2 k] \sum_{n_3=0}^{N_3-1} \exp[2\pi i n_3 \ell]$ 

Then,

$$LL^* = \frac{\sin^2(\pi N_1 h) \sin^2(\pi N_2 k) \sin^2(\pi N_3 \ell)}{\sin^2(\pi h) \sin^2(\pi k) \sin^2(\pi \ell)}$$
(II-32)

where  $L^*$  is complex conjugate of L.

At  $N_1$ ,  $N_2$ ,  $N_3 >>1$ , Eq. (II-32) becomes a periodic function termed as Laue function, when Eq. (II-33) is satisfied, in which h, k,  $\ell$  are well-known as Miller index. These are very important conditions to raise X-ray diffraction. Eq. (II-33) is also termed as Laue conditions, which is indispensable rule different from usual scattering.

(II-31)

25

$$\mathbf{S} \bullet \mathbf{a} = h$$
,  $\mathbf{S} \bullet \mathbf{b} = k$ ,  $\mathbf{S} \bullet \mathbf{c} = \ell$  (*h*, *k*,  $\ell$ : integer) (II-33)

Many text books explain the reason why Eq. (II-33) is indispensable for X-ray diffraction.

However, Eq. (II-32) is one of the special cases of X-ray scattering represented by Eq. (II-1) generally.

Based on Eq. (II-33), Eq. (II-28) is rewritten as Eq. (II-31). Laue function  $LL^*$  in WAXD is in connection to crystal size and is also discontinuous part in X-ray scattering. Eq. (II-33) is the second important thing to induce Eq. (II-32) for WAXD.

As one-dimensional direction,  $L_1(h)L_1 * (h) = L_1^2(h) = \sin^2(\pi N_1 h)/\sin^2(\pi h)$  is shown in Figure 5. The result indicates that the diffraction peak becomes sharper and higher as  $N_1$  increases. The maximum value is  $L_1^2(h) = N_1^2$  (h = 0, 1, 2, ---)



Figure 5. Laue function in one-dimensional direction at  $N_1$ =100. [2]

On the other hand,  $F(S)F^*(S) = |F(S)|^2$  termed as crystal structural factor is related to the scattering from the total atoms in a crystal unit.

To satisfy Laue conditions in Eq. (II-33),  $(\mathbf{s}'-\mathbf{s}_o)/\lambda = \mathbf{S}$  must be represented by reciprocal lattice vectors  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$  in a crystal unit, which is given by

$$\frac{\mathbf{s'}-\mathbf{s}_{o}}{\lambda} = \mathbf{S} = h\mathbf{a}^{*} + k\mathbf{b}^{*} + \ell\mathbf{c}^{*}, \quad S = |\mathbf{S}| = \frac{2\sin\theta}{\lambda} = \frac{1}{d} \quad (\text{II-34}) \quad (h, k, \ell : \text{ integer})$$

where

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

*V* is the volume of a crystal unit. Again, it must be noted that *h* in Eqs. (II-31) ~ (II-34) is integer different from  $4\pi \sin \theta / \lambda$  used in this paper. Eq. (II-34) is the third important thing to pursue the mathematical treatment for WAXD.

The reciprocal space for Eq. (II-34) is represented as Ewald sphere with radius of  $1/\lambda$  ( $\lambda$ : 0.1542 nm for X-ray generated from Cu target) in Figure 6(a) and the representation for real space  $2d \sin \theta_B = \lambda$  corresponds to Bragg equation  $2d \sin \theta_B = n\lambda$  (n = 1, 2-----).



Figure 6. (a) Ewald sphere representing Laue condition in reciprocal space. (b) Bragg equation representing X-ray diffraction in real space

Now, Eq. (II-29) can be written as follows:

$$F(S) = F(h,k,\ell) = \sum_{i} f_{i} \exp\{2\pi i \left(h\mathbf{a}^{*} + k\mathbf{b}^{*} + \ell\mathbf{c}^{*}\right) \left(x_{i}\mathbf{a} + y_{i}\mathbf{b} + z_{i}\mathbf{c}\right)\}$$
(II-35-1)

By using the relationship ( $aa^* = bb^* = cc^* = 1$ , the others, zero), Eq. (II-35-1) is generally represented as follows:

$$F(h,k,\ell) = \sum_{i} f_{i} \exp\left[2\pi i(hx_{i} + ky_{i} + \ell z_{i})\right] \qquad \text{Unit cell} \qquad (\text{II-35-2})$$

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

Atom •	1	2	3	N
Coordinate	<i>x</i> <sub>1</sub> , <i>y</i> <sub>1</sub> , <i>z</i> <sub>1</sub>	<i>x</i> <sub>2</sub> , <i>y</i> <sub>2</sub> , <i>z</i> <sub>2</sub>	<i>x</i> <sub>3</sub> , <i>y</i> <sub>3</sub> , <i>z</i> <sub>3</sub>	$x_N, y_N, z_N$
Atomic scattering	5			
factor	$f_1$	$f_2$	$f_3$	$f_N$

Thus, we have

$$F(h,k,\ell) = F_{hk\ell} = f_1 \exp\{2\pi i (hx_1 + ky_1 + \ell z_1)\} + f_2 \exp\{2\pi i (hx_2 + ky_2 + \ell z_2)\} + f_3 \exp\{2\pi i (hx_3 + ky_3 + \ell z_3)\} + \dots + f_N \exp\{2\pi i (hx_N + ky_N + \ell z_N)\}$$
(II-36)

$$\left|F_{hk\ell}\right|^{2} = F_{hk\ell}F_{hk\ell} * \qquad I \propto \left|F_{hk\ell}\right|^{2} \qquad \text{(II-37)}$$

Here every crystal plane is not involved in X-ray diffraction. Some crystal planes contribute to the reflection, but some do not contribute on the basis of extinction rule. Eq. (II-36) is the fourth important thing to pursue the mathematical treatment for WAXD.

Extinction rule		
Bravais lattice	Reflection	No eflection
Primitive	all	non
Base centered	<i>h, k</i> , all odd or all even	h, k  h  or  k  odd (or even)
body æntered	$(h+k+\ell)$ even	$(h+k+\ell)$ odd
face centered	$h, k, \ell$ all odd	$h, k, \ell  h, k, \ell \text{ odd (or even)}$
	or all even	

A number of textbooks refer to the calculation procedures of  $|F_{hk\ell}|^2$  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  $NaC\ell$  unit.

Practice problem

Describe the structural factor of  $NaC\ell$  unit and discuss extinction rule.



Figure 7. Crystal unit of  $NaC\ell$ 

Answer

The coordinate Na<sup>+</sup> and  $C\ell^{-}$  are as follows:

Na<sup>+</sup> : 
$$(0, 0, 0)$$
,  $(0, \frac{1}{2}, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, \frac{1}{2})$ ,  $(\frac{1}{2}, \frac{1}{2}, 0)$   
C $\ell^{-}$  :  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, 0)$ ,  $(0, \frac{1}{2}, 0)$ ,  $(0, 0, \frac{1}{2})$ 

Using Eq. (II-36), the crystal structural factor F(S) for  $NaC\ell$  is given by

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

By considering Extinction rule,

	$\left(4(f_{Na^{+}}+f_{C\ell^{-}})\right)$
$F(h,k,\ell) = \langle$	$4(f_{Na^+} - f_{C\ell^-})$

 $k, h, \ell$ , all even $k, h, \ell$ , all odd $k, h, \ell$ , even and odd mixing

alsul

For example

The diffraction from the (111) plane

The diffraction from the (220) plane  $4(f_{Na^+} + f_{C\ell^-})$ 

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

 $4(f_{Na^+} - f_{C\ell^-})$ 

Anyway, the diffraction intensity (II-25) is written by using Eqs. (II-32) and (II-37) as follows:

$$I(h,k,\ell) = I_e \frac{\sin^2(\pi N_1 h) \sin^2(\pi N_2 k) \sin^2(\pi N_3 \ell)}{\sin^2(\pi h) \sin^2(\pi k) \sin^2(\pi \ell)} |F_{hk\ell}|^2 \quad \text{(II-38)}$$

Here it may be noted that the irradiation volume of X-ray is much bigger than the crystallite size associated with  $N_1$ ,  $N_2$  and  $N_3$  and then the sizes of many crystallites are not same and the actual X-ray diffraction reflects the distribution of  $N_1$ ,  $N_2$  and  $N_3$ . If  $N_1$ ,  $N_2$ , and  $N_3$  are fixed, many vice maxima must be appeared in the observed diffraction

intensity. However, such phenomenon has never been observed actually. This is due to size distribution of crystallites (particles) existed in the irradiation volume. This phenomenon has been described elsewhere. [4-7] Of course, the consideration for interparticle interference effect for crystallites is negligible for WAXD, since the effect is almost independent of the wide angle  $2\theta_B$ .

#### III. 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 in Figure 1. As described already, the scattered intensity from *K*-th particle can be evaluated by using Eq. (II-4).

For SAXS, Eq. (II-4) is rewritten as follows:

$$E_{K}(h) = E_{e} \exp(i\mathbf{h} \cdot \mathbf{R}_{K}) \int \rho(\mathbf{r}_{k}) \exp[i(\mathbf{h} \cdot \mathbf{r}_{k})] dr_{k} \equiv E_{e} F_{K}(h) \exp(i\mathbf{h} \cdot \mathbf{R}_{K})$$
(III-1)

where  $E_e$  is amplitude from one electron corresponding to *K* in Eq. (II-4) and  $I_e = E_e^2$ , and  $F_K(h)$  is given by

$$F_{K}(h) = \int \rho(\mathbf{r}_{k}) \exp[i(\mathbf{h} \bullet \mathbf{r}_{k})] d\mathbf{r}_{k}$$
(III-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  $O_K$  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

$$E_{s}(h) = \sum_{K=1}^{N} E_{K}(h) = E_{e} \sum_{K=1}^{N} F_{K}(h) \exp(i\mathbf{h} \cdot \mathbf{R}_{K})$$
(III-3)

In stead of  $O_{k+1}$  in Figure 1,  $O_j$  particle (position different from the neighbor particle) is set in this section as general representation. Putting  $R_{KJ} = R_J - R_K$ , the scattered intensity I(h) becomes

$$I(h) = I_e \sum_{K=1}^{N} \sum_{J=1}^{N} F_K(h) F_J^*(h) \exp(i\mathbf{h} \cdot \mathbf{R}_K) \exp(-i\mathbf{h} \cdot \mathbf{R}_J)$$
  
$$= I_e \sum_{K=1}^{N} \sum_{J=1}^{N} F_K(h) F_J^*(h) \exp(-i\mathbf{h} \cdot \mathbf{R}_{KJ})$$
  
$$= I_e \left\{ \sum_{K=1}^{N} \left| F_K^2 \right| + \sum_{K \neq J}^{N} \sum_{J}^{N} F_K(h) F_J^*(h) \exp(-i\mathbf{h} \cdot \mathbf{R}_{KJ}) \right\}$$
(III-4)

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. (III-4) can be written

$$I(h) = I_e \left\{ N \left\langle F^2 \right\rangle + \left\langle F \right\rangle^2 \sum_{K \neq J}^N \sum_{J}^N \exp(-i\mathbf{h} \cdot \mathbf{R}_{KJ}) \right\}$$
  
=  $I_e N \left[ \left\langle F^2 \right\rangle - \left\langle F \right\rangle^2 \right] + I_e \left\langle F \right\rangle^2 \left[ N + \sum_{K \neq J}^N \sum_{J}^N \exp(-i\mathbf{h} \cdot \mathbf{R}_{KJ}) \right]$  (III-5)

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 Eq. (III-5), 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 8.

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  $dv/v_1$ .

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  $dP(r) = P(r)dv/v_1$ . 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  $\{P(\mathbf{r}) - 1\}$  has the fluctuation, the double summation in Eq. (III-5) cannot be carried out by the same weight for pair of each two-atoms and the summation must be represented by weight  $\frac{1}{\nu_1} \{P(\mathbf{r}) - 1\}$ .

Matsut In Figure 1, let's consider  $\mathbf{R}_{KJ}$  as continuous scale in statistical group, the integration can be done in stead of summation of

$$\sum_{K\neq J} \sum_{J} \exp\left(-i\mathbf{h} \bullet \mathbf{R}_{KJ}\right) = \frac{1}{\upsilon_1} \int_0^\infty \{P(R_{KJ}) - 1\} \exp\left(-i\mathbf{h} \bullet \mathbf{R}_{KJ}\right) d\upsilon$$
$$= \frac{4\pi}{\upsilon_1} \int_0^\infty \{P(R_{KJ}) - 1\} \frac{\sin(hR_{KJ})}{h} R_{KJ} dR_{KJ}$$

Hence Eq. (II-5) an bewritten a follows:

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

$$= I_e N \left[ \left\langle F^2 \right\rangle - \left\langle F \right\rangle^2 \right] + I_e \left\langle F \right\rangle^2 \left[ N + \frac{4\pi}{\upsilon_1} \int_0^\infty \left\{ P(R_{KJ}) - 1 \right\} \frac{\sin(hR_{KJ})}{h} R_{KJ} dR_{KJ} \right]$$

$$= I_e N \left[ \left\langle F^2 \right\rangle - \left\langle F \right\rangle^2 \right] + I_e \left\langle F \right\rangle^2 \left[ N + \frac{4\pi}{\upsilon_1} \int_0^\infty \left\{ P(R) - 1 \right\} \frac{\sin(hR)}{h} R dR \right]$$

$$= I_e N \left[ \left\langle F^2 \right\rangle - \left\langle F \right\rangle^2 \right] + I_e N \left\langle F \right\rangle^2 \left[ 1 + \frac{4\pi}{V} \int_0^\infty \left\{ P(R) - 1 \right\} \frac{\sin(hR)}{h} R dR \right]$$
(III-6)

The scattered intensity from congested polyatomic molecules is given by the electron density distribution P(R) as a function of distance R between molecules in textbooks. The normal rewriting from  $\mathbf{R}_{KI}$  denoting vector between K and J to R in Eq. (III-6) means the difficulty in distinguishing between atoms within a molecules as well as between atoms in other molecule in congested system.

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  $\rho_o = 1/V$ . Hence Eq. (III-6) can be rewritten as follows:

$$I(h) = I_e N \langle F \rangle^2 \left[ 1 + 4\pi \int_0^\infty \{ \rho(R) - \rho_o \} \frac{\sin(hR)}{hR} R^2 dR \right] \quad \text{(III-7)}$$

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

$$I(h) = I_e N \langle F \rangle^2 \left[ 1 + 4\pi \int_0^\infty P(R) \frac{\sin(hR)}{hR} R^2 dR \right]$$
(III-8)

In Eq. (III-8), P(R) termed as radial distribution function becomes positive and negative as reported many text books.

From Eq. (III-8),

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

$$I'(h) = \frac{I(h) - I_o}{I_o} = \int_0^\infty 4\pi R^2 P(R) \frac{\sin(hR)}{hR} dR \qquad \text{(III-9)}$$

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 of Eq. (III-9)',

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

Let's consider Eq. (III-2) for a sphere with radius *a*. From  $\rho(r) = \rho_o$  at  $r \le a/2$ and  $\rho(r) = 0$  at  $r \ge a/2$ , the intensity is given by

(III-9)'

$$F(h) = \int \rho(\mathbf{r}) \exp[i(\mathbf{h} \cdot \mathbf{r})] d\mathbf{r} = \rho_o \int_0^{2\pi} \int_0^{\pi} \int_0^{\alpha} r^2 \cos[hr \cos\alpha] \sin\alpha dr d\alpha d\phi$$
  
=  $3V(\sin U - U \cos U)/U^3$   
 $I(h) = I_e \rho_o |F(h)|^2$  (III-10-1)

$$I(h) = 9I_e \rho_o V^2 (\sin U - U \cos U)^2 / U^6 = I(q)$$
(III-10-2)

where  $U = ha = (4\pi a/\lambda)\sin\theta = 2\pi qa$   $(q = \sin\theta/\lambda)$  and  $V = 4\pi a^3/3$ .

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, many scattered peaks of I(h) (I(q)) 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.

#### **Guinier** law

Now, let's consider Guinier law [8], 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 Eq. (III-9),

$$I'(h) = \frac{I(h) - I_o}{I_o} = \int_0^\infty 4\pi R^2 P(R) \frac{\sin(hR)}{hR} dR$$
  
=  $4\pi \left\{ \int_0^D P(R) R^2 dR - \frac{h^2}{6} \int_0^D P(R) R^4 dR + \frac{h^4}{120} \int_0^D P(R) R^6 dR - --- \right\}$  (III-10)  
=  $4\pi \int_0^D P(R) R^2 dR \left\{ 1 - \frac{h^2}{3} \left[ \frac{\int_0^D P(R) R^4 dR}{2 \int_0^D P(R) R^2 dR} \right] + --- \right\}$ 

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

$$I(0) = 4\pi \int_{0}^{D} P(R)R^{2} dr$$
  
and  
$$R_{g}^{2} = \frac{1}{2} \frac{\int_{0}^{D} P(R)R^{4} dR}{\int_{0}^{D} P(R)R^{2} dR}$$
(III-11)

Accordingly

$$I'(h) = I(0) \left\{ 1 - \frac{h^2}{3} R_g^2 + \frac{1}{2} \left( \frac{h^2}{3} R_g^2 \right)^2 - \right\} \approx I(0) \exp\left( -\frac{h^2 R_g^2}{3} \right)$$
(III-12-1)  
$$I'(s) = I(0) \exp\left( -\frac{(2\pi s)^2 R_g^2}{3} \right)$$
(III-12-2)

 $R_g$  is termed as radius gyration. Rewriting I'(s) as I(s), Figure 9(a) and (b) show the plots of I(s) vs. s and ln[I(s)] vs. s<sup>2</sup>, respectively.  $R_g$  can be obtained by plotting ln[I(s)] vs. s<sup>2</sup>. When P(R) is used for a concrete particle, it is generally termed as

correlation function Q(R). The overlapped particles K and K+1 are separated as shown in Figure 1 and the separation for two spheres is shown in Figure 10.

ASUC

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

$$x2 + y2 = a2$$
$$(x-a)2 + y2 = a2$$

Then evaluation for volume V of revolution along x is given by

$$V = \int_{r/2}^{a} 2\pi \left( \sqrt{a^2 - x^2} \right)^2 dx$$

When  $r \rightarrow R$ , the correlation function of sphere with radius *a* is given by

$$Q(R) = \rho^2 \frac{4\pi a^3}{3} \left[ 1 - \frac{3}{4} \frac{R}{a} + \frac{1}{16} \left( \frac{R}{a} \right)^3 \right] = P(R)$$

By using Eq. (III-11), the radius of gyration of sphere is given as follows:  $D \rightarrow 2a$ ,

$$R_g^2 = \frac{1}{2} \frac{\int_0^D Q(R) R^4 dR}{\int_0^{2a} Q(R) R^2 dR} = \frac{1}{2} \frac{\int_0^{2a} Q(R) R^4 dR}{\int_0^{2a} Q(R) R^2 dR} = \frac{1}{2} \frac{2a^5/5}{a^3/3} = \frac{3a^2}{5} \qquad R_g = \sqrt{\frac{3}{5}a} \qquad \text{(III-13)}$$



Figure 9. (a) SAXS scattering profiles of the full-length barley SGT1 protein in solution at different concentrations. (b) Guinier plot to obtain  $R_g$ . Doi:10.1371/journal.pone.0093313.g007.



Figure 10. The schematic diagram to induce the correlation function for spheres.

Here it may be emphasized again that Guinier plots can be utilized, when many particles exist in the medium without any inter-particles interference effect. That is, many particles must be isolated in the medium. Table 1 lists radius gyration  $R_g$  for several particles.

Table 1. Radius gyration  $(R_g)$  for several particles

Particle shape, size	radius gyration $(R_g)$
Sphere with radius <i>a</i>	$\left(\frac{3}{5}\right)^{\frac{1}{2}}a$
Spheroid ( <i>a</i> , <i>a</i> , v <i>a</i> )	$a\left(\frac{2+v^2}{5}\right)^{\frac{1}{2}}$
Cylinder (2H: height, R adius)	$\left(\frac{R^2}{2} + \frac{H^2}{3}\right)^{1/2}$
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.[9] As shown in Figure 11(a), there exist lattice points  $a_1$ ,  $a_2$ ,  $a_3$ , -----. When existence probability of  $a_1$  at the tip of vector  $\mathbf{y}$  from origin O is  $H(\mathbf{y})$ , the possibility of  $a_2$  at the tip of vector  $\mathbf{z}$ from  $a_1$  is  $H(\mathbf{y})H(\mathbf{z})$ . In this case, the possibility of  $a_2$  at the tip of vector  $\mathbf{x} (= \mathbf{y} + \mathbf{z})$ from O is not  $H(\mathbf{y})H(\mathbf{z})$  but  $\int H(\mathbf{y})H(\mathbf{x}-\mathbf{y})d\mathbf{y}$ . Here we shall consider one-dimensional

problem in Figure 11(b) to simplify the mathematical treatment. In this case, the lattice points  $a_1, a_2, a_3,$ ----- exist on vector **x** and then  $H(\mathbf{x})$  may be replaced on scalar  $H(\mathbf{x})$ . The existence possibility of the tip of vector **x** at  $a_2$  is given by

$$H_2(x) = \int H(y)H(x-y)dy = H(x)^{\circ}H(x)$$
 (III-14)

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

$$H_n(x) = H(x)^{\cap} H(x)^{\cap} H(x)^{\cap} - --$$
(convolution of (n-1) times) (III-15)

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:

$$\int_0^\infty H(x)dx = 1$$

The average value  $\overline{a}$  for the closest distance is

$$\overline{a} = \int_0^\infty x H_1(x) dx$$

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



Figure 11. (a) Schematic diagram for lattice points arranged in one-dimensional direction. (b) Statistical existence possibility z(x) of lattice particles in one-dimension.

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

$$z(x) = \delta(x-0) + \sum_{n=1}^{\infty} H_n(x) + \sum_{n=1}^{\infty} H_n(-x)$$
(III-16)

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  $F(X) = \int_0^\infty H(x) \exp[i\mathbf{h} \cdot \mathbf{x}] dx$ ,  $[F(X)]^n = \int_0^\infty H_n(x) \exp[i\mathbf{h} \cdot \mathbf{x}] dx$  $F^*(X) = \int_0^\infty H(-x) \exp[-i\mathbf{h} \cdot \mathbf{x}] dx$ ,  $[F^*(X)]^n = \int_0^\infty H_n(-x) \exp[-i\mathbf{h} \cdot \mathbf{x}] dx$  (III-17)  $1 = \int_{0^-}^0 \delta(x-0) \exp[i\mathbf{h} \cdot \mathbf{x}] dx$ 

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

$$Z(X) = 1 + F(X) + F^{2}(X) + \dots + F^{*}(X) + [F^{*}(X)]^{2} + \dots + F^{*}(X) + [F^{*}(X)]^{2} + \dots + F^{*}(X) = 1 + \frac{F(X)}{1 - F(X)} + \frac{F^{*}(X)}{1 - F^{*}(X)} = \operatorname{Re}\left[\frac{1 + F(X)}{1 - F(X)}\right] = \frac{1 - |F|^{2}}{1 + |F|^{2} - 2|F|\cos(\mathbf{h} \cdot \overline{\mathbf{a}})}$$
(III-18)

When lattice points  $a_1, a_2, a_3$  ---- are set on vector **h**,  $\overline{\mathbf{a}}$  is written as vector.  $F(X) = |F| \cos(\mathbf{h} \cdot \overline{\mathbf{a}}) = |F| \cos(h\overline{a})$  (III-19)

Eq. (III-19)  $(n \rightarrow \infty)$  is related to scattered (or diffraction) intensity profile from lattice factors along point sequence.

Assuming H(x) to be Gauss function at the center  $\overline{a}$ ,[9]

$$H(x) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left\{-\frac{(x-\overline{a})}{2\sigma^2}\right\}$$
(III-20)  
$$F(X) = \exp\left[2\pi i X \overline{a}\right] \int_{-\infty}^{\infty} H(x) \exp\left[2\pi i X \left(x-\overline{a}\right)\right] dx = \exp\left[2\pi i X \overline{a}\right] \exp\left[-2\pi^2 X^2 \sigma^2\right]$$
(III-21)

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

representing as  $X (= p / \overline{a})$ ,

$$|F| = \exp\left[-2\pi^2 X^2 \sigma^2\right] = \exp\left[-2\pi^2 g^2 p^2\right]$$
 (III-22)

Hence Eq. (III-18) can be also represented as follows:

$$Z(p) = \frac{1 - \exp\left[-4\pi^2 g^2 p^2\right]}{\left[1 - \exp\left\{-2\pi^2 g^2 p^2\right\}\right]^2 + 4\sin^2(\pi p)\exp\left\{-2\pi^2 g^2 p^2\right\}}$$
(IV-23)

Figure 12 shows that the scattered peaks (or diffraction peaks) becomes smaller and broader as the fluctuation g becomes larger. Of course, the peak profile shown in Figure 12 is similar to Laue function at  $g \rightarrow 0$  but different, since Eq. (III-23) was induced at  $N \rightarrow \infty$ .



Figure 12. 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 Eq. (III-5), the lattice points  $a_1$ ,  $a_2$ ,  $a_3$  ---  $a_n$  in Figure 11 can be replaced by the center of gravity of each scattering element.

Hence the last term in Eq. (III-5) is given by [4-5]

$$N + \sum_{K \neq J}^{N} \sum_{J}^{N} \exp(-i\mathbf{h} \cdot \mathbf{R}_{KJ})$$
  
=  $N + \operatorname{Re}\left[\frac{NF}{1-F} - \frac{F(1-F^{N})}{(1-F)^{2}} + \frac{NF^{*}}{1-F^{*}} - \frac{F^{*}(1-F^{*N})}{(1-F^{*})^{2}}\right]$   
=  $N\operatorname{Re}\left[\frac{1+F}{1-F} + \frac{2F(1-F^{N})}{N(1-F)^{2}}\right]$ 

Accordingly, the scattered intensity from N elements arranged in one-dimensional direction.

$$I(h) = I_e N \left[ \left\langle F^2 \right\rangle - \left\langle F \right\rangle^2 \right] + I_e \left\langle F \right\rangle^2 \left[ N + \sum_{K \neq J}^N \sum_{J}^N \exp(-i\mathbf{h} \cdot \mathbf{R}_{KJ}) \right]$$
  
$$= I_e N \left[ \left\langle f^2 \right\rangle - \left\langle f \right\rangle^2 \right] + I_e \left\langle f \right\rangle^2 \left[ N + \sum_{K \neq J}^N \sum_{J}^N \exp(-i\mathbf{h} \cdot \mathbf{R}_{KJ}) \right]$$
  
$$= I_e N \left[ \left\langle f^2 \right\rangle - \left\langle f \right\rangle^2 \right] + I_e N \left\langle f \right\rangle^2 \left[ \frac{1+F}{1-F} + \frac{2F(1-F^N)}{N(1-F)^2} \right]$$
  
(III-24)

As one example, numerical calculation by using Eq. (III-24) 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.[10] The calculation was carried out in accordance with Babonet's reciprocity theorem. In stead of Eq. (II-3),  $\rho(\mathbf{r}) = (\rho_s - \rho_o)\sigma(\mathbf{r}) + \rho_o = \rho_s\sigma(\mathbf{r})$  is adopted at  $\rho_o = 0$  to analyze SAXS pattern from ellipsoidal voids.

To avoid confusion between  $[\langle F^2 \rangle, \langle F \rangle^2, F$  in Eq. (III-18)] and  $[\langle F^2 \rangle$  and  $\langle F \rangle^2$  concerning structural amplitude in Eq. (III-24)] are rewritten as  $\langle f^2 \rangle$  and  $\langle f \rangle^2$ . Figure 13 shows the geometrical coordinate for the calculation. 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  $d_{i-1}$ ,  $d_i$ ,  $d_{i+1}$ . The average distance is  $\overline{d}$  and the parameter is set to be  $\overline{d}/a$ . In Case I, b/a (= P) is variable but  $a/\lambda$  (= Q) is a constant. In Case II, b/a is constant but  $a/\lambda$  is variable.



Figure 13. Geometrical arrangement of ellipsoidal voids along *j* axis. Assembly of voids for (a) Case I and (b) Case II; (c) coordinate to calculate scattering from an ellipsoidal void, in which the major axis of the ellipsoid  $V_3$  is on the *kj* plane. [10]

The calculation of I(h) in Eq. (III-24) must be modified in the two cases. To do so, the two kinds of intensity in Case I and in Case II are rewritten as  $I_P(h)$  and  $I_q(h)$ , respectively. By considering the size distribution of voids denoted by P and q,  $I_P(h)$  and  $I_q(h)$  are written as  $\langle I_P(h) \rangle_{av}$  and  $\langle I_q(h) \rangle_{av}$ , respectively. That is, the particle size in the assembly is given as Gaussian distribution as follows:

30

Case I 
$$N(P) = \frac{\exp\left[-\frac{(P-\overline{P})^2}{2\sigma_p^2}\right]}{\sum_{p=1}^{2\overline{P}-1} \exp\left[-\frac{(P-\overline{P})^2}{2\sigma_p^2}\right]} \quad \langle I_p(h) \rangle_{av} = \sum_{p=1}^{2\overline{P}-1} N(P)I_p(h) \quad (\text{HI-25-1})$$
  
Case I  $N(q) = \frac{\exp\left[-\frac{(q-\overline{q})^2}{2\sigma_p^2}\right]}{\frac{4\overline{q}-1}{2\sigma_q^2}} \quad \langle I_q(h) \rangle_{av} = \sum_{q=1}^{4\overline{q}-1} N(q)I_q(h) \quad (\text{HI-25-2})$ 

The voids are oriented to their own fiber axes (the k-axis) predominantly. The orientation function  $p(\beta)$  of the long axis is given by

$$p(\beta) = \exp\left(-\sigma_{\beta}^{2}\sin^{2}\beta\right) \quad \text{(III-26)}$$
  
Hence  $\langle f^{2} \rangle$  and  $\langle f \rangle^{2}$  are given by  $\int_{0}^{2\pi} p(\beta)E^{2}(\beta)d\beta / \int_{0}^{2\pi} p(\beta)d\beta$  and  $\left\{\int_{0}^{2\pi} p(\beta)E(\beta)d\beta / \int_{0}^{2\pi} p(\beta)d\beta\right\}^{2}$ , respectively.  $E(\beta)$  is the scattering amplitude from a void and it is described elsewhere [10]

void and it is described elsewhere.[10]

Figure 14 shows the observed SAXS pattern from carbon fibers and two examples of theoretical patterns in Case II. The theoretical patterns are in good agreement with the observed pattern.



Figure 14. The observed SAXS pattern (a) from a specimen prepared by stabilization at 260°C and carbonization at 1200°C. The two patterns calculated from Case II  $(\overline{d}/a = 0.5)$ , (b) $\sigma/\overline{d} = 0.01$  and (c)  $\sigma/\overline{d} = 0.5$ . The common parameters; b/a=10,  $\overline{q} = 3$ , N=10. [10]

The reasonable approach to analyze SAXS intensity distribution is that the electron density fluctuation must be evaluated on the average density of the specimen. This concept has been used for neutron scattering. Such treatment was proposed in terms of the relationship between electron density distribution about crystal and amorphous phases and the autocorrelation function in one-dimensional direction by Stroble and Schneider [11]. This method is convenience to determine the thicknesses of real crystal lamella and crystal boundary layer in addition to identity period (long period). Their method can be applied precisely in the case where the stacked lamellae are arranged perfectly in a particular direction of the sample.

The recent drastic speed-up of the calculation by computer made it possible to more strict treatment. Figure 15 shows the model that the electron density fluctuation must be evaluated on the average density  $\overline{\rho}$  of the specimen, in which the transition region between crystal and amorphous is represented as  $(t_1 + t_2)$ . [7] This model is similar to the concept proposed by Stroble and Schneider. [11]



Figure 15 (a) lamellar assembly on two-dimensional plane. (b) density variation of two phases by positive and negative deviations from the average density  $\overline{\rho}$  of the system represented by an arbitrary function. (c) density variation represented by a trapezoidal function.[7]

The complicated mathematical treatment is represented elsewhere.[7] The results calculated by computer at the above optimum conditions are in good agreement with the observed results for the two-dimensional patterns as shown in Figure 16. The observed pattern was observed for dry gel films prepared by decalin and paraffine solutions, when the X-ray beam was inserted parallel to the surface of stacked dry gel films. [12] The parameter fitting was easy because of rapid calculation speed of recent computers.

The parameters to give the best fittings are as follows:

Decalin

$$\overline{Y}/\overline{L} = 0.02$$
,  $\overline{X}/\overline{L} = 0.03$ ,  $\sigma_y/\overline{Y} = 0.11$ ,  $\sigma_z/\overline{Z} = 0.11$ ,  $\overline{N} = 5$ ,  $\sigma_N = 3$ ,  $\sigma_\alpha = 3$ ,  $t_1/\overline{X} = 0.051$ ,  $t_2/\overline{X} = 0.166$ 

Paraffin

th Matsulo  $\overline{Y}/\overline{L} = 0.02$ ,  $\overline{X}/\overline{L} = 0.03$ ,  $\sigma_y/\overline{Y} = 0.15$ ,  $\sigma_z/\overline{Z} = 0.15$ ,  $\overline{N} = 8$ ,  $\sigma_N = 3$ ,  $\sigma_{\alpha} = 5, \ t_1 / \overline{X} = 0.047, \ t_2 / \overline{X} = 0.129$ 



Figure 16. Observed and theoretical SAXS intensity distributions in the vertical direction; (a) Dry gel films prepared in decalin; (b) dry gel films prepared in paraffin; (c) SAXS patterns (edge) from stacked decalin films; (d) SAXS image patterns (edge) from stacked paraffin film; (e) Theoretical SAXS patterns from the decalin films; (f) Theoretical SAXS patterns from the paraffin films.[12]

Incidentally, the good fitting of scattered intensity for two-dimensional pattern is generally very difficult in the case where the medium density is set to be zero because of appearance of the very unusual peaks, even if the good fitting along the vertical direction was achieved as shown in frames (a) and (b). [5] Incidentally, it should be emphasized that Babonet's theorem can be satisfied in the case where the two phases for model (c) in Figure 15 have no fluctuation in thickness in addition to no orientation fluctuation of lamellar assembly.[7]

# **IV** 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.

Figures 17(a) and (b) show the arrangement of polarizer and analyzer under Hv and Vv scatterings, respectively.



Figure 17. Schematic diagrams (a) Hv light scattering, (b) Vv scattering

Incidentally, the following idioms are related to the polarization conditions. [13]

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

Advantage of small angle light scattering (SALS) under polarization is to recognize the structure shape of isolated particles in polymer films and liquid crystal very rapidly by using a simple home-made instrument under Hv polarization.

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

$$E_{s}(h) = \sum_{i=1}^{N} E_{i} \exp[i(\mathbf{h} \bullet \mathbf{r}_{i})]$$
$$= (4\pi^{2}/R_{o}^{2}\lambda_{o}^{2})\sum_{i=1}^{N} (\mathbf{M} \bullet \mathbf{O}) \exp[i(\mathbf{h} \bullet \mathbf{r}_{i})] = K \int (\mathbf{M} \bullet \mathbf{O}) \exp[ik(\mathbf{s} \bullet \mathbf{r})] d\mathbf{r} \quad (IV-1)$$

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  $\mathbf{M}_{i} \sin \gamma_{i}$  is the characteristic term of visible light different from X-ray.  $\mathbf{M}_{i}$  is induced dipole moment of *i*-th scattering element and  $\gamma_{i}$  is interior angle between  $\mathbf{M}_{i}$ and  $\mathbf{R}_{i}$  vectors.  $\mathbf{M}_{i}$  is given by  $\boldsymbol{\alpha}_{i}\mathbf{E}_{o}$ , in which  $\boldsymbol{\alpha}_{i}$  is tensor for polarizability and  $\mathbf{E}_{o}$  is electric vector. Accordingly,  $\gamma_{i}$  is dependent upon polarizability ellipsoid and the orientation. On observation of scattering beam through analyzer as shown in Figure 17, the polarization direction of analyzer denoting as unit vector  $\mathbf{O}$  can be detected among the tangential component of  $\mathbf{M}_{i}$  for  $\mathbf{R}_{i}$ . 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.

In stead of **h** in Eq. (II-7), **s** in Eq. (IV-1) has been normally used to represent the following notation for light scattering in a number of papers and textbooks. It should be noted that scattering angle for PALS is represented as  $\theta$  in stead of  $2\theta$  for X-ray scattering. [13]

$$\mathbf{s} = \mathbf{s}_{\mathbf{o}} - \mathbf{s}' \quad k = 2\pi / \lambda \quad |s| = 2k \sin(\theta / 2)$$

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, cattered intensity for SALS is given by

$$I = K^{2} \int (\mathbf{M}_{i} \cdot \mathbf{O})(\mathbf{M}_{j} \cdot \mathbf{O}) \exp[-ik(\mathbf{r}_{i} \cdot \mathbf{s})] \exp[ik(\mathbf{r}_{j} \cdot \mathbf{s})] d\mathbf{r}_{i} d\mathbf{r}_{j}$$

$$= K^{2} \int \int (\mathbf{M}_{i} \cdot \mathbf{O})(\mathbf{M}_{j} \cdot \mathbf{O}) \exp[ik(\mathbf{r}_{ij} \cdot \mathbf{s})] d\mathbf{r}_{i} d\mathbf{r}_{ij}$$

$$= K^{2} \int \int (\mathbf{M}_{i} \cdot \mathbf{O})(\mathbf{M}_{j} \cdot \mathbf{O}) \{\cos[k(\mathbf{r} \cdot \mathbf{s})] + i\sin[k(\mathbf{r} \cdot \mathbf{s})]\} d\mathbf{r}_{i} d\mathbf{r}$$

$$= K^{2} \int \int (\mathbf{M}_{i} \cdot \mathbf{O})(\mathbf{M}_{j} \cdot \mathbf{O}) \cos[k(\mathbf{r} \cdot \mathbf{s})] d\mathbf{r}_{i} d\mathbf{r}$$

$$= K^{2} \int \{\int (\mathbf{M}_{i} \cdot \mathbf{O})(\mathbf{M}_{j} \cdot \mathbf{O}) d\mathbf{r}_{i}\} \cos[k(\mathbf{r} \cdot \mathbf{s})] d\mathbf{r}$$

$$= K^{2} V \int \langle (\mathbf{M}_{i} \cdot \mathbf{O})(\mathbf{M}_{j} \cdot \mathbf{O}) \rangle_{\mathbf{r}} \cos[k(\mathbf{r} \cdot \mathbf{s})] d\mathbf{r}$$
(IV-2)

where  $\mathbf{r} = \mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$  and  $\langle \rangle_{\mathbf{r}}$  is the average of the product of scattering elements with separation distance  $\mathbf{r}$ , 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 [13]

$$\boldsymbol{M}_{i} = \boldsymbol{E}_{o} \left\{ \boldsymbol{\delta}_{i} \left( \mathbf{t}_{p} \bullet \mathbf{a}_{i} \right) \mathbf{a}_{i} + (\boldsymbol{b}_{i})_{i} \mathbf{t}_{p} \right\}$$
(IV-

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

Furthermore,

$$\delta_i = (\alpha_{\prime\prime\prime})_i - (\alpha_{\perp})_i, \qquad (b_t)_i = (\alpha_{\perp})_i - \alpha_s \qquad (\text{IV-4})$$

 $(\alpha_{\prime\prime})_i$  and  $(\alpha_{\perp})_i$  are polarizabilities parallel and perpendicular to optical axis (the unit vector  $a_i$ ), respectively.  $\alpha_s$  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  $t_p = \mathbf{j}$  for horizontal polarization direction. Normally,  $\mathbf{t_p} = \mathbf{k}$ .

As for the observation of vertical and horizontal components of scattered intensity,  $O_V = k$  and  $O_H = j$  can be constructed approximately. Hence,

$$(\mathbf{M} \bullet \mathbf{O})_{H_{V}} = (\mathbf{M} \bullet \mathbf{O})_{V_{h}} = E_{o} \delta_{i} (\mathbf{a}_{j} \bullet j) (\mathbf{a}_{i} \bullet \mathbf{k}) \qquad (\text{IV-5-1})$$
$$(\mathbf{M} \bullet \mathbf{O})_{V_{V}} = E_{o} \{\delta_{i} (\mathbf{a}_{i} \bullet \mathbf{k})^{2} + (b_{t})_{i}\} \qquad (\text{IV-5-2})$$
$$(\mathbf{M} \bullet \mathbf{O})_{H_{h}} = E_{o} \{\delta_{i} (\mathbf{a}_{i} \bullet j)^{2} + (b_{t})_{i}\} \qquad (\text{IV-5-3})$$

Here, as described in Eq. (IV-2), it should be noted that the center of coordinate must be set in the center of particle on the theoretical calculation. In this case, sin term disappears.

As described before, X-ray scattered intensity is given by

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

 $Q(\mathbf{r})$  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  $\langle (\mathbf{M}_i \bullet \mathbf{O})(\mathbf{M}_j \bullet \mathbf{O}) \rangle_{\mathbf{r}}$  in Eq. (IV-2). Hence the model analysis and/or statistical analysis must be adopted to compare the theoretical results with observed ones.

The scattering analyses for spherulites [13-14] and rods [15-16] have been reported in a number of papers and then this paper does not deal with the analyses. 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. To confirm the concept, the schematic diagram is proposed for the observed Hv pattern corresponding to polarized microscopy in Figure 18 [17-18] and the detailed geometrical arrangement is shown in Figure 19 to pursue the theoretical calculation.[18] The scattered intensity provides the same style as Eq. (III-14) for SAXS.

The variations of the length  $L_j$ , the width  $D_j$  and the adjacent distance  $X_i$  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  $\overline{L}$ ,  $\overline{D}$  and  $\overline{X}$  and their standard deviations  $\sigma_{E}$ ,  $\sigma_d$  and  $\sigma_x$ .

$$h(L_j) = \frac{1}{\sqrt{2\pi\sigma_\ell^2}} \exp\left\{\frac{-(L_j - \overline{L})^2}{2\sigma_\ell^2}\right\}$$
(IV-6-1)  
$$M(D_j) = \frac{1}{\sqrt{2\pi\sigma_d^2}} \exp\left\{\frac{-(D_j - \overline{D})^2}{2\sigma_d^2}\right\}$$
(IV-6-2)  
$$H(X_j) = \frac{1}{\sqrt{2\pi\sigma_x^2}} \exp\left\{\frac{-(X_j - \overline{X})^2}{2\sigma_x^2}\right\}$$
(IV-6-3)

Generally, each rod in the assembly has the orientation distribution and then it is defined that the *j*-th rod is oriented at angle  $\xi$  between  $Z_j$  axis (width direction of *j*-th rod) and  $Z_2$  axis (the line to connect each rod gravity), which is given by

$$p(\xi) = \exp\left[-\sigma_{\xi}^{2}\sin^{2}(\xi - \xi_{o})\right] \qquad (\text{IV-7})$$

where  $\sigma_{\xi}$  is a parameter associated with the shape of  $p(\xi) \cdot p(\xi)$  shows a sharp distribution with increasing  $\sigma_{\xi}$  and  $\alpha = \xi_o - \gamma - \pi/2$  or  $\alpha = -\xi_o + \gamma + \pi/2$ .

Through Eqs. (IV-6) – (IV-7),  $\langle f^2 \rangle$ ,  $\langle f \rangle^2$  and *F* in Eq. (III-24) corresponding to SAXS are written for SALS as follows:  $I = I_B - I_C$  (IV-8) where  $I_B = \operatorname{Re}\left[\langle f^2 \rangle - \langle f \rangle^2 + \frac{1+F}{1-F} \langle f \rangle^2\right]$  (IV-9-1) SAXS are written for SALS as follows:

$$I = I_B - I_C \qquad (IV-8)$$

where

$$I_{B} = \operatorname{Re}\left[\left\langle f^{2} \right\rangle - \left\langle f \right\rangle^{2} + \frac{1+F}{1-F} \left\langle f \right\rangle^{2}\right] \qquad \text{(IV-9-1)}$$

$$I_{C} = \operatorname{Re}\left[\frac{2F(1-F^{N})}{N(1-F)^{2}} \left\langle f \right\rangle^{2}\right] \qquad \text{(IV-9-2)}$$

$$\left\langle f^{2} \right\rangle = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{0}^{2\pi} p(\xi) M(D_{j}) h(L_{j}) f_{j}^{2} d\xi dD_{j} dL_{j}}{\int_{0}^{2\pi} p(\xi) d\xi} \qquad \text{(IV-10)}$$

$$\left\langle f \right\rangle = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{0}^{2\pi} p(\xi) M(D_{j}) h(L_{j}) f_{j} d\xi dD_{j} dL_{j}}{\int_{0}^{2\pi} p(\xi) d\xi dD_{j} dL_{j}} \qquad \text{(IV-11)}$$

$$F = \int_{-\infty}^{\infty} H(X_j) \exp(ihX_j) dX_j = \int_{-\infty}^{\infty} H(X_j) \exp(-2\pi i sX_j) dX_j \qquad \text{(IV-12)}$$

The structural amplitude from the *j*-th rod is given by

$$f_{j} = \frac{1}{2} K \delta_{o} \cos \rho_{2} \sin\{2(\xi + \omega_{o})\} \frac{\sin[\pi L_{j} \sin \theta \sin(\mu + \xi - \gamma)/\lambda]}{\pi L_{j} \sin \theta \sin(\mu + \xi - \gamma)/\lambda} \frac{\sin[\pi D_{j} \sin \theta \cos(\mu + \xi - \gamma)/\lambda]}{\pi D_{j} \sin \theta \cos(\mu + \xi - \gamma)/\lambda}$$

(IV-13) Eq. (IV-13),  $\delta_o$  is anisotropy In of the scattering element and  $\cos \rho_2 = \cos \theta / (\cos^2 \theta + \sin^2 \theta \sin^2 \mu)^{1/2} . [14]$ 

In a real system [18], the position of the samples irradiated by the laser beam contains distribution of the number of rods N. This concept must be introduced to smear out the many subsidiary maxima that appear at lower scattering angle. The distribution is generally written as

$$P(N) = \exp\left\{-\frac{(N-\overline{N})^2}{2\sigma_N^2}\right\} / \sum_{N=1}^{2\overline{N}-1} \exp\left\{-\frac{(N-\overline{N})^2}{2\sigma_N^2}\right\}$$
(IV-14)

In the present system [18], we will assume the same type of distribution of N. Then, the average value of the term  $I_{\rm C}$  in Eq. (IV-8) is given by

$$\left\langle I_{C}\right\rangle = \sum_{N=1}^{2\overline{N}-1} I_{C} P(N) \tag{IV-15}$$

Of course, as described before, this concept is introduced essentially by theoretical calculation for SAXS intensity as particle size parameter P or q in Case I and Case II, respectively in Figure 13. Incidentally,  $\omega_o$  is fixed to be  $0^\circ$ .



Figure 18. Schematic diagram for Hv scattering patterns and oriented rod assembly. (a) schematic representation of Hv pattern; (b) schematic representation of arrangement for rods: (c) observed Hv pattern from poly(tetramethylene oxide)-poly(tetramethylene terephthalate) film with draw ratio of 1.5; (d) polarized micrograph observed for the film. [17-18]



Figure 19. Model used for the theoretical analysis of scattered intensity distribution.[18]

Figure 20 shows the calculated Hv patterns. The patterns are sensitive to the variation of  $\xi_o$  but is hardly affected by  $\sigma_{\xi}$ . For the calculation,  $\gamma$  is fixed to be 10° from the relationship shown in Figure 18 and also  $\alpha = 60^{\circ}$  and  $\alpha = -60^{\circ}$  are satisfied at  $\alpha = -\xi_o + \gamma + 90^{\circ}$  and  $\alpha = \xi_o - \gamma - 90^{\circ}$  in the case of  $\xi_o = 40^{\circ}$ , indicating the justice of the geometrical relationship between the broad and sharp scattering lobes and arrangement of the rod assembly.

The Hv pattern provides no direct information about sample morphology as explained by using Eq. (III-24) for SAXS pattern but the accumulated knowledge for SALS can indicate the important information about morphology with rapid and easy measurement as shown in Figure 17.



Figure 20. Hv patterns with change in  $\xi_o$  and  $\sigma_{\xi}$  in which the other parameters are fixed at  $\sigma_{\ell}/\overline{L} = \sigma_d/\overline{D} = 0.001$ ,  $\sigma_x/\overline{X} = 0.5$ ,  $\overline{D}/\overline{L} = 0.05$ ,  $\overline{X}/\overline{D} = 40$ ,  $\overline{L}/\lambda = 40$  and  $\gamma = \pm 10^{\circ}$  at small scattering angle up to 5°. [18]

Another treatment for SALS is statistical approach model. [19-20] The statistical approach 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 [21-22] and amorphous films [23-24]. 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 of frosted glass (as shown in Figure 21(a)), since the very weak light scattered from the gels could not pass through the analyzer. [20] The pattern was observed on the sample surface by the reflection from the analyzer, and then photographs were taken using a commercial camera, as shown in Figure 21 (b).



Figure 21. Light scattering pattern afforded by polymer gels. (a) usual method to photograph the pattern; (b) pattern reflected on the gel surface by using a commercial camera. [20]

The actual patterns were observed for poly(vinylalcohol) (PVA) gel [21] and  $\kappa$ -carrageenan gel [22]. As an example, Figure 22 shows the gelation process of  $\kappa$ -carrageenan solution by quenching at 30°C. After quenching the solution, the pattern

appeared from the polymer rich phase by progression of concentration fluctuation and the pattern became clearer with elapsing time. Incidentally, the pattern disappeared after a week later. [21-22]



Figure 22. Change of  $\mu_{I}(I)$  at  $\theta = 15^{\circ}$  and Hv patterns with respect to time measured for the 1.0 and 2.5%  $\kappa$  -carrageenan aqueous solutions after quenching at 30°C.[22]

Judging from the appearance of the X-type pattern, a new concept is needed. Light scattering from anisotropic density fluctuation was first developed by Debye and Bueche and the theory was expanded to the scattering of light from a polymer film with randomly correlated orientation fluctuations of anisotropic elements by Stein and Wilson. [19] By using the geometrical coordinate in Figure 23, the following equations are formulated.

$$I_{Hv} = \frac{1}{15} K \delta^2 \int_0^\infty \mu(r) f(r) \frac{\sin(hr)}{hr} r^2 dr \qquad \text{(IV-16)}$$

and

$$I_{Vv} = K \int_0^\infty \left\{ \left\langle \eta^2 \right\rangle_{av} \gamma(r) + \frac{4}{45} \delta^2 f(r)_{r_{ij}} \mu(r) \right\} \frac{\sin(hr)}{hr} r^2 dr \quad \text{(IV-17)}$$

In Eqs. (IV-16) and Eq. (IV-17),  $\gamma(r)$  is a correlation function associated with the mean square fluctuation in average polarizability  $\langle \eta^2 \rangle_{av}$ . f(r) is an orientation correlation function of the principal axes between two scattering elements and  $\mu'(r)$  is given by

$$\mu'(r) = 1 + \frac{\left\langle \Delta^2 \right\rangle_{av}}{\delta^2} \psi(r) \qquad \text{(IV-18)}$$

where  $\delta$  is the average anisotropy and  $\langle \Delta^2 \rangle_{av}$  is a mean square fluctuation in average optical anisotropy and  $\psi(r)$  is the correlation function associated with the fluctuation in the magnitude of the anisotropy normalized by  $\langle \Delta^2 \rangle_{av}$ .



Figure 23. The coordinate system for the principal polarizabilities of the scattering elements proposed by Stein and Wilson. [19]

From Eq. (IV-16) and (IV-17), the following relation can be derived.

$$I_{V_{\nu}} - \frac{4}{3}I_{H_{\nu}} = K \left\langle \eta^2 \right\rangle_{a\nu} \int_0^\infty \gamma(r) \frac{\sinh r}{hr} r^2 dr \qquad (\text{IV-19})$$

In the actual analysis, the correlation distance estimating the extension of the inhomogeneities can be obtained by assuming that  $\gamma(r)$  in Eq. (V-17) and/or Eq. (V-19) has been described by a sum of Gaussians. [22]

In Eqs. (V-16) and (V-17), however, the orientation function is defined as polar angle associated with the correlation distance between two scattering elements and the theoretical Hv pattern shows a circular type different from Figure 22. The adoption of  $\gamma(r)$  is limited to the system that optical axes between scattering elements orient randomly with respect to the vector along distance between the center of gravities of the optical elements. That is, the optical axes rotate freely around  $\mathbf{r}_{ij}$  independent of correlation length  $r_{ij}$ . This is obviously abnormal.

To resolve the discrepancy, the more detailed analysis is needed for the azimuthal angle as shown in Figure 24. [20]



Figure 24. Optical coordinate system of light scattering concerning the principal polarizabilities of the scattering elements, in which the optical axes separated with  $r_{ij}$  have optical fluctuations for polar and azimuthal angles. [20]

As for the statistical method in Figure 24, the scattered intensity obtained after very complicated mathematical treatment is given by [20]

$$\begin{split} I_{H\nu} &= K\delta^2 \int_0^{\pi} \int_0^{\infty} \mu \left( r \right) \left\{ \frac{1}{15} f(r) + g(r) \left( 1 - f(r) \right) \right. \\ & \times \left[ \frac{1}{720} \left( 5\cos^4 \alpha + 30\cos^2 \alpha - 11 \right) - \frac{1}{144} \cos^2 \frac{\theta}{2} \left( 5\cos^4 \alpha + 6\cos^2 \alpha - 3 \right) \right] \right. \\ & \left. + \frac{1}{576} \cos^4 \frac{\theta}{2} \sin^2 2\mu \left( 35\cos^4 \alpha - 30\cos^2 \alpha + 3 \right) \right] \right\} \cos \left[ hr \cos \alpha \right] r^2 \sin \alpha dr d\alpha \\ \text{By omitting the dummy subscript } ij \text{ for } r_{ij}, f(r) \text{ is given by } [20] \\ & f(r) = \left\langle \frac{3\cos^2 \omega_{ij} - 1}{2} \right\rangle_r \qquad (\text{IV-21-1}) \end{split}$$

By omitting the dummy subscript *ij* for  $r_{ij}$ , f(r) is given by [20]

$$f(r) = \left\langle \frac{3\cos^2 \omega_{ij} - 1}{2} \right\rangle_r \qquad \text{(IV-21-1)}$$
$$f(r) = \exp\left(-\frac{r^2}{a^2}\right) \qquad \text{(IV-21-2)}$$

where the average is taken over all pairs of volume elements (i and j) separated by a constant scalar distance r. f(r) = 1 for parallel orientation ( $\omega_{ij} = 0^{\circ}$ ) and 0 for random orientation ( $\omega_{ij}$  : random), and it varies between these limits as r changes from zero to infinity.

Furthermore, as discussed before, it is important to consider that azimuthal angle which the projection of the *j*-th principal axis onto a plane perpendicular to the principal axis of the *i*-th element makes, is also given as a correlation of the distance between the two elements. The correlation function g(r) is defined as [20]

$$g(r) = \left\langle 2\cos^2 \phi_{ij} - 1 \right\rangle_r \qquad \text{(IV-22-1)}$$
$$g(r) = \exp\left(-\frac{r^2}{b^2}\right) \qquad \text{(IV-22-2)}$$

where the average is taken over all pairs of volume elements (i and j) separated by a constant scalar distance r. g(r) = 1 for parallel orientation ( $\phi_{ij} = 0^{\circ}$ ), and g(r) = 0 for random orientation ( $\phi_{ij}$  : random), and it varies between these limits as r changes from zero to infinity. At g(r) = 0, Eq. (IV-18) reduces to Eq. (IV-16). [20]

Figure 25 shows the Hv patterns at the indicated b/a, in which a/ $\lambda$  is fixed to be 3. The four lobes taking an X-type become sharper with increasing b/a, indicating that the pattern is strongly affected by azimuthal angle dependence for the correlation distance. The pattern is in good agreement with the pattern observed at initial stage of the

formation of polymer rich phases by concentration fluctuation in the crystalline polymer solutions [20-22] and initial crystallization process of polyethylene (terephthalate). [23-24]



Figure 25. Hv light scattering patterns calculated by Eq. (III-20) as a function of b/a : (a) 1, (b) 3, (c) 5 and (d) 10 at a/  $\lambda$  =3. [20]

Of course, the concept shown in Figure 24 was applied to the systems concerning spherulite and rod. [25] The theoretical patterns were in good agreement with the observed patterns.

# V. Fatal defect about the recent X-ray instrument termed as "simultaneous SAXS and WAXD measurement instrument"

Recently, small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD) intensities have been measured by using X-ray beam generated in one direction. The brand name of the instrument is "a simultaneous SAXS and WAXD measurement instrument". The X-ray beam generated by the instrument has surely high

luminance providing high degree resolution of peak profiles by diffraction and/or scattering. The sample stage and detector, however, are fixed, since the intensities for SAXS and WAXD are obtained by the digital display of the number of photons detected on the imaging plate. Such optical system contains serious fatal defect on evaluating orientation of crystallites parallel to the surface of films prepared by T-die and inflation methods, which shall be discussed elsewhere. [26]

This chapter points out the serious defect for evaluating most probable distance between adjacent amorphous molecular chains taking preferred orientation with respect to the reference axis of the fiber and film. The focus is concentrated on importance of incoherent scattering to evaluate radial distribution function of amorphous chains but the intensity measurement up to very wide Bragg angle is impossible by imaging plate.

When X-ray photons with wavelength  $\lambda_o$  collide with stationary electrons in atom, two X-ray beams with the same wavelength  $(\lambda_o)$  and with longer wavelength  $(\lambda)$  are scattered. As an approximation, the following relationship can be obtained. [2]

$$\lambda = \lambda_o + \frac{h}{m_e c} (1 - \cos \theta_B) = \lambda_o + 0.002426 (1 - \cos \theta_B) = \lambda_o + \lambda_c (1 - \cos \theta_B) \quad (\text{unit} : nm)$$
(V-1)

where

*h* (Planck's constant) =  $6.626 \times 10^{-27}$  [erg · sec] *m<sub>e</sub>* (stationary electron mass) =  $9.109 \times 10^{-26}$  [gr] *c* (velocity of light) =  $2.998 \times 10^{10}$  [cm/sec]

The constant  $\lambda_c$  for incoherent (inelastic) scattering is termed as Compton wavelength. The characteristics are three points. The incoherent scattered intensity becomes higher, when 1) the wavelength of incident X-ray is shorter, 2) scattering angle  $\theta_B$  is wider, and 3) atomic number becomes lower.

For amorphous polymer solid, intensity distribution *I* as a function of  $2\theta_B$  for Cu target has generally three peaks at least because of ordering of adjacent amorphous chains as shown in Figure 26, in which frames (a) and (b) show the intensity distribution for polyethylene (PE). Figure 26(a) indicates X-ray scattering from amorphous film with no crystal phase maintained at 110°C by Joule heat under electric field [27], in which experimental curve is obtained after corrections for air scattering, background noise, polarization and absorption. The first, second and third peaks appears at  $2\theta_B(2\theta) = 18.5$ , 43.4, 78.9°, respectively. Such peaks have been observed for undrawn amorphous polymer films. [28] The appearance of the second and third peaks

indicates the ordered arrangement of adjacent amorphous chains. The curve could not be obtained beyond  $120^{\circ}$ , since  $60^{\circ}$  was the limit rotation of sample stage on goniometer under  $\theta - 2\theta$  scanning.

The intensity distribution  $I(2\theta)$  up to  $180^{\circ}$  was indispensable to obtain smooth radial distribution function. As shown in Figure 26, the experimental curve is almost flat in  $2\theta$  range from 100 to  $120^{\circ}$  indicating that the intensity >  $100^{\circ}$  is attributed to incoherent intensity as well as coherent intensity independent of ordering amorphous chains. Here it may be noted that the incoherent intensity tends to level off at  $2\theta > 120^{\circ}$  and then the profile is determined on the basis of the postulation that the coherent intensity at  $\theta = 180^{\circ}$  is equal to value at  $\theta = 0^{\circ}$  and the incoherent intensity at  $2\theta = 180^{\circ}$  is equal to the difference between supposition intensity and coherent intensity. [8-9]

The coherent intensity by the above method as a function of  $2\theta$  is represented by  $I'(s)(=I(s)/I_o - 1)$  generally as a well-known profile in frame (b), in which s is given by  $\sin \theta/\lambda$ . This relation was discussed in Eq. (III-9)' already. The I'(s) vs. s obtained by same treatment was shown in Figures 26(c) and (d) for polyethylene terephthalate (PET) and poly(phthalazinone ether ketone) (PPEK), respectively.



Figure 26. (a) : Process to obtain coherent intensity. (b) I'(s) vs. *s* curve of undrawn amorphous PE [27] (c) I'(s) vs. *s* curve of undrawn amorphous PET. [28] (d) I'(s) vs. *s* 

curve of undrawn amorphous PPEK [28], where  $h = 2\pi s$ .

Here it should be noticed that the scanning angle  $\theta = 60^{\circ}$  by Cu target corresponds to  $\theta = 23.5^{\circ}$  by Mo target, since the wavelengths ( $\lambda$ ) of X-ray beam generated from Cu and Mo targets are 0.154 and 0.071073 *nm*, respectively. Certainly, Mo target is better than Cu target to obtain accuracy of the experimental intensity I(h)for evaluating the radial distribution function, since I(h) up to 180° can be measured directly without the suppuration intensity shown in Fig. 10(a). Even for Mo target, the very wide width of imaging plate for the recent X-ray instrument is needed and the fine treatment as shown in Fig. 26(a) is impossible.

The radial distribution function P(r) for random orientation system can be given by

$$4\pi r P(r) = \frac{2}{\pi} \int_0^\infty h I'(h) \sin(hr) dh$$
 (V-2-1)  
$$4\pi r P(r) = 32\pi \int_0^\infty s I'(4\pi s) \sin(4\pi s r) ds$$
 (V-2-2)

In Eq. (V-2-2),  $h = 4\pi \sin \theta / \lambda$  was replaced as  $s = h / 4\pi$  in actual calculation

Figure 27 shows radial distribution functions of the amorphous PE, PET and PPEK films. The functions are important to evaluate the most probable distance between adjacent amorphous chains corresponding to the existence probability of electron density. As discussed elsewhere [28], the average distances obtained for the PET and PPEK at room temperature are reasonable in relation to their bulky structure of monomer unit. On the other hand, the average distance between amorphous PE chains maintained at 110°C by Joule heat under electric field [27] is wider than the distances about PET and PPEK chains at room temperature. [28]



Figure 27. Radial distribution function of (a) undrawn PE [27], (b) PET [28], (c) PPEK [28]

As for the oriented system for amorphous chains, most of the evaluation is associated with the orientation function of amorphous peak magnitude as a function of angle between the reference axis and stretching axis. [28]

Here it should be noted that that the most probable distance between adjacent amorphous main chains depends on the orientation degree of the chains in the fiber. On the other hand, as a well-known fact, the lattice constants of crystal units for most of crystallite polymers provide their intrinsic values independent of orientation of crystallites in the elongation material under no external stress at room temperature. Hence orientation modes of crystallites can be evaluated according to the intrinsic distance between established crystal planes relating to the different shapes of crystal unit such as orthorhombic [29-33], monoclinic [34-35], triclinic [36-37] etc. Namely, the different distance between the adjacent chains in the crystal unit, is independent of the crystallite orientation directions in bulk associated with compression and expansion modes provide different distances between their adjacent chains. Such phenomenon is shown as a model in Figure 28. Such oriented mode cannot be represented by one dimensional radial distribution function P(r) for an isotropic system. [27-28]

To obtain most probable possibility of adjacent amorphous chain distance with the model in Figure 28, the intensity must be measured as a function of tilting angle  $\kappa$  with respect to the fiber axis. The radial distribution can be expanded as a function of  $\kappa$  as follows:

$$4\pi r P(r,\kappa) = \frac{2}{\pi} \int_0^\infty h I'(h,\kappa) \sin(hr) dh = 32\pi \int_0^\infty s I'(4\pi s,\kappa) \sin(4\pi s r) ds$$
(V-3)

 $(h,\kappa)$  is the scattered intensity detected at  $\mu = 90^{\circ}$  in Figure 2.



Figure 28. Orientation modes of amorphous chains existed in the different directions with respect to the spinning fiber direction. The distance between adjacent chains oriented at  $45^{\circ}$  with respect to the fiber axis (the X<sub>3</sub> axis) can be evaluated by scattered intensity in the horizontal direction.

Figure 29 shows the results of PPEK fibers prepared by dry spinning method [28], since PPEK is perfectly amorphous polymer which is not crystallized by elongation and thermal treatment. By the  $\theta - 2\theta$  scanning,  $I'(s,\kappa)$  can be obtained easily by measuring intensity at angle  $\kappa$  fixed with interval 10° in the range of  $0 \sim 90^\circ$ , since the intensity corrections concerning air scattering, absorption coefficient and incoherent scattering at each  $\kappa$  are not complicated as like treatments shown in Figure 26(a) for the undrawn PE film. The intensity height is dependent upon tilting angle  $\kappa$ . The  $\kappa$  dependence of peak magnitude indicates that the distance between the adjacent amorphous chains at the different orientations is different as shown in Figure 28.



Figure 29.  $I'(s) \sim s$  curves of the PPEK spinning fibers against the indicated angles  $\kappa (\varphi = \pi/2 - \kappa)$ . [28]

As discussed already, Figure 2 shows general representation of X-ray scattering system for flat image. The intensity depends on the OP distance. Therefore the accurate scattered intensity can be obtained only by the spherical image. Of course, the distance correction must be done for flat image and curved image in addition to the corrections for air scattering, absorption and polarization factor. To simplify these corrections, it is important to satisfy two conditions: 1) sample rotation with respect to the vertical reference axis V in Figure 2 to detect the intensity in the horizontal direction and 2) the  $\theta - 2\theta$  rotation about sample and detector. The geometrical arrangement to satisfy the above two conditions is shown in Figure 30.



Figure 30. Geometrical arrangement to calculate two-dimensional radial distribution function of oriented PPEK amorphous chains, in which  $\kappa$  is the tilting angle of fiber

direction with respect to the vertical direction (the V axis) and  $\alpha$  is the angle between the vector **r** perpendicular to adjacent amorphous chain arrangement (see Figs. 28) and fiber axis (the X<sub>3</sub> axis). [28]

Based on the geometrical coordinate in Figure 30, the contour map of the two-dimensional radial distribution function  $Q(r, \alpha)$  can be obtained by using Eq. (V-3) after somewhat complicated mathematical treatments, in which the experimental data of  $I'(s, \varphi)$  is given in Figure 29.

$$Q(r,\alpha) = \int_{0}^{\infty} \int_{0}^{2\pi} \int_{0}^{\pi} s^{2} I'(s,\varphi) \left[ \sum_{n=0}^{\infty} J_{2n}(4\pi sr)(-1)^{n} (4n+1) P_{2n}(\cos\varphi) P_{2n}(\cos\alpha) \right] \sin\varphi d\varphi d\psi ds$$
  

$$= \sum_{n=0}^{\infty} P_{2n}(\cos\alpha) 2\pi (4n+1)(-1)^{n} \int_{0}^{\infty} s^{2} J_{2n}(4\pi sr) \left[ \int_{0}^{\pi} I'(s,\varphi) P_{2n}(\cos\varphi) \sin\varphi d\varphi \right] ds$$
  

$$= \sum_{n=0}^{\infty} P_{2n}(\cos\alpha) \int_{0}^{\infty} 4\pi s^{2} (-1)^{n} J_{2n}(4\pi sr) \left[ \frac{(4n+1)}{2} \int_{0}^{\pi} I'(s,\varphi) P_{2n}(\cos\varphi) \sin\varphi d\varphi \right] ds$$
  

$$= \sum_{n=0}^{\infty} 4\pi P_{2n}(\cos\alpha) \int_{0}^{\infty} (-1)^{n} s^{2} J_{2n}(4\pi sr) I_{2n}(s) ds$$
  

$$= \sum_{n=0}^{\infty} P_{2n}(\cos\alpha) W_{2n}(r)$$
  
(V-3)

where

$$I_{2n}(s) = \frac{4n+1}{2} \int_0^{\pi} I'(s,\phi) P_{2n}(\cos\phi) \sin\phi d\phi$$
 (V-4)

and

$$W_{2n}(r) = 4\pi (-1)^n \int_0^\infty s^2 I_{2n}(s) J_{2n}(4\pi sr) ds \qquad (V-5)$$

 $( \land )$ 

where  $P_{2n}(x)$  is Legendre polynomial and  $J_{2n}(x)$  is Bessel function.

Figure 31 shows the contour map of  $Q(r, \alpha)$  for PPEK spinning fibers with low chain orientation ( $F_{200}^{am} = 0.0546$ ). [28] The density magnitude is normalized by the lowest

magnitude which is drawn in the contour map. Namely, the lowest magnitude is represented as a unit in the map. It may be postulated that the most probable distance at each polar angle  $\alpha$  approximately corresponds to that at angle  $\varphi$ , although the physical meanings of  $\alpha$  and  $\varphi$  are different as shown in Figure 30. At  $\kappa = 0^{\circ}$ ,  $\varphi$ must be 90° to detect X-ray beam by horizontal scanning of scintillation counter and the vector **r** associated with the adjacent chain distance direction must exist on the horizontal plane ( $\alpha = 90^{\circ}$ ). The most probable distance *r* between adjacent chains is 0.486 *nm* at  $\alpha = 0^{\circ}$  for chains oriented parallel to the spinning fiber direction because of tension under dry spinning, while *r* at  $\alpha = 90^{\circ}$  is 0.473 *nm* for chains oriented perpendicular to the spinning fiber direction because of the compression. In the map, each inflection point of contour lines almost corresponds to the average distance *r*. Anyway, this paper emphasizes that such detailed analysis must be done by using  $\theta - 2\theta$  scanning instrument up to wide angle.



Figure 31. Contour map  $Q(r, \alpha)$  of the radial distribution function associated with electron density distribution for a PPEK fiber  $(0.1 \times r nm)$ . [28]

Different from WAXD, the recent instrument has great advantage to evaluate SAXS intensity from large domains with high order arrangement in order to detect high order scattering peaks as well as to evaluate a single crystal structure analysis, since it provide high X-ray brightness. Also high brightness assures the incident beam through point focus and the scattered and diffraction intensity can use without slit correction.

Summary

The present paper is based on a course taught by the authors (MS program) of Department of Polymer Material at Dalian University of Technology. The course covered a wide range including the difference between continuous and characteristic X-rays in terms of fundamental quantum mechanics as well as synchrotron light and X-ray-absorption fine structure spectroscopy (XAFS) etc. In the course, the application examples for WAXD, SAXS and SALS were described in comparison with more detailed observed and theoretical results.

To shorten the course taught, this paper picks up the similarity and difference between SAXS and SALS by simple mathematical treatment to facilitate understanding as much as possible for students and young scientists who are not familiar with X-ray and visible light beams. 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. Most of SAXS patterns from materials must be analyzed by considering inter-particle interference effect except scattered intensity from isolated particles evaluating Guinier law. SAXS patterns from materials must be analyzed by considering inter-particle interference effect except scattered intensity from isolated particles evaluating Guinier law. The further description is pointed out the serious defect of the recent machine termed as simultaneous measuring instrument of WAXD and SAXS. By using the instrument, the evaluation of incoherent intensity is difficult on evaluating scattered intensity at wide angle region.

### References

- 1) B.D. Cullity, "Elements of X-ray Diffraction", Addition –Wesley Publishing Company, Inc., Reading (1956)
- 2) T. Masuko, "X-ray Diffraction from Polymers, a set of lectures" in Japanese, 1993.
- 3) B.E. Warren, "X-ray Diffraction" Addition Wesley, Reading (1969)
- 4) Jun Liu, Yuezhen Bin, Masaru Matsuo, "Magnetic Behavior of Zn-doped Fe3O<sub>4</sub> Nanoparticles Estimated in Terms of Crystal Domain Size"
  J. Phys. Chem. C 116(1) 134-143 (2012)

- M. Matsuo, M. Tsuji, R.S. Manley, "Ultradrawing at Room Temperature of High Molecular Weight Polyethylene. 3. Theoretical Analysis of SAXS Patterns of Unannealed and Annealed Samples. Macromolecules, 16, 1505-1514, 1983
- M. Matsuo, C. Sawatari, M. Tsuji, R.S. Manley "One-dimensional Mathematical Treatment of Small-angle X-ray Scattering from a System of Alternating Lamellar Phase" J. Chem. Soc., Faraday Trans. 2, 1593-1605, 79, 1983
- M. Matsuo, C. Kitayama, "Two-Dimensional Mathematical Treatment of Small-Angle X-Ray Scattering from a System of Alternating Lamellar Phases with orientation Distribution" Polymer J. 17, 479-497 1985
- 8) A. Guinier; G. Fournet, "Small Angle Scattering of X-ray" John Wiley & Sons, New York (1955)
- 9) R. Hosemann, S.N. Bagchi, "Direct Analysis of Diffraction by Matter", North-Holland(1962)
- M. Kaburagi; M. Kaburagi; Y. Bin; D. Zhu, C. Xi "Small Angle X-Ray Scattering from Voids within Fibers during the Stabilization and Carbonization Stages" Carbon 41, 915-926 (2003)
- G. R. Stroble; M. Schneider, "Direct Evaluation of the Electron Density Correlation Function of Partially Crystalline Polymers". Polym Sci. Polym. Phys. Ed., 18, 1343 (1980)
- 12) X. Shi; Y. Bin; D. Hou; Y. Men; M. Matsuo "Gelation/Crystallization Mechanisms of UHMWPE Solutions and Structures of Ultradrawn Gel Film" Polymer J. 46, 21-35, (2014)
- 13) R.S. Stein, M.B. Rhodes, "Photographic Light Scattering by Polyethylene Films" J. Appl. Phys. 31 1873-1884 (1960)
- 14) S. Clough; J.J. van Aartsen; R.S. Stein, "Scattering of Light by Two-dimensional Spherulite", 36, 3072- 3085 (1965)
- 15) M. B. Rhodes and R. S. Stein, "Two forms of poly(tetrafluoroethylene) spherulites and their scattering patterns "J. Polym. Sci., Part B, 1, 663-667 (1963).
- M. Moritani, N. Hyashi; A. Tsuo; H. Kawai "Light Scattering Pattern from Collagen Films in Relation to the Texture of a Random Assembly of Anisotropic Rods in Three Dimensions Polymer J. 2 74-87 (1971)
- C. Sawatari; T. Muranaka, M. Matsuo "Morphological Studies on Optically Anisotrpiv Rodlike Textures of Poly(butylene terephthalate) Polymer J. 15, 33-47 (1983)
- C. Sawatari; M. Iida; M. Matsuo "Light Scattering Studies on the Morphology and Deformation Mechanism of Poly(tetramethylene-oxide-Poly(tetramethylene

terephthalate) Block Polymer" Macromolecules 17, 1765-1773 (1984)

- R.S. Stein; P.R. Wilson, "Scattering of Light by Polymer Films Possessing Correlated Orientation Fluctuations" J. Appl. Phys. 33, 1914-1922 (1962)
- 20) M. Matsuo; S. Miyoshi; M. Azuma; Y. Nakano; Y. Bin "Polazied Small-Angle Light Scattering From Gels Estimated in Terms of a Statistical Approach" Phys. Rev. E 72, 041403 (2005)
- 21) Y. Bin; Y. Tanabe; C. Nakabayashi, H. Kurosu, M. Matsuo "Morphology and Mechanical Properties of Awolen Gels and Dry Gel Films of Poly(vinyl alcohol) Prepared by Crystallization from Solutions under Simultaneous Biaxially Stretching" Polymer 42, 1183-1200 (2001)
- 22) M. Matsuo, T. Tanaka, L. Ma "Gelation Mechanism of Agarose and  $\kappa$  carrageenan Solutions Estimated in Terms of Concentration Fluctuation" Polymer 43, 5299-5309 (2002)
- 23) T. Xu; Y. Bin; Y. Nakagaki; M. Matsuo "Densityy Fluctuation of the Amorphous Region of Poly(ethylene terephthalate) Fulms by Quasi-Spinodal Decomposition" Macromolecules 37, 6985-6993
- 24) M. Matsuo; Y. Luo; A. Galeski "Gauche-trans Transitions in Amorphous Polymers under Annealing: Lattice Model and Polarized Light Scatering" Phys. Rev. E 79, 041801 (2009)
- 25) Y. Luo; S. Kayakabe; Y. Xi; Y. Bin; C, Xu: M. Matsuo "Characteristics of Several Kinds of Polyethylene Gel Estimated by Samll-Angle Light Scattering Under Cross Polarization" J. Polym. Scie. Polym. Phys. Ed. 49, 384-397 (2011)
- 26) M. Matsuo; Y. Bin In preparation
- 27) R. Zhang; Y. Bin; W. Yang; S. Fan; M. Matsuo "Appearance of Perfect Amorphous Linear Bulk Polyethylene under Applied Electric field and the Analysis by Radial Distribution Function and Direct Tunneling Effect" J. Phys. Chem. B. 118 2226-2237 (2014)
- 28) W. Yang; Y. Bin; Y. Yuan; M. Matsuo "Evaluation for Most Probable Distance between Adjacent Amorphous Molecular Cahins Taking Preferred Orientation with Respect to a Spinning Fiber" Polymer 103, 112-123 (2016)
- 29) W. Krigbaum, R.J. Roe "Crystallie Orientation in Materials Having Fiber Texture. II. A Study of Strained Samples of Crosslinked Polyethylene" J. Chem. Phys. 41, 737-748 (1964)
- R.J. Roe "Description of Crystalline Orientation in Polycrystalline Materials. III. General Solution to Pole Figure Inversion" J. Appl. Phys. 36, 2024-2031, (1965)
- 31) K. Fujita, S. Suehiro, S. Nomura, H. Kawai, Polymer J. 14, 545 (1982)

- 32) M. Matsuo, X. Chunye "Defprmation Mechanism of Polyethylene Spherulites Estimated by Crystal Orientation Distribution Function and Small Angle Light Scattering under Hv Polarization Condition" Polymer 17, 4311-4318 (1997)
- 33) Y. Bin; A. Koganemaru; T. Nakashima; M. Matsuo "Segmental Orientation under Simultaneous Biaxially Stretching Using a Lattice Model and Application of oriented Crystallization of Ultra-high Molecular Weight Polyethylene Films Prepared by Gelation/crystallization from Solution" Polymer J. 37, 192-205 (2005)
- 34) M. Matsuo; C. Sawatari; Y. Iwai; F. Ozaki "Effect of Orientation Distribution and Crystallinity on the Measurement by X-Ray Diffraction of the Crystal Lattice Moduli of Cellulose I and II. Macromolecules 23, 3266-3275 (1990)
- 35) M. Matsuo; R. Sato; Y. Shimizu "Effect of Molecular Orientation Distribution and Crystallinity on the Measuremnt of the Crystal Lattice Modulus of Nylon y by X-Ray Diffraction" Colloid Polym. Sci. 271, 11-21 (1993)
- 36) M. Matsuo; R. Adachi; X. Jiang; Y. Bin "Orientation Behavior of the Three Principal Crystallographic Axes of Poly(butylene terephthalate) Estimated in Terms of Orientation Distribution Function of Crystallites" Macromolecules 37, 1324-1332 (2004)
- 37) Y. Bin; K. Oishui; K. Yoshida; T. Nakashima; M. Matsuo "Orientation Distribution Functions of the Three Principal Crystallographic Axes as well as Crystallites of Poly(ethylene terephthalate) Films under Biaxially Stretching" Polymer J. 36, 394-402 (2004)