Simulation of images and electron diffraction patterns

TEM image and electron-diffraction pattern simulation methods were originally developed for interpreting experimental HRTEM images and diffraction patterns. They are used, for example, to explain why atoms sometimes appear in black and sometimes in white in an image. Image-simulation techniques are now used for different purposes such as to:

- interpret experimental HRTEM images;
- verify the possible structure model(s) by comparing experimental and calculated images and electron-diffraction patterns;
- predict how the images and diffraction patterns will look under certain microscope conditions for a particular structure in a particular orientation;
- predict the resolution required for a particular microscope to resolve the atoms in a particular structure;
- find out the experimental conditions under which an image was taken;
- find out the optimal experimental conditions of a particular microscope for a particular structure.

Since image formation includes two steps: interaction of electrons with the specimen and image formation by lenses, image simulation is also divided into two steps: calculation of the wave function at the exit surface of the specimen (exit wave) and calculation of the images.

The Fourier transform of the exit wave can be interpreted as the diffraction pattern. Electron-diffraction simulations can be used for extraction of quantitative crystallographic information including crystal structure solution and refinement.

12.1 Main parameters that affect HRTEM images and ED patterns

Analysis of the HRTEM images and electron-diffraction patterns is quite a hard task due to complexity of the theory of electron diffraction (Cowley and Moodie, 1957). The mathematical base present in analysis of electron diffraction includes a lot of equations and parameters. The main parameters that affect both HRTEM images and ED patterns are listed below:
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- *Crystal structure* – unit-cell dimensions, space group, atomic coordinates, occupancy, atomic displacement parameters and possible inclusion of defects;
- *Crystal orientation* – the sample orientation (e.g. the zone axis and crystal tilt);
- *Crystal thickness*;
- *Microscope parameters* – accelerating voltage, etc.;
- *Optical conditions* – the optical system of a microscope (HRTEM images) including beam divergence, defocus, etc.

The following parameters would affect the simulated HRTEM images only since all these parameters are related to the imaging system of an electron microscope:

- *Microscope parameters* – spherical aberration constant $C_s$, chromatic aberration constant $C_c$, coma and 3rd-order spherical aberration $C_3$;
- *Optical conditions* – defocus, astigmatism and focus spread.

### 12.2 Exit-wave calculation

Two methods are used for calculating the exit-wave function: the multislice method and the Bloch-wave method.

#### 12.2.1 The multislice method

The multislice method is based on the physical optical approach by Cowley and Moodie, 1957. A crystal of thickness $t$ is sliced (in the computer) into many thin slices of thickness $\Delta t$ as shown in Figure 12.1. As was shown later by Goodman and Moodie (1974), the multislice formulation is identical to the Schrödinger equation in the limiting case when $\Delta t \to 0$. In practice, the thickness $\Delta t$ is chosen to be so small ($< 4 \, \text{Å}$) that the phase-object approximation is valid for each slice. For each slice, the potential is projected onto a plane and the corresponding projected potential is calculated. The propagation of the electron wave from the exit surface of one slice to the incident surface of the next slice (over a distance $\Delta t$) is considered as Fresnel propagation in vacuum. The final exit-wave function is obtained when all the slices have been taken into account.

The scheme of the multislice calculations can be described as follows.

![Fig. 12.1](image_url)

Illustration of the multislice approximation.
Exit-wave calculation

- calculate projected potential \( \varphi(x, y) \);
- calculate Fresnel propagator \( F(u, v) \);
- calculate phase object function \( q(x, y) \);
- calculate incident wave function \( \Psi_0(u, v) \);
- perform multislice iterations.

\[
\Psi_n = F(F^{-1}(\Psi_{n-1} \cdot P_n) \cdot q_n) \tag{12.1}
\]

where \( F \) and \( F^{-1} \) denote forward and inverse Fourier transforms (FT), respectively;

- calculate the exit-wave function \( \Psi_{ex}(u, v) \);
- calculate focal plane image wave \( \psi(xy) \);
- apply the contrast transfer function (CTF) to the image wave \( \psi(xy) \) to calculate the HRTEM image.

The multislice calculation includes some approximations but has the advantage that it can be used for very complicated structures, and even for defects and interfaces. The multislice iterations use the fast Fourier transform (FFT) in order to improve the speed of calculations (see Lynch and O’Keefe, 1972; Ishizuka and Uyeda, 1977 and Ishizuka, 2004).

The crystal structure or the structural model is known before the image simulation starts. The knowledge of the structure assumes that the unit-cell parameters, the atomic coordinates and the space group are available. One can also include the parameters of thermal vibration, occupancies of atoms, etc.

The structure-factor calculation can be performed on the crystal structure data using

\[
F(u) = \sum_{j=1}^{N_{as}} f_j \cdot \exp \left[ -B_j \left( \sin^2 \theta_{hkl} \right) / \lambda^2 \right] \cdot \frac{occ_j \cdot n}{m} \cdot \sum_{s=1}^{m} \exp \left[ 2\pi i \left( \mathbf{u} \cdot \left( \mathbf{R}_s \cdot \mathbf{r}_j + \mathbf{t}_s \right) \right) \right] \tag{12.2}
\]

where \( N_{as} \) is number of symmetry independent atoms, \( f_j \) is the atomic scattering factor of an atom \( j \), \( B_j \) is the Debye–Waller factor, \( \theta_{hkl} \) is the scattering angle, \( \lambda \) is the wavelength, \( occ_j \) is the occupancy factor, \( n \) is the Wyckoff number, \( m \) is the space group order, \( \mathbf{u} = (h \ k \ l) = ha^* + kb^* + lc^* \) is a reciprocal lattice vector, \( \mathbf{r}_j = (x_j y_j z_j) = x_j \mathbf{a} + y_j \mathbf{b} + z_j \mathbf{c} \) is the vector of fractional coordinates for each atom in the asymmetric unit, \( \mathbf{R}_s \) and \( \mathbf{t}_s \) are the rotation matrix and the translation vector, respectively for the \( s \)th symmetry element of the space group.

The Fourier expansion of the crystal potential is

\[
\varphi(xyz) = \sum_h \sum_k \sum_l F(hkl) \cdot \exp \left[ 2\pi i \left( hx + ky + lz \right) \right] \tag{12.3}
\]

where \( h, k \) and \( l \) are integers over which the Fourier series is summed.

The potential projected onto a plane, for example onto the \( xy \)-plane, can be calculated using the following equation
\[ \varphi(xy) = c \int_0^1 \sum_h \sum_k \sum_l F(hkl) \cdot \exp[2\pi i (hx + ky + lz)] dz \] (12.4)

where \( c \) is the unit-cell parameter.

Here, the integral is different from zero only when \( l = 0 \). Thus, eqn (12.4) can be simplified and rewritten in the following form

\[ \varphi(xy) = c \cdot \sum_h \sum_k F(hk0) \cdot \exp[2\pi i (hx + ky)] \] (12.5)

There are several methods of the unit-cell slicing described in the literature based on the following principles:

- The whole unit cell is projected onto the plane and then all slices are equal and are \( 1/n \) (\( n \) is the number of slices) of the full projected potential.
- The potential of each slice is formed by only atoms which belong to that particular slice.

In the second case the effects of high-order Laue zones (HOLZ) reflections can be taken into account.

The phase object function can be calculated by

\[ q(xy) = \exp[-i\sigma \varphi(xy) \cdot \Delta z] \] (12.6)

where \( \sigma \) is the interaction constant, which can be calculated by

\[ \sigma = \frac{2\pi m_0 e}{h^2} \lambda \left( 1 + \frac{eE_0}{m_0 c^2} \right) \] (12.7)

The Fresnel propagator \( P(hk) \) can be calculated by

\[ P(hk) = \exp[2\pi i \Delta z \xi(hk)] \] (12.8)

where \( \Delta z \) is the slice thickness and \( \xi(hk) \) is the excitation error that, in the small-angle approximation, is given by

\[ \xi(hk) = \frac{\lambda}{2} \cdot \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} \right) \] (12.9)

where \( a \) and \( b \) are the unit-cell parameters. This equation is given for orthogonal cells.

### 12.2.2 The Bloch wave method

The Bloch-wave method solves directly the time-independent Schrödinger equation

\[ \nabla^2 \psi(xyz) + \frac{8\pi^2 me}{h^2} [U + \varphi(xyz)] \psi(xyz) = 0 \] (12.10)

where \( \psi(xyz) \) is the electron wave function, \( U \) the accelerating voltage, \( \varphi(xyz) \) the potential in the crystal, \( m \) the relativistically corrected mass of the electron, \( e \) the electron charge and Planck’s constant \( h \).
The lattice potential can be expanded into a Fourier series and the electron wave inside the crystal for an arbitrary wavevector $\mathbf{k}$ can be written as a Bloch wave,

$$\psi(\mathbf{r}) = \sum g C_g \exp \left[ 2\pi i (\mathbf{g} + \mathbf{k}) \cdot \mathbf{r} \right]$$  \hspace{1cm} (12.11)

where $C_g$ are called Bloch-wave coefficients.

Substituting $\psi(\mathbf{r})$ into the wave equation gives the following form,

$$\sum g \left[ \left( k_0^2 - (\mathbf{k} + \mathbf{g})^2 \right) C_g + \sum_{h \neq g} U_{g-h} C_h \right] \exp \left[ 2\pi i (\mathbf{g} + \mathbf{k}) \cdot \mathbf{r} \right] = 0$$  \hspace{1cm} (12.12)

or

$$\left( k_0^2 - (\mathbf{k} + \mathbf{g})^2 \right) C_g + \sum_{h \neq g} U_{g-h} C_h = 0$$  \hspace{1cm} (12.13)

where $U_g$ is defined as

$$U_g = \frac{2m \hbar V_g}{\hbar^2}$$  \hspace{1cm} (12.14)

and $V_g$ is the structure factor for electrons.

This equation can be represented in a matrix form as

$$\frac{1}{2k_0} \left[ \begin{array}{cccc} -k_0^2 & U_{-g} & U_{-h} & \cdots \\ U_g & - (\mathbf{k} + \mathbf{g})^2 & U_{g-h} & \cdots \\ U_h & U_{h-g} & - (\mathbf{k} + \mathbf{h})^2 & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{array} \right] \left[ \begin{array}{c} C_0 \\ C_g \\ C_h \\ \cdots \end{array} \right] = \lambda \left[ \begin{array}{c} C_0 \\ C_g \\ C_h \\ \cdots \end{array} \right]$$  \hspace{1cm} (12.15)

or in a more compact form as

$$\mathbf{A} \cdot \mathbf{C} = \lambda \cdot \mathbf{C}.$$  \hspace{1cm} (12.16)

The final problem can be solved using matrix diagonalization to determine the wavevectors, $\mathbf{k}$ (related to the eigenvalues $\lambda$) and all the Bloch coefficients, $C_g$.

The scheme of the Bloch wave calculations can be described as follows.

- Select all beams $\mathbf{g}$ within the given resolution and maximum excitation error ($S_g$) value.
- Calculate $U_g$, $U_{-g}$, $U_{g-h}$, etc. for all combinations of $\mathbf{g}$ and fill the matrix $\mathbf{A}$ in eqn (12.16);
- Solve the matrix eqn (12.16) for eigenvalues $\lambda$ and eigenvectors $\mathbf{C}$;
- Calculate the excitation coefficients $c$ by solving a linear equation $\phi_g(0) = c \cdot C_g$ with $\phi_g(0)$ as the wave at the entrance surface of the crystal (thickness $t = 0$);
- Calculate the wave amplitude at any given crystal thickness $t$ using $\phi_g(t) = \sum c \cdot C_g \cdot \exp (2\pi i \lambda t)$.

There are several ways to speed up the calculations, especially in the case when the type of calculations is set to the CBED disk with a large number of points.
The following parameters affect the results of the Bloch-wave calculation:

- $g_{\text{max}}$: limits the total resolution of the simulated diffraction pattern. Reflections with $g_{hkl} > g_{\text{max}}$ will not be included in the calculations.

- **Voltage**: the curvature of the Ewald sphere increases with the decrease of accelerating voltages ($V_{\text{acc}} < 2V_{\text{acc}}$). Decreasing the voltage can increase the total number of reflections, provided that other parameters remain unchanged.

- $S_{g,\text{max}}$: increasing excitation error $S_{g,\text{max}}$ will increase the number of reflections, which will be counted as *exact* (black reflections in Figure 12.2) and will participate in the matrix diagonalization.

- $S_{g,\text{Bethe}}$: increasing $S_{g,\text{Bethe}}$ will increase the number of reflections, which will be counted as *Bethe* (grey reflections in Figure 12.2) and will participate only in the generalized Bethe approximation.

- **Number of points**: the total number of matrix diagonalizations in the case of CBED disk calculation mode can be approximately evaluated by the following equation:

$$N_{\text{total}} = \text{round} \left( \pi \cdot N_{\text{points}}^2 \right) \cdot N_{\text{beams}}$$  \hspace{1cm} (12.17)

where $N_{\text{beams}}$ is the total number of the exact beams in the diffraction pattern. In the case of other calculation types the $N_{\text{total}}$ will vary.

- **HOLZ layers**: changing the number of HOLZ layers will increase the total number of reflections within the given $g_{\text{max}}$ value.

### 12.2.3 Calculation of ED patterns

In the multislice method, ED patterns are calculated directly from the Fourier transform of the exit-wave function (Anstis, 1977), taking into account the beam divergence. Since the lenses change mainly the phase of the electron wave, the condition of the lenses, such as defocus and astigmatism will have little affect on the intensities in the diffraction pattern. In the case of the Bloch-wave method the diffraction intensities will be

$$I_g = |\phi_g(t)|^2$$  \hspace{1cm} (12.18)

Some examples of simulated electron-diffraction patterns are given in Figure 12.3. The best fit of the experimental SAED pattern in Figure 12.3a with the
12.2 Exit-wave calculation

Experimental and simulated electron-diffraction patterns of K$_2$O·7Nb$_2$O$_5$ (same as Figure 5.22a). (a) experimental SAED pattern (200 kV), (b) The result of the dynamical refinement (wedge sample shape of the crystal with maximum thickness $t = 374$ Å) that fits (a) the best. (c) simulated pattern at thickness $t = 20$ Å, (d) simulated pattern at thickness $t = 100$ Å.

Simulation including dynamical refinement (Figure 12.3b) was found using the eSlice module within the eMap software package (Oleynikov, 2011). The simulations shown in Figures 12.3c and d were obtained with the multislice method using the eMap software package (Oleynikov, 2006). Please note that it is quite hard to find the best match between experimental and simulated electron-diffraction patterns. This is due to the fact that in reality, experimental SAED patterns are usually taken from a wedge that has variation of thickness values starting from a very thin part at the edge of the crystal (Figure 12.3c) and continuing with inclusion of thicker parts up to 100–300 Å (Figure 12.3d).

Simulated CBED patterns of silicon in [111] zone axis orientation for the thickness $t = 1000$ Å, 200 kV are presented in Figure 12.4. Simulations were done with Bloch wave method using the eMap software package (Oleynikov, 2006). Note that the blurred low frequency features in the ZOLZ disks have 6mm symmetry while the fine features (HOLZ lines) exhibit 3m symmetry (see Figure 5.33 and Section 5.10 for similar example).

12.2.4 Comparison of multislice and Bloch-wave methods

The Bloch-wave method is mainly used for relatively simple structures (MgO, GaAs, etc.), since otherwise the computation becomes too time consuming.
12.2.5 Formation of an HRTEM image

The contrast transfer function is applied to the exit wave, and images corresponding to different optical conditions are calculated, as shown in Figure 12.5.
The resulting images should match reasonably the experimental images if the structure model and the optical parameters are correct.

In image simulation, dynamic scattering has been taken into account. We can use image simulation to check the influence of dynamic scattering on the final HRTEM image under different conditions. However, because image simulation cannot take into account all the experimental parameters, simulated images and diffraction patterns usually do not fit perfectly experimental images.

References


