X-Ray Diffraction Theory (A survey of polymer crystallization by X-ray diffraction . chapter 2)

Chapter 2. X-Ray Diffraction Theory

2.1 Basic Theory

2.1.1 Basics for X-ray diffraction

We shall now discuss the nature of X-ray diffraction and make relationship of the diffraction pattern to the structure of matter. We first consider X-ray diffraction from elementary charged particles like electrons. In our discussion, we assume that the incident X-ray beam is monochromatic. We also use the Fraunhofer approximation during interference of X-rays. Then, we consider parallel waves both in the incident and scattered directions. Furthermore, we ignore the case of re-scattering of the scattered wave. Finally, we consider interference effects due to coherent scattering without changing the wavelength.

2.1.2 Scattering by a single electron

According to the classical electromagnetic (CE) theory, X-rays can be represented by a transverse wave, consisting of electric and magnetic fields perpendicular to propagating direction [1]. When the X-ray is incident to the material, atomic electrons interact with the electric field. As a result of the interaction, the bound electron is oscillated with the same frequency to the incident X-ray. According to the CE theory, an accelerated electron will radiate electromagnetic wave having the same frequency with the incident wave. Thus, when the electric field interacts with an electron, a secondary wave, having the same frequency of the field, is emitted due to the oscillation of the bound electron. This secondary wave is called the scattered wave. The intensity of the scattered X-ray beam is proportional to the square of the amplitude of the incident electric field.
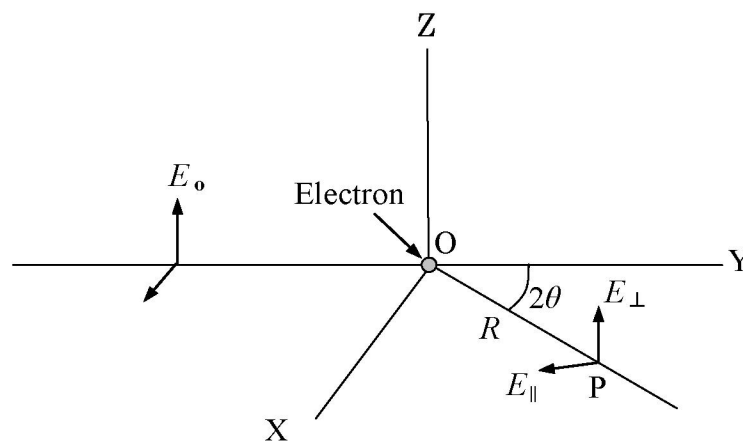

Fig. 2.1 Schematic drawing of scattering phenomena from an electron

Using the CE theory, Thomson derived an expression of the scattered wave by a single electron [2]. In Fig. 2.1, the electron is located at point O. At first, we consider the case of the polarized X-ray whose electric field, E_o, parallel to the Z-axis. At a point P of distance R from O, the component of the scattered field polarized perpendicular to the XY plane is given by:

$$E_\perp = E_o \left(\frac{e^2}{mc^2} \right) / R , \quad\text{...} \quad (2.1)$$

where e and m are the charge and mass of the electron, c the velocity of light. Then we consider the incident X-ray field, E_o, polarized parallel to the X-axis. The induced scattering field polarized parallel to the XY-plane becomes:

$$E_\parallel = E_o \left(\frac{e^2}{mc^2} \right) cos\, 2\theta \; / \; R \quad\text{....................................} \quad (2.2)$$

where, 2θ is the scattering angle as illustrated in Fig.2.1. As the intensity of X-ray is calculated by square of the electric field, the incident intensity of the X-ray beam is:

$$I_o = E_o^2 \quad\text{..}(2.3)$$

Since the incident X-ray beam is unpolarized, then the scattered intensity, I_s , is derived by an average of the scattered electric field:

$$I_s = \frac{E_\perp^2 + E_\parallel^2}{2} = I_o \frac{e^4}{m^2 c^4 R^2} \left(\frac{1 + cos^2 2\theta}{2} \right) \quad\text{.......................} \quad (2.4)$$

In Eq. (2.4), the factor in the parentheses is called the polarization factor. This condition holds equal for other charged particles. If we consider the case of a proton, the mass becomes far heavier than an electron. Then, we can neglect X-ray scattering by a proton, because the intensity shows inverse square dependence on the mass.

2.1.3 Scattering by an atom consisting of many electrons

Now, we consider an atom containing Z electrons. If all these Z electrons are located at the same point in space, the scattered waves from them with charge Ze will be in phase, and Eq. (2.3) readily gives:

$$I_{Ze} = Z^2 I_s \quad\text{...} \quad (2.5)$$

However, the wavelengths used in X-ray diffraction are of the order of the atomic diameter. Therefore, if the electrons in an atom are located at different distances, the scattered waves are not completely in phase. As a result of the destructive interference, the net intensity will become less than that of Eq.(2.5). It is possible to consider that the actual amplitude will correspond to a number of F_a electrons less than Z. Then, the amplitude of the electric field scattered from an atom will be:

$$E_a = F_a E. \quad\text{...} \quad (2.6)$$

The quantity F_a is called the atomic scattering factor.

According to Eqs.(2.3) and (2.4), the scattering intensity from the atom becomes:

$$I_a = F_a F_a^* I_s , \quad\text{.......................................} \quad (2.7)$$

where F_a^* is a complex conjugate of F_a, as a result of the Fourier transformation (See Eq.(2.15)). For a macroscopic sample, the diffracted intensity will be proportional to the

irradiated volume. We, therefore, define absolute intensity per unit volume:

$$i = F_a F_a^* I_s / V \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (2.8)$$

For calculating F_a, we consider interference by two electrons located at A and C, separated by a distance r. In Fig.2.2, the direction of incident and scattered beams is indicated by the unit vector $\mathbf{S_o}$ and $\mathbf{S}$, respectively. The angle $,2\theta$, between the two vectors is the scattering angle.
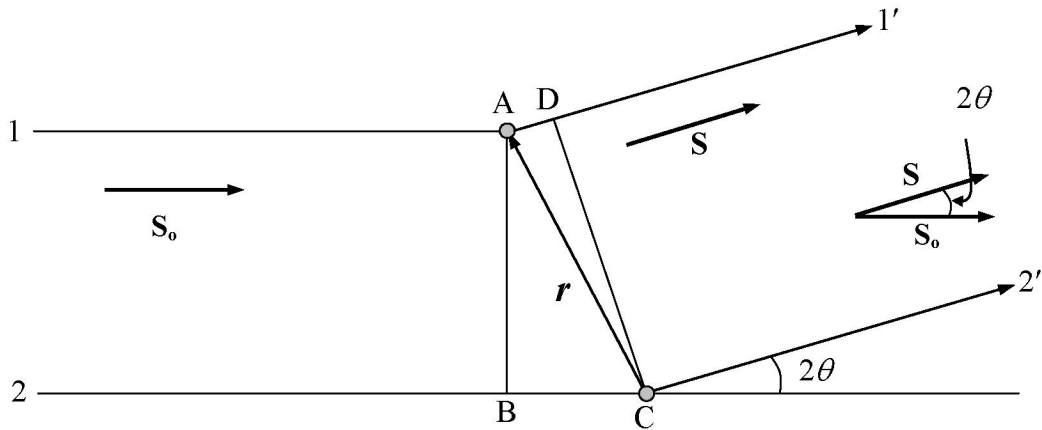

Fig. 2.2 Schematic drawing of the scattering by two electrons

According to the figure,

$$\text{AD} = -\,\mathbf{S} \cdot r \qquad \text{and} \qquad \text{BC} = -\,\mathbf{S_o} \cdot r.$$

The path difference between the rays 11′ and 22′ is measured by:

$$\delta = \text{AD} - \text{BC} = -\,(\mathbf{S} - \mathbf{S_o}) \cdot r.$$

Then, the phase difference between the two rays becomes:

$$\phi = \frac{2\pi}{\lambda} \times \delta = -\frac{2\pi}{\lambda} \times (\mathbf{S} - \mathbf{S_o}) \cdot r \quad \dots \dots \dots \dots \dots \dots \dots \dots \quad (2.9)$$

We define here the scattering vector s in the reciprocal space;

$$s = \frac{\mathbf{S} - \mathbf{So}}{\lambda} \quad \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad (2.10)$$

The magnitude of s is a function of the scattering angle:

$$|s| = \left| \frac{\mathbf{S} - \mathbf{So}}{\lambda} \right| = \frac{2\sin\theta}{\lambda} \cdot \quad \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad (2.11)$$

Then, the resulting amplitude of the scattered X-rays from the two electrons will be:

$$E_a = Ee^0 + Ee^{-2\pi i s \cdot r_i} \qquad (2.12)$$

If we consider an atom containing Z electrons, and if the distance of electrons from the origin is represented by vectors r_i, then the resultant scattered amplitude will be:

$$E_a(s) = \sum_{i=1}^{Z} E_i e^{-2\pi i s \cdot r_i} \qquad (2.13)$$

Thus, according to Eq.(2.6), the structure factor F_a can be expressed by:

$$F_a(s) = \frac{E_a(s)}{E} = \sum_{i=1}^{Z} F_i e^{-2\pi i s \cdot r_i} \qquad (2.14)$$

In the atom, electrons are considered to be continuously distributed. If $\rho(\mathbf{r})$ is the electron density in the volume element dv, then Eq. (2.14) changes to:

$$F_a(s) = \int \rho(\mathbf{r}) \, e^{-2\pi i s \cdot r} \, dv \qquad (2.15)$$

This equation was derived by Fourier before the diffraction theory was discussed. This equation demonstrates that *the scattering amplitude of X-ray is the Fourier transform of the electron density*. For calculating $F_a(s)$, the integration is performed inside the atom.

For the X-ray diffraction theory including Fourier transform, the reader may refer the text of general theory [3,4] and its applicaton to polymers [5-8].

2.2 Fourier Transformation

2.2.1 Relation in the Fourier transform

Following the Fourier transform derived in Eq.(2.15), it is possible to introduce the generalized theory applicable to all material phases such as solids, liquids and gases. In the generalized theory, relations of the structure factor, $F(s)$, and total intensity, $I(s)$, of the material are derived as follows:

$$F(s) = \int \rho(\mathbf{r}) e^{-2\pi i s \cdot r} dv, \qquad (2.16)$$

$$I(s) = iV = I_s \, F(s) \, F^*(s), \qquad (2.17)$$

where $F^*(s)$ is the complex conjugate of $F(s)$.

The most striking property of the Fourier integral is that $\rho(\mathbf{r})$ is connected to $F(s)$ by the reverse formula:

$$\rho(\mathbf{r}) = \int F(s) e^{2\pi i s \cdot r} \, dv_s, \qquad (2.18)$$

where dv_s is the volume element of the reciprocal space. Equation (2.18) indicates that there exists a relation of reciprocity between $F(s)$ in the reciprocal space and $\rho(\mathbf{r})$ in the real space. If we know the relation between the two spaces, it is convenient to understand the relationship between the structure and its scattering pattern.

Using analytical results of the Fourier transform, it is possible to discuss the relationship of the structure of a substance with the X-ray scattering pattern. Here, we will present some examples of characteristic functions and their Fourier transforms.

2.2.2 Examples of the Fourier transform

We imagine here that $f(x)$ is a one-dimensional electron density profile as a structure model in the real space. The corresponding diffraction pattern in the reciprocal space is deduced by $I(s)$ using Eq.(2.17). In case of an even function, $F^2(s)$ is used instead of $F(s)\,F^*(s)$.

(a) Delta function

Delta function is defined by $\delta(x) = 0$ at $x \neq 0$, and $\delta(x) = \infty$ at $x=0$.

If $f_1(x) = \delta(x)$, then $F_1(s) = \int \delta(x) \mathrm{d}v_x = 1$.

(i)   (ii)
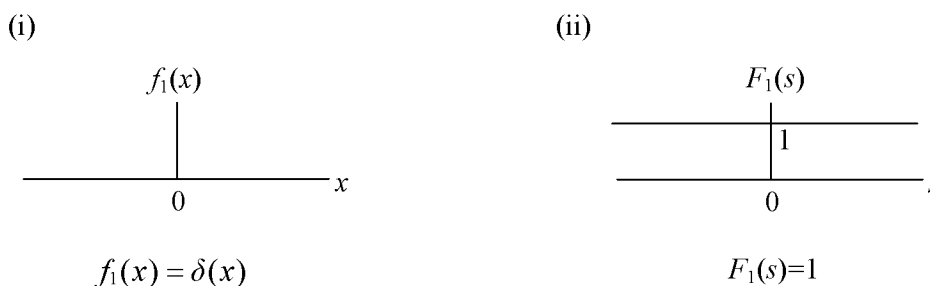
$$f_1(x) = \delta(x)$$

$$F_1(s)=1$$

Fig. 2.3   The illustrations of (i) delta function and (ii) Fourier transform ; $F_1(s)$.

(b) Row of the delta functions

If we suppose the row of the delta functions separated by a regular distance 'a' :

$$f_2(x) = \sum_n \delta(x - na) \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2.19)$$

The Fourier transform of the $f_2(x)$ becomes:

$$F_2(s) = \sum_n e^{-2\pi i s n a} = \frac{\sin \pi s N a}{\sin \pi s a}, \quad\dots\dots\dots\dots\dots\dots\dots(2.20)$$

where N is the total number of the row. In case of the large number of N, $F_2(s)$ becomes a row of delta functions separated by $1/a$:

$$F_2(s) = \frac{\sin \pi s N a}{\sin \pi s a} = \frac{1}{a} \sum_n \delta(s - \frac{h}{a}) \quad\dots\dots\dots\dots\dots\dots(2.21)$$

(c)   Application of the delta function in polymers

Combining the above relations discussed in (a) and (b), X-ray diffraction patterns by polymers can be estimated.   If we imagine a linear-polymer molecule, the periodic monomer repetition is aligned along the vertical direction.   An array of the periodic points (f_3) is characterized by f_1 in the horizontal direction (x) and f_2 in the vertical direction (y). Then, the two dimensional function $f_3(x,y)$ illustrated in Fig.2.4(i) is transformed into $F_3(s_x, s_y)$ like layer lines separated by $1/a$ shown in Fig.2.4(ii). In the polymer molecule, distance of the monomer is in the order of several Å.   Then, the reflection of the layer line will appear in the order of $Å^{-1}$, which can be detected by wide angle X-ray scattering (WAXS).

In the chapter 4, we will discuss a diffraction pattern of the oriented polyethylene terephthalate (PET). The cold-drawn PET molecules are aligned parallel to the draw direction, defined by f_3.   The corresponding pattern shows diffuse layers (See Figs.4.1 (a), (b) and (c), pp32).
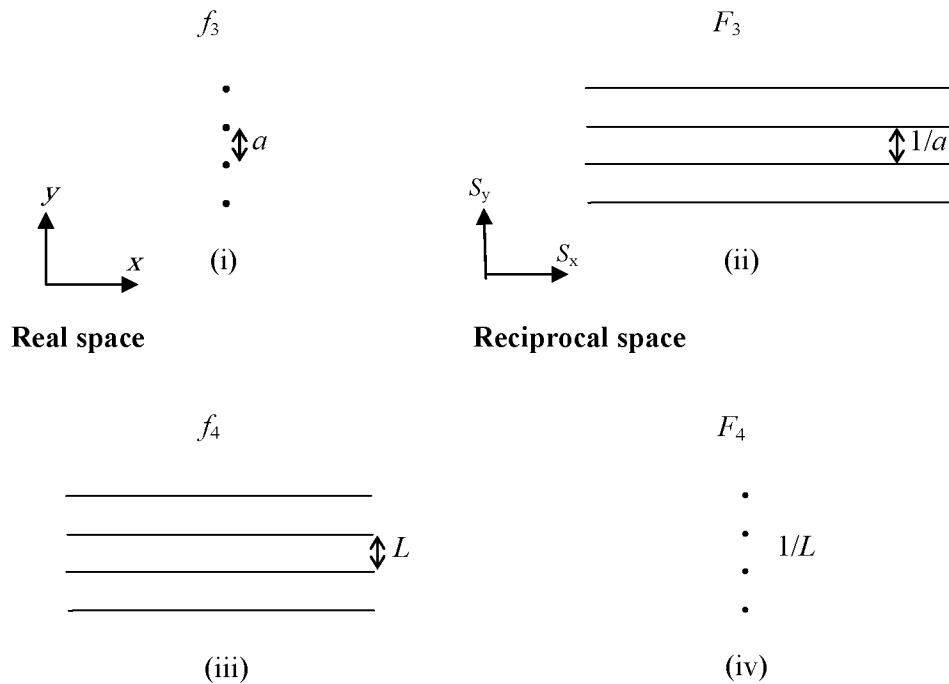

Fig. 2.4   (i) Function of the periodic points, f_3, and (ii) the Fourier transform, F_3.

(iii) Function of the periodic layers, f_4, and (iv) the Fourier transform F_4.

(d) Reverse transformation

In the Fourier transformation, it is possible to obtain the relation of reverse transformation: The function, $f_4(x,y)$, showing the row of layer lines in the real space will be transformed into $F_4(s_x,s_y)$ corresponding row of delta functions along the vertical direction.   If we consider a lamellar structure separated by L (Fig. 2.4(iii)), the diffraction pattern becomes the row of points separated by $1/L$ as shown in Fig. 2.4(iv). As the lamellar structure is in the order of 100 Å , the diffraction pattern has a order of 0.01 Å $^{-1}$, which can be detected by small angle X-ray scattering (SAXS). Examples of the F_4 function are shown in Fig.4.12 (pp42) and section 4.8 (pp44-46).

(e) Crystal function:

Expanding the one dimensional function f_2 into three dimensions, the crystal lattice function f_5 is transformed into the reciprocal lattice function (F_5).

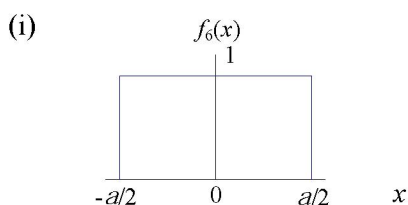According to the definitions,

$$f_5 = p\mathbf{a} + q\mathbf{b} + r\mathbf{c} \qquad \text{and}$$

$$F_5 = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \text{ , as expressed in Eq.(1.1) and Eq.(1.6).}$$

This fact indicates that the crystalline structure has a diffraction pattern appeared on the reciprocal lattice.
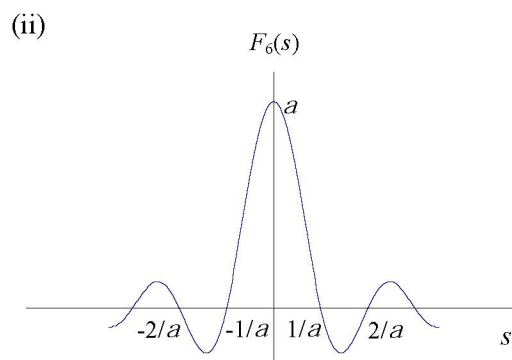
(f) Rectangular function

If we imagine an electron distribution on a rectangular function $f_6(x)$ shown in Fig.2.5(i), the corresponding diffraction function is analytically calculated by $F_6(s)$.

(i)

(ii)

$$f_6(x) = \begin{cases} 1 \text{ when } |x| < \dfrac{a}{2} \\[2mm] 0 \text{ when } |x| > \dfrac{a}{2} \end{cases}$$

$$F_6(s) = a \, \frac{\sin \pi s a}{\pi s a}$$

(Real space)　　　　　　　　**(Reciprocal space)**

Fig. 2.5　(i) The rectangular function $f_6(x)$ and (ii) the Fourier transform: $F_6(s)$.

The rectangular function is a model of molecular entity or crystalline shape, which will be used in the convolution theory. (See in section 2.3.3(b), pp 20)

(g) Gaussian function

The Gaussian function is a basic function to consider distribution of electron density or molecular movements. The main feature of the Gaussian is that the curve width is reversely transformed by the Fourier transformation. As a result, the sharp Gaussian will be transformed into a broad one. We use this function to discuss thermal movements of crystalline molecules using a convolution theory (See in section 2.3.3(a), pp18-19).
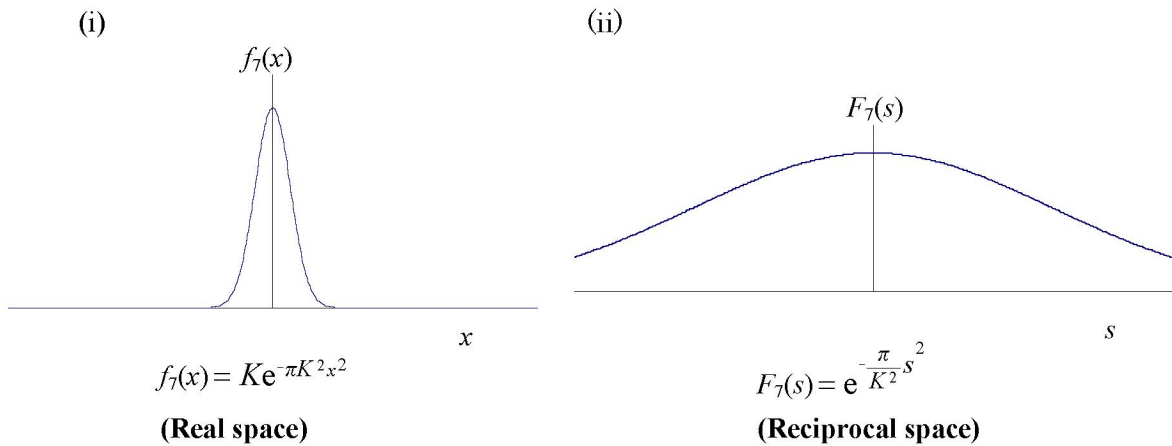
(i)

$$f_7(x)$$

$$x$$

$$f_7(x) = K e^{-\pi K^2 x^2}$$

(Real space)

(ii)

$$F_7(s)$$

$$s$$

$$F_7(s) = e^{-\frac{\pi}{K^2} s^2}$$

(Reciprocal space)

Fig.2.6   (i) The Gaussian function $f_7(x)$ and (ii) the Fourier transform $F_7(s)$.

(vi) Spherulitic function

This function is a model of the electron distribution of an atom. It is known that a spherulitic material in the real space has a spherical symmetry in the scattered intensity around the center ($s = 0$).
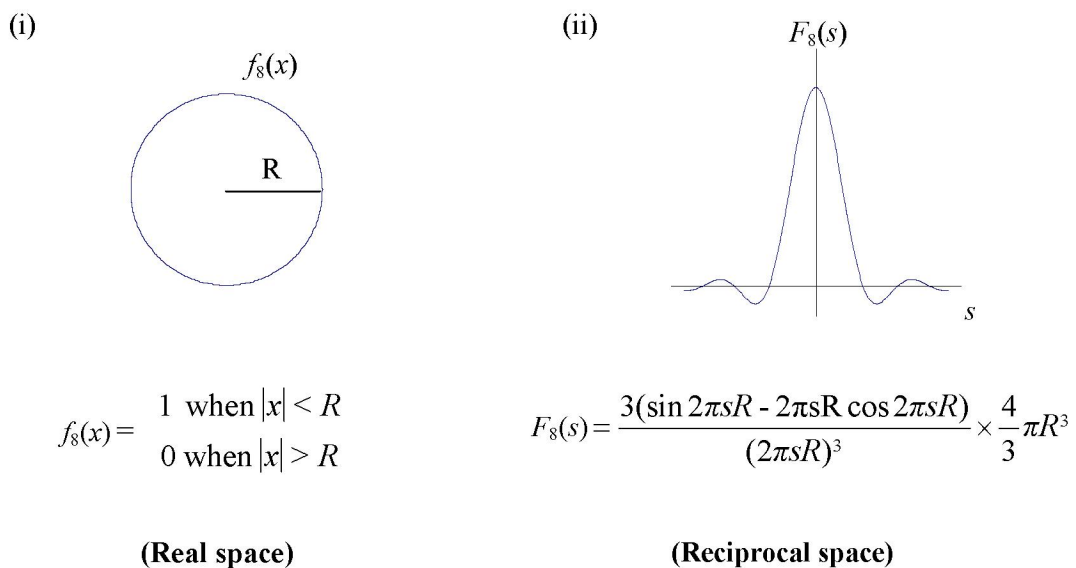
(i)

$$f_8(x)$$

R

$$f_8(x) = \begin{cases} 1 & \text{when } |x| < R \\ 0 & \text{when } |x| > R \end{cases}$$

(Real space)

(ii)

$$F_8(s)$$

$$s$$

$$F_8(s) = \frac{3(\sin 2\pi sR - 2\pi sR \cos 2\pi sR)}{(2\pi sR)^3} \times \frac{4}{3}\pi R^3$$

(Reciprocal space)

Fig. 2.7   (i) The spherulitic function $f_8(x)$ and (ii) Fourier transform $F_8(s)$.

2.3. The Convolution Theory

2.3.1 Convolution function

The one-dimensional convolution function, $h(x)$, of the two functions $f(x)$ and $g(x)$ is defined by;

$$h(x) = \int f(u)g(x-u)dv_u \quad\text{..}\quad (2.22)$$

The convolution function is expressed by;

$$h(x) = f(x) * g(x) \quad\text{..}\quad (2.23)$$

In the case of $f(x) = \delta(x)$, then $f(x) * g(x) = g(x)$. This relation is extended using the periodic delta function showing lattice periodicity ($f(x) = f_2(x)$). In this case, the convolution, $f(x) * g(x)$, represents the periodic array of $g(x)$. Extending to the three dimensions, the crystalline state, arranged atoms or molecules on the lattice, can be expressed by the convolution of $f_s(r)$ and a characteristic electron density $g(r)$.

2.3.2 Fourier transform of the convolution

Fourier transform, $\mathscr{F}$, of the convolution function is defined as

$$Y(s) = \mathscr{F}[f(x) * g(x)] = \iint f(u)g(x-u)dv_u\, e^{-2\pi i s \cdot x} dv_x dv_u \quad\text{....................}\quad (2.24)$$

Here, the variables u and x are changed into $U=u$ and $W=x-u$. In this case, product of the volume elements $dv_x dv_u$ is equivalent to $dv_U dv_W$.
Then,

$$Y(s) = \iint f(U)g(W)e^{-2\pi i s(U+W)} dv_U dv_W$$

$$= \int f(U)e^{-2\pi i s U} dv_V \int g(W)e^{-2\pi i s W} dv_W = F(s) \cdot G(s), \quad\text{.............}\quad (2.25)$$

where $F(s) = \mathscr{F}[f(x)]$ and $G(s) = \mathscr{F}[g(x)]$.

Accordingly, *the Fourier transform of the convolution function is equal to the product of the transformed functions:*

$$\mathscr{F}[h(x)] = \mathscr{F}[f(x) * g(x)] = F(s) \cdot G(s) \quad\text{....................................}\quad (2.26)$$

Using the reverse relation of the Fourier transformation, *the product function is transformed into the convolution of the transformed functions:*

Thus $\quad \mathscr{F}[f(x) \cdot g(x)] = F(s) * G(s) \quad\text{..}\quad (2.27)$

2.3.3 Application of the convolution theory

(a) Thermal motion of the crystalline molecules

At high temperatures, crystalline molecules are displaced from the regular positons. Due to the thermal motion, it is considered that the diffraction would be disturbed into a diffuse pattern. However, the result shows sharp reflection peaks with decreasing intensity at higher angles (*s*). This fact is possible to explain by the convolution theory.

The crystalline structure has a regular packing of atoms or molecules. We represent this state using the convolution of the two functions: the lattice function $f_2(x)$ (or $f_5(r)$ in the three dimensions) and electron density function, $f_7(x)$, distributed by the Gaussian. Then, the feature of thermal motion on the regular lattice separated by '*a*' is shown by $f_2(x) * f_7(x)$ as illustrated in Fig.2.8 (a).
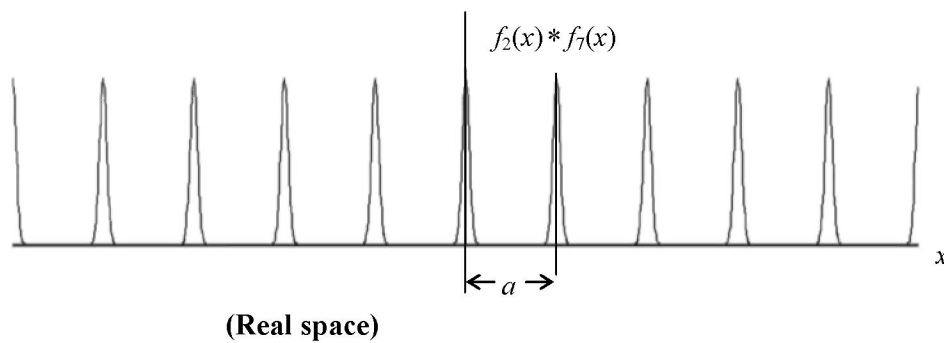

(Real space)

Fig.2.8 (a)　Electron density profiles on the regular lattice separated by '*a* '

The diffraction pattern of the above state can be calculated by Eq.(2.26). The transformed function $F_2(s)$ is a row of delta functions separated by $1/a$ (or reciprocal lattice in the three dimensions). On the other hand, the transformed function $F_7(s)$ is a Gaussian having a broad half width. The product of the both functions will be the row of the delta functions cut off by the Gaussian curve shown in Fig.2.8(b). As a result, the diffraction pattern has a sharp reflection peaks whose intensity will decrease at higher angles (large *s* values)
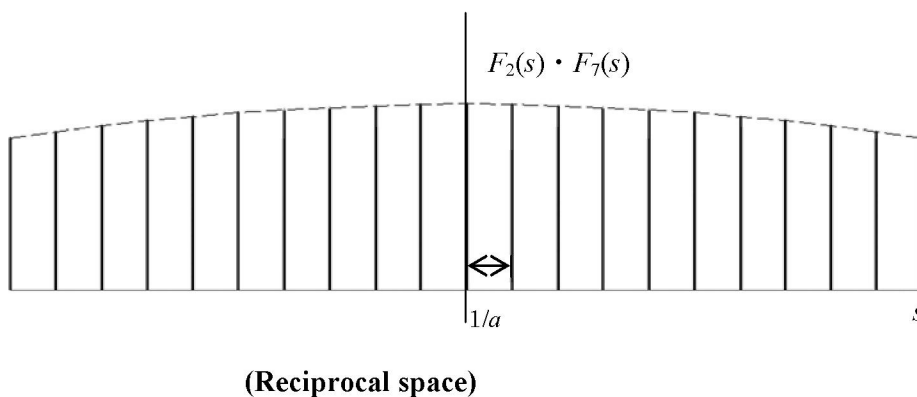

(Reciprocal space)

Fig.2.8(b)　Feature of the diffraction by the structure shown in Fig.2.8(a)

Considering the larger thermal motion at higher temperatures, atoms are oscillated randomly from the lattice points. Then, the crystalline regularity will be broken in the short range structure. However, followed by the Ergodic theorem in the thermodynamics, a time average structure is coincident with a space average structure. Then the effect of the thermal motion is possible to discuss using the broader distribution of $f_7(x)$.

$$f_2(x) * f_7(x)$$

$$\leftarrow a \rightarrow$$

$$x$$
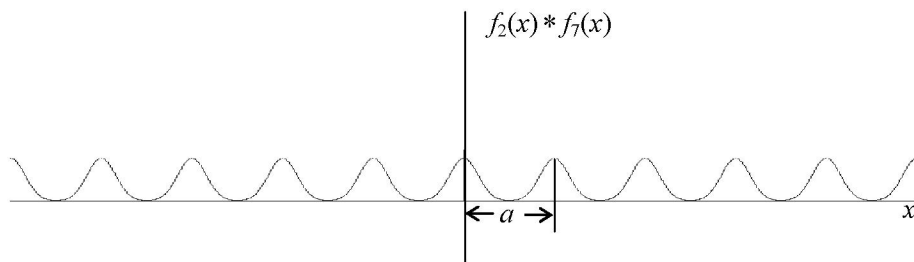
(Real space)

Fig.2.8(c)   Wider distribution of electron density by the thermal motion.

The effect of the thermal motion is emphasized in Fig.2.8(c), where the half width of $f_7(x)$ becomes wider than that in Fig.2.8(a). The resultant diffraction pattern in Fig.2.8(d) shows that the sharp diffraction peaks are rapidly cut off by $F_7(s)$. ***Despite of the thermal motions, sharpness of the diffraction pattern does not change at higher temperatures.***

$$F_2(s) \cdot F_7(s)$$

$$1/a$$

$$s$$
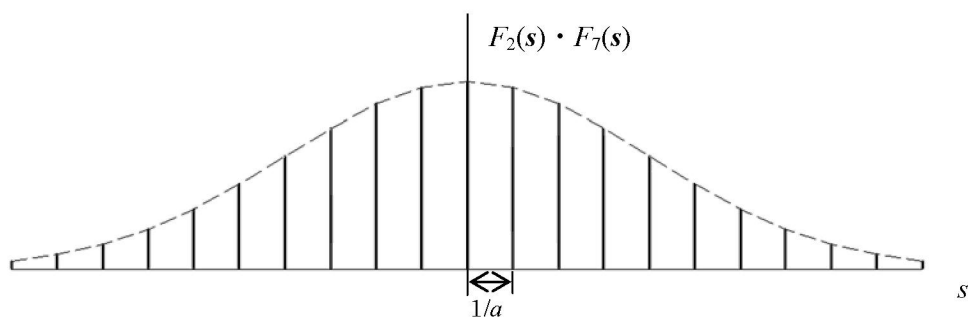
(Reciprocal space)

Fig.2.8(d)   Effect of the thermal motion: The sharp peaks are cut by $F_7(s)$,
showing that the peak intensity will weakened at high diffraction angle.

(b) Effect of the crystalline shape

The appearance of diffraction peaks is affected by the crystalline shape. It is possible to explain the effect of the crystalline size (or ordered region) by the convolution theory. If we consider two functions $f_2(x)$ and $f_6(x)$, which represent crystalline periodicity and shape of the crystal, respectively. Considering the multiple of the both functions, $f_2(x) \cdot f_6(x)$ indicates the effect of the crystalline shape. As shown in Fig. 2.9(a), the crystalline repetition $(f_2(x))$ is cut by the edge of $f_6(x)$ with total length of L.
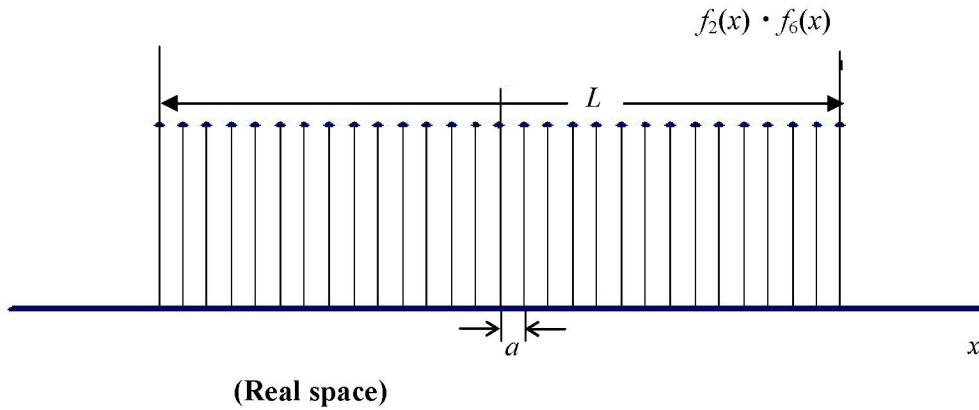
$$f_2(x) \cdot f_6(x)$$

(Real space)

Fig.2.9 (a)   Features of the crystalline shape: the crystalline regularity, $f_2(x)$,
is cut by the crystalline shape function, $f_6(x)$.

The above structure defined by the multiple function, $f_2(x) \cdot f_6(x)$, has a diffraction pattern transformed by Eq.(2.27):

$$\mathscr{F} [f_2(x) \cdot f_6(x)] = F_2(s) * F_6(s). \dots\dots\dots\dots\dots\dots\dots(2.28)$$

The diffraction intensity of the above structure will have a regular peaks on the reciprocal lattice separated by $1/a$. The peak has a width depending on $1/L$ as shown in Fig.2.9(b). In the case of a small crystal having low L value, the peak width is broadened by $1/L$. This fact clearly indicates that *the crystalline size is closely related to the sharpness of the diffraction peak.*
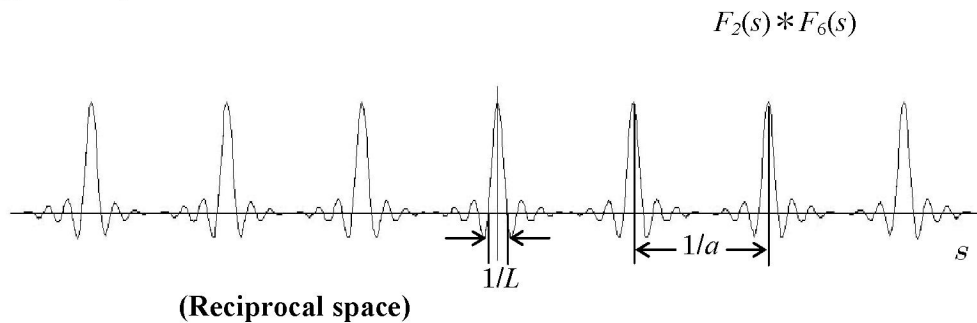
$$F_2(s) * F_6(s)$$

(Reciprocal space)

Fig. 2.9 (b)   Effect of the crystalline shape: the diffraction peaks are broadened
in the small crystal depending on the factor 1/L.

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